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# Capstone Report

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

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## **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

|   |      |
|---|------|
| Abstract .....  | ii   |
| List of Tables .....  | vi   |
| List of Figures .....   | viii |
| Acknowledgments .....   | x    |
| Executive Summary and Conclusions .....   | xi   |
| <br>  |      |
| Chapter 1 Introduction .....  | 1    |
| <br>  |      |
| Chapter 2 Literature Survey .....   | 5    |
| Paint Definition and Composition .....  | 5    |
| Paint Manufacture and Use Statistics .....  | 7    |
| Paint Emissions Exposure and Health Effects .....   | 9    |
| Small Chamber Emissions Testing Procedures .....  | 13   |
| <br>  |      |
| Chapter 3 Standardized Test Methods for Characterizing Organic Compounds Emitted from<br>Paint Using Small Environmental Chambers ..... | 16   |
| Test Facilities .....   | 16   |
| Construction of the Small Chamber .....   | 17   |
| Air Mixing .....  | 19   |
| Surface Velocity .....  | 19   |
| Clean Air Generation System .....   | 19   |
| Temperature Control .....   | 20   |
| Humidity Control .....  | 20   |
| Lighting Control .....  | 20   |
| Environmental Measurement and Control Systems .....   | 21   |
| Automatic Systems .....   | 21   |
| Sample Collection and Analysis .....  | 22   |
| Principal Components of the “Standard Practice” for Testing Paint Emissions .....   | 25   |
| Storing and Handling Paint Prior to Analysis .....  | 26   |
| Analyzing Paint in Bulk (As a Liquid) .....   | 27   |
| Selecting and Preparing a Suitable Paint Substrate .....  | 28   |
| Applying Paint to a Substrate to Create a Test Specimen .....   | 29   |
| Operating the Small Chamber .....   | 31   |
| Sampling the Specimen’s Gaseous Emissions .....   | 31   |
| Using Instruments to Measure Chemicals Present in the Emissions Sample ...  | 34   |
| Analyzing the Results of the Analytical Instruments .....   | 34   |
| Reporting the Experimental Results .....  | 38   |
| Conducting Quality Assurance/Quality Control .....  | 40   |

## Table of Contents (Continued)

|   |     |
|---|-----|
| Chapter 4 Characterization of Emissions of Volatile Organic Compounds from Interior Alkyd Paint ..... | 42  |
| Experimental Work .....   | 43  |
| Bulk Product Analysis by GC/MS .....  | 44  |
| Small Chamber Emission Test Methods .....   | 44  |
| Sampling and Analysis Methods .....   | 46  |
| Results and Discussion .....  | 48  |
| VOC Content Determined by GC/MS .....   | 48  |
| Emission Tests - Mass Balance Calculations .....  | 50  |
| Emission Test Results .....   | 55  |
| Conclusions .....   | 65  |
| Chapter 5 Methyl Ethyl Ketoxime Emissions from Alkyd Paint .....                                      | 68  |
| Experimental Work .....   | 69  |
| Results and Discussion .....  | 70  |
| MEKO Contents .....   | 70  |
| Chamber Emission Data .....   | 71  |
| MEKO Emission Model .....   | 74  |
| Indoor Air Quality Impact Assessment .....  | 75  |
| Exposure Reduction Assessment .....   | 78  |
| Conclusions .....   | 79  |
| Chapter 6 New Findings About Aldehyde Emissions from Alkyd Paint .....                                | 81  |
| Experimental Work .....   | 82  |
| Results and Discussion .....  | 84  |
| Bulk Analysis for Hexanal .....   | 84  |
| Chamber Emission Data .....   | 85  |
| Hexanal Formation Mechanism .....   | 91  |
| Hexanal Emission Model .....  | 92  |
| Indoor Air Quality Simulation .....   | 96  |
| Conclusions .....   | 96  |
| Chapter 7 Substrate Effects on VOC Emissions from a Latex Paint .....                                 | 99  |
| Experimental Work .....   | 100 |
| Results and Discussion .....  | 102 |
| Paint Composition .....   | 102 |
| Substrate Effects on VOC Emissions .....  | 104 |

## Table of Contents (Continued)

|   |     |
|---|-----|
| Substrate Effects on Composition of VOC Emissions .....   | 108 |
| Emission Models .....   | 108 |
| Emission Mechanisms .....   | 110 |
| Long-Term Emission Data .....   | 113 |
| Conclusions .....   | 113 |
| Chapter 8 Experimental Work to Evaluate Low-VOC Paints .....  | 116 |
| Experimental Work .....   | 117 |
| Results and Discussion .....  | 119 |
| Bulk Analysis .....   | 119 |
| Emissions .....   | 121 |
| Performance Evaluation .....  | 126 |
| Conclusions .....   | 127 |
| Chapter 9 Experimental Work to Characterize and Reduce Formaldehyde Emissions from<br>Low-VOC Paint .....   | 129 |
| Experimental Procedure .....  | 130 |
| Experimental Data .....   | 131 |
| Emission Model .....  | 133 |
| Data Analysis .....   | 136 |
| Source Investigation .....  | 140 |
| Biocide Replacement .....   | 142 |
| Conclusions .....   | 143 |
| Chapter 10 References .....   | 144 |
| Appendix A A Proposed Standard Practice for Testing and Sampling of Volatile Organic<br>Compounds (Including Carbonyl Compounds) Emitted from Paint Using Small<br>Environmental Chambers ..... | A-1 |

## List of Tables

|     |  |     |
|-----|--|-----|
| 2-1 | Wall Paint Production by Type from 1997 to 2000 .....  | 8   |
| 3-1 | Quality Control Objectives .....   | 40  |
| 4-1 | Concentrations of the Predominant VOCs in the Liquid Primer and Three Interior Alkyd Enamel Paints .....                         | 49  |
| 4-2 | Matrix of Tests Performed in the Program .....   | 51  |
| 4-3 | Percent of the Applied VOC Mass Recovered in Emissions During 2-week Small Chamber Tests with Alkyd Primer and Paints .....      | 53  |
| 5-1 | Recovery of MEKO .....   | 71  |
| 5-2 | Estimated Values of Model Parameter and Goodness-of-Fit to the Chamber Concentration Data .....                                  | 75  |
| 6-1 | Information About the Primer and Three Test Paints .....   | 83  |
| 6-2 | The Total Emissions for the Three Most Abundant Aldehydes (in mg/g paint) .....  | 86  |
| 6-3 | Hexanal Concentration in Test Chamber for Alkyd Paint A-1 .....  | 87  |
| 6-4 | Hexanal Concentration in Test Chamber for Alkyd Paint A-2 .....  | 88  |
| 6-5 | Hexanal Concentration in Test Chamber for Alkyd Paint A-3 .....  | 89  |
| 6-6 | Estimated Model Parameters for Hexanal Formation from the Three Alkyd Paints Tested .....  | 95  |
| 7-1 | Determination of Volatile Organic Compounds in the Latex Paint by ASTM Methods (ASTM, 1989) .....                                | 103 |
| 7-2 | Total and Individual VOCs Determined by GC Analysis Concentration Units (mg/g) .   | 103 |
| 7-3 | Comparison of Peak Concentrations Measured In the Environmental Chambers (in mg/m <sup>3</sup> ) .....                           | 104 |
| 7-4 | Weight Percentage of VOC in the Latex Paint Emitted in the First 336-Hour Testing Period .....                                   | 108 |
| 7-5 | Summary of Parameters of the Double Exponential Model for VOC Emissions from Painted Gypsum Board .....                          | 111 |
| 7-6 | Summary of Parameters of the Double Exponential Model for VOC Emissions from Painted Stainless Steel (R <sub>20</sub> = 0) ..... | 111 |
| 8-1 | The Low-VOC Latex Paints Tested .....  | 118 |
| 8-2 | ASTM Methods Used for Performance Testing .....  | 120 |
| 8-3 | Results of Bulk Analyses (mg/g) .....  | 121 |

## List of Tables (Continued)

|     |   |     |
|-----|---|-----|
| 8-4 | Results of Performance Testing .....  | 126 |
| 9-1 | Estimated Values of Parameters of Equation (9-4) .....  | 138 |
| 9-2 | Comparison of Quantitative Measures of Goodness of Model with ASTM Criteria<br>(ASTM, 1995) ..... | 139 |
| 9-3 | Estimated Amount of Formaldehyde in the Paint Applied .....                                       | 139 |
| 9-4 | Calculated Formaldehyde Content in Three Paints Tested .....                                      | 142 |

## List of Figures

|     |  |     |
|-----|--|-----|
| 3-1 | Small chamber paint testing facility. . . . .  | 18  |
| 4-1 | Decane emissions from alkyd primer and Paint A-1 for first 20 hours after application to glass, gypsum board, or pine board substrates. . . . .                              | 56  |
| 4-2 | Effect of primer on short-term decane emissions from Paint A-1 applied to pine board; data presented for first 20 hours after paint application. . . . .                     | 59  |
| 4-3 | Comparison of TVOC emissions from three alkyd paints for first 20 hours after application to a pine board previously coated with primer. . . . .                             | 61  |
| 4-4 | Effect of wet film thickness on short-term decane emissions from Paint A-1 during first 20 hours following application to pine board previously coated with primer. . . . .  | 63  |
| 4-5 | Effect of air exchange rate on short-term decane emissions during small chamber tests with Paint A-1 applied to pine board previously coated with primer. . . . .            | 64  |
| 4-6 | Long-term hexanal emissions from three paints applied to pine board coated 48 hours earlier with alkyd primer. . . . .   | 66  |
| 5-1 | Chamber concentrations resulting from the MEKO emissions from Paint A-1. . . . .   | 72  |
| 5-2 | Chamber concentrations resulting from the MEKO emissions from Paint A-2. . . . .   | 72  |
| 5-3 | Chamber concentrations resulting from the MEKO emission from Paint A-3. . . . .  | 73  |
| 5-4 | Cumulative MEKO emissions for Paint A-2 (calculated from chamber concentration data). . . . .  | 73  |
| 5-5 | Comparison of the predicted test house MEKO concentrations with the suggested indoor exposure thresholds. . . . .  | 77  |
| 5-6 | Predicted test house MEKO concentrations at high (3.0 h <sup>-1</sup> ) air exchange rate. . . . .   | 79  |
| 6-1 | Hexanal emission from Paint A-1 and modeling results. . . . .  | 90  |
| 6-2 | Hexanal emission from Paint A-2 and modeling results. . . . .  | 90  |
| 6-3 | Hexanal emission from Paint A-3 and modeling results. . . . .  | 91  |
| 6-4 | Predicted hexanal concentration in a typical house after alkyd paint application. . . . .  | 97  |
| 7-1 | Effect of substrate on ethylene glycol emissions. . . . .  | 105 |
| 7-2 | Effect of substrate on propylene glycol emissions. . . . .   | 105 |
| 7-3 | Effects of substrate on 2-(2-butoxyethoxy)ethanol emissions. . . . .   | 106 |
| 7-4 | Effect of substrate on TPM emissions. . . . .  | 106 |
| 7-5 | VOC composition in chamber air with stainless steel substrate (relative abundance = weight percentage in TOC). . . . .   | 109 |
| 7-6 | VOC composition in chamber air with stainless steel substrate (relative abundance = weight percentage in TVOC). . . . .  | 109 |
| 7-7 | Long-term VOC emissions from painted gypsum board. . . . .   | 114 |
| 8-1 | Comparison of TVOC emission profile of paint L-2 with that of paint 0 (a conventional latex paint). The method detection limit for TVOC was 0.02 mg/m <sup>3</sup> . . . . . | 122 |



## List of Figures (Continued)

|     |   |     |
|-----|---|-----|
| 8-2 | Aldehyde emission profiles of paint L-1. The method detection limits was 0.0007 mg/m <sup>3</sup> for formaldehyde and acetaldehyde, and 0.0014 mg/m <sup>3</sup> for benzaldehyde. . . . .     | 124 |
| 8-3 | Aldehyde emission profiles of paint L-3. The method detection limit was 0.0007 mg/m <sup>3</sup> for formaldehyde, acetaldehyde, and propanal, and 0.0014 mg/m <sup>3</sup> for benzaldehyde. . | 125 |
| 9-1 | Comparison of chamber data with model predictions. Note that model predications for paints with no biocide and with a different biocide are not differentiable. . . . .                         | 132 |
| 9-2 | Schematic of the first-order decay in-series model. . . . .   | 134 |
| 9-3 | Fraction of formaldehyde remaining in the paint. . . . .  | 141 |

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## **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<sup>3</sup>. The chamber used at NRMRL is 53 L (0.053 m<sup>3</sup>) in volume. Chambers with volumes greater than 5 m<sup>3</sup> 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  $\pm 20\%$  in measuring these recoveries.

Due to the relatively high VOC content and fast emission pattern, peak concentrations of total VOC as high as  $10,000 \text{ mg/m}^3$  were measured during small chamber emissions tests with a loading factor of  $0.5 \text{ m}^2/\text{m}^3$  and an air exchange rate of  $0.5 \text{ h}^{-1}$ . 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 [ $\text{CH}_3\text{C}(\text{NOH})\text{C}_2\text{H}_5$ , 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  $152^\circ\text{C}$ ), 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  $0.1 \text{ mg/m}^3$  for all three paints. The predicted MEKO concentrations also exceeded the lower limit of a suggested sensory irritation range of 4 to  $18 \text{ mg/m}^3$  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.

## **Chapter 1**

### **Introduction**

The purpose of the report is to present the results of the U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory (NRMRL) Indoor Source Characterization Research Program between 1995 and 1999. The focus of the research program during this period was on emissions of volatile organic compounds (VOCs), including hazardous air pollutants (HAPs), from architectural coatings. Among architectural coatings, the focus of research was mainly on interior paints. Experimental work was conducted at EPA's Small Chamber Source Characterization Facilities by the Indoor Environment Management Branch of the Air Pollution Prevention and Control Division.

Americans spend about 90% of their time indoors. Concentrations of pollutants are often much higher indoors than outdoors. Risk assessment and risk management studies (U.S. EPA 1987, 1990) have found that indoor environmental pollution is among the greatest risks to human health and have advised EPA to address this problem. In response to these studies, EPA established the Indoor Source Characterization Research Program and Experimental Facilities in the late 1980s. Initial research was conducted to characterize organic emission profiles of common indoor materials and products to facilitate the identification of high-risk indoor sources.

In the early 1990s, EPA's Office of Pollution Prevention and Toxics (OPPT) developed an Indoor Air Source Ranking Database (SRD) as part of the Indoor Air Source Characterization Project (Cinalli et al., 1993). The objectives were to categorize product classes and to score and rank product classes based on relative risks. The SRD scores could be used to assign priorities to product classes for further data development and risk screening. Based on formulation data, emission profiles, use patterns, and health hazard data, architectural coatings, mainly interior paints, were ranked as one of the top priority, high-risk indoor air pollution sources.

Between 1995 and 1999, NRMRL's paint emission characterization research program was devoted to the development, verification, and demonstration of a standard test method for measurement of organic emissions from the two types of commercially available, most commonly used indoor architectural coatings – latex and alkyd paints. A literature survey indicated that there was a lack of reliable and consistent paint emission data needed to develop and evaluate effective risk management options to address exposure risks and health concerns. Further investigation showed that a standard test method was required for testing laboratories, researchers, and paint manufacturers to generate and report emission data that were complete, consistent, and comparable.

The research program produced a standard method for testing organic emissions from paints and six technical papers published in peer-reviewed journals (Chang et al., 1997; Chang et al., 1998; Chang and Guo, 1998; Fortmann et al., 1998; Chang et al., 1999; and Chang et al., 2001). A Standard Practice (Appendix A), based on the standard test method, was developed and submitted to the American Society for Testing and Materials (ASTM) for adoption as the national standard. In 2000, the research program won an Agencywide Pollution Prevention Leadership Award (James Craig Award) for identifying a major source of formaldehyde emissions and successfully preventing air pollution by those formaldehyde emissions with paint reformulation.

This report is divided into 10 chapters and an appendix. Chapters 1 and 2 provide background information:

- Chapter 1, Introduction, summarizes the paint emission research program and the scope, purpose, and organization of this report.
- Chapter 2, Literature Survey, provides background information from selected literature about interior paint consumption data, latex and alkyd paint properties, exposure and health risk concerns, and the need for a standard test protocol.

Chapter 3 focuses on testing methods:

- Chapter 3, Standardized Test Methods, presents the developed standard test method for characterizing organic compounds emitted from paint using small environmental chambers. The coded Standard Practice is provided in the Appendix. This chapter provides a detailed description of the test facilities and the rationale of critical experimental procedures.

Chapters 4, 5, and 6 focus on alkyd paint:

- Chapter 4, Characterization of Emissions of Volatile Organic Compounds from Interior Alkyd Paint, provides experimental data to demonstrate the usefulness of the small chamber test method. Results are presented for a series of tests performed to evaluate factors that may affect organic emissions from interior alkyd paints.
- Chapter 5, Methyl Ethyl Ketoxime (MEKO) Emissions from Alkyd Paint, shows how the standard test method can be used to measure the emission rate of a toxic chemical compound, MEKO, from three different alkyd paints. The chamber data were used to establish an emission model which predicted indoor MEKO concentrations during and after painting. The effectiveness of risk management options, including selection of lower MEKO paints and higher ventilation during painting, was also evaluated by the model.
- Chapter 6, New Findings About Aldehyde Emissions from Alkyd Paint, describes the use of a small chamber test method to characterize the emissions of odorous aldehydes that were produced by autoxidation reactions during the curing (drying) process. This chapter also demonstrates how to employ the chamber data to simulate indoor air quality impact and evaluate exposure risk.

Chapters 7, 8, and 9 focus on latex paint:

- Chapter 7, Substrate Effects on VOC Emissions from a Latex Paint, discusses how the small chamber test method was used to discover the significant effects of two substrates -- a stainless steel plate and a gypsum board -- on the VOC emission rates and patterns from a latex paint.
- Chapter 8, Experimental Work to Evaluate Low-VOC Paints, reports the test results of four commercially available low-VOC latex paints, evaluated as substitutes for conventional latex paints.
- Chapter 9, Experimental Work to Characterize and Reduce Formaldehyde Emissions from Low-VOC Paint, illustrates how the Standard Practice was employed to investigate the contributing sources of formaldehyde emissions from a latex paint. This chapter also demonstrates that small chambers can be used as a tool to conduct pollution prevention research to reduce formaldehyde emissions by paint reformulation.

and

- Chapter 10, References, lists the references cited in the report.

## **Chapter 2**

### **Literature Survey**

This chapter summarizes scientific research pertaining to the measurement of paint emissions and the evaluation of paints' effects on indoor air quality. It provides a context for NRMRL's work on developing standard test practices and it illustrates the fact that these practices met a pressing need within the community of indoor air scientists. The literature survey begins by describing the content of paint; it then summarizes both the patterns of paint use in the United States and the health problems that might result from that use. It concludes by describing the state of small chamber paint emissions testing at the time when NRMRL began its research into standardizing the practice.

#### **Paint Definition and Composition**

Paint is a mechanical dispersion of pigments or powders with a liquid or solvent known as a vehicle. The vehicle portion of the paint consists of a non-volatile portion and a volatile portion. After application of a paint, the non-volatile portions of the vehicle (e.g., resin polymers, film-formers, and binders) remain as a film on the coated surface, and the volatile portion evaporates (U.S. EPA, 1997). In addition to pigments and vehicles, paints contain other chemicals (called additives) that enhance their physical properties and make them easier to apply. Wall paint vehicles can be alkyd (solvent/oil-based) or latex (water-based). A paint's vehicle affects the ease with which it can be applied. Most paints are applied by brush, roller or spray.

Solvents perform the following three functions:

- They dissolve the chemicals that, when dried, form the coating's film.

- They dilute the paint solution or emulsion to achieve a proper solids content ratio and viscosity.
- Their evaporation rate controls the paint's rate of drying.

Different types of solvents have varying characteristics:

- **Aliphatic hydrocarbon** solvents are used in alkyd paints. These solvents are petroleum fractions containing mostly aliphatic hydrocarbons with small amounts of aromatic hydrocarbons. These solvents are commonly referred to as naphthas, or mineral spirits. About 75% of the aliphatic hydrocarbons used in alkyd wall paint are mineral spirits (U.S. EPA, 1997).
- In the past, **ethylene glycol** was the organic primary solvent used in latex flat paint. There is a current market trend towards replacing ethylene glycol with propylene glycol in both latex and alkyd paints. This substitution allows manufacturers to develop formulations containing less organic solvent. These new formulations, in turn, have lower and less hazardous organic compound emissions.
- **Glycol ethers and esters** are fully soluble in water. They also aid the freeze-thaw stability, coalescence, and wet-edge control in latex paints. They also make it easier to spread paints on the surface to be coated. These compounds are relatively volatile.
- **Alcohol, ketone, and ester** solvents are used in wall paints. Methyl ethyl ketone and methyl isobutyl ketone are the most common compounds used (NPCA, 1992a).
- **Xylenes** are aromatic hydrocarbons used in alkyd paints. Aromatics have been largely phased out of wall paint use.

Other paint additives that can affect emissions of paint during application include pigments, fillers, thickeners, plasticizers, surfactants, driers, stabilizers, and biocides. Any of these additives can affect emissions through direct emissions or reaction with paint components to produce volatile byproducts that evaporate into the air (U.S. EPA, 1997).

Interior latex paints are usually not considered to be in the same VOC category as alkyd paints because they can be cleaned with water and are non-flammable. Nevertheless, latex paints



contain volatile and semivolatile organic chemicals in the range of 3.5% to 9.5% (U.S. EPA, 1997). In general, latex paints are favored over alkyd paints indoors because they release much less odor, cost less, dry faster, and are easier to clean up.

Alkyd paints are used indoors primarily for high-gloss applications or for situations in which a particular surface or condition necessitates their use. For example, alkyd paint may be needed when high moisture resistance is required to minimize mold growth. Alkyd paints are used on a variety of substrates such as metal, plastic, wood, or glass.

### **Paint Manufacture and Use Statistics**

The total volume of alkyd and latex coatings used in the United States has remained around 650 million gallons per year between 1998 and 2000 (U.S. Census, 2000, 2001). More than 60% of this volume was paint applied to indoor surfaces (NPCA, 1992b; U.S. Census, 2000, 2001). Alkyd paint represents a small part (12%) of the total interior wall paint market. Latex paint makes up over 87% of indoor wall paints produced in 2000.

Table 2-1 shows a breakdown of wall paint production between 1997 and 2000. Latex flat paints comprised 98% of all flat wall paints. Latex semi-gloss paints comprise 90% of all semi-gloss wall paints in 2000. For comparison purposes, in 1973, latex flat and latex semi-gloss wall paints comprised 90% and 45% of the flat and semi-gloss wall paint market, respectively. In 1981, those figures were 93% and 70%, respectively, and in 1992 those figures were 97% and 75%, respectively (U.S. Census, 2000, 2001).

**Table 2-1. Wall Paint Production by Type from 1997 to 2000**

| Interior Type                   | Quantity (thousands of gallons) |                |                |                |
|---------------------------------|---------------------------------|----------------|----------------|----------------|
|                                 | 2000                            | 1999           | 1998           | 1997           |
| Alkyd (solvent based)           | 47,521                          | 51,181         | 49,514         | 52,432         |
| Flat                            | 3,239                           | 3,322          | 3,512          | 3,727          |
| Gloss                           | 3,216                           | 3,409          | 3,679          | 6,067          |
| Semi-gloss                      | 14,122                          | 12,355         | 11,548         | 11,803         |
| Primers and Sealers             | 18,781                          | 19,503         | 18,796         | 18,111         |
| Miscellaneous                   | 8,163                           | 12,592         | 11,979         | 12,724         |
| Latex (water based)             | 347,281                         | 339,225        | 315,636        | 335,035        |
| Flat                            | 149,252                         | 150,931        | 137,781        | 149,115        |
| Semi-gloss                      | 130,872                         | 125,002        | 114,602        | 120,635        |
| Primers                         | 33,381                          | 31,581         | 29,148         | 26,131         |
| Miscellaneous<br>Stains/Sealers | 33,776                          | 31,711         | 34,105         | 39,154         |
| <b>Total Interior</b>           | <b>394,802</b>                  | <b>390,406</b> | <b>365,150</b> | <b>387,467</b> |

Alkyd paint is composed primarily of organic solvents. Aliphatic and aromatic hydrocarbon solvents make up about half the solvents in alkyd products. These solvents include benzene, toluene, xylene, naphthas, and mineral spirits. The use of oxygenated solvents, including ketones, alcohols, esters, glycol ethers, and glycols, is growing. Ketones (primarily methyl ethyl ketone [MEK], methyl isobutyl ketone [MIBK], and acetone) comprise about 15 % of the coatings solvents market (Markarian, 2000). Alcohols, such as ethanol, butanol, propanol, and methanol, also hold about 15% of the market (Markarian, 2000).

While alkyd paint use is decreasing, emissions from alkyd paints still present a significant potential health risk due to the types of volatile compounds that these emissions contain. Per unit of volume, latex paints contain less hazardous volatile material than alkyd

paints do. However, the volume of latex paints used nationwide each year is extremely large (much larger than the volume of alkyd paints). Thus, widespread exposure to latex paint emissions is still an important source of indoor air pollution. Even though paint composition and consumption are moving away from alkyd paint and towards water-based (latex) paint, the health effects from both types of paint are still under investigation.

Health effects assessments and environmental regulations are focused on the hydrocarbons and hazardous air pollutants (HAPs) contained in both latex and alkyd paint. For example, the hydrocarbons in paint are such significant contributors to photochemical smog formation that California's South Coast Air Quality Management District (SCAQMD) developed legislative standards for paint hydrocarbon content. These standards seek to eliminate 21.8 of the estimated 59 million tons per day of hydrocarbon emission to the ambient air from paint in the South Coast district (Sissell, 1999). At the federal level, the Architectural and Industrial Maintenance (AIM) regulation took effect in 1999. It limits hydrocarbons in architectural coatings and industrial maintenance applications (Markarian, 2000). Both hydrocarbon reductions and HAP regulations are gradually becoming more stringent (Markarian, 2000).

### **Paint Emissions Exposure and Health Effects**

Indoor air exposure of painters and occupants to paint emissions is a health concern (U.S. EPA, 1997). Conventional paints contain VOCs that vaporize, dispersing into the air we breathe. Exposure to VOCs can result in irritation of the eyes, nose, and skin; respiratory problems; headaches; nausea; and dizziness (Pennybaker, 1999; Wieslander et al., 1999). Many of the VOC compounds in paint (such as benzene, formaldehyde, toluene, and xylene) are hazardous. Some of these VOCs are carcinogens or neurotoxins (Pennybaker, 1999; U.S. EPA, 1993).

People are exposed to indoor air pollutants for 90% of the time. They frequently complain about their health or well-being after moving into new or remodeled buildings. However, it can be difficult to interpret the public health significance of these reports since no federal or state air quality standards exist to limit the exposure of pollutants in non-industrial

indoor air. Health threshold limits have not been set for long-term exposure to compounds found in paint emissions. For this reason, the types of compounds and their emission concentration are important to the long-term study of indoor health effects of wall paint exposure.

In Germany, 2 months after a renovated building received occupants, a total VOC concentration of 2,000-3,000  $\mu\text{g}/\text{m}^3$  was measured. After 10 months, the concentration decreased to 900-1,300  $\mu\text{g}/\text{m}^3$  due to intense ventilation (Pitten et al., 2000). It was suggested that even this lower concentration could pose serious threats to well being and health risk to vulnerable occupants such as children with asthma and allergies. Since measurement methods for total VOCs (TVOCs) are not standardized, different measurements of the same emissions can produce significantly different values. Therefore, interpretation of these measurements should proceed only with great caution.

Emissions from newly painted building interiors have been associated with respiratory inflammation, asthma, and eye irritation. Many VOCs, such as terpenes and formaldehyde, are often present in the indoor air of new buildings. However, it is difficult to determine which of these chemicals are causing specific health effects because of the confounding effects of other contemporaneous construction, such as new woodwork and floor coverings. Wieslander and coauthors, from the Swedish Department of Occupational and Environmental Medicine, have reported that these confounding effects prevented them from determining if the solvent-free water-based paints used in renovating and reconstructing a building contributed to the health effects identified in the building's occupants (Wieslander et al., 1999). NRMRL research provides the standard procedures to characterize both the composition and concentration of paint emissions over time. With validated models from NRMRL, health researchers can disentangle the effects of paint emissions from other indoor air emission sources.

Asthma has been reported as a health concern associated with VOC emissions from newly painted indoor surfaces (Wieslander et al., 1997). Wieslander measured exposure to formaldehyde and VOCs at 62 dwellings. The relationships among exposures, asthma, and

clinical signs were calculated by multiple linear or logistic regression, adjusting for possible influence of age, gender, and tobacco smoking. The prevalence of asthma was elevated among subjects with domestic exposure to newly painted surfaces, particularly newly painted wood details and kitchen painting. A significantly increased prevalence of symptoms related to asthma was also observed in relation to workplace exposure to newly painted surfaces. The indoor concentrations of aliphatic compounds (C<sub>8</sub>-C<sub>11</sub>), butanols, and 2,2,4-trimethyl 1,3-pentanediol diisobutyrate (TPD also known as TXIB) were significantly elevated in newly painted dwellings. The total indoor VOC concentration was about 100 µg/m<sup>3</sup> higher in dwellings that had paint coats less than a year old. A significant increase in formaldehyde concentration was observed in dwellings with newly painted wood details. These results indicate that exposure to chemical emissions from indoor paint is related to asthma and that some VOCs may cause inflammatory reactions in the airways (Wieslander et al., 1997).

While many health professionals have focused on symptoms reported by painters and occupants in new or renovated spaces, EPA has investigated the potential risks associated with individual pollutants in the emissions from paint. Using paint emission test results and models from NRMRL, EPA has found that:

- Based on emission chamber work, the approximate 8-hr time weighted average (TWA) for TVOC levels can exceed 2,000 mg/m<sup>3</sup>.
- Xylene emissions from some paint samples approached the exposure levels at which neurologic effects are often seen.
- The high solvent exposures indicated by TVOC measurements from chamber studies lead to concern about the possibility of chronic central nervous system (CNS) effects in professional painters.
- TVOC exposure levels indicate a high likelihood of complaints about indoor air quality during and shortly after painting.
- For MEKO, the risk posed by the Maximum Occupational Exposure (MOE) during typical use presents concerns regarding developmental toxicity health effects.

- The risk of cancer among consumers and professional painters from the inhalation of MEKO during paint application and drying is a concern (U.S. EPA, 1997).

For latex paints, EPA determined that acute and chronic risks exist for professional painters based on exposure to latex paint emissions. They found that:

- TVOC levels are in the range that may result in complaints about indoor air quality. All samples and test conditions in the chamber studies resulted in TVOC levels exceeding  $40 \text{ mg/m}^3$  as an approximate 24-hr TWA.
- Some latex paint is the source of formaldehyde and acetaldehyde. Neither the exact concentrations of these chemicals nor the exact reason these chemicals are emitted from latex paint had been well characterized by studies completed before 1993.
- Acetaldehyde exposure presents a chronic health risk.
- Acetaldehyde exposure also raises possible concern for cancer risk with risk estimates around  $10^{-4}$  based on current potency estimates.
- Formaldehyde exposure raises a marginal concern for cancer risk to professional painters. Risk estimates based on unit risk values using data from emissions tests are around  $10^{-6}$  to  $10^{-4}$ .
- Formaldehyde also presents an acute irritation concern for both consumers and professional painters.

EPA recognizes that the paint industry has been in a state of flux and that it is lowering the VOC content of paint—mainly due to existing regulations that aim to reduce ground-level ozone levels. The marketplace has made a major switch from solvent- to water-based paint over the last 30 years. In addition, the use of mercury as the biocide of choice in paints has been discontinued, based partly on emission tests done by NRMRL (Tichenor et al., 1991). Industry is aware of indoor air problems—for example, some companies have developed and marketed “no-VOC” latex paints that have less odor. Although industry has made significant improvements to address EPA’s concerns, not all the factors in the risk analysis have been addressed, and further research on emissions reduction and health effects is still necessary.

## Small Chamber Emissions Testing Procedures

A number of studies have indicated the need for standard test practices for paint emissions. Tichenor and Sparks describe how to manage exposure from indoor air pollutants in residential and office environments. They find that intelligent source management requires knowledge of the sources' emissions characteristics, including their chemical compositions, emission rates, and emission decay rates. As an example, Tichenor describes several scenarios that cover full-time occupancy, part-time occupancy, room ventilation, and room size. For each of these scenarios, Tichenor predicts exposure of occupants to paint emissions. Tichenor concludes that individual exposure to indoor air pollutants is affected by several parameters, including source emission characteristics, source use, occupancy patterns, and ventilation options. Standardized measurement of these parameters is necessary to choose source management options that effectively decrease exposure (Tichenor and Sparks, 1996).

Saarela, in a review of papers describing the emissions from building construction materials, shows that measurement and evaluation of emissions from indoor materials are more meaningful when there are published guidelines for testing and policies for the use of emissions data. According to Saarela, chamber test methods are becoming more important for material classification, product development, and marketing. Therefore, it is important to develop and standardize these measurement methods to ensure that emission measurements, regardless of where in the world they are made, are comparable. There is a need to define all of the testing parameters and analytical procedures in detail so as to generate reliable emissions test data. These data, in turn, are required for developing selection guidelines for building material (Saarela and Sandell, 1991).

Levin first reported on the use of emissions testing for product selection during the design of a large office building (Levin, 1987a, 1987b, 1987c). In 1988, neither environmental chamber testing nor any other product evaluation method provided more than limited data. Even where test data were available, differing methodologies, the testing of non-comparable specimens, or changes in product formulations decreased the data's value for product selection

purposes. Levin points out that environmental chamber test results can be used by manufacturers during product development to determine the potential magnitude, composition, and health effects of exposure to their products' emissions. Therefore, Levin found that a standard protocol was needed to guide the emissions testing used for product development, pollution prevention, and exposure assessment programs. Levin presents the basic requirements for a well-designed small environmental chamber, including the pros and cons for several design and monitoring options. He also presents the major obstacles to adequate product documentation and the comparability of test results (Levin, 1989a and b).

In 1991 Levin reviewed the protocols, applications, and problems associated with using environmental chambers to determine VOC emissions from indoor air pollutant sources. His review covered the efforts of NRMRL to develop a small chamber test method that would standardize test procedures. It also covered the consensus American Society for Testing and Materials (ASTM) standard D-5116-90 that NRMRL developed in cooperation with ASTM. Levin compared the small chamber method development work performed by various groups to the large-chamber and whole-house approaches used to characterize emissions from a variety of home construction and decoration materials. Standards development efforts for low- or reduced-VOC products are burdened by the large differences in testing requirements that exist within this diverse group of products. In his review he concludes that the lack of standardized test protocols makes data interpretation and comparison of test results difficult for most product types (Levin, 1991).

Chemical reactions further complicate the procedures for using small chambers to evaluate paint emissions. Many chemical and physical transformations or reactions can occur, both while the paint is stored in the container and after it is applied to a surface. In-can preservatives and freeze/thaw protectants are incorporated into many paint formulations for quality control purposes. So-called "natural" paints based on casein have been known to deteriorate in the can, resulting in a "spoiled milk" odor after application. Homogeneous and heterogeneous reactions occur after the paint is applied to building interior surfaces. Once there, the change in the composition of the paint due to the evaporation of the volatile contents and the



increased concentration of the non-volatile components creates a new chemical balance among the remaining constituents with potential for chemical reactions. One example of this is the large burst in emission of hexanal from latex paints 24 hours after application, as seen in the research described in detail later in this report (Chang and Guo, 1998b).

## Chapter 3

### Standardized Test Methods for Characterizing Organic Compounds Emitted from Paint Using Small Environmental Chambers

A set of experimental methods was developed for testing the emissions properties of household indoor paints. Those experimental methods have been documented and submitted to ASTM for adoption as a standard practice. “A Proposed Standard Practice for Testing and Sampling of Volatile Organic Compounds (Including Carbonyl Compounds) Emitted from Paint Using Small Environmental Chambers” is included in the appendix of this report. This chapter describes the principal elements of the standard practice and provides detailed information about the background and the rationale of those methods. The goal of the standard practice is to generate quantitative and comparable emissions data. These data, in turn, may be used for:

- Selecting paints for specific purposes
- Establishing paint specifications
- Conducting quality control checks of paint
- Developing new low-emissions paints
- Supporting any future paint labeling programs
- Conducting indoor air quality analyses
- Conducting exposure risk assessments

#### Test Facilities

The purpose of this section is to provide an overview of the test facilities used for evaluating paint emissions. The design principles and major functions of critical components of the test facilities are also discussed. The small environmental chamber system employed by NRMRL is used as an example. Currently there are no commercially available chamber systems, but investigators can design their own test facilities by following the same principles to suit their

own needs. More technical discussions on small environmental chamber systems can be found in ASTM D5116-97.

The core experimental apparatus with which NRMRL conducts its paint emissions testing 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 cubic meters. The chamber used at NRMRL is 53 L (0.053 m<sup>3</sup>) in volume. Chambers with volumes greater than 5 m<sup>3</sup> 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. Figure 3-1 illustrates a system with two test chambers.

### ***Construction of the Small Chamber***

Small environmental test chambers should have non-adsorbent, chemically inert, smooth interior surfaces so as not to adsorb or react with compounds of interest. Care must be taken in their construction to avoid the use of caulks and adhesives that emit or adsorb VOCs. As an example, electropolished stainless steel and glass may be used for interior surfaces. The chamber must have an access door with air-tight, non-adsorbent seals. The chambers must be fitted with inlet and outlet ports for air flow. Ports for temperature and humidity probes may also be required. Ports for sample collection are needed only if the sampling is not conducted in the outlet air.

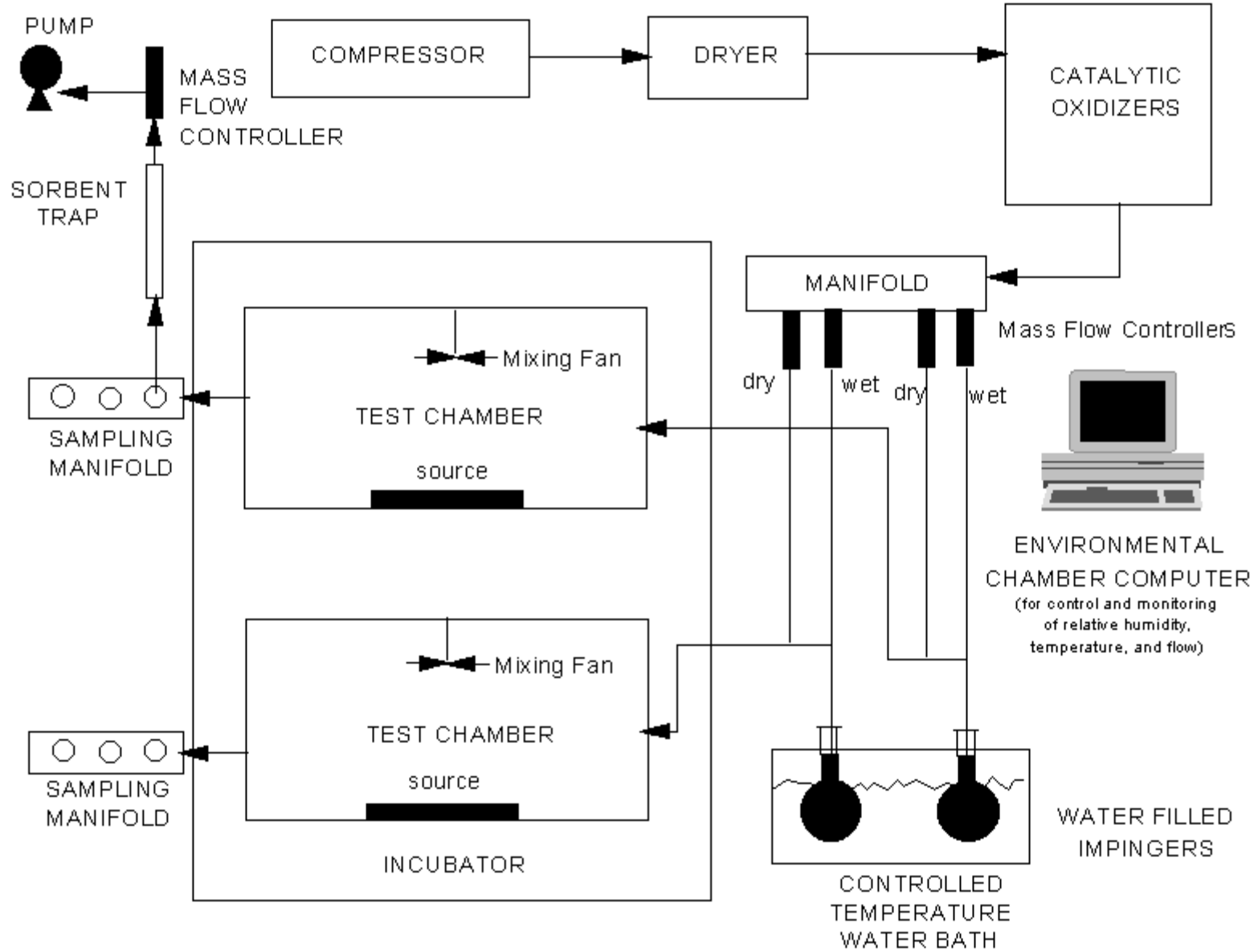


Figure 3-1. Small chamber paint testing facility.

## ***Air Mixing***

The chamber and its air-moving components need to be designed to ensure good mixing of the incoming air with the chamber air. While contaminant concentration gradients are expected to exist in the chamber, particularly in the boundary layer near the emissions source, the mixing issue concerns only the uniformity of the concentration in the bulk air inside the chamber. The use of mixing fans and multi-port inlets and outlets are two techniques that have been used successfully to ensure adequate mixing of air in the chamber.

## ***Surface Velocity***

The air's velocity near the surface of the material being tested can affect the mass transfer rate. Thus, sources with evaporative emissions (e.g., wet paints) are tested under typical indoor velocities (for example, 5-10 cm/s). A small fan can be used to achieve such velocities. A diffuser should be used to eliminate the calm spot downstream of the fan hub. Velocity measurements can be made with hot wire or hot film anemometers.

## ***Clean Air Generation System***

Clean air must be generated and delivered to the chambers to provide adequate background for conducting tests. A typical clean air system might use an oilless compressor drawing in ambient air followed by removal of moisture (for example, using a membrane dryer) and trace organics (for example, by catalytic oxidation units). Other options include gas cylinders or charcoal-filtered outdoor or laboratory air. If granular media (for example, charcoal) are used for control of organics, a particle filter should be used downstream to remove particulate matter. Calculations should be performed to determine the amount of air flow required before a decision is reached on the supply system. For most sources to be tested, extremely clean air is needed. Inlet concentrations should not exceed  $2 \mu\text{g}/\text{m}^3$  for any single compound or  $10 \mu\text{g}/\text{m}^3$  for the sum of all VOCs. The purity of the air should be verified by routine analysis of background air samples from a clean chamber.

## ***Temperature Control***

Temperature can be controlled by placing the test chambers in incubator cabinets or other controllable constant-temperature environments. The temperature of the inlet air can be controlled by using conditioning coils.

## ***Humidity Control***

The humidity of the chamber air is controlled by adding deionized water or high-performance liquid chromatography (HPLC) grade distilled water to the air stream. Injection by syringe pumps followed by heating to vaporize the water can achieve desired humidity levels. Other types of pumps (for example, HPLC) might also provide sufficient accuracy. The chamber air can be humidified by bubbling a portion of the airstream through deionized water at a controlled temperature (for example, in a water bath). The saturated air is then mixed with dry air to achieve the desired humidity. Steam humidification can also be used. Coiled lines inside the constant-temperature environment can be used to equilibrate the inlet temperature before delivery to the test chambers.

## ***Lighting Control***

Small chambers are normally operated without lights. If the effect of lighting on emissions is to be determined, appropriate interior illumination should be provided. If the heat generated by lighting is a concern, a transparent chamber lid with a light source placed outside the chamber may be an option.

## ***Environmental Measurement and Control Systems***

Measurement and control are required for air flow, temperature, and humidity. Air flow can be automatically monitored and controlled by electronic mass flow controllers, or manual flow control (for example, a needle valve or orifice plate) and measurement (for example, a bubble meter or rotameter) can be used. Temperature can be measured automatically via thermocouples or thermistors; manual dial or stem thermometers can also be used. Humidity control depends on the humidification system employed. If liquid injection is used, water flow is controlled by the pump setting. Control of humidity by saturated air requires temperature control of the water and flow control of the saturated air stream. Humidity can be measured by several types of sensors, including dew point detectors and thin-film capacitors. Temperature and humidity sensors should be located inside the chamber at least 5 cm from the inside wall and near the midpoint between the air inlet and outlet ports.

## ***Automatic Systems***

Microcomputer-based measurement and control systems can be used to set air flow rates and monitor temperature, relative humidity, and air flow during the experiments. Analog signals from temperature, relative humidity, and flow sensors are converted to digital data that can be stored by a microcomputer-based system, then processed to engineering units using appropriate calibration factors. In this way, chamber environmental data can be continuously monitored, then compiled and reduced for archival storage or display with minimal operator effort. Automatic systems are also capable of certain control functions. Digital signals can be output to control valves or converted to analog signals and sent out as setpoint signals to mass flow controllers. A graphics overlay program can be used to show current setpoints and measured values on a system schematic displayed on the microcomputer's monitor.

## **Sample Collection and Analysis**

Indoor sources of organic emissions such as paints vary widely in both the strength of their emissions and the type and number of compounds emitted. Differences in emissions rates of several orders of magnitude among sources are not unusual. To characterize organic emissions fully, the sample collection/analysis system must be capable of quantitative collection and analysis of volatile, semi-volatile, polar, and non-polar compounds. Any small chamber sampling and analysis technique or strategy developed must consider the emission characteristics of the specific source being evaluated. The design and operation of sample collection and analysis systems must be appropriate for the organic compounds (and their concentrations) being sampled. Such systems generally include sampling devices, sample collectors, and analytical instruments. The remainder of this section discusses the alternatives available for small chamber sampling and analysis of organic emissions.

### **Sampling Devices**

The exhaust flow (for example, chamber outlet) is normally used as the sampling point, although separate sampling ports in the chamber can be used. A multiport sampling manifold can provide flexibility for duplicate samples. A mixing chamber between the test chamber and the manifold can be used to permit addition and mixing of internal standard gases with the chamber air stream (note that the effective chamber volume should be the sum of the test chamber and the mixing chamber or manifold). Sampling ports with septums are needed if syringe sampling is to be conducted. The sampling system should be constructed of inert material (for example, glass, stainless steel), and the system should be maintained at the same temperature as the test chambers. The exhaust from the sampling system should be ducted into a fume hood, ensuring that any hazardous chemicals emitted by the test materials are isolated from the laboratory environment.

Samples can be drawn into gas-tight syringes, gas chromatograph (GC) sampling loops, evacuated canisters, or through sorbent cartridges using sampling pumps. Gas-tight syringes and



closed loops are frequently used when chamber concentrations are high and sample volumes must be small to prevent overloading the analytical instrument. Larger volume samples can be pulled through sorbent cartridges using sampling pumps. Flow rate can be controlled by an electronic mass flow controller (MFC) or other means. The sampling flow rate should be regulated to prevent instabilities in the chamber system flow. Generally, this will require that the sampling flow rate be limited to <50 % of the chamber flow rate. Valves and a vacuum gauge may be incorporated into the system to permit verification of system integrity before samples are drawn. The entire system can be connected to a programmable electronic timer to permit unattended sample collection.

## Sample Collectors

Selection of appropriate sample collectors will depend on factors such as boiling point, polarity, and concentration ranges of the compounds of interest, as well as the amount of water vapor in the sample airstream. No single sample collection, concentration, and delivery system will be adequate for all analytes of interest, and the user must understand the limitations of any system used to characterize source emissions. If the sample is collected by way of syringe or closed-loop sampling, it is injected directly into an instrument for analysis. Collection in a sampling bag (for example, Tedlar) or vessel (for example, glass, stainless steel) allows larger samples to be collected and subsequently concentrated and analyzed. For many small chamber evaluations of indoor paints, the fact that some of the compounds of interest are present only at low concentrations requires the concentration of large-volume samples and collection on an appropriate adsorbent medium. Several sorbent materials are available for use, singly or in combination, including activated carbon (charcoal), glass beads, Ambersorb, Tenax (polyphenylene oxide), graphitized carbon, and XAD-2. The selection of the sorbent (or sorbent combination) depends on the compound(s) to be collected. XAD-2 resin can be used to collect compounds considered to be semi- or non-volatile (i.e., boiling points above 180°C). If sorbent collection is used, the laboratory must be equipped with appropriate storage capabilities. Air-tight glass tubes or chemically inert bags are both appropriate. Flushing the storage containers with

high purity nitrogen prior to use will help ensure their cleanliness. Samples should be stored in a freezer at  $-20^{\circ}\text{C}$ .

When sorbents are used for sample collection, desorption and concentration are necessary. For example, a clamshell oven can be used to thermally desorb sorbent (e.g., Tenax) cartridges with the vapors fed to the concentrator column of a purge and trap concentrator that thermally desorbs the organic compounds. Another example is solvent extraction and dilution of samples collected by charcoal cartridges. If possible, sorbent samples destined for thermal desorption should be processed and analyzed within 48 h of collection. Samples requiring solvent extraction should be processed within 7 to 14 days and analyzed within 40 days of extraction.

## Organic Analysis Instrumentation

Several analytical instruments are available for determining the concentration of the organics sampled from the chamber: GCs are the most commonly used. GCs have a wide variety of columns available for separating organic compounds. Gas chromatography separates materials based on the differences between their vapor pressures. Compounds “distill” from a GC column based on how readily they remain in the vapor phase. Capillary columns are generally preferred because they allow more opportunity for compounds to vaporize, condense, and separate from a mixture before exiting the column to the detector. Several detectors can be used depending on the purpose of the test and the compounds of interest. Mass spectrometers (MS) are the most versatile and can be used in the scan mode to identify unknown compounds. When used in the scan mode, a conventional MS has a sensitivity of about  $10^{-9}$  g. An ion trap may have a sensitivity approaching  $10^{-12}$  g in the scan mode. If conventional MS is being used to analyze known compounds, it can be operated in the selective ion mode where its sensitivity increases to  $10^{-12}$  g. MS can be made even more sensitive via negative chemical ionization. Flame ionization detectors (FIDs) are also widely used. They respond to a wide variety of organic compounds and have a sensitivity of  $10^{-11}$  g. Electron capture detectors (ECD) are used for analyzing electronegative compounds (for example, halogenated organics) and have a sensitivity of  $10^{-13}$  g.

Some compounds are not easily measured with GCs; for example, low molecular weight aldehydes. Analysis of these compounds requires other instrumentation. High Performance Liquid Chromatography (HPLC) is one technique used to analyze compounds that are very polar, thermally unstable, or of a high molecular weight. HPLC separations are based on the differential solubility of compounds in a sample. Generally the compounds are derivatized before injection. Once a sample is injected into the HPLC column, compounds dissolve into the solvent pumped through the column. Solubility can be increased by automatically changing the solvent mixture. A variety of packed solid-phase columns are available for separation of different classes of compounds by HPLC. HPLC can be combined with any of several detector types including ultraviolet (UV), visible (VIS), and infrared (IR) spectrometers. Much like gas chromatography, data collected from HPLC analysis using these optical detectors consist of the specific retention time of a compound (which indicates its identity) and the specific detector response (which indicates the quantity of compound in the sample). HPLC can also be coupled with a mass spectrometer (MS) to generate coordinated retention time, concentration, and molecular fingerprint information.

## Standards Generation and System Calibration

Calibration gas may be added to the test chamber or sampling manifold from permeation ovens, gas cylinders, or dilution bottles. Calibration (or tracer) gas is added through the test chamber in tests to determine chamber mixing, check for leaks, or to evaluate chamber “sink” effects (i.e., the interactions between pollutants and chamber surfaces). Internal standards for analysis quality control may be added at the head of the sampling system. The internal standard should not be added to the chamber due to the potential for adsorption on the material being tested. Quality control can also be achieved by spiked samples.

## **Principal Components of the “Standard Practice” for Testing Paint Emissions**

The purpose of this section is to provide a detailed description of the experimental procedures included in the standard practice developed by NRMRL for measuring the emission

rates of various organic compounds from indoor paints. The practice is applicable to both alkyd and latex paints and primers. The following laboratory procedures are covered in the practice:

- Storing and handling paint prior to analysis
- Analyzing paint in bulk (as a liquid)
- Selecting and preparing a suitable paint substrate
- Applying paint to a substrate to create a test specimen
- Operating the small chamber
- Sampling the specimen's gaseous emissions
- Using instruments to measure chemicals present in the emissions sample
- Analyzing the results of the analytical instruments
- Reporting the experimental results
- Conducting quality assurance/quality control

### ***Storing and Handling Paint Prior to Analysis***

The purpose of this procedure is to ensure that the origin and history of each paint tested are clearly documented and that the properties of each paint remain constant throughout the testing process.

To ensure that paint is properly documented, NRMRL recommends that, upon acquiring a new batch of paint, the investigator should record pertinent receipt information on a label attached to the paint. The receipt information includes:

- The date of acquisition
- The source of the paint
- The manufacturer and lot number

Repeatedly opening a large can of paint and extracting small samples from it allows organic compounds to escape from the paint over time. To guard against the possibility of the paint substantially changing in composition while it is being stored for analysis, the investigator should open the can of paint only once and then immediately divide the paint into aliquots. Each of these aliquots should be intended for a single application of paint to a sample. Although this

procedure does not altogether eliminate the problem of uncontrolled vapor loss, it minimizes it and standardizes it across all samples.

It is essential to ensure that the paint within a new can is homogenous before it is divided into aliquots. Over time, unshaken paint may separate into layers with different chemical compositions. Before opening a new paint can and drawing aliquots, the investigator should homogenize the paint; e.g., using a commercial paint shaker. Stainless steel mixing balls may be added to each aliquot to aid in the re-homogenization of the sample immediately before use.

NRMRL investigators store paint and primer aliquots in clean, amber glass vials. The caps of these vials are lined with Teflon<sup>®</sup>. The vials, once filled, are stored at room temperature, away from light. The investigators take care to use them before the expiration of the shelf-life specified by the paint manufacturer. These procedures guard against the deterioration of the paint while it is in storage at the laboratory.

### ***Analyzing Paint in Bulk (As a Liquid)***

As a step preliminary to the design and implementation of an emissions test, the bulk composition of the paint in question may be analyzed. NRMRL has adopted a slightly modified version of Method 311 (1996) as its protocol for bulk analysis of paints. NRMRL chose this method because it is a standard EPA method, it has been developed to be flexible, and it provides consistent, comparable, and reproducible results with known performance for a wide variety of materials. NRMRL investigators perform this analysis on an aliquot of every paint investigated in its small chamber research program. By performing a bulk organic compound analysis of every candidate paint, the research program is assured of an initial chemical composition analysis that is consistent, realistic, and comparable to other paint materials tested in the program. The purpose of this analysis is to ascertain the identities and relative abundance of the chemicals likely to be emitted from the paint into the air. The concentrations of VOCs in the bulk paint can also be used with an emissions source model to predict VOC concentrations in the small chamber during testing. All of this information is useful in the design of the emissions test because it gives the

investigators choices of the kinds of sampling and analytical techniques that can be used. Proper sampling techniques, for example, vary depending upon the kinds and concentrations of chemicals one expects to be present.

Investigators proceed with this method by diluting an aliquot of paint with an appropriate solvent and centrifuging the mixture to remove solid matter. Potentially suitable solvents for this step include dimethylformamide, methylene chloride (for alkyd paints), or acetone or acetonitrile (for latex paints). The investigator may need to perform several initial tests to ascertain which solvent most effectively dilutes the paint. The interested reader may refer directly to Method 311 (1996) for more specific details on procedures and quality control checks for analyzing the supernatant.

A portion of the supernatant is injected into a GC/MS. The investigator's choice of GC column and operating procedure depends on his or her initial assumptions about what kind of chemicals are present in the supernatant. One general rule serves as a foundation for these assumptions and is particularly noteworthy. It is that alkyd primers and paints primarily contain relatively non-polar aromatic and aliphatic VOCs, while latex paints contain a significant amount of polar compounds (e.g., glycols, glycol ethers, and alcohols).

### ***Selecting and Preparing a Suitable Paint Substrate***

The purpose of NRMRL's procedures for selecting and preparing paint substrates is to provide a realistic, representative, and adequate substrate for painting. Traditional substrates, such as glass, stainless steel, and aluminum plates, are not realistic and representative for interior paints. NRMRL suggests that investigators use common indoor materials such as gypsum board and wood. A substrate should be sufficiently large to generate adequate loading, it should not be contaminated, and its edges should be sealed (with sodium silicate or Teflon<sup>®</sup> tape) to minimize edge effects.

The investigator should procure substrate material and cut it to an appropriate size (which depends on the loading rate desired in the small chamber). For example, a 16 by 16 cm square of substrate (a 0.0256 m<sup>2</sup> square) would provide a loading of 0.48 m<sup>2</sup>/m<sup>3</sup> for a small chamber with a volume of 0.053 m<sup>3</sup>. The surface of the substrate must be smooth to facilitate the application of a smooth layer of paint—when necessary, an appropriate abrasive should be used to produce a smooth surface before the paint is applied.

The sides of the substrate (which are neither painted nor counted as part of the substrate's area) should be sealed to prevent them from allowing the escape of organic vapors. At NRMRL, this is accomplished by coating them with a solution of sodium silicate.

Until the substrates are ready to be used, they must be protected from exposure to ambient organic vapors which might contaminate them and bias emissions tests. Two ways of doing this are: (1) storing the substrate in an area with very low levels of VOCs, or if this is not possible, (2) storing the substrate in an airtight container. For at least 24 hours prior to use, the substrates should be conditioned in the small chamber at exactly the temperature and humidity at which the sampling will be conducted. The purpose of this process is to make sure that the substrate is already “conditioned” (in steady state with its environment) when it is painted.

### ***Applying Paint to a Substrate to Create a Test Specimen***

One of the key objectives of NRMRL's paint testing practice is to apply paint in a controlled fashion that is realistic, quantifiable, and comparable. The first part of this objective is to apply paint in a way that is realistic—that is, in a manner similar to how it would be applied by actual house painters. In addition, the results of the emissions tests should be analyzed with reference to a quantitative measurement of the mass of paint applied. Finally, in order for different tests to be comparable, they must consistently involve approximately the same mass and thickness of paint.

With these goals in mind, NRMRL recommends using a roller or a brush under most circumstances and a slit applicator for perfectly smooth surfaces such as glass. The slit applicator will not leave a smooth coat on rougher surfaces such as gypsum board or wood because it cannot compensate for valleys and ridges in the substrate. NRMRL did not find other applicators to be particularly useful. Electronic applicators, for example, are expensive and they do not produce a film that is sufficiently smooth and reproducible. Another applicator device, the spray gun, is impractical given the small size of the test specimen, the waste from overspray, and the loss of VOCs during spraying.

An investigator should begin the paint application process by determining the mass of paint to be applied, using product data listed on the paint container label. One can calculate the mass of paint needed using the spreading rate (ft<sup>2</sup>/gal.), the density of the paint, and the area to be painted:

$$M_p = \frac{A(D_p)}{SR} \quad (3-1)$$

Where:

- $M_p$  = target mass of paint to be applied (g),
- $A$  = area of the substrate (cm<sup>2</sup>),
- $D_p$  = density of the paint (g/mL), and
- $SR$  = spreading rate, generally listed on container or data sheet as ft<sup>2</sup>/gal. (cm<sup>2</sup>/mL).

The appropriate mass of paint can then be weighed out into a tray. At this point, the uncoated substrate should also be weighed. The paint may then be applied to the substrate using the roller (or alternate applicator). Once application is complete, the amount of paint applied is determined either by measuring the increase in the substrate's weight or the decrease in the roller and tray's weight. The final weight of the paint applied should be within 10% of the target application amount originally calculated.



## ***Operating the Small Chamber***

The purpose of this phase of NRMRL's standard practice is to provide a controlled environment for conducting emissions testing that can reflect common indoor air conditions.

Therefore, NRMRL recommends that the small chamber should be set to maintain an environment within the following operating ranges:

|                    |   |
|--------------------|---|
| Temperature:       | 20 to 25°C                                |
| Air Exchange Rate: | 0.3 to 2 h <sup>-1</sup>                  |
| Air Speed:         | 5 to 10 cm/s                              |
| Loading:           | 0.3 to 1.5 m <sup>2</sup> /m <sup>3</sup> |

The relative humidity of inlet air should be maintained at 50% unless defined otherwise. These operating ranges were chosen to match the actual conditions under which interior house painting is likely to take place.

Prior to each use, the environmental test chamber, the sampling manifold, and all other internal hardware should be cleaned to remove any chemicals which may have adhered over the course of previous use. NRMRL uses alkaline detergent and deionized water as its cleaning agents. The environmental conditions used for testing should be maintained for 24 hours prior to the beginning of the test.

## ***Sampling the Specimen's Gaseous Emissions***

This part of the chamber operation and sample collection is critical to a successful emissions evaluation. With new or unusual coating materials, some trial and error experimentation may be necessary to develop a method that ensures complete and accurate collection of the paint emissions.

## Sampling Protocol

As a test progresses, the experimenter may need to periodically adjust the airflow controllers for the sorbent tubes and the length of sampling. At any given time, an important goal of sampling is to deliver a precisely measured volume of air to the sampling media that conveys an optimal mass of VOCs. An optimal mass of VOCs is one that is small enough to avoid overloading the sorbent yet large enough to be detected by the analytical instrument.

During the early stages of a test, VOC emissions are often so high that they quickly overwhelm sampling media. These conditions necessitate the collection of small sample volumes, which can be difficult to measure precisely. The precision of the measurement of small sample volumes should be maximized by adjusting the two settings that determine it: rate of airflow and period of sampling. These two settings must multiply to produce the required sample volume—particular settings should be chosen so as to maximize the *overall* precision of the measured sample volume. Typical small-sample collection times range from 5 to 10 minutes. In some cases, the investigator may choose to sample through two sorbent cartridges in series. A separate analysis of the second sorbent cartridge will reveal whether or not overloading (i.e., “breakthrough”) has occurred in the first cartridge.

Higher airflow rates and longer sample collection periods may be required in later stages of the test as the concentrations of VOCs decrease in the chamber air. Again, the objective of the selection of sampling time and flow rate is to collect sufficient organic material to be within the sensitivity range of the analysis procedure yet avoid exceeding the sampling media capacity. The total sampling flow rate must be less than 50% of the airflow from the chamber (e.g., less than 220 mL/min for a 53 L chamber with an air exchange rate of 0.5 h<sup>-1</sup>).

Air samples should be collected at predefined intervals during the test. The duration of the test and the frequency of sample collection will vary, since they are determined by the objectives of the test. A high frequency of sampling will be required if the objective of the test is to develop or evaluate source emission models. A lower frequency of sampling may be appropriate for other

test objectives. If resources are available, NRMRL's recommended sampling times for collection of data for model development during a 2-week test with alkyd paint are at 0.25, 0.5, 1, 1.5, 2, 4, 6, 8, 10, 12, 24, 48, 72, 96, 144, 192, 264, and 336 hours following the start of the test. NRMRL's recommended sampling times during a 2-week test with latex paint are at 2, 4, 8, 12, 24, 48, 72, 96, 144, 192, 264, and 336 hours following the start of the test. After sampling, one should carefully seal sample tubes and record sampling flow rates and durations on them.

## Sampling Media

During the first 10 to 20 hours after application of an alkyd primer or paint, air samples for determination of VOCs may need to be collected on charcoal cartridges. These cartridges, if used, are subsequently extracted with organic solvent. The use of charcoal cartridges may be necessary because the very high concentrations of the VOCs in initial emissions can preclude the use of Tenax and thermal desorption methods (due to the potential for breakthrough on the sorbent media and overloading of the analytical instrument). Charcoal cartridge extracts can be diluted if the emission sample concentration is too high for the analysis equipment. After the initial drying period, the concentrations of VOCs will decrease to levels amenable to collection on Tenax.

In addition to charcoal and Tenax sampling, air samples may be collected on silica gel for the measurement of certain carbonyl-bearing compounds. A fourth sampling method (which allows collection of aldehydes) uses silica gel coated with acidified 2,4-dinitrophenylhydrazine (DNPH). Samples collected on sorbent media or DNPH-silica gel cartridges should be analyzed as soon as possible and no later than 30 days after collection. If they must be stored, they should be refrigerated at lower than 4 °C.

## ***Using Instruments to Measure Chemicals Present in the Emissions Sample***

The overall goal of the analysis of an emissions sample is to determine the amount and kind of VOCs that the sample contains. Examples of the sampling and analysis methods followed by NRMRL for monitoring paint emissions include:

- GC/MS is used for compound identification. GC/MS is applicable to samples collected on charcoal, Tenax, and silica gel. Compound identification is based on chromatographic retention time and molecular fragmentation patterns from the unknown compounds. Compound identification is confirmed by comparison with the National Institute of Standards and Technology (NIST) mass spectral library data base. The advantage of GC/MS is its ability to use an established data base of mass spectra for a variety of organic compounds.
- GC/FID is used for quantification of non-polar compounds such as alkanes, alkenes, and aromatic compounds. Like GC/MS, GC/FID can be used to quantify compounds collected on charcoal, Tenax, and silica gel. Compound identification is confirmed using relative chromatographic retention times determined by GC/MS. Compound quantification is based on calibration using at least five standard concentrations covering the quantification range of the instrument. GC/FID has the advantages of being less expensive than GC/MS and able to quantify compounds over a wider concentration range.
- HPLC/UV is used for identification and quantification of polar compounds such as ketones and aldehyde that GC/FID cannot determine easily. HPLC is applicable to samples collected on dinitrophenylhydrazene (DNPH). Compound quantification is based on calibration with nine carbonyl compounds: formaldehyde, acetaldehyde, propanal, benzaldehyde, pentanal, m-tolualdehyde, methyl isobutyl ketone, hexanal, and heptanal. Additional carbonyl compounds can be analyzed with this technique if the appropriate standards are available for calibration.

## ***Analyzing the Results of the Analytical Instruments***

One of the purposes of analyzing the results of the sampling instruments is to convert the analytical results (chamber concentrations) into emission rates (ERs) and emission factors (EFs).

The two technical terms commonly used to describe the rate of emissions from indoor materials, ER and EF, are related as follows:

$$ER = A(EF) \quad (3-2)$$

where:

|    |   |  |
|----|---|--|
| ER | = | emission rate (mg h <sup>-1</sup> ),                   |
| A  | = | source area (m <sup>2</sup> ), and                     |
| EF | = | emission factor (mg m <sup>-2</sup> h <sup>-1</sup> ). |

### Calculating VOC Emission Rates and Emission Factors

Once the chamber concentration data are obtained, the emission factor can be calculated by three methods:

- Direct calculation from individual data points (Equation 3-3)
- Direct calculation from the time/concentration profile (Equations 3-4 and 3-5)
- Using an explicit chamber model (Equation 3-6)

Selection of the most suitable method or methods depends on several factors, such as the type of source, data quality, and sampling frequency.

If the emissions rate is nearly constant and the chamber has reached steady state, the emission factor can be calculated from a single data point:

$$EF = C_s \left( \frac{N}{L} \right) \quad (3-3)$$

where:

|                |   |   |
|----------------|---|---|
| C <sub>s</sub> | = | steady state chamber concentration (mg m <sup>-3</sup> ), |
| N              | = | air change rate (h <sup>-1</sup> ), and                   |
| L              | = | loading factor (m <sup>-1</sup> ).                        |

Note that this method may have significant error if the emission rate is not constant and/or the chamber has not reached steady state.

Where the emission rate is not constant but there are enough chamber concentration vs. time data points (for example, 10 or more) and the data are relatively smooth, a time-dependent emission factor profile can be obtained directly from the concentration data:

$$EF(t_i) = \frac{\frac{\Delta C_i}{\Delta t_i} + NC_i}{L} \quad (3-4)$$

where:

- EF(t<sub>i</sub>) = emission factor at time t<sub>i</sub> (mg h<sup>-1</sup>),
- C<sub>i</sub> = chamber concentration at time t<sub>i</sub> (mg m<sup>-3</sup>), and
- ΔC<sub>i</sub>/Δt<sub>i</sub> = the slope of the time/concentration curve at time t<sub>i</sub> (mg m<sup>-3</sup> h<sup>-1</sup>).

The slope is approximated by the average of the slopes of two adjacent intervals:

$$\Delta C_i / \Delta t_i = \frac{\frac{C_i - C_{i-1}}{t_i - t_{i-1}} + \frac{C_{i+1} - C_i}{t_{i+1} - t_i}}{2} \quad (3-5)$$

Thus, if there are  $n + 1$  data points for concentration,  $n - 1$  emission factor values may be obtained by this method. Such calculations can be easily carried out in an electronic worksheet. Before making the calculations, make sure that replicate samples are replaced by the average values to avoid dividing by zero.

The results from this method (Equations 3-4 and 3-5) are independent of any source emission models. Additional benefits of these direct calculations include the fact that the results can be used to check the validity of a chosen model, and that they can help select the most appropriate model for further data analysis (see the following section on Using Emissions Models). Note that differential methods such as this have the potential for high levels of uncertainty. If there are sufficient data points but the random error is significant, a data smoothing process can be considered before using this method.

## Using Emissions Models

Another technique that NRMRL used to analyze the sampling results is to relate those data to models of paint emission. Those mathematical models are useful for the purpose of predicting (i.e., interpolating and extrapolating) emission rates, calculating their effect on indoor air quality (when used as input to an indoor air quality model), and conducting exposure risk assessment. When existing models, usually of an empirical nature, are not adequate, NRMRL develops new mathematical simulations (as illustrated in Chapters 5 to 9) of the time-dependent concentration data.

The simplest model that is very useful for simulating short-term paint emissions assumes that the chamber is an ideal continuously stirred tank reactor (CSTR) and that the change in emission factor can be approximated by a first-order decay, as shown below:

$$EF = (EF_0)e^{-kt} \quad (3-6)$$

where:

$$\begin{array}{ll} EF_0 & = \text{initial emissions factor, mg m}^{-2} \text{ h}^{-1}, \text{ and} \\ k & = \text{first-order decay rate constant, h}^{-1}. \end{array}$$

The corresponding chamber model is:

$$dC/dt = L(EF_0)e^{-kt} - NC \quad (3-7)$$

Which has the following solution under the condition that  $C=0$  when  $t=0$  and  $N \neq k$ :

$$C = \frac{L(EF_0)(e^{-kt} - e^{-Nt})}{N - k} \quad (3-8)$$

Equation 3-8 is the model to be used to fit the chamber concentration data using non-linear regression techniques. Using a curve-fitting program implemented on a computer requires the user to provide initial values for the parameters to be estimated (that is,  $EF_0$  and  $k$ ).

### ***Reporting the Experimental Results***

The purpose of guidelines for reporting is to ensure consistent and complete compilation of results so that other investigators can compare or repeat emissions testing on similar or new coating materials. NRMRL recommends the use the following template for the purpose of ensuring that the experimental conditions and results are documented clearly and completely:



- **Test objectives.** This section provides a clear description of the purpose of the testing program. This section should also clearly state the data quality objectives and the limiting assumptions made during the experimental design and testing phases of the research.
- **Facilities and equipment.** Here, the report gives a description of the test chambers, clean air systems, environmental measurement and control techniques, sample collection (including sorbents if used), analytical instrumentation, and standards generation and calibration.
- **Experimental design.** This section describes the test conditions, including temperature, humidity, air exchange rate, and material loading. It includes a test matrix if appropriate.
- **Sample descriptions.** This section provides a complete description of the sample(s) tested, including type of material/product, size or amount of material tested, product history, brand name (if appropriate), and sample selection process. For wet samples, one describes the sample substrate. The section also includes information about sample conditioning, including duration and environmental conditions.
- **Experimental procedures.** Here, the experimental procedures used during the testing are described. The section includes details of the sampling and analysis techniques. For wet samples, information about application method is provided here.
- **Data analysis.** This section shows the methods, including appropriate models and equations, used to analyze the chamber data to produce emission factors.
- **Results.** This section provides emission factors for each type of sample tested and for each environmental condition evaluated. Emission factors can be provided for individual organic compounds or for all organic compounds, or both. For sources with variable emission rates, the section provides appropriate rate constants.
- **Discussion and Conclusions.** Here, one discusses the relevance of the findings and provides conclusions. For example, one might describe the effect of temperature or air exchange rate on the emission factor.
- **Quality Assurance/Quality Control.** This section describes the data quality objectives and discusses the test's adherence to acceptance criteria. These are described for both environmental variables and the chemical results. The results of duplicate sampling and replicate analysis are provided here, as well as the outcome of any audits.

## Conducting Quality Assurance/Quality Control

One should prepare a quality assurance and quality control (QA/QC) plan to specify the quality requirements of the measured and reported data obtained during testing. The plan should include all facets of the measurement program from sample receipt to final review and issuance of reports. ASTM Guide D 5116 describes QA/QC activities applicable to testing emissions from paint.

NRMRL's QA/QC plan is based on established data quality objectives. These objectives are listed in Table 3-1.

**Table 3-1. Quality Control Objectives**

| Parameter                  | Precision              | Accuracy       | Completeness |
|----------------------------|------------------------|----------------|--------------|
| Temperature                | ± 0.5 °C               | ± 0.5 °C       | >90%         |
| Relative Humidity          | ± 5.0%                 | ± 10.0%        | >90%         |
| Air Flow Rate              | ± 1.0%                 | ± 2.0 %        | >90%         |
| Substrate Area             | ± 1.0%                 | Not Applicable | >90%         |
| Sample Weight <sup>a</sup> | ± 10.0%                | Not Applicable | >90%         |
| Organic Concentration      | ± 20% RSD <sup>b</sup> | Not Applicable | >90%         |
| Emission Rate              | ± 20% RSD              | Not Applicable | >90%         |

<sup>a</sup> For wet samples

<sup>b</sup> RSD=relative standard deviation=(s/m) \* 100 %, where s=estimate of the standard deviation and m=mean.

To determine the accuracy of chamber test conditions and operating parameters (temperature, air flow rate, and relative humidity), measuring devices should be calibrated with NIST-traceable primary sources. Accuracy should be established for organic concentrations by analyzing spiked samples, and a data quality objective should be established based on the data needs of the project.

The chamber's background concentrations of VOCs, formaldehyde, and other carbonyl compounds should be measured at the start of each test without the substrate in the chamber.

NRMRL's QA/QC guidelines specify that the empty chamber background should be below the following criteria:

- For total VOCs,  $10 \mu\text{g}/\text{m}^3$  or one-sixth of the lowest concentration to be measured, whichever is lower.
- For individual VOCs,  $2 \mu\text{g}/\text{m}^3$  or one-sixth of the lowest concentration to be measured, whichever is lower.

Field blanks, consisting of sorbent tubes and silica gel cartridges that are not used for sampling, should be analyzed to verify that they have not been contaminated during handling and storage.

The precision of the sampling and analysis should be determined by collecting multiple samples. Duplicate samples should be collected concurrently at selected time periods during the test. The number of duplicates for each type of sampling media should represent approximately 10% of the number of samples collected. Due to the limited volume of air available, duplicate samples can be collected for only one type of media during a sampling period, especially when low VOC concentrations dictate high sample volumes. Results from duplicate samples provide a measure of bias between samples. Replicate analysis of duplicate samples (when possible) provides a measure of precision for the analysis procedures used in the investigation.

## Chapter 4

### Characterization of Emissions of Volatile Organic Compounds from Interior Alkyd Paint

To demonstrate the usefulness of the small environmental chamber test method, this chapter describes NRMRL's technical approach to characterizing emissions from interior alkyd paints. It also provides results from NRMRL's bulk analysis of liquid paints and its measurement of VOC emissions following application. Experimental data are presented for a series of tests performed to evaluate factors that may affect emissions of VOCs from paints. Finally, the chapter describes the use of a mass balance approach to evaluate emissions test results.

Building materials are recognized as important sources of indoor air contaminants (Levin, 1989a). 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. EPA has evaluated wall paint as a source of indoor air pollution under the Indoor Air Source Characterization Project (IASCP) (Cinalli et al., 1993). 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 cited 13 references on emissions of VOCs from lacquer, paint, and varnish in his review of sources and emissions of VOCs (Wolkoff, 1995). Tichenor reported major organic compounds in a variety of building materials, including polyurethane finish, latex paint, and wood stain (Tichenor, 1987). Products with petroleum-based solvents contained alkanes (nonane, decane,

undecane), substituted alkanes, and aromatics. Emissions data have been reported for wood stain, varnish, latex paints, and alkyd paints (Tichenor and Guo, 1991; Howard et al., 1997; Krebs et al., 1995; Fortmann et al., 1998). Data from these studies have been used to develop methods and models for predicting VOC emissions from coatings used indoors (Sparks et al., 1996, Guo et al., 1996a).

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 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.

## **Experimental Work**

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 the section titled Emission Tests - Mass Balance Calculations. The liquid product was analyzed using 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).

## ***Bulk 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 (40 CFR 1996), but the analysis was not limited to quantification of only the 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 to 250 °C. The coatings were extracted by diluting 1 g of paint with 10 mL of methylene chloride. The sample was shaken for several minutes, then centrifuged for 5 minutes to remove the solids. The supernatant was analyzed by GC/MS. The compounds were identified by matching spectra using the 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 to 20 of the predominant VOCs. Blanks (solvent) and spiked controls were analyzed as part of the QA program.

## ***Small Chamber Emission Test Methods***

Small chamber emission tests were performed to measure the emission rates of the selected VOCs from the primer and paints following application to test substrates. (The basic procedures of small chamber testing are described in Chapter 3 of this document.) The emissions chamber operating conditions for the 15 tests conducted for this project were:

|                    |   |
|--------------------|---|
| Temperature:       | 23 ± 0.5 °C ,   |
| Relative humidity: | 50 ± 5% (chamber inlet air),  |
| Air exchange rate: | 0.5 ± 0.05 h <sup>-1</sup> , for a nominal ventilation rate of 0.442 L/min, and |
| Air speed:         | 10 cm/s (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 x 16 cm for a total area of 0.0256 m<sup>2</sup>, which gave a loading factor of approximately 0.5 m<sup>2</sup>/m<sup>3</sup> in the 53 L chamber. (The same loading was

used with glass.) The edges of these test specimens were sealed with sodium silicate. The bottoms 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% relative humidity (RH) for at least 24 hours 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 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. The average mass applied was  $2.8 \pm 0.3 \text{ g}/256 \text{ cm}^2$  (89  $\mu\text{m}$  wet film thickness) for the primer and  $2.3 \pm 0.3 \text{ g}/256 \text{ cm}^2$  (68  $\mu\text{m}$  wet film thickness) for the paint. The application rates were slightly lower than the manufacturer's recommended rates for wet film thickness of 100  $\mu\text{m}$  for the primer and 76  $\mu\text{m}$  for the paint, but were realistic based on the application method and visual observation. Paint was applied to the glass with a slit applicator. The slit applicator does not work well with the substrates (gypsum and pine board) the edges of which are sealed with sodium silicate because of the rough edge. 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 hour, after which the test specimen was removed from the chamber and the paint applied. In subsequent tests, the drying time was extended to 48 hours 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 effect of drying time on the recovery of VOCs during the tests. Most tests were 2 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 HPLC. During the first 10 to 20 hours 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 (EPA, 1997). 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 2-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 (ASTM, 1996) and NIOSH Method 1500 (NIOSH, 1994a). Samples were collected on commercial sorbent tubes 6 mm O.D. x 70 mm long containing two sections (50 mg/100 mg) of coconut shell charcoal. Air sample volumes of 0.5 to 3.0 L were collected at a flow rate of 200 cm<sup>3</sup>/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<sub>10</sub> 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 x 70 mm long, consisting of two sections (150 mg and 75 mg) of activated silica gel (20/40 mesh). The sampling and analysis method was a modification of NIOSH Method 2010 (NIOSH, 1994b). 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 x 6 mm O.D. containing 250 mg of 60/80 mesh Tenax TA. Sample volumes of 0.5 to 8.0 L were collected at flow rates of 50 to 200 cm<sup>3</sup>/min. The samples were analyzed by thermal desorption/GC/MS. The method was based on the EPA TO-1 method (Winnberry et al., 1988).

## DNPH-Silica Gel Samples

Air samples were collected on commercially available silica gel coated with acidified DNPH. Sample volumes of 2 to 30 L were collected at flow rates of 200 to 400 cm<sup>3</sup>/min. Analysis was performed by HPLC. The sampling and analysis method was based on EPA Method TO-11 (Winberry et al., 1988). 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 4-1). 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 TVOC content of the primer. Undecane, o-ethyltoluene, decane, and dodecane were the most abundant VOCs in Paint A-1, the paint used in most tests. The four compounds constituted 20% of the TVOC of Paint A-1. Paint A-2, with undecane, decane, o-ethyltoluene, and dodecane as the predominant compounds, was very similar to Paint A-1. Paint A-3 differed from Paints A-1 and A-2. The concentrations of the straight chain C-8 to C-12 alkanes were substantially lower in Paint A-3, and this paint contained more branched alkanes. A number of aromatics were 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

**Table 4-1. Concentrations of the Predominant VOCs in the Liquid Primer and Three Interior Alkyd Enamel Paints**

| ID | Compound                | mg/g <sup>a</sup> |            |            |            |
|----|-------------------------|-------------------|------------|------------|------------|
|    |                         | Primer            | Paint A -1 | Paint A -2 | Paint A -3 |
| 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 <sup>b</sup>  | 0.92       | 2.93       | 1.34       |
| 4  | ethylbenzene            | 0.29              | 1.10       | 1.54       | 2.05       |
| 5  | m,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       | -- <sup>c</sup>   | --         | --         | 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       |

<sup>a</sup> Mean concentration of analyses of triplicate aliquots

<sup>b</sup> BDL = below method detection limit

<sup>c</sup> Not detected

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.

The TVOC concentration, calculated by integration of all peaks in the chromatogram between toluene and tetradecane and using the average 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 determined for the primer and Paint A-1 by EPA Method 24, a gravimetric method (40 CFR 1994). The results were 333 mg/g for the primer and 331 mg/g for Paint A-1, results consistent with the manufacturer's reported volatile content of 332 mg/g and 328 mg/g for the primer and Paint A-1, respectively. The TVOC concentrations estimated for the primer (316 mg/g) and Paint A-1 (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 4-2, and include evaluation of the effect of substrate, primer, paint, previous coat, film thickness, air exchange rate, and air speed at the substrate surface.

For each test, the total mass of the individual VOCs and TVOC emitted during the 2-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 also be used to compare results from tests performed under different conditions (e.g., air exchange rate) or with different test parameters (e.g., film thickness, substrate). The mass balance was calculated as the total amount (in milligrams) of the TVOC or individual VOCs emitted during the test versus the amount (in milligrams) of the TVOC or

**Table 4-2. Matrix of Tests Performed in the Program**

| Test No. | Substrate   | Primer           | Paint | Notes                  | Test for Effect of: |
|----------|-------------|------------------|-------|------------------------|---------------------|
| 1        | Glass       | Yes <sup>a</sup> | A-1   |                        | Substrate           |
| 2        | Gypsum      | Yes <sup>a</sup> | A-1   |                        | Substrate           |
| 3        | Pine        | Yes <sup>a</sup> | A-1   |                        | Substrate           |
| 4        | Glass       | Yes              | None  |                        | Substrate           |
| 5        | Gypsum      | Yes              | None  |                        | Substrate           |
| 6        | Pine        | Yes              | A-1   |                        | Substrate           |
| 7        | Pine        | Yes              | A-1   | Replicate - Test 6     | Precision           |
| 8        | Pine        | None             | A-1   |                        | Primer              |
| 9        | Pine-Test 3 | None             | A-1   | Apply second coat      | Two coats           |
| 10       | Pine        | Yes              | A-2   |                        | Paint               |
| 11       | Pine        | Yes              | A-3   |                        | Paint               |
| 12       | Pine        | Yes              | A-1   | Velocity~3cm/s         | Air velocity        |
| 13       | Pine        | Yes              | A-1   | AER <sup>b</sup> =1.12 | AER                 |
| 14       | Pine        | Yes              | A-1   | Heavier application    | Thickness           |

<sup>a</sup> Primer dried for 1 hour before application of paint in Tests 1-3; dried for 48 hours in all other tests

<sup>b</sup> Air exchange rate, h<sup>-1</sup>

individual VOCs applied. The total mass of primer or paint applied was determined gravimetrically at the time of application. Concentration data for TVOC 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 TVOC and individual VOCs emitted was calculated as:

$$\text{Amount Emitted (mg)} = A_c(Q)$$

where:

$A_c$  = the area under the time/concentration curve, mg•h/m<sup>3</sup>; and

$Q$  = the chamber air exchange flow rate, m<sup>3</sup>/h.

The mass balance, reported as the percent of the applied VOC or TVOC 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 2-week test period. The results of the mass balance calculations are summarized in Table 4-3. The average percent TVOC recovered in the 14 tests was  $111\% \pm 20\%$ . The median recovered was 103%. The recovery of TVOC ranged from 84% to 146%, but was 84% to 110% in nine of those tests. The reason for the high recoveries in five of the tests could not be determined.

There are no criteria for determining what is an acceptable mass balance. The error in the mass balance calculation is a function of the analytical errors associated with analysis of both the liquid product and the air samples. Because more than 90% of the VOCs are emitted during the first 10 hours, the data for the samples collected on the charcoal sorbents have the greatest effect on the mass balance. Analyses of duplicate samples collected on charcoal during each test gave an average %RSD ranging from 2% to 19%. The median %RSD was below 10% for all but 1 of the 20 VOCs. ASTM Standard Practice D3687 for analysis of VOCs collected with the charcoal tube method states that a relative precision of  $\pm 15\%$  can be expected for the method (ASTM D3687, 1996).

TVOC concentrations were 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 quantification. Recoveries of 85% to 115% were achieved.

The percentage recoveries for individual VOCs were highly variable. As shown in Table 4-3, the median percentage recovered ranged from 30% for toluene to 190% for 1,3,5-trimethylbenzene. Eleven of the 20 VOCs had median recoveries between 74% and 120%. The average percentage recovery was between 80% and 127% for 12 of the 20 VOCs. Data are presented in Table 4-3 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.

**Table 4-3. Percent of the Applied VOC Mass Recovered in Emissions During 2-week Small Chamber Tests with Alkyd Primer and Paints**

| Compound                            | Amt. <sup>a</sup> | % of Applied Mass Recovered |         |         | Std. Dev. | Median |
|-------------------------------------|-------------------|-----------------------------|---------|---------|-----------|--------|
|                                     |                   | Minimum                     | Maximum | Average |           |        |
| 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-decahydronaphthalene          | 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 <sup>b</sup>         | 5                 | --                          | --      | --      | --        | --     |
| 1,2,3-trimethylbenzene <sup>c</sup> | 18                | --                          | --      | --      | --        | --     |
| isopropylbenzene <sup>d</sup>       | --                | --                          | --      | --      | --        | --     |

<sup>a</sup> Amt. = Relative amount in primer/Paint A-1 system listed in order with 1 being the most abundant VOC

<sup>b</sup> Mass balance not calculated due to analytical problems with this compound

<sup>c</sup> Most air concentrations below practical quantification limit; mass balance not calculated

<sup>d</sup> Present only in Paints A-2 and A-3; mass balance not calculated

The column, labeled “Amt.” is the relative abundance of the VOC in the primer/Paint A-1 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 4-1). 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, ethylbenzene, *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 to 4 minutes 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-1 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 4-3 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  $\pm 20\%$  is probably reasonable. This assumes that all of the VOCs are emitted from the test specimen and that the duration of the small chamber emission 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 emission 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. Geherig et al. (1993) reported that compounds with polar oxygen-containing functional groups showed reduced emissions from a low-VOC paint applied to gypsum board or wall paper as compared to applications to glass plate. They did not observe any significant effect for less polar alkanes and aromatics. Guo et al. reported similar results for latex paint applied to gypsum board (Guo et al., 1996b). 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-1) 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-1 applied to glass, gypsum board, or pine board. Emissions of decane, the most abundant VOC in the primer/Paint A-1 coating system, are depicted in Figure 4-1 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 1060, 926, and 1450 mg/m<sup>3</sup> 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<sup>3</sup> for the three substrates. There were slight differences in the mass applied during the three tests. If the peak concentrations of decane were normalized for the amount of primer and paint applied, the difference between the

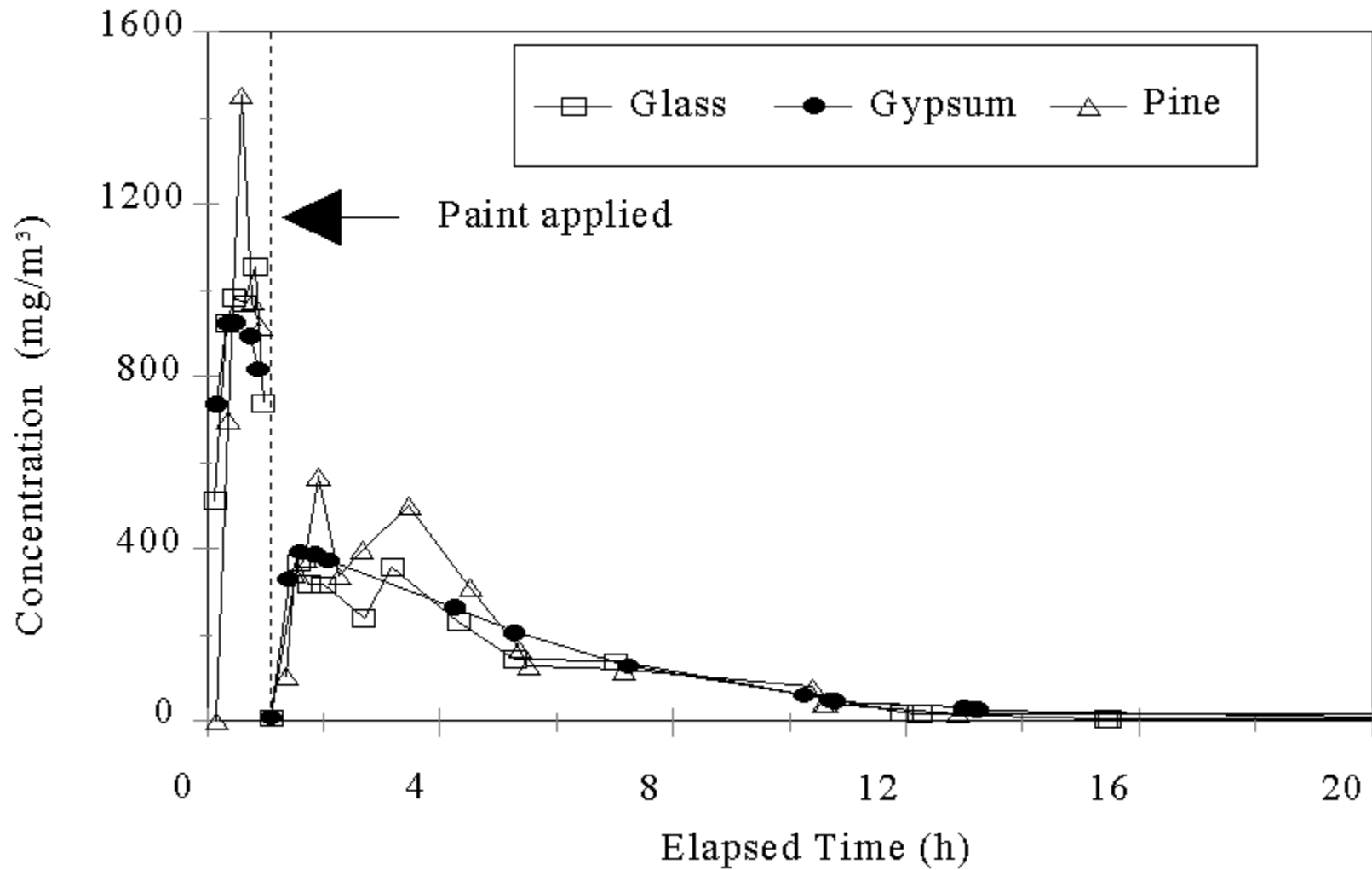


Figure 4-1. Decane emissions from alkyd primer and Paint A-1 for first 20 hours after application to glass, gypsum board, or pine board substrates.

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 the peak concentrations, the concentrations of decane in the emissions after 4 hours 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.

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 TVOC recovered in the emissions was 84%, 97%, and 133% for glass, gypsum board, and pine board, respectively. Recoveries greater than 100% occur due to substantial background emissions from the substrate or the inaccuracy 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. Therefore, the variation in recovery, ranging from 84% to 133% in these tests, is likely related to the errors associated with estimating TVOC in the product and in the emissions, as discussed in the previous section. For decane, the most abundant VOC in the primer/paint A-1 coating system, the recoveries were 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 TVOCs.

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 were not substantial when compared to the differences observed in previous tests with latex paint (Krebs et al., 1995). 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 2-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-1 to a pine board without application of the primer and comparing the results to a standard test involving application of the primer followed 48 hours later by application of Paint A-1. Results of the comparison for decane emissions are depicted in Figure 4-2. The peak concentrations and the rate of emissions during the first 20 hours 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-1 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-1 applied over the primer and 102% for Paint A-1 applied to a pine board coated with primer and Paint A-1 3 months prior to application of the second coat of Paint A-1.

### 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

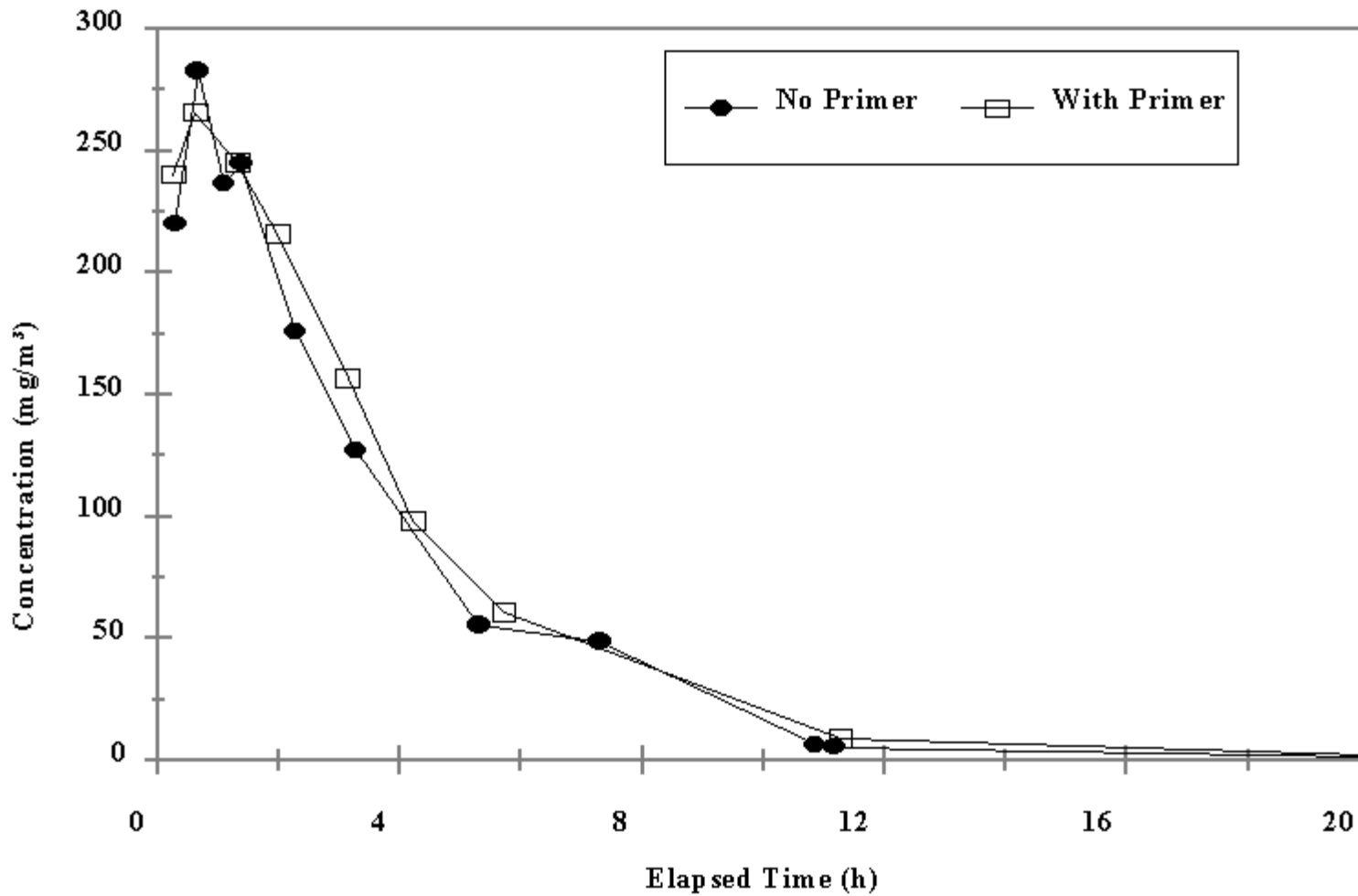


Figure 4-2. Effect of primer on short-term decane emissions from Paint A-1 applied to pine board; data presented for first 20 hours after paint application

concentration were similar in the liquid Paints A-1 and A-2 (Table 4-1). Paint A-3 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 4-3 depicts the emissions of TVOC for the three paints (the emissions from the primer applied 48 hours prior are not depicted in the figure). The TVOC emission profile was similar for Paints A-2 and A-3. The emissions from Paint A-1 were somewhat lower during the initial 4 hours 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 2-week tests. TVOC recoveries were 104%, 110%, and 94% for Paints A-1, A-2, and A-3, respectively. For decane, the recoveries were 110%, 119%, and 100%.

The emission profile depicted in Figure 4-3 was typical for the tests with the alkyd paints. The peak concentration of TVOC occurred within an hour after application. Calculated cumulative emissions showed that approximately 90% of the TVOCs were emitted during the first 10 hours following application of either the primer or paint. Within 100 hours after application, concentrations of VOCs in the test chamber dropped by 3 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 hours following application of the primer or paint and the concentrations then decreased rapidly (e.g., Figure 4-3).

### Effect of Film Thickness

The effect of film thickness on emissions has not been studied in detail (Wolkoff, 1995). Clausen 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 (Clausen, 1993). The effect of film thickness on VOC emissions from the solvent-based

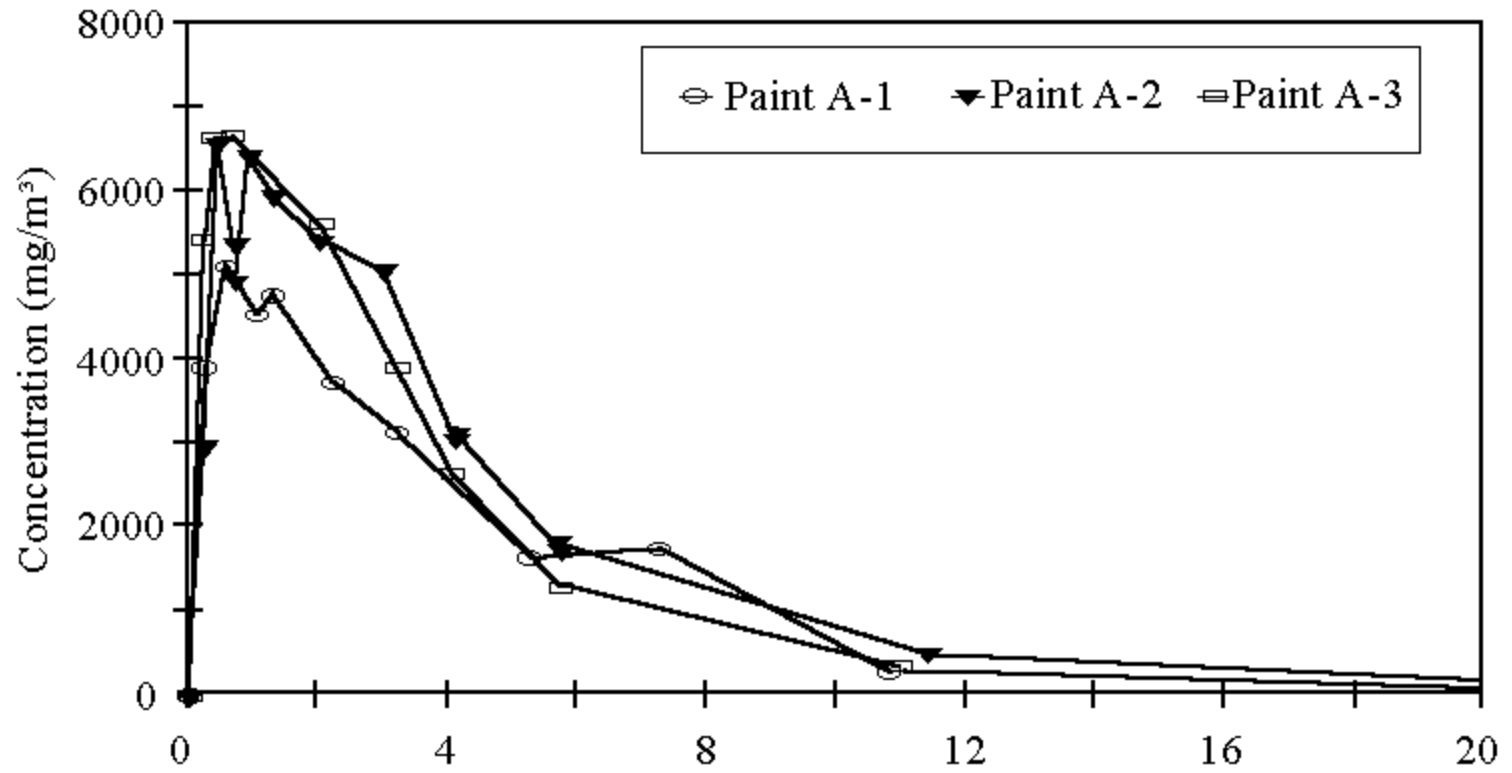


Figure 4-3. Comparison of TVOC emissions from three alkyd paints for first 20 hours after application to a pine board previously coated with primer.

Paint A-1 was evaluated by comparing an application with a paint film thickness of 59  $\mu\text{m}$  with a film thickness of Paint A-1 of 82  $\mu\text{m}$ , both on previously primed pine boards. The effect of wet film thickness on emissions of decane is depicted in Figure 4-4. 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 Air Exchange Rate

The emission rates of VOCs from wet coatings, which may be controlled by evaporation, have been shown to be affected by the air exchange rate (Tichenor, 1991; Tichenor, 1995; Wolkoff et al., 1993). For evaporative emissions, increased air exchange rates (i.e., increased ventilation) can be expected to result in lower peak VOC concentrations in the test chamber and earlier occurrence of the peak concentration. Results of the test with Paint A-1 in tests with air exchange rates of 0.5 and 1.0  $\text{hr}^{-1}$  were consistent with these predictions, as depicted in Figure 4-5 for decane.

### Effect of Air Velocity at the Surface

To evaluate the effect of air velocity at the surface on emissions, one test was conducted at 0.5 air change per hour (ACH) with a mixing fan in the chamber. With the fan, the air speed at the surface is approximately 10 cm/s. 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/s, the minimum speed that can be measured with the hot-wire anemometer. Based on theoretical predictions for gas-phase mass-transfer-controlled emissions (Tichenor et al., 1991), 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  $\text{mg}/\text{m}^3$  at 1.29 hours



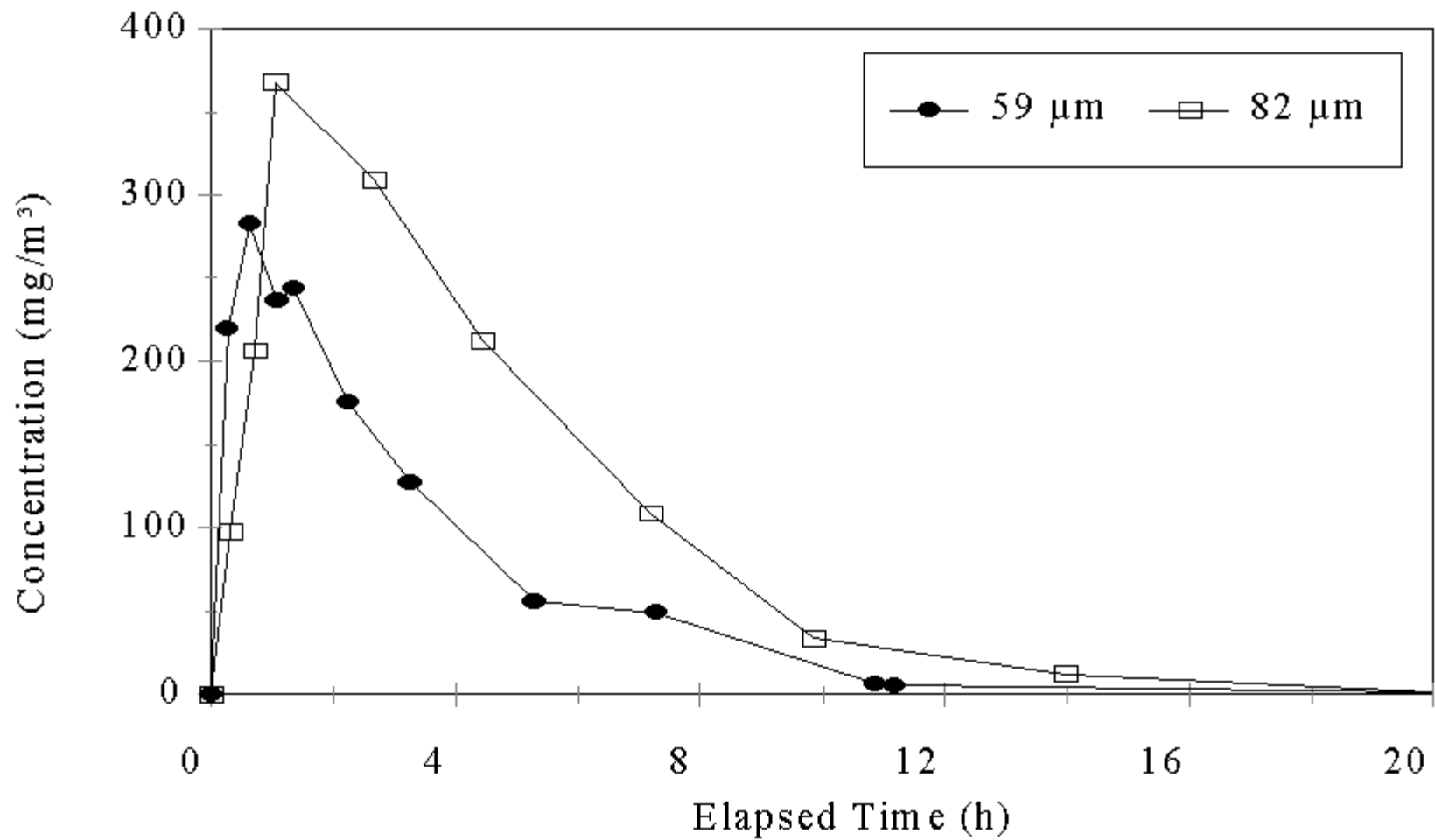


Figure 4-4. Effect of wet film thickness on short-term decane emissions from Paint A-1 during first 20 hours following application to pine board previously coated with primer.

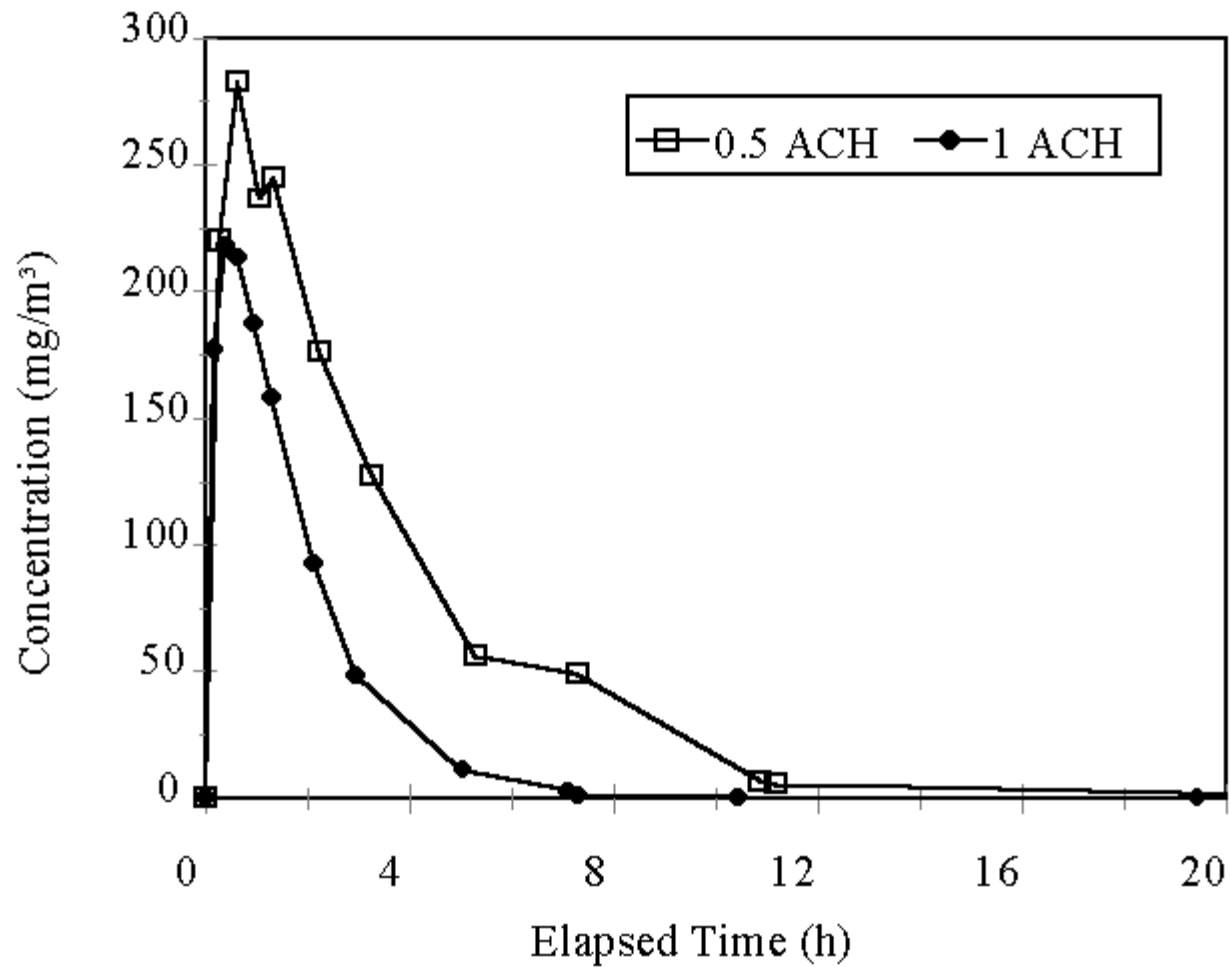


Figure 4-5. Effect of air exchange rate on short-term decane emissions during small chamber tests with Paint A-1 applied to pine board previously coated with primer.

after application, and the peak concentration of decane from the paint was 245 mg/m<sup>3</sup> at 1.36 hours after application. But in the test without the fan, the peak decane concentrations were 523 mg/m<sup>3</sup> at 2.44 hours after primer application and 164 mg/m<sup>3</sup> at 2.23 hours after paint application.

## Emissions of Aldehydes

In addition to the solvent VOCs, aldehydes—formaldehyde, acetaldehyde, propanal, pentanal, and hexanal—were detected in the emissions from the primer and paint. 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<sup>3</sup>, which was at least 2 orders of magnitude lower than the peak hexanal concentrations during the tests. The hexanal was apparently formed by oxidation (Hancock et al., 1989a and 1989b). An example of the hexanal emissions for the primer and three paints is presented in Figure 4-6. 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 2-week test periods was similar for the three paints, and (3) unlike the VOCs, hexanal emissions were not significant until about 10 hours after paint application and peaked at about 20 to 24 hours for Paint A-1. Figure 4-6 is included in this chapter for illustrative purposes only; results of the aldehyde emissions are presented in detail in Chapter 6.

## 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. Paint A-3 contained more branched alkanes. All four coatings contained low levels of aromatic compounds.

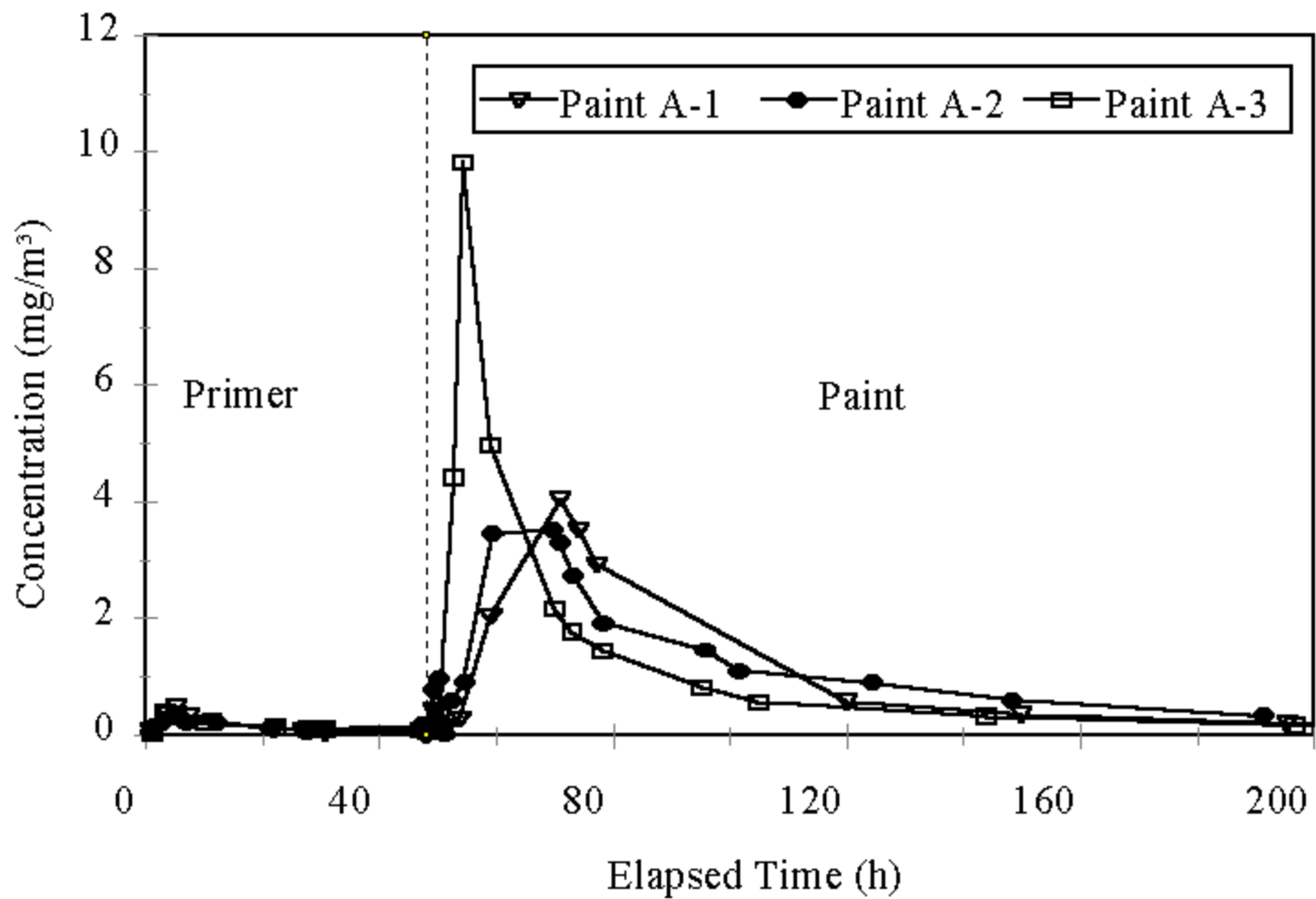


Figure 4-6. Long-term hexanal emissions from three paints applied to pine board coated 48 hours earlier with alkyd primer.

The three paints contained methyl ethyl ketoxime, but the primer did not. The TVOC 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 manufacturers' data.

Small chamber emissions tests, conducted by coating glass, gypsum board, or pine board with primer followed by application of the paint 1 hour later, demonstrated that the substrate did not have a substantial effect 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 hours 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 effects of other variables, including air velocity, air exchange rate, 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; i.e., there was 100% recovery. The data for the most abundant compounds in the paint suggest that errors of  $\pm 20\%$  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.

## Chapter 5

### Methyl Ethyl Ketoxime Emissions from Alkyd Paint

The previous chapter outlined how NRMRL's test methods have been used to characterize overall VOC emissions from alkyd paints. The goal of the present chapter is to provide an example of how these methods can be used to monitor a single chemical of concern.

Methyl ethyl ketoxime (MEKO), another name for 2-butanone oxime or ethyl methyl ketoxime [ $\text{CH}_3\text{C}(\text{NOH})\text{C}_2\text{H}_5$ , CAS Registry No. 96-29-7], is often used by paint manufacturers as an additive to interior alkyd paints (Weismantel, 1981; Turner, 1988). MEKO 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 should be less than 0.5% (Krivanek, 1982). Due to its relatively high volatility (152°C boiling point), 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. Impacts of MEKO emissions on indoor air quality and associated exposure risk are significantly affected by source characteristics such as emission rates and patterns.

MEKO has been found to be a moderate eye irritant (Krivanek, 1982). It has also been the subject of a Section 4 test rule under the Toxic Substances Control Act (Fed. Regist., 1986). Testing conducted under the test rule (Fed. Regist., 1989) has evaluated a number of toxicological endpoints for the chemical. MEKO demonstrated carcinogenic activity in long-term inhalation studies, causing liver tumors in both rats and mice. MEKO did not cause gene or chromosome mutations in standard genotoxicity studies. Nielsen et al. (1997) reviewed and evaluated

published toxicological data on noncarcinogenic effects of MEKO. No data were found on effects in humans, and inhalation studies concordant with effects in oral studies were not available. Using a safety factor to extrapolate from animals to humans, Nielsen et al. (1997) proposed a tentative health hazard indoor air exposure limit of  $0.1 \text{ mg/m}^3$  for MEKO and suggested a range of sensory irritation thresholds of 4 to  $18 \text{ mg/m}^3$ . Those indoor exposure threshold values were recommended to facilitate the evaluation of building materials and indoor climate.

The objective of NRMRL's research was to characterize the MEKO emissions from alkyd paints. Alkyd paint in general contains significant amount (e.g., 40%) of organic solvent. While solvent emissions were discussed by other papers (Fortmann et al., 1998; Chang and Guo, 1998), this research focuses on MEKO. Small environmental chambers (ASTM, 1995) were used to measure the MEKO emissions from three commonly available alkyd paints applied to pine boards. The chamber data were interpreted by a first-order decay model to simulate the time-varying emission rates. This emission model was used as input to an indoor air quality (IAQ) model to evaluate the effectiveness of exposure reduction options.

## Experimental Work

Experiments were designed to generate MEKO emission data from a newly applied alkyd paint as it dried for more than 24 hours under controlled experimental conditions. Tests were conducted in the EPA's small chamber source characterization facilities consisting of electropolished stainless steel chambers (Tichenor, 1989). The facilities allowed close control of temperature, relative humidity, and air flow rate in the chambers. Small fans were used in the chambers to provide a velocity near (1 cm above) the test surface of 5 - 10 cm/s which is typical of indoor environments. The standard test conditions were:

|                                     |                                      |
|-------------------------------------|--------------------------------------|
| Air exchange rate (N)               | $0.5 \text{ h}^{-1}$                 |
| Temperature                         | $23^\circ\text{C}$                   |
| Inlet relative humidity             | 50%                                  |
| Nominal wet paint film thickness    | $80 \mu\text{m}$                     |
| Substrate specimen surface area (A) | $0.0256 \text{ m}^2$ (0.16 x 0.16 m) |
| Chamber volume (V)                  | $0.053 \text{ m}^3$                  |
| Loading ( $L = A/V$ )               | $0.48 \text{ m}^{-1}$                |

Three commonly used alkyd paints (designated as paints A-1, A-2, and A-3) were selected, acquired, and dispensed as described in Chapter 6.

The primer and the paints were analyzed for MEKO contents by extracting a sample (usually 1g in 10 mL) of methylene chloride and analyzing the extract by GC/MS.

A pine board substrate was used in the experiments. It was prepared, loaded with paint, and placed into the small chamber as described in Chapter 6. The MEKO concentration in the clean air flowing into the chamber was virtually 0. Any MEKO emissions from the substrate would be reflected by the detection of MEKO in the exit air from the chamber.

Air samples at the chamber exit were collected on silica gel cartridges, 8 mm OD x 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 (NIOSH, 1994b). The samples were extracted with methanol and analyzed by GC/MS.

## **Results and Discussion**

### ***MEKO Contents***

Bulk analysis results showed that the primer had no detectable amount of MEKO, but all three alkyd paints tested contained an appreciable amount of MEKO. The MEKO contents of paints A-1, A-2, and A-3 were 0.96, 2.93, and 1.34 mg/g of paint, respectively. It is believed that the MEKO contents in these three paints cover the typical range of alkyd paints available in the marketplace.



## Chamber Emission Data

No MEKO was detected in the chamber air during the substrate conditioning and primer drying periods. The data indicated that there were no MEKO emissions from either the pine board or the primer, which confirmed the bulk analysis results that the primer contained no MEKO. However, significant MEKO emissions were measured for all three alkyd paints tested. The concentration profiles (time/concentration curves) of MEKO in the environmental chambers from paints A-1, A-2, and A-3 are shown in Figures 5-1, 5-2, and 5-3, respectively. It is seen that MEKO emissions occurred immediately after painting, with the chamber concentration peaking within 1 hour. Using paint A-2 as an example, Figure 5-4 shows that more than 90% of the MEKO emitted was released in less than 10 hours. The fast release of MEKO resulted in a decrease of chamber concentration by more than 2 orders of magnitude in 24 hours.

Table 5-1 lists material balance results represented by the recovery (as the ratio between MEKO emitted in the chambers and applied with the paint). The amount of MEKO applied to the pine board was estimated by multiplying the MEKO content and the quantity of each paint applied. The total amount of MEKO emitted from each paint was estimated by a procedure which integrates the concentration profile from time 0 to 24 hours. Table 5-1 indicates that the recovery ranged from 68% to 105%, which suggests that most of the MEKO in the paints was emitted.

**Table 5-1. Recovery of MEKO**

|           | MEKO Applied,<br>mg/m <sup>2</sup> | MEKO Emitted <sup>a</sup> ,<br>mg/m <sup>2</sup> | Recovery<br>(Emitted/Applied),<br>% |
|-----------|------------------------------------|--|-------------------------------------|
| Paint A-1 | 64.4                               | 43.5   | 68                                  |
| Paint A-2 | 241                                | 252  | 105                                 |
| Paint A-3 | 110                                | 97.8   | 89                                  |

<sup>a</sup> Estimated by integration of the first 24 h chamber concentration data.

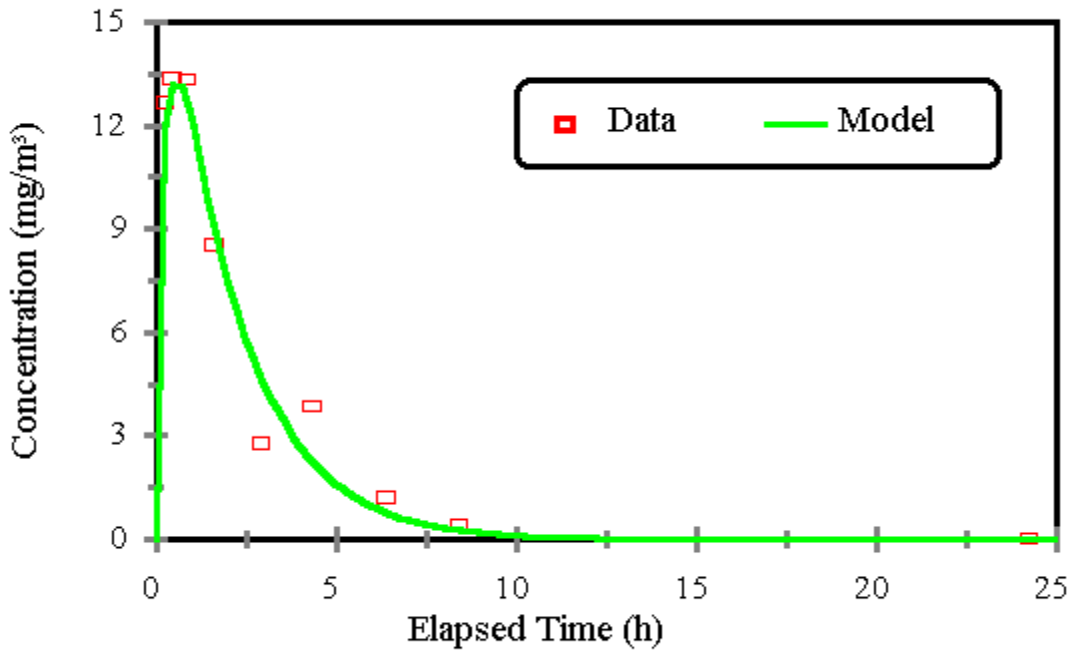


Figure 5-1. Chamber concentrations resulting from the MEKO emissions from Paint A-1.

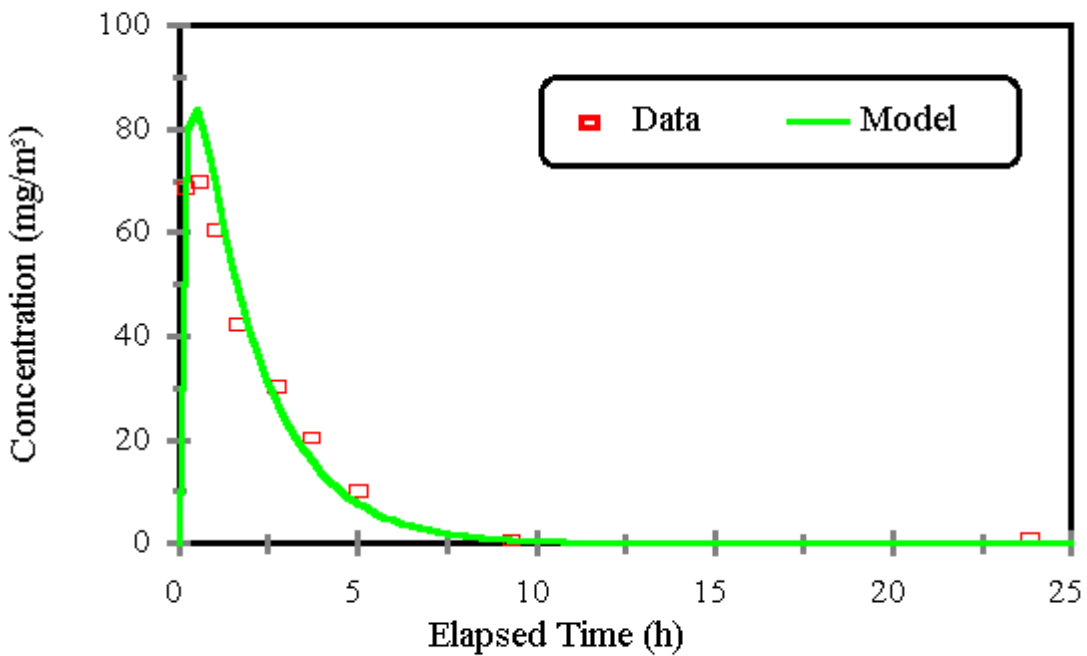


Figure 5-2. Chamber concentrations resulting from the MEKO emissions from Paint A-2.

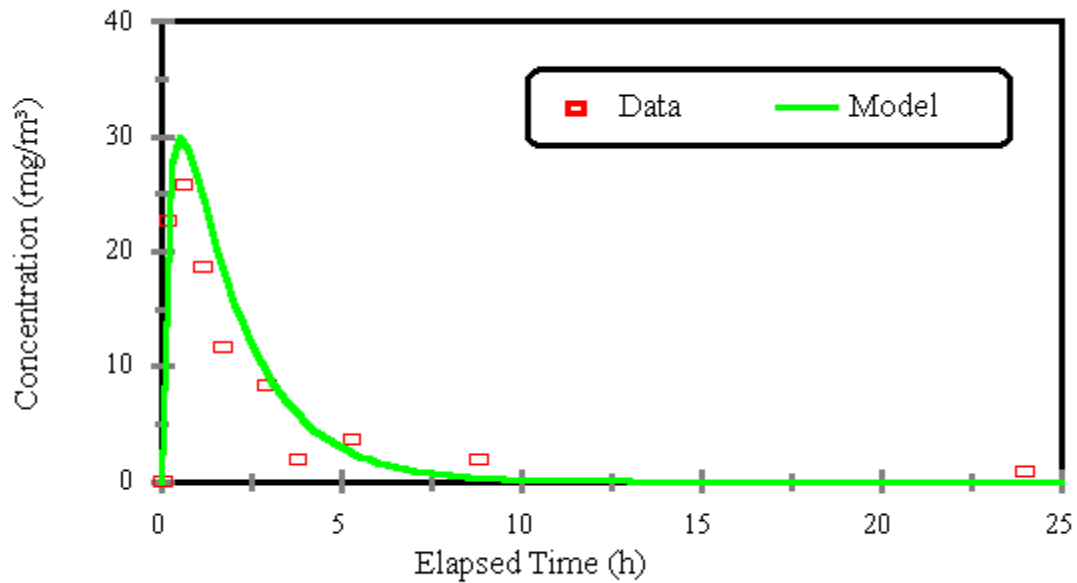


Figure 5-3. Chamber concentrations resulting from the MEKO emission from

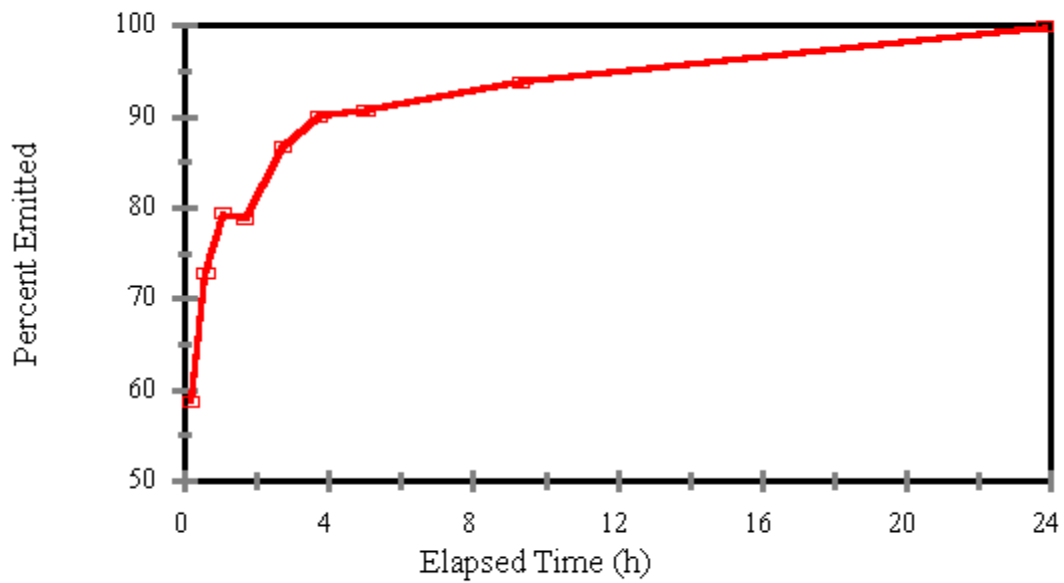


Figure 5-4. Cumulative MEKO emissions for Paint A-2 (calculated from chamber concentration data).

## **MEKO Emission Model**

Assuming the MEKO emissions are an evaporation-like process controlled by gas-phase mass transfer, it was found that the chamber concentration data can be simulated by a first-order decay model (Guo et al., 1990; Clausen, 1993).

$$EF = M_o k e^{-kt} \quad (5-1)$$

where

|                |   |  |
|----------------|---|--|
| EF             | = | MEKO emission factor (mg/m <sup>2</sup> /h),                   |
| M <sub>o</sub> | = | initial amount of MEKO in the paint film (mg/m <sup>2</sup> ), |
| k              | = | first-order decay rate constant (h <sup>-1</sup> ), and        |
| t              | = | time elapsed (h).  |

Assuming the chamber air was well-mixed, mass balance equations give the following expression for the chamber air MEKO concentration, C:

$$C = \frac{L M_o k}{N - k} (e^{-kt} - e^{-Nt}) \quad (5-2)$$

If one uses the total amount of MEKO emitted listed in Table 5-1 as the value of M<sub>o</sub> for each paint, there is only one unknown parameter, k, in Equation (5-2). The values of the unknown parameter were estimated by the best fit of Equation (5-2) to the chamber concentration profiles shown in Figures 5-1 to 5-3 using a non-linear regression method.

Table 5-2 shows the estimated values of k and normalized mean square error (NMSE) which is a parameter recommended by a standard guide of the American Society for Testing and Materials (ASTM, 1995) to reflect the goodness-of-fit of the model for each paint tested. Comparing the value of k with the MEKO content in each paint, the data seem to suggest that there is a linear relationship between them. The values of k shown in Table 5-2 are also within the range expected for emissions controlled by the gas-phase mass transfer process (Sparks et al., 1996). The goodness-of-fit of the model was represented by NMSE which is a measure of the

**Table 5-2. Estimated Values of Model Parameter and Goodness-of-Fit to the Chamber Concentration Data**

|           | <b>k, h<sup>-1</sup></b> | <b>Normalized Mean Square Error<sup>b</sup></b> | <b>MEKO in Paint, mg/g</b> |
|-----------|--------------------------|---|----------------------------|
| Paint A-1 | 3.83±0.59 <sup>a</sup>   | 0.056   | 0.96                       |
| Paint A-2 | 5.19±1.20 <sup>a</sup>   | 0.071   | 2.93                       |
| Paint A-3 | 4.17±1.48 <sup>a</sup>   | 0.219   | 1.34                       |

<sup>a</sup> Mean ± standard deviation

<sup>b</sup> A value of 0 indicates perfect agreement for all pairs of observed and predicted values. A value near 0.2 indicates differences of about 50%.

magnitude of prediction error relative to the predicted and measured values (ASTM, 1995). The ASTM standard guide suggests that, considering the potential consequences of measurement uncertainties, a NMSE value of 0.25 or less can be taken as generally indicative of adequate model performance (ASTM, 1995). Table 5-2 shows that the NMSE values for the three paints tested are all less than 0.25, which indicates that the first-order decay model is adequate for predicting MEKO emissions.

### ***Indoor Air Quality Impact Assessment***

The impact of alkyd paint MEKO emissions on indoor air quality (IAQ) was assessed by a case study which assumed that an alkyd paint was used to paint the trim, cabinetry, inside doors, and frames of an EPA IAQ test house. The test house is an unfurnished, single-story, wood-frame house with a central heating and air-conditioning system. The house contains three bedrooms, a kitchen, a living room, a dining area, a den, and two full baths. The detailed floor plan of the IAQ test house was reported elsewhere (Chang and Guo, 1994). The volume of the house (not including the attic and the crawl space) was estimated to be 305 m<sup>3</sup>. The total area to be painted (trim, cabinetry, and inside doors and frames) was estimated to be 80 m<sup>2</sup>. The painting was assumed to be performed in two periods (one in the morning and the other in the afternoon) in a single day. The morning period started (t = 0) at 9 AM and lasted for 3 h. There was a 1 h lunch

break between the morning and the afternoon periods. The afternoon period started at 1 PM and lasted for another 3 h. The painting was conducted continuously and evenly throughout the two 3 h working periods.

To simplify the calculations, the indoor air in the whole house was assumed to be well-mixed and can be represented by a one-compartment model. No sink effects were accounted for due to the lack of sink data. To assess the impact of MEKO emissions on IAQ, a continuous-application source model was used. The model assumed that one coat of the alkyd paint was applied to the surfaces at a constant rate. The approach was to break up the application into many differential areas, and each area began emitting once the paint was applied. Evans (1996) established the mathematical models for three types of continuous-application emission sources. The analytical solution of the one-compartment model with a first-order decay emission source is:

$$C(t) = \frac{a(t) - a(t - q) H(t - q)}{V} \quad (5-3)$$

$$a(t) = \frac{k M_{tot}}{q} \left[ \frac{1}{Nk} + \frac{1}{k(k - N)} e^{-kt} - \frac{1}{N(k - N)} e^{-Nt} \right] \quad (5-4)$$

$$H(t - q) = \begin{cases} 0, & t < q \\ 1, & t \geq q \end{cases} \quad (5-5)$$

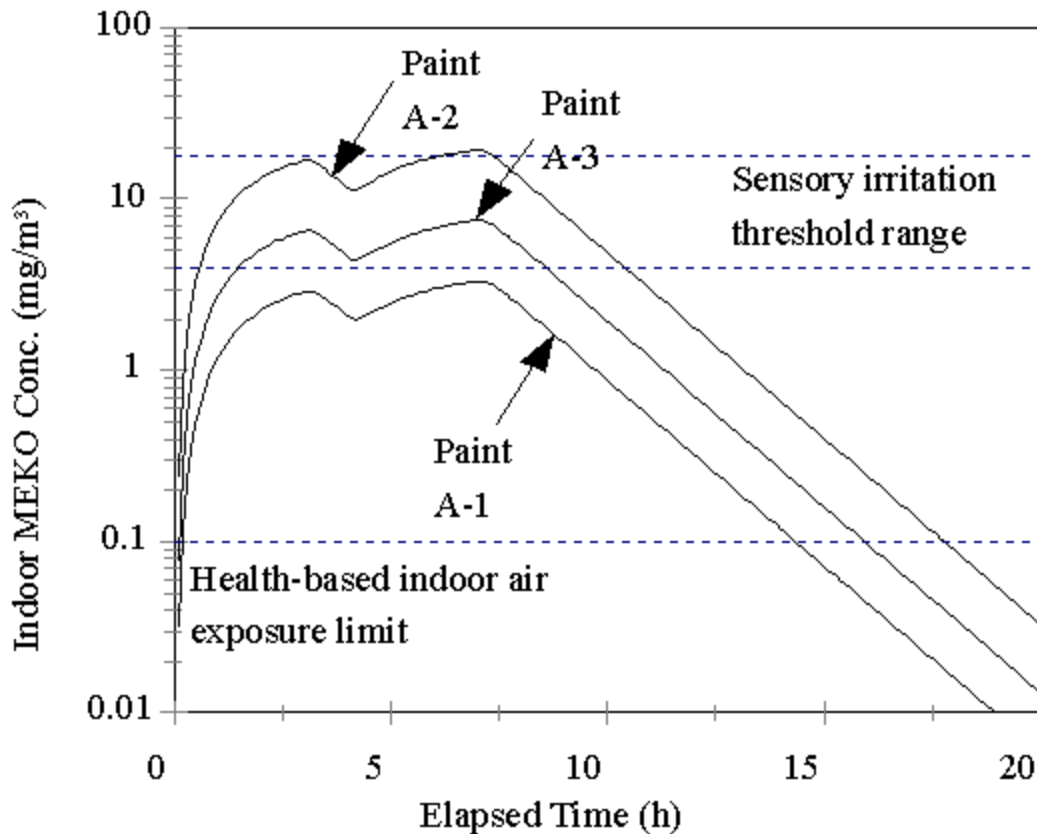
where

- q = the paint application time of each painting period (h),
- a(t) = time shift term in Equation (5-3),
- H(t-q) = Heaviside operator (O'Neil, 1991),
- V = volume of the test house (m<sup>3</sup>), and
- M<sub>tot</sub> = total amount of emittable MEKO in the applied paint during each painting period (mg).

The MEKO concentrations in the test house with an air exchange rate of 0.5 h<sup>-1</sup> during and after the painting, as predicted by the model for the three alkyd paints, are shown in Figure 5-5. It is seen that the MEKO concentration rises sharply right after the painting started and reaches a

peak at the end of the morning period. The MEKO concentration declines slightly between the 4th and 5th h which reflects the 1 h lunch break. The MEKO concentration rises again after the afternoon painting period started and reaches another peak at the end. After all the painting is finished, the MEKO concentration decreases continuously.

Compared with the suggested indoor air exposure limit of  $0.1 \text{ mg/m}^3$ , Figure 5-5 shows that the test house MEKO concentration exceeded the limit for all three alkyd paints. The episode of IAQ deterioration started at the beginning of the painting and lasted for more than 7 h after the



**Figure 5-5. Comparison of the predicted test house MEKO concentrations with the suggested indoor exposure thresholds.**

painting. The test house MEKO concentration also exceeded the lower limit of the suggested sensory irritation range when paints A-2 and A-3 were used.

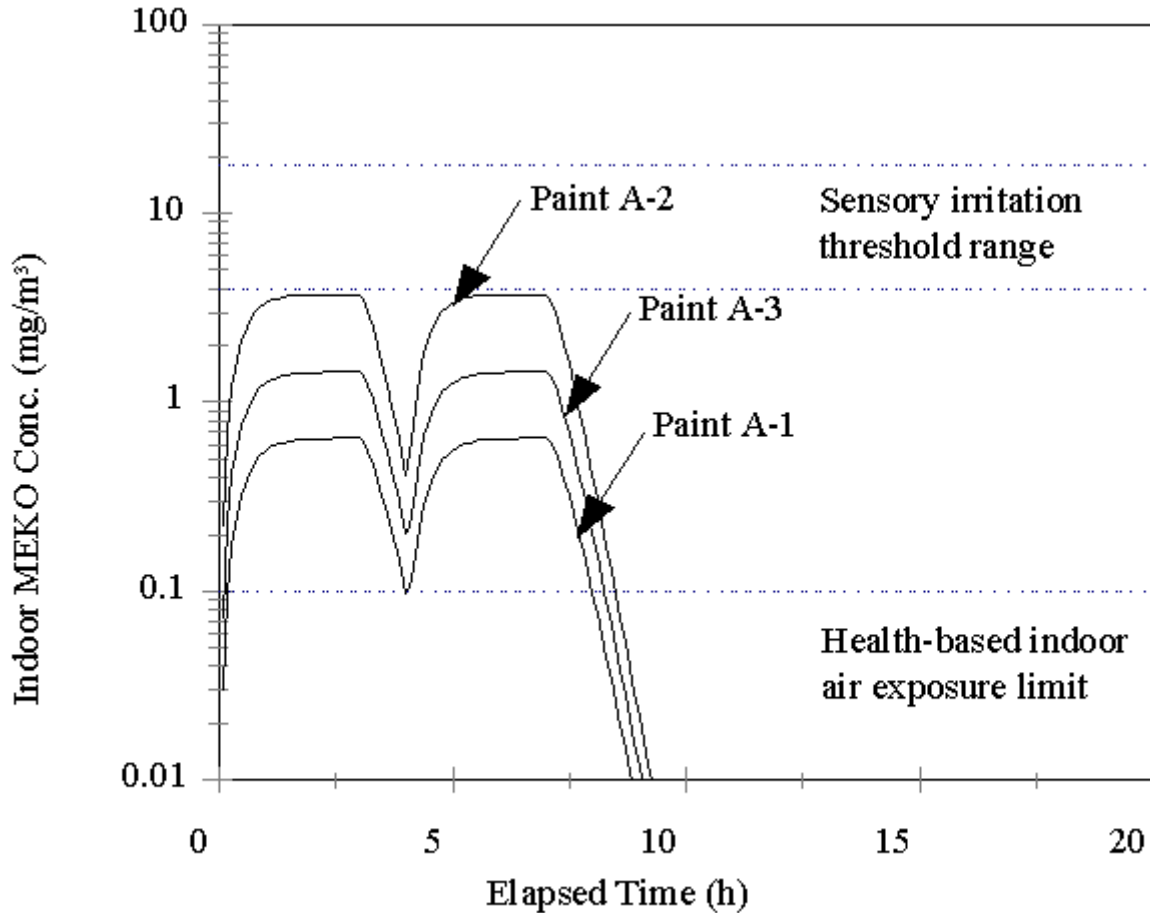
## ***Exposure Reduction Assessment***

To reduce the exposure potential, alkyd paint with lower MEKO content should be selected. Figure 5-5 shows that the peak MEKO concentration was reduced by more than 80% when paint A-1 (with 0.96 mg of MEKO/g of paint) was used instead of paint A-2 (with 2.93 mg of MEKO/g of paint). Figure 5-5 also shows that using the paint with lower MEKO content can decrease the duration of concentration elevation after the painting.

The exposure potential to MEKO can also be reduced by increased ventilation. Figure 5-6 shows that, if the air exchange rate of the case previously discussed were increased to  $3.0 \text{ h}^{-1}$ , the test house MEKO concentration could be maintained below the sensory irritation threshold range during and between the two painting periods (hour 0 to 7 in Figure 5-6) even when paint A-2 was used. The test house MEKO concentration also decreased rapidly after the painting, and fell below the suggested indoor air exposure limit of  $0.1 \text{ mg/m}^3$  within 2 h (between hours 7 and 9 in Figure 5-6).

Since Equations (5-3) and (5-4) indicate that the indoor MEKO concentration increases are proportional to the total amount of emittable MEKO in the applied paint ( $M$ ), another exposure reduction option can be the division of the whole paint work into several small jobs. Only a small area is painted during each paint job, and plenty of air-out time (more than 12 h) should be allowed between the jobs. For example, when paint A-1 is used and the painted area is





**Figure 5-6. Predicted test house MEKO concentrations at high (3.0 h<sup>-1</sup>) air exchange rate.**

<1.6 m<sup>2</sup>, the test house MEKO concentration can be maintained < 0.1 mg/m<sup>3</sup> at an air exchange rate of 3.0 h<sup>-1</sup>. The MEKO concentration in the test house can be further reduced if the source room can be isolated from the rest of the house and high local ventilation (e.g., 3 h<sup>-1</sup>) is implemented in the source room.

**Conclusions**

Bulk analysis showed that the MEKO content in alkyd paints can be as high as several milligrams per gram. Material balance from the chamber tests indicated that the majority (more

than 68%) of the MEKO in the paint applied was emitted. Due to the relatively fast emission pattern, more than 90% of the MEKO emissions occurred within 10 hours after painting. The alkyd paint MEKO emissions can be simulated by a first-order decay model. The model indicated that the MEKO emission is mostly gas-phase mass transfer controlled.

The first-order decay model can be used as 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. The IAQ model indicated that MEKO emitted from alkyd paints can cause indoor MEKO concentration to exceed suggested indoor exposure limits. The elevated MEKO concentrations can last for more than 10 h after the painting is finished. The indoor MEKO concentration can be reduced by selection of lower MEKO alkyd paint, implementation of higher ventilation, and isolation of the source room with local ventilation. The higher ventilation should be maintained about 2 h after the painting is finished to avoid exposure to residual MEKO emissions.

## Chapter 6

### New Findings About Aldehyde Emissions from Alkyd Paint

Using the small chamber apparatus as the basis of their testing methods, NRMRL staff have made significant discoveries about the behavior and emissions of alkyd paints in the *actual conditions* in which they are used. For example, NRMRL found that some alkyd paints release odorous aldehyde compounds that are generated as the paint dries in a film. Only by analyzing the gaseous emissions of a test material covered with alkyd paint was NRMRL able to detect and model the generation of such compounds.

The unpleasant “after-odor” which can persist for weeks after application of alkyd paint has been the cause of customer complaints and indoor air quality (IAQ) concerns. Hancock et al. (1989a and 1989b) investigated the byproducts produced during the drying of a number of oil-modified alkyd resins. They found that a number of odorous aldehydes were produced from the reactions between unsaturated fatty acids and oxygen during the drying process of an alkyd-based paint film

The unsaturated fatty acids, mostly derived from naturally occurring vegetable oils, are usually included in alkyd paints to facilitate the formation of a polymer film. After alkyd paint is applied to a surface at room temperature, the unsaturated fatty acids in the paint undergo spontaneous reactions with atmospheric oxygen (autoxidation reaction) to produce hydroperoxides (Porter et al., 1980). Under the influence of suitable promoters (catalysts) such as cobalt, lead, benzil, or methanesulphonic acid, the hydroperoxides decompose to give free radicals. The free radicals generated are responsible for the subsequent cross-linking of the polyester polymers (the alkyd resins) by hydrogen abstraction, dimerization, or some other mechanism to form a paint film with desirable physical/chemical properties. However, the hydroperoxides not only generate free radicals, but also decompose by fragmentation to give

byproducts, mainly aldehydes with lesser amount of ketones and alcohols. These byproducts are responsible for the characteristic acrid odor during the drying process of alkyd paint since many of the aldehydes formed are volatile and have pungent odors.

The objective of the research work described in this chapter of the report is to characterize aldehyde emissions from alkyd paints. Small environmental chambers (ASTM D5116, 1990) were used to measure the aldehyde emissions from three commercially available alkyd paints applied to pine boards. The major aldehyde species emitted were identified, and the emission rates of the most abundant one, hexanal, were quantified. The chamber data were analyzed by a consecutive first-order reaction model to identify the rate-controlling step. The model, finally, was used to simulate IAQ for the prediction of hexanal concentrations.

## Experimental Work

Experiments were designed to generate aldehyde emission data from a newly applied alkyd paint as it dried for more than 100 hours under controlled experimental conditions. Tests were conducted in EPA's small chamber source characterization facilities consisting of electropolished stainless steel chambers (Tichenor, 1989). The facilities allowed close control of temperature, relative humidity, and air flow rate in the chambers. Small fans were used in the chambers to provide a velocity near (1 cm above) the test surface of 5 -10 cm/s which is typical of indoor environments. The standard test conditions were:

|                                  |                                       |
|----------------------------------|---------------------------------------|
| Air exchange rate (N)            | 0.5 h <sup>-1</sup>                   |
| Temperature                      | 23°C                                  |
| Inlet relative humidity          | 50%                                   |
| Nominal wet paint film thickness | 80 μm                                 |
| Substrate specimen surface area  | 0.0256 m <sup>2</sup> (0.16 x 0.16 m) |
| Chamber volume                   | 0.053 m <sup>3</sup>                  |
| Loading (L)                      | 0.48 m <sup>2</sup> /m <sup>3</sup>   |

Three commonly used alkyd paints, designated as paints A-1, A-2, and A-3, manufactured by three major U.S. paint companies were acquired for testing (Table 6-1). Those

**Table 6-1. Information About the Primer and Three Test Paints**

| <b>Product Code Name</b>       | <b>Primer</b>      | <b>Paint A -1</b> | <b>Paint A -2</b>  | <b>Paint A -3</b>                                |
|--------------------------------|--------------------|-------------------|--------------------|--|
| Paint Type                     | --                 | semi-gloss        | gloss              | gloss  |
| Color                          | white              | seafoam           | no pigment         | no pigment                                       |
| Density (g/cm <sup>3</sup> )   | 1.33               | 1.26              | 1.10               | N/A <sup>a</sup>                                 |
| Recommended Wet Film Thickness | 4 mils<br>(102 μm) | 3 mils<br>(76 μm) | 4 mils<br>(102 μm) | 46.4-51.0 m <sup>2</sup> /gal.<br>(74.2-81.4 μm) |

<sup>a</sup> not available

alkyd paints were selected after consulting with paint suppliers on the popularity of medium-priced paints. The purchased paint was mixed in cans and then split into 150 mL amber vials. Each vial was used for only one test.

The paints were analyzed for hexanal (the most abundant aldehyde emitted) contents by extracting a paint sample (usually 1 g) in 10 mL methylene chloride and analyzing the extract by GC/MS.

A pine board purchased from a local lumber supplier was used as the substrate. The board was cut into 16 x 16 cm sections and the exposed edges were sealed with sodium silicate solution to minimize any adsorption of aldehydes. For each experiment, the pine board substrate was first treated with a primer recommended by paint suppliers. Experimental data showed that the primer (Table 6-1) emits far less (more than an order of magnitude) hexanal than the paints. After 48 hours of drying, an alkyd paint was applied to one side (the side to be exposed to chamber air) of the substrate specimen using a roller. The mass applied was determined using a protocol involving weighing of the substrate before and after the application. The painted samples were placed in the chamber promptly (within 3 minutes after paint application). The test start time (t=0) was established when the door to the chamber was closed. The chamber was flushed with clean air (<5 μg/m<sup>3</sup> VOCs) before each test. A typical test lasted for about a week with the clean air flow through the chamber continued at a controlled rate.

Air samples in the chamber outlet were collected based on EPA Method IP-6A (Winnberry et al., 1990) using 55 to 105  $\mu\text{m}$  chromatographic-grade silica gel coated with acidified 2,4- dinitrophenylhydrazine (DNPH). Sample volumes ranged from 2 to 30 L with sample flow in the range of 200 to 400  $\text{cm}^3/\text{min}$  controlled by mass flow controllers. Each sample was extracted with 5 mL acetonitrile (ACN). Twenty-five  $\mu\text{L}$  of extract was analyzed on a Hewlett Packard 1090 high-performance liquid chromatograph (HPLC). Chromatography was performed with a C-18 reverse-phase column (4.6 x 250 mm) using a gradient program of 45% ACN to 30 minutes, then 75% ACN to 35 minutes, then 100% ACN to 41 minutes, and finished with 45% ACN to 55 minutes.

The HPLC was calibrated for nine carbonyl compounds: formaldehyde, acetaldehyde, propanal, benzaldehyde, pentanal, m-tolualdehyde, methyl isobutyl ketone, hexanal, and heptanal. The nine targeted compounds were identified by comparison of their chromatographic retention times with those of the derivatized standards. Quantification was performed using an external standard method with a five-point calibration based on peak area of derivatized standards. Performance of the instrument was verified each day by analysis of a quality control check sample prior to starting the sample analysis.

## **Results and Discussion**

### ***Bulk Analysis for Hexanal***

No detectable amount of hexanal was found in any of the three alkyd paints tested. The detection limit of bulk analysis was determined by the analytical instrument, the sample size, and the extraction/dilution procedures. Typically, the instrument detection limit for hexanal was about 3 ng. Taking into account the 1.0  $\mu\text{L}$  injection and the 10 mL extraction of 1 g of paint, this detection limit corresponds to 0.03 mg of hexanal per gram of paint. Therefore, the bulk analysis results indicated that the hexanal content in any of the three alkyd paints tested was below 0.03 mg/g.

## ***Chamber Emission Data***

Significant aldehyde emissions were detected by DNPH sampling of the chamber air for all three alkyd paints tested. All nine carbonyl compounds that HPLC was calibrated with were detected in the chamber air samples. The three most abundant carbonyl compounds detected from each paint are listed in Table 6-2. The emission profiles (time/concentration curves) of the common most-abundant aldehyde, hexanal, from paints A-1, A-2, and A-3 are presented in Tables 6-3 to 6-5 and Figures 6-1 to 6-3. It is seen that, for each paint, the hexanal concentration in the chamber remained low for the first few hours after painting. Later, the hexanal concentration increased to reach a peak followed by a relatively slow decay which lasted for more than 100 hours.

The total amount of hexanal emitted from each paint, as shown in Table 6-2, was estimated by integrating the time/concentration curves from time 0 to 200 h. The amount of hexanal emitted was greater than 2 mg/g which confirms that hexanal was formed after painting since the bulk analysis did not detect any hexanal.

**Table 6-2. The Total Emissions for the Three Most Abundant Aldehydes  
(in mg/g paint)**

|          | <b>Paint A -1</b> | <b>Paint A -2</b> | <b>Paint A -3</b> |
|----------|-------------------|-------------------|-------------------|
| Hexanal  | 2.04              | 2.33              | 2.48              |
| Pentanal | 0.26              | 0.33              | 0.48              |
| Propanal | 0.08              | 0.26              | 0.30              |



**Table 6-3. Hexanal Concentration in Test Chamber for Alkyd Paint A-1**

| <b>Elapsed<br/>Time (h)</b> | <b>Concentration<br/>(mg/m<sup>3</sup>)</b> |
|-----------------------------|---|
| 1.14                        | 0.045                                       |
| 2.30                        | 0.032                                       |
| 2.30                        | 0.035                                       |
| 3.37                        | 0.029                                       |
| 4.54                        | 0.043                                       |
| 6.24                        | 0.321                                       |
| 6.24                        | 4.67  |
| 10.93                       | 5.12  |
| 20.38                       | 4.16  |
| 22.49                       | 3.53  |
| 26.79                       | 1.56  |
| 26.79                       | 1.25  |
| 30.45                       | 0.768                                       |
| 48.00                       | 0.225                                       |
| 53.86                       | 0.114                                       |
| 71.47                       | 0.118                                       |
| 173.74                      | 0.079                                       |

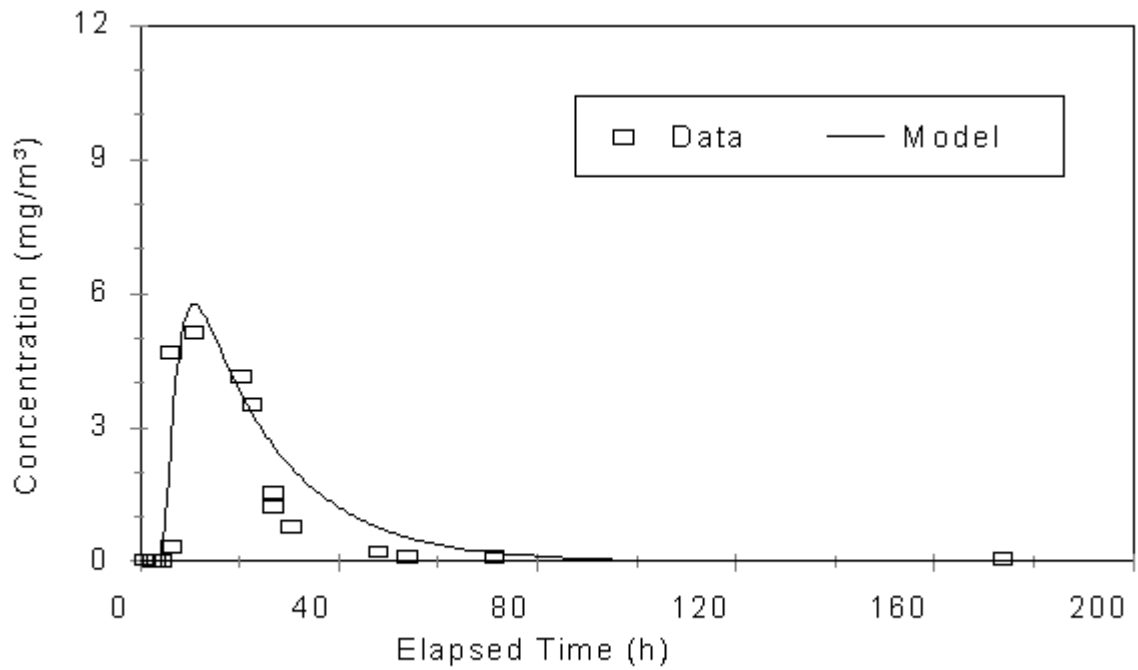
**Table 6-4. Hexanal Concentration in Test Chamber for Alkyd Paint A-2**

| <b>Elapsed<br/>Time (h)</b> | <b>Concentration<br/>(mg/m<sup>3</sup>)</b> |
|-----------------------------|---|
| 1.20                        | 0.777                                       |
| 2.30                        | 0.975                                       |
| 2.30                        | 0.930                                       |
| 4.56                        | 0.570                                       |
| 6.55                        | 0.785                                       |
| 6.55                        | 1.02  |
| 11.43                       | 3.44  |
| 21.61                       | 4.46  |
| 21.61                       | 2.59  |
| 23.07                       | 3.29  |
| 25.20                       | 2.85  |
| 25.20                       | 2.62  |
| 30.51                       | 1.92  |
| 47.83                       | 1.45  |
| 53.63                       | 1.10  |
| 76.41                       | 0.896                                       |
| 100.37                      | 0.590                                       |
| 143.61                      | 0.328                                       |

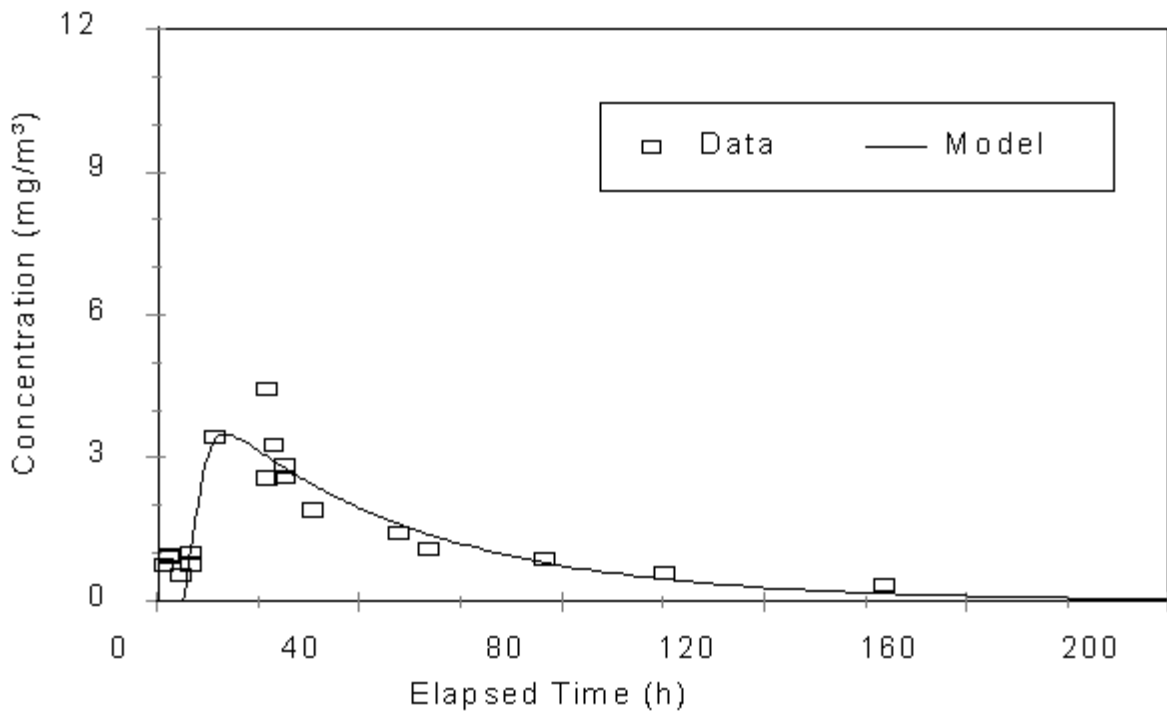
**Table 6-5. Hexanal Concentration in Test Chamber for Alkyd Paint A-3**

| <b>Elapsed Time (h)</b> | <b>Concentration (mg/m<sup>3</sup>)</b> |
|-------------------------|---|
| 0.33                    | 0.051 <sup>a</sup>                      |
| 1.26                    | 0.142                                   |
| 2.37                    | 0.375                                   |
| 4.63                    | 4.42                                    |
| 6.38                    | 9.82                                    |
| 10.99                   | 4.98                                    |
| 22.19                   | 2.15                                    |
| 25.00                   | 1.77                                    |
| 30.13                   | 1.44                                    |
| 47.17                   | 0.811                                   |
| 56.80                   | 0.562                                   |
| 95.88                   | 0.325                                   |
| 148.96                  | 0.167                                   |
| 195.83                  | 0.122                                   |

<sup>a</sup> Below practical quantification limit, but above method detection limit.



**Figure 6-1. Hexanal emission from Paint A-1 and modeling results.**



**Figure 6-2. Hexanal emission from Paint A-2 and modeling results.**

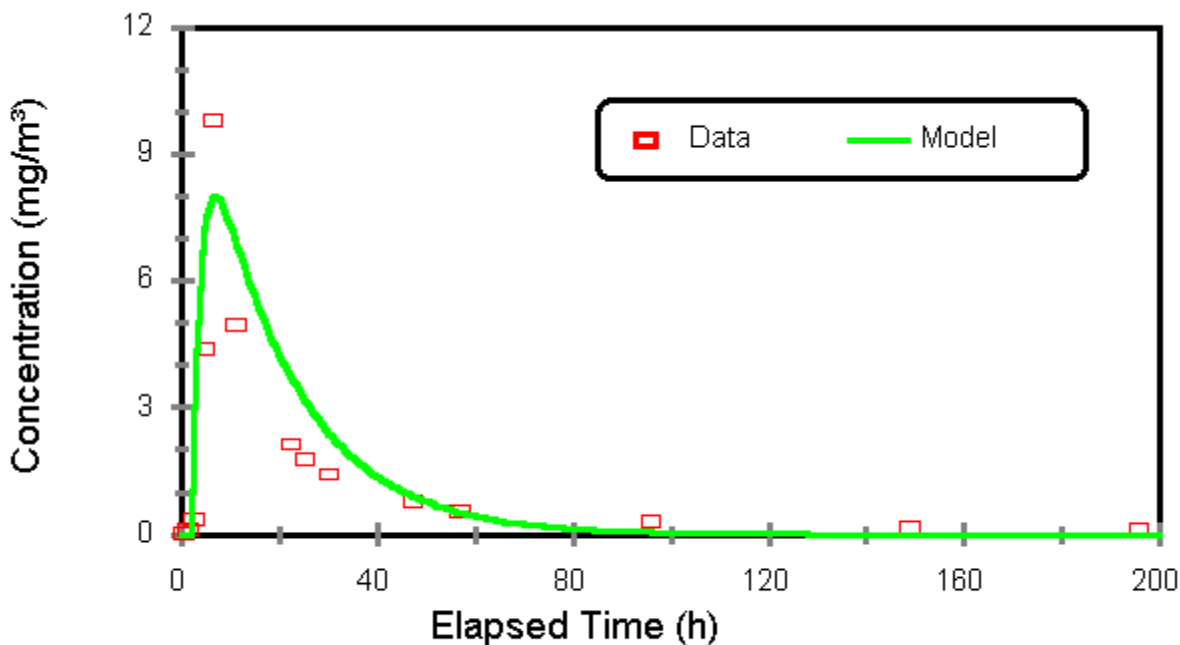
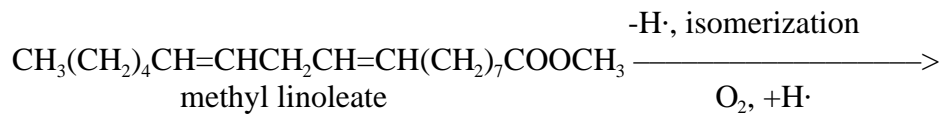
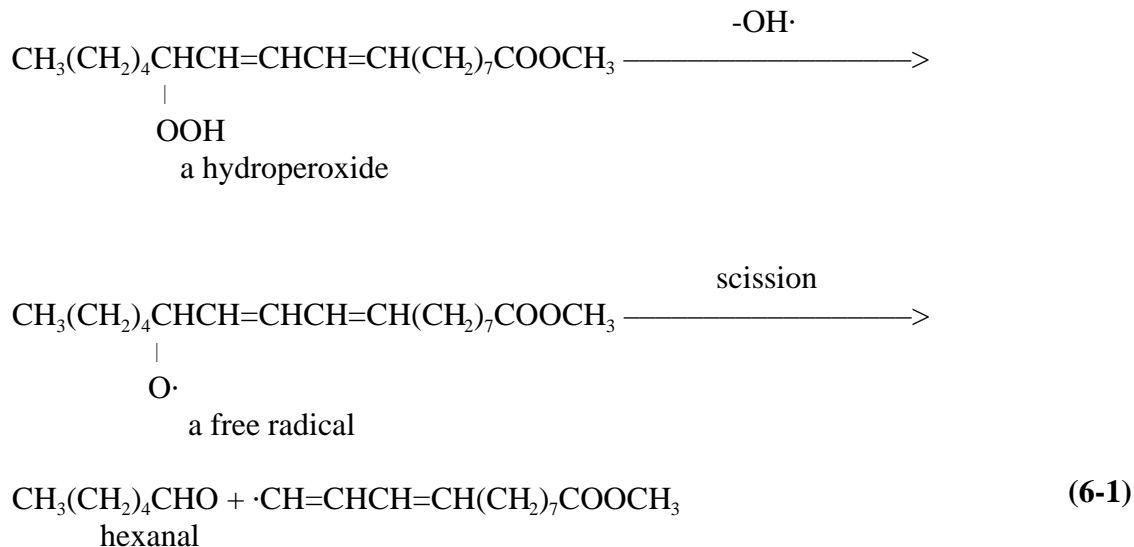


Figure 6-3. Hexanal emission from Paint A-3 and modeling results.

### Hexanal Formation Mechanism

Hancock et al. (1989a and 1989b) found hexanal as one of the major volatile byproducts resulting from the autoxidation reaction of fatty acids. The autoxidation and hexanal formation process can be accounted for by a chain reaction mechanism as illustrated by the following fragmentation scheme involving the ester of a fatty acid, methyl linoleate.





The above-mentioned hexanal formation mechanisms indicate that oxygen from the air is needed for the autoxidation reactions. It is known that, after the alkyd paint is applied to a substrate, there is an induction period before the alkyd coating begins to take up oxygen from the air (Byrnes, 1996). This induction period caused a delay of hexanal production from the alkyd paints tested in current experiments and was reflected by the low hexanal concentration in chamber air for the first few hours after painting. The mechanisms also involve a series of intermediate reactions, and hexanal is the one of the final byproducts. Chemical kinetic theories (Charles, 1977) indicate that, for consecutive reactions, the formation rate of the end products should always exhibit a pattern including a peak followed by a relatively slow decay. This pattern of time/formation rate relationship was also reflected by the hexanal concentration profiles in the chamber air shown in Figures 6-1 to 6-3.

### ***Hexanal Emission Model***

Assuming that the formation of hexanal can be described by a set of simplified consecutive first-order reactions:



where

- [A] = alkyd resins related to hexanal formation (mg/m<sup>2</sup>),  
 [I] = intermediates related to hexanal formation (mg/m<sup>2</sup>),  
 [H] = hexanal formed (mg/m<sup>2</sup>),  
 k<sub>1</sub> = first order reaction rate constant (h<sup>-1</sup>), and  
 k<sub>2</sub> = first order reaction rate constant (h<sup>-1</sup>).

Assume that there is a delay t<sub>a</sub> before the initiation of the formation reaction. The reaction rates can then be expressed as

$$\frac{d[A]}{dt} = -k_1 [A] U_a(t) \quad (6-3)$$

$$\frac{d[I]}{dt} = (k_1 [A] - k_2 [I]) U_a(t) \quad (6-4)$$

$$\frac{d[H]}{dt} = k_2 [I] U_a(t) \quad (6-5)$$

where U<sub>a</sub>(t) represents the unit step function reflecting the time lag t<sub>a</sub> and its value is 1 if t > t<sub>a</sub>, otherwise 0.

The initial conditions of Equations (6-3) to (6-5) are: [I] = [H] = 0 and [A] = A<sub>0</sub> at t = 0. Solving Equation (6-3) by integrating from an initial condition of t = 0 and [A] = A<sub>0</sub> yields

$$[A] = A_0 e^{-k_1 (t-t_a) U_a(t)} \quad (6-6)$$

Substituting Equation (6-6) into (6-4) and solving (6-4) by Laplace transform yields

$$[I] = \frac{k_1 A_0}{k_2 - k_1} ( e^{-k_1 (t-t_a)} U_a(t) - e^{-k_2 (t-t_a)} U_a(t) ) \quad (6-7)$$

Substituting Equation (6-7) into (6-5) and assuming that hexanal emission is controlled by the chemical reactions and all the hexanal formed is emitted, which means that the emission factor EF(t) is the formation rate for H, yields:

$$EF(t) = k_2 [I] = \frac{k_1 k_2 A_0}{k_2 - k_1} ( e^{-k_1 (t-t_a)} U_a(t) - e^{-k_2 (t-t_a)} U_a(t) ) \quad (6-8)$$

or

$$EF(t) = EF_0 ( e^{-k_1 (t-t_a)} U_a(t) - e^{-k_2 (t-t_a)} U_a(t) ) \quad (6-9)$$

where  $EF_0 = \frac{k_1 k_2 A_0}{k_2 - k_1}$

As the proposed source model for aldehyde emissions from alkyd paint, Equation (6-9) has the following characteristics: 1) It gives an initial emission factor of zero when  $t \leq t_a$ ; 2) It gives the maximum emission factor  $EF_{max}$  at  $t = t_a + \ln(k_2/k_1) / (k_2 - k_1)$ ; and 3) After reaching the maximum, the emission factor decays slowly.

The concentration profile of hexanal in a well-mixed chamber can be obtained by material balance with Equation (6-9) as the source term:

$$\frac{dC}{dt} = -N C + L EF(t) \quad (6-10)$$

where

- C = hexanal concentration (mg/m<sup>3</sup>),
- N = air exchange rate (h<sup>-1</sup>), and
- L = loading (m<sup>-1</sup>).



Solving Equation (6-10) yields

$$C = L EF_0 \left( \frac{e^{-k_1 (t-t_d)} U_a(t) - e^{-N (t-t_d)} U_a(t)}{N - k_1} - \frac{e^{-k_2 (t-t_d)} U_a(t) - e^{-N (t-t_d)} U_a(t)}{N - k_2} \right) \quad (6-11)$$

The parameter  $A_0$  in Equation (6-9) reflects the total hexanal emitted which can be obtained by integrating the concentration/time curves shown in Figures 6-1 to -3. The estimated values of  $A_0$  of the three alkyd paints tested are listed in Table 6-2. The values of the three remaining parameters ( $k_1$ ,  $k_2$ , and delay time  $t_d$ ) can be estimated by the best fit of Equation (6-11) to the time/concentration curve using a non-linear regression method. The estimated values of the three parameters by fitting Equation (6-11) to the concentration profiles shown in Figures 6-1 to 6-3 for the three alkyd paints tested are listed in Table 6-6. It is seen that each paint has a different set of values for  $k_1$  and  $k_2$  which reflects the fact that the fatty acids and promoters in the three paints are different from each other. Also the values of  $k_1$  are smaller than those of  $k_2$  which indicates that the formation rate of intermediates is much slower than that of hexanal. Therefore, the hexanal emissions were mostly controlled by the chemical reaction step during which intermediates were formed.

**Table 6-6. Estimated Model Parameters for Hexanal Formation from the Three Alkyd Paints Tested**

|  | <b>Paint A-1</b> | <b>Paint A-2</b> | <b>Paint A-3</b> |
|--|------------------|------------------|------------------|
| $EF_0$ (mg/m <sup>2</sup> /h) <sup>a</sup> | 9.41             | 4.8              | 11.9             |
| $k_1$ (h <sup>-1</sup> )                   | 0.056±0.012      | 0.024±0.002      | 0.056±0.009      |
| $k_2$ (h <sup>-1</sup> )                   | 0.744±0.414      | 0.617±0.332      | 1.52±1.60        |
| $t_d$ (h)                                  | 4.3±1.4          | 5.0±1.0          | 2.1±0.78         |

<sup>a</sup> Estimated from integrating the time/concentration curves.

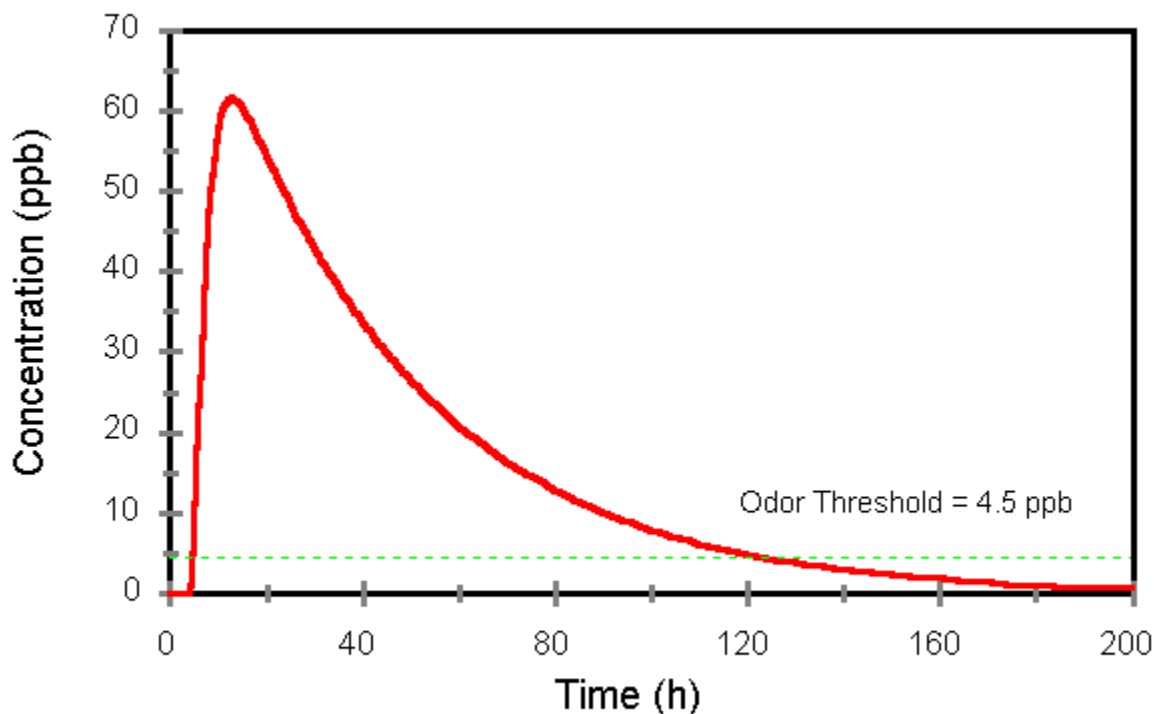
## ***Indoor Air Quality Simulation***

Simple IAQ simulation was performed by using Equation (6-11) to estimate hexanal concentration after indoor use of alkyd paint in an example house, assuming that alkyd paint A-2 is used to paint the kitchen and bathroom cabinets (with a total area of 10 m<sup>2</sup> being painted) of a residential house (with a volume of 300 m<sup>3</sup>). The indoor air of the house is well-mixed with an air exchange rate of 0.5 h<sup>-1</sup>. The estimated values of model parameters for paint A-2 shown in Table 6-6 were used for the simulation. Figure 6-4 shows the indoor air hexanal concentrations predicted by the simulation results. Also shown is the hexanal odor threshold (4.5 ppb) reported in the literature (ASTM, 1978). It is seen that the indoor hexanal level remained above the odor threshold for about 120 hours.

Table 6-2 indicates that hexanal is not the only aldehyde emitted. Other aldehyde emissions such as pentanal and propanal also have very low odor threshold values, 12 and 9 ppb, respectively (ASTM, 1978). The combination of those aldehydes and indoor sink effects can result in a strong and irritating odor that lasts for weeks.

## **Conclusions**

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. Reaction kinetics and mass balance calculations indicate that the aldehydes emitted should be produced after the paint was applied to a substrate. The aldehydes emission patterns are consistent with the theory that they were formed as byproducts from spontaneous autoxidation reactions of unsaturated fatty acids (in the applied paint) with atmospheric oxygen. Chamber data showed that the major volatile byproducts from the three alkyd paints tested were hexanal, propanal, and pentanal.



**Figure 6-4. Predicted hexanal concentration in a typical house after alkyd paint application.**

The hexanal formation and emission rates can be simulated by a consecutive first-order reaction model with an initial time lag. The time lag reflects an induction period after painting during which little oxygen was taken up by the alkyd coating. As the final byproduct of a series of consecutive first-order reactions, the hexanal emission rate should increase from zero to reach a peak followed by a slow decay as confirmed by chamber concentration data. The modeling results also showed that the hexanal emissions were mostly controlled by the chemical reactions to form intermediates as the precursors to hexanal production.

The slow-decay aldehyde emission pattern results in prolonged exposure by 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. Prolonged

occupant exposure to the aldehydes emitted from an alkyd paint could cause sensory irritation and other health concerns.

## Chapter 7

### Substrate Effects on VOC Emissions from a Latex Paint

NRMRL's paint testing practices are applicable to indoor latex paints as well as alkyd paints. This and the following two chapters present examples of how latex paint emissions have been studied using the small environmental chamber. The present chapter describes how NRMRL discovered the important effect that choice of substrate has on the chemical profile of VOC emissions.

Interior architectural coatings can increase indoor air pollution due to emissions of VOCs (WHO, 1989; Clausen et al., 1991). As of 1992, more than 85% of the interior coatings used in the United States were latex paint (National Paint & Coatings Association, 1992a and b). Methods of assessing latex paint emissions have been developed to determine cumulative mass emissions of VOCs for purposes of assessing their impact on the ambient air, specifically for their contributions to photochemical smog (Brezinski, 1989). In indoor environments, the concern is directed to determining the time-varying exposure of occupants to TVOCs, as well as specific VOCs.

Environmental test chambers have been used to measure the VOC emission profiles under simulated indoor conditions. These emission profiles can be used as a basis for exposure risk assessment (ASTM D5116, 1990). The tests involve applying the selected latex paint to a substrate and monitoring the chamber VOC concentration changes resulting from emissions of the painted substrate as a function of time. The test substrates used by most previous emission tests include stainless steel (Clausen et al., 1991; and Clausen, 1993) and glass (Sheldon and Naugle, 1994). Other substrates such as aluminum pans (Stromberg and Wind, 1968; Hansen, 1974) and glass plates (Rosen and Andersson, 1990; Sullivan, 1975) were also used to study the solvent evaporation and drying mechanisms of latex paints. Those substrates have the advantages

of being non-porous, non-absorbent, and easy to handle. However, latex paint is seldom applied to these substrates in real indoor environments. The surfaces most commonly painted with latex paint in the United States are walls and ceilings made of gypsum board. The gypsum board has a porous surface and absorbs liquid; this characteristic can alter the behavior of applied latex paint and change the VOC emission patterns.

To evaluate the substrate effects on time-varying VOC emissions, environmental chamber tests were conducted to measure the emissions from a latex paint applied to two different substrates -- a stainless steel plate and a gypsum board -- under identical experimental conditions (Tichenor, 1995; Krebs et al., 1995). The objective of this research is to report the summarized experimental data and to assess the substrate effects on latex paint VOC emissions.

## **Experimental Work**

Experiments were designed to generate VOC concentration data from newly applied latex paint as it dried for several hundred hours under controlled experimental conditions. Tests were conducted in EPA's small chamber source characterization facilities consisting of electropolished stainless steel chambers (Tichenor et al., 1990). The facilities allowed close control and monitoring of temperature, relative humidity, and air flow rate in the chambers. Small fans were used in the chambers to provide a velocity near (1 cm above) the test surface of 5 - 10 cm/s which is typical of indoor environments. The standard testing conditions were:

|                                  |                                       |
|----------------------------------|---------------------------------------|
| Air exchange rate (N)            | 0.5 h <sup>-1</sup>                   |
| Temperature                      | 23°C                                  |
| Inlet relative humidity          | 50%                                   |
| Nominal wet paint film thickness | 100 μm                                |
| Substrate specimen size (A)      | 0.0256 m <sup>2</sup> (0.16 × 0.16 m) |
| Chamber volume (V)               | 0.053 m <sup>3</sup>                  |
| Chamber loading (L = A/V)        | 0.48 m <sup>2</sup> /m <sup>3</sup>   |

The latex paint used in this study was selected after consulting with local paint suppliers on the popularity of medium-priced paints. Sufficient paint from the same lot was purchased to

conduct the small chamber tests. The purchased paint was mixed in cans and then split into 150 mL amber vials. Each vial was used for only one test.

The paint was analyzed for water content, VOCs, and density by ASTM Standard Test Methods (ASTM, 1989) and other related methods. Because the ASTM methods did not give information on the individual VOCs, these compounds were analyzed by extracting a paint sample in acetone and analyzing the extract by GC/MS and GC/FID. These analyses allowed the individual VOC compounds to be identified by MS and quantified by FIDs. Paint samples were periodically analyzed by GC to assess the stability of the target compound concentrations.

The substrates evaluated were newly purchased bare stainless steel and gypsum board. The gypsum board was paper-coated with a total thickness of 0.127 cm (0.5 in.) commonly used for walls and ceilings in residential and commercial buildings. The edges of the gypsum board samples were sealed with sodium silicate to minimize any adsorption of the VOCs. The latex paint was applied to the substrate specimen by a roller. It was estimated that 4.2 and 3.6 g of the paint were applied to the stainless steel and the gypsum board, respectively. The mass applied was determined using a protocol involving weighing of the substrate, the paint, and the roller before and after the application. The painted samples were placed in the chamber shortly (within 5 minutes) after the paint was applied. The test start ( $t=0$ ) was established when the door to the chamber was closed. The chamber was flushed with clean air (with less than  $5 \mu\text{g}/\text{m}^3$  TVOC) before each test. A typical test lasted for about 2 weeks with the clean air flow through the chamber continued at a controlled rate. The test duration was prolonged to more than 11 months for a long-term test.

VOCs in the chamber outlet were collected on Tenax sorbent tubes and analyzed by GC/FID. The desorption unit was a combination of an Envirochem Multisorbent Desorber and Unacon sample concentrator. The analytical column was a J&W 30 m  $\times$  0.53 mm (Megabore) DB-Wax operated at 40°C for 5 minutes and ramped at 5°C per minute to 240°C. The lower quantification limits (i.e., the lowest calibration levels) for the target compounds were from 26 to 37 ng on GC column, which is equivalent to a chamber concentration range of 0.0026 to 0.0037

mg/m<sup>3</sup> for 10-L samples. Of the VOC samples collected, 16% were duplicates. The average relative standard deviation between duplicates was 5% to 17% for individual compounds and 9% for TVOCs.

## **Results and Discussion**

### ***Paint Composition***

Table 7-1 shows the paint composition obtained by ASTM methods (ASTM, 1989). Table 7-2 shows five major VOCs (propylene glycol, ethylene glycol, 2-(2-butoxyethoxy)ethanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TPM also known as Texanol), and diethylene glycol) detected by GC analysis. The TVOC content in the bottom of each column in Table 7-2 was the sum of the five VOC contents in the same column. Comparison between Tables 7-1 and 7-2 indicates that the TVOC contents determined by the ASTM methods are lower than those by GC analysis. Since the ASTM TVOCs were determined by the relatively small difference between total volatiles and water content, it is suspected that the results from the ASTM analysis are biased for latex paint. Besides, the ASTM gravimetric method determining total volatiles (including water) involves heating the diluted sample in an oven at 110±5°C for 60 min. However, the boiling points (ranging from 187°C for propylene glycol to 244°C for TPM) for the VOCs in the paint are much higher than the oven temperature. It is suspected that the evaporation in the oven was incomplete at the specified temperature. Furthermore, at temperatures over 100°C, the paint polymerization is accelerated and may form a film over the residue which could significantly decrease evaporation. The GC VOC data are believed to be more reliable than the ASTM values and will be used for mass balance calculations.



**Table 7-1. Determination of Volatile Organic Compounds in the Latex Paint Tested by ASTM Methods (ASTM, 1989)**

|                               | Sample ID |        |        | Mean   |
|-------------------------------|-----------|--------|--------|--------|
|                               | 1         | 2      | 3      |        |
| Non-Volatiles                 | 57.23%    | 57.16% | 57.14% | 57.20% |
| Total Volatiles (incl. water) | 42.77%    | 42.84% | 42.86% | 42.8%  |
| Water Content <sup>a</sup>    | 39.91%    | 40.31% | 39.93% | 40.1%  |
| Density (g/mL)                | 1.41      | 1.42   | 1.43   | 1.42   |
| TVOC Content (mg/g)           | 28.6      | 25.3   | 29.3   | 28.0   |

<sup>a</sup> ASTM method D4017 (Karl Fischer)

**Table 7-2. Total and Individual VOCs Determined by GC Analysis Concentration Units (mg/g)**

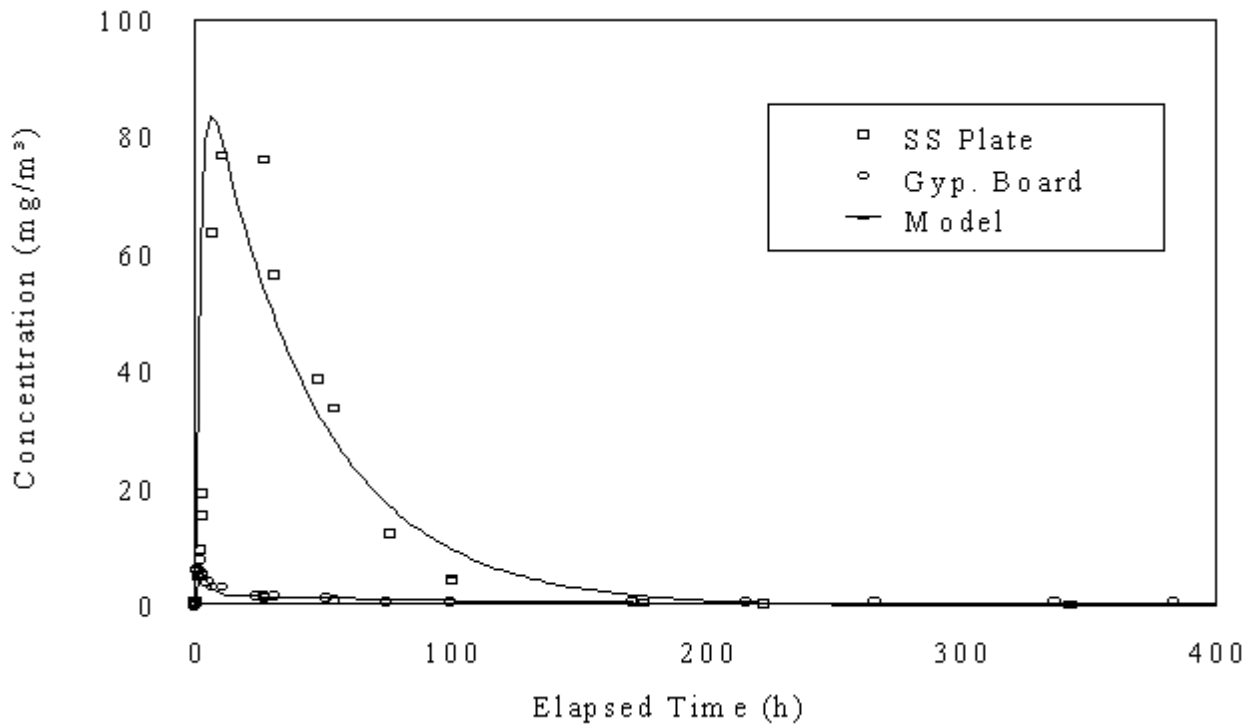
| Compound            | Sample ID |      |      |      | Mean |
|---------------------|-----------|------|------|------|------|
|                     | 1a        | 1b   | 4d   | 4e   |      |
| Propylene Glycol    | 2.52      | 2.46 | 2.14 | 2.16 | 2.32 |
| Ethylene Glycol     | 23.6      | 25.8 | 23.3 | 23.3 | 24.0 |
| Butoxyethoxyethanol | 5.20      | 5.15 | 4.88 | 4.68 | 4.98 |
| TPM                 | 14.0      | 14.0 | 13.2 | 12.6 | 13.5 |
| Diethylene Glycol   | 0.98      | 0.56 | 0.43 | 0.37 | 0.59 |
| TVOCs               | 46.3      | 48.0 | 44.0 | 43.1 | 45.4 |

### **Substrate Effects on VOC Emissions**

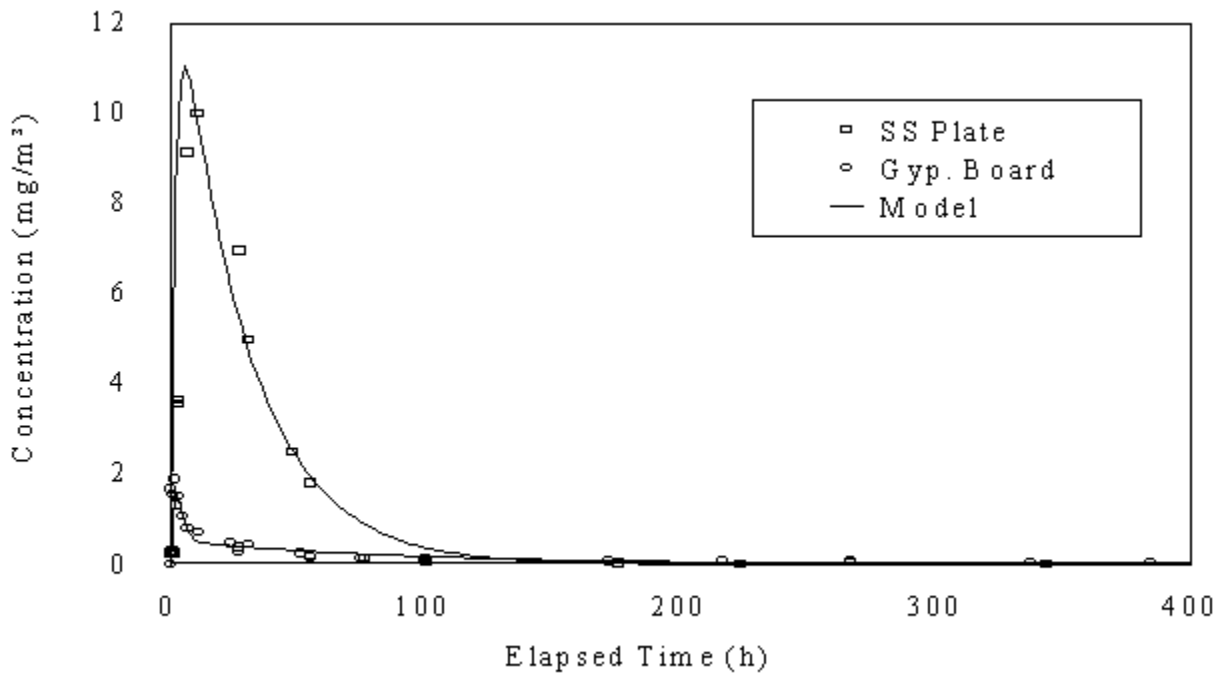
Figures 7-1 to 7-4 show the chamber air VOC concentration profiles (concentration vs. time curves) during the 2-week test period for the four major VOCs emitted from the latex paint applied to the two substrates. A significant substrate effect on latex paint VOC emissions is evidenced by comparing the VOC concentration profiles between stainless steel and gypsum board tests. Figures 7-1 to 7-4 indicate that, for each VOC, the chamber concentrations resulting from the gypsum board substrate were considerably lower than those from the stainless steel substrate during the 2-week test period. Table 7-3 shows the comparison of peak VOC concentrations measured from the two tests. When the latex paint was applied to the gypsum board instead of the stainless steel plate, the peak concentrations of propylene glycol, ethylene glycol, butoxyethoxyethanol, and TPM decreased by 81%, 90%, 56%, and 23%, respectively.

**Table 7-3. Comparison of Peak Concentrations Measured In the Environmental Chambers (in mg/m<sup>3</sup>)**

| <b>Compound</b>  | <b>Stainless Steel Plate</b> | <b>Gypsum Board</b> |
|------------------|------------------------------|---------------------|
| Ethylene Glycol  | 76.8                         | 7.88                |
| Propylene Glycol | 10.0                         | 1.88                |
| BEE              | 11.6                         | 5.14                |
| TPM              | 23.3                         | 18.0                |
| TVOCs            | 122                          | 32.9                |



**Figure 7-1. Effect of substrate on ethylene glycol emissions.**



**Figure 7-2. Effect of substrate on propylene glycol emissions.**

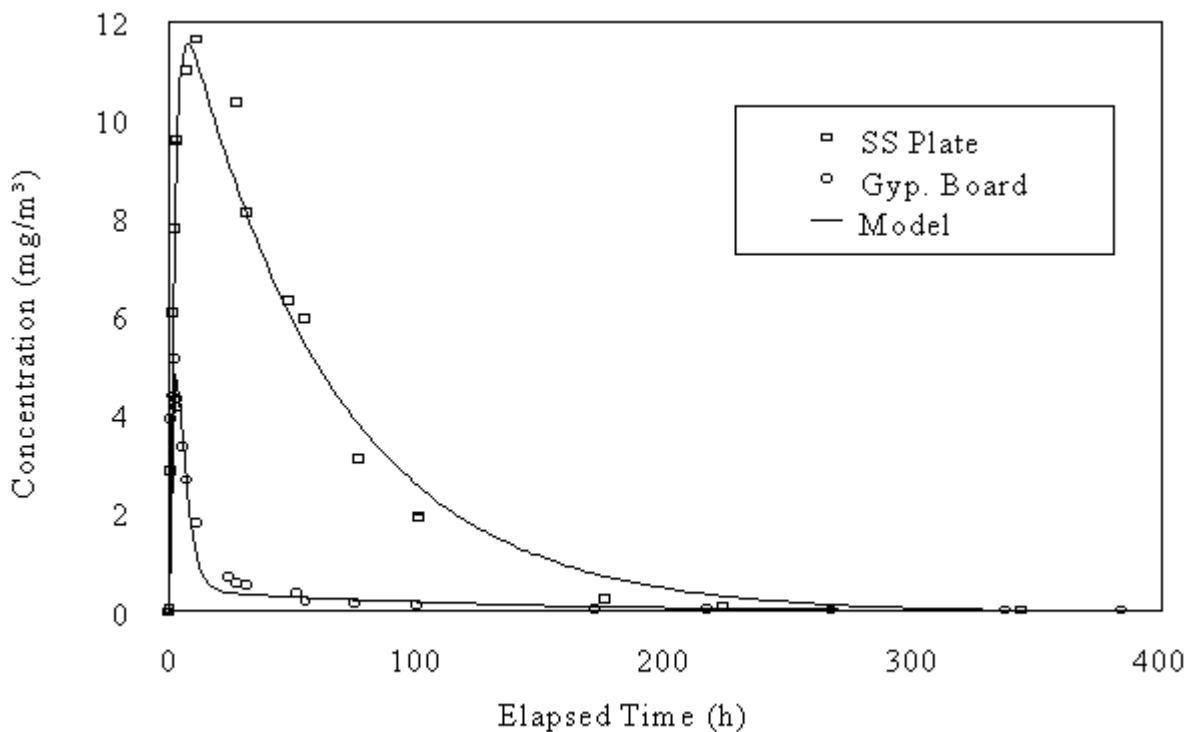


Figure 7-3. Effects of substrate on 2-(2-butoxyethoxy)ethanol emissions.

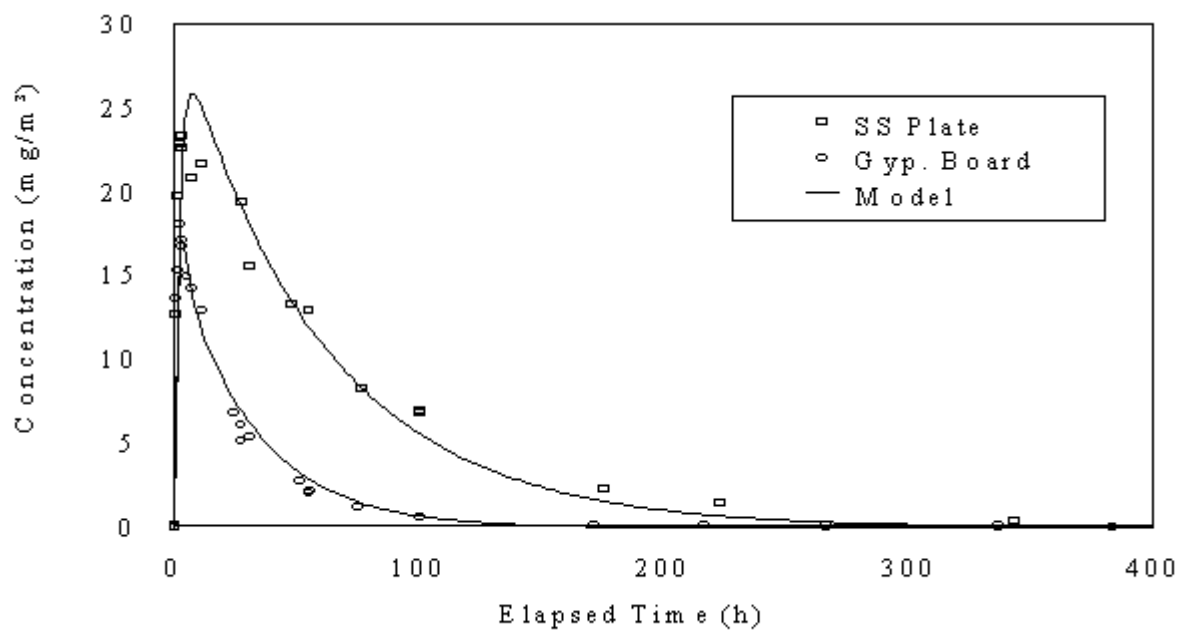


Figure 7-4. Effect of substrate on TPM emissions.

The differences are also reflected by the amount of each compound emitted. The amount of each VOC emitted from the latex paint in the 2-week test period ( $W$ ) was estimated by integrating the concentration curve (Colombo and De Bortoli, 1992; Guo et al., 1996b):

$$W = \frac{Q}{2} \sum_{i=1}^{n-1} [(C_i + C_{i+1}) (t_{i+1} - t_i)] \quad (7-1)$$

where

- $Q$  = air exchange flow rate ( $\text{m}^3/\text{h}$ ),
- $C$  = chamber concentration of a given compound ( $\text{mg}/\text{m}^3$ ),
- $t$  = time (h), and
- $n$  = total number of data points.

and the percent of each VOC emitted in the 2-week test period can be calculated as:

$$\text{Percent emitted} = \frac{W}{W_0} \cdot 100\% \quad (7-2)$$

where

- $W_0$  = The amount of VOCs in the latex paint applied (mg).

Table 7-4 shows that 89% to 100% of the VOCs were emitted when stainless steel was the substrate. However, only 9% to 29% of the VOCs were emitted during the same period when gypsum board was the substrate. Similar to the peak concentration reduction, the total emission reduction was not uniform among the four major species. Ethylene glycol had the largest reduction (from 100% to 9%) and TPM the smallest (from 89% to 29%). The other significant difference in emission patterns is that the peak concentrations appeared earlier with gypsum board than with stainless steel and this happened for all the individual compounds (see Figures 7-1 to 7-4).

**Table 7-4. Weight Percentage of VOC in the Latex Paint Emitted in the First 336-Hour Testing Period (in %)**

| Compound         | Stainless Steel Plate | Gypsum Board |
|------------------|-----------------------|--------------|
| Ethylene Glycol  | 100                   | 9            |
| Propylene Glycol | 89                    | 17           |
| BEE              | 93                    | 14           |
| TPM              | 89                    | 29           |
| TVOCs            | 97                    | 20           |

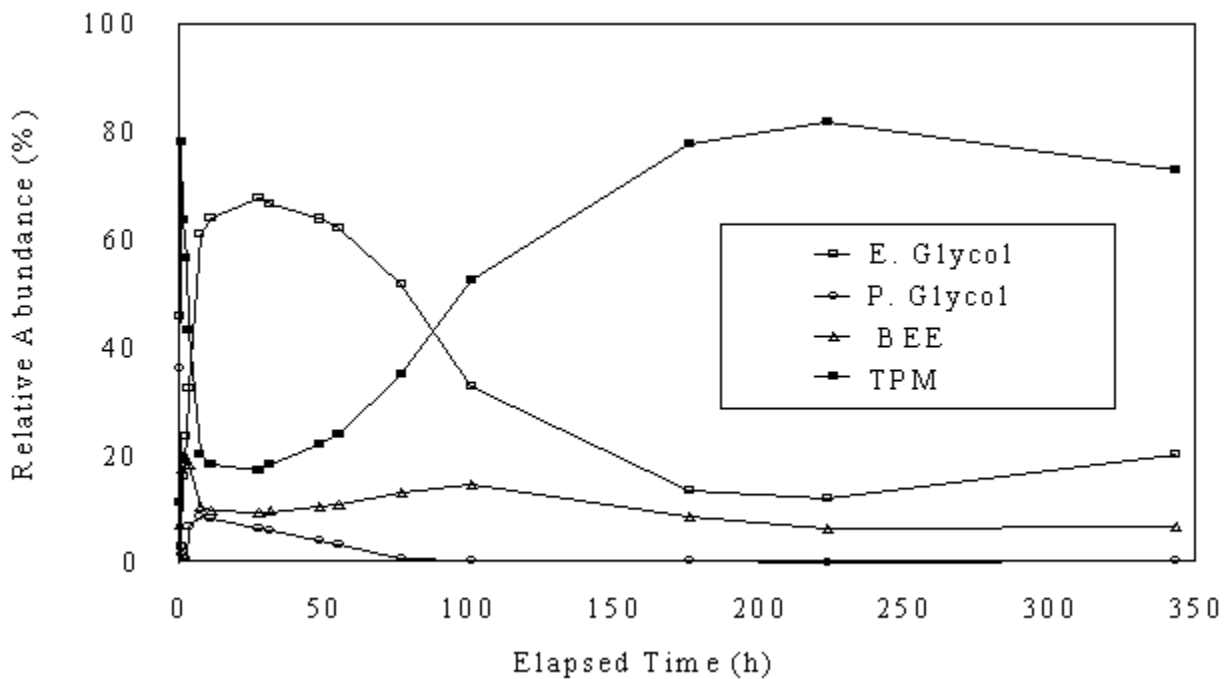
### ***Substrate Effects on Composition of VOC Emissions***

When the same paint was applied to the two substrates, the compositions of VOC emissions were dramatically different. As shown in Figure 7-5, when stainless steel was the substrate, ethylene glycol dominated the VOC emissions for the first 100 h, and TPM was the dominant VOC after that. On the other hand, when the gypsum board was the substrate, the trend was reversed. TPM became the dominant VOC emitted for the first 100 h, and ethylene glycol dominated the VOC emissions after that (Figure 7-6).

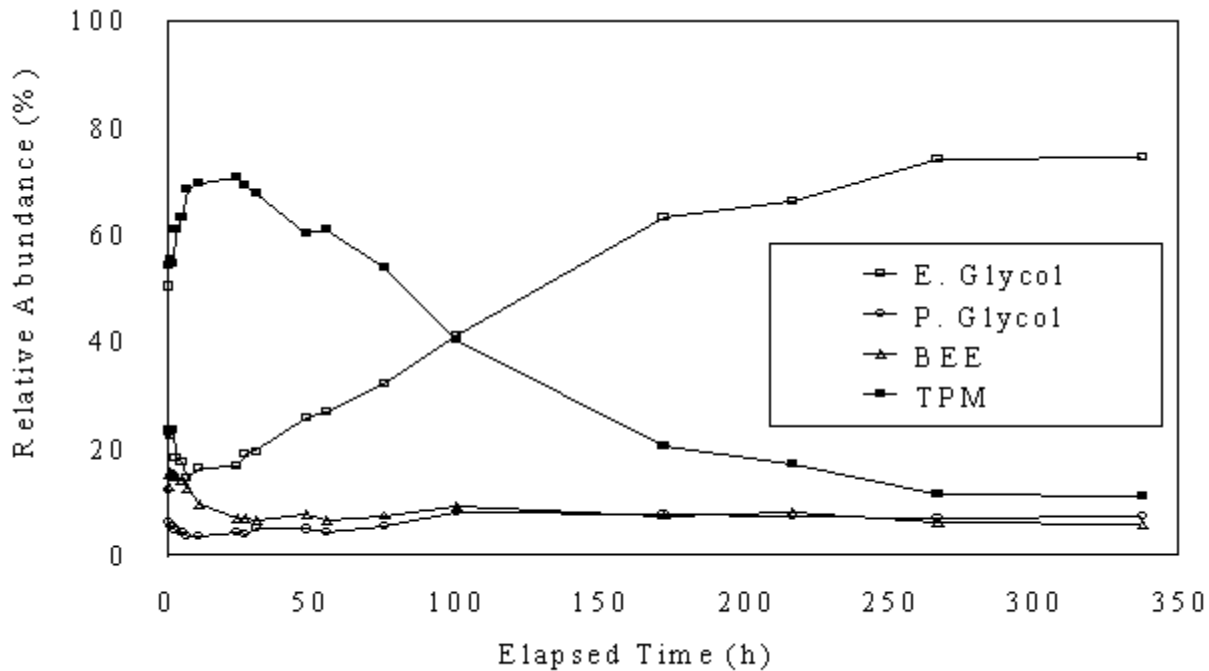
### ***Emission Models***

Chang and Guo (1992b) analyzed wood stain emission data that look similar to current gypsum board data, by using a double-exponential model:

$$EF(t) = R_1 + R_2 = R_{10} e^{-k_1 t} + R_{20} e^{-k_2 t} \quad (7-3)$$



**Figure 7-5. VOC composition in chamber air with stainless steel substrate (relative abundance = weight percent in TVOC).**



**Figure 7-6. VOC composition in chamber air with stainless steel substrate (relative abundance = weight percentage in TVOC).**

where

|                 |   |   |
|-----------------|---|---|
| EF(t)           | = | Emission factor of a VOC (mg/m <sup>2</sup> /h),            |
| R <sub>1</sub>  | = | Phase 1 emission factor (mg/m <sup>2</sup> /h),             |
| R <sub>2</sub>  | = | Phase 2 emission factor (mg/m <sup>2</sup> /h),             |
| R <sub>10</sub> | = | Phase 1 initial emission factor (mg/m <sup>2</sup> /h),     |
| k <sub>1</sub>  | = | Phase 1 emission rate decay constant (h <sup>-1</sup> ),    |
| R <sub>20</sub> | = | Phase 2 initial emission factor (mg/m <sup>2</sup> /h), and |
| k <sub>2</sub>  | = | Phase 2 emission rate decay constant (h <sup>-1</sup> ).    |

Integrating the chamber mass balance equation with the source term defined by Equation (7-3) and assuming an initial concentration of zero gives:

$$C = L \left[ \frac{R_{10} (e^{-k_1 t} - e^{-Nt})}{N - k_1} + \frac{R_{20} (e^{-k_2 t} - e^{-Nt})}{N - k_2} \right] \quad (7-4)$$

Based on the techniques suggested by Chang and Guo (1992b), the double exponential model was used to analyze the chamber data using a non-linear regression curve fit routine implemented on a microcomputer. It was found that Equation (7-4) provides an adequate representation of the chamber concentration profiles resulting from gypsum board VOC emissions (see Figures 7-1 to 7-4). The stainless steel emission data can also be described by the double exponential model by assuming that the phase 2 emissions are negligible ( $R_{20} = 0$ ). Tables 7-5 and 7-6 list the values of parameters estimated by the non-linear regression fit.

### ***Emission Mechanisms***

Chang and Guo (1992b) indicated that the double exponential model can represent a two-phase emission process. In this previous work, wood stain was applied to hardwood. The phase 1 emissions,  $R_1$ , correspond to the period shortly after the stain was applied while it was still relatively wet. During this phase, it appeared that VOC emissions were related to evaporation processes, characterized by relatively fast emissions. These fast emissions caused a rapid



**Table 7-5. Summary of Parameters of the Double Exponential Model for VOC Emissions from Painted Gypsum Board**

| Compound         | $R_{10}$<br>(mg/m <sup>2</sup> /h) | $k_1$<br>(h <sup>-1</sup> ) | $R_{10}/k_1$<br>(mg/m <sup>2</sup> ) | $R_{20}$<br>(mg/m <sup>2</sup> /h) | $k_2$<br>(h <sup>-1</sup> ) | $R_{20}/k_2$<br>(mg/m <sup>2</sup> ) |
|------------------|------------------------------------|-----------------------------|--------------------------------------|------------------------------------|-----------------------------|--------------------------------------|
| Ethylene Glycol  | 18.5                               | 0.696                       | 26.6                                 | 1.96                               | 0.00694                     | 282                                  |
| Propylene Glycol | 4.78                               | 0.724                       | 6.60                                 | 0.561                              | 0.0115                      | 48.8                                 |
| BEE              | 10.8                               | 0.331                       | 32.6                                 | 0.475                              | 0.00767                     | 61.9                                 |
| TPM              | 29.7                               | 0.795                       | 37.4                                 | 15.9                               | 0.0317                      | 502                                  |

**Table 7-6. Summary of Parameters of the Double Exponential Model for VOC Emissions from Painted Stainless Steel ( $R_{20} = 0$ )**

| Compound         | $R_{10}$<br>(mg/m <sup>2</sup> /h) | $k_1$<br>(h <sup>-1</sup> ) | $R_{10}/k_1$ (mg/m <sup>2</sup> ) |
|------------------|------------------------------------|-----------------------------|-----------------------------------|
| Ethylene Glycol  | 100                                | 0.0235                      | 4255                              |
| Propylene Glycol | 14.0                               | 0.0368                      | 380                               |
| BEE              | 13.4                               | 0.0166                      | 807                               |
| TPM              | 30.0                               | 0.0169                      | 1775                              |

depletion of organic compounds on the surface of the wood, resulting in a rapid rise and decline of the chamber concentrations. A similar phenomenon was observed in the latex paint data for the first 50 to 100 h, as shown in Figures 7-1 to 7-4.

The phase 2 emissions,  $R_2$ , corresponded to the period when the wood stain applied was relatively dry. There was evidence that the emissions were controlled by diffusion through a solid (the wood), making the emission rates low, but the emission lasted for a long time. The latex paint behaved in a similar fashion, as reflected by the small values of  $R_{20}$  and  $k_2$  (compared with the corresponding  $R_{10}$  and  $k_1$  values) as shown in Table 7-5.

According to the model,  $R_{10}/k_1$  and  $R_{20}/k_2$  represent the total quantities of organic species emitted in phases 1 and 2, respectively. The values of those two parameters estimated from the chamber data are also listed in Table 7-5. It is seen that for gypsum board, the VOCs emitted in phase 2 far exceeded those in phase 1. It is likely that the majority of the latex paint VOCs penetrated into the relatively porous gypsum board and became relatively dry shortly after application. Only a small fraction of the paint VOCs stayed wet on the surface of the gypsum board, resulting in the relatively short phase 1 emissions. The rest of the VOCs applied were probably imbedded in the gypsum board and had to diffuse through the substrate to be emitted as the phase 2 emissions.

However, the opposite was observed when the stainless steel plate was the substrate. Almost all of the VOCs in the latex paint applied were emitted in phase 1. The phase 2 emissions were so small that, for modeling purposes, the emission rate was negligible and the value of  $R_{20}$  was set at 0 (see Table 7-6). This is most likely due to the fact that the stainless steel was impervious and all of the latex paint applied remained on the surface. As a result, it took longer for the latex paint to dry, and the majority of the VOCs were emitted rather rapidly while the paint was still relatively wet.

## **Long-Term Emission Data**

Figure 7-7 shows the temporal history of the composition of the VOC emissions from a painted gypsum board over an 11-month period. As mentioned in the section above, entitled “Substrate Effects on Composition of VOC Emissions,” TPM had the highest initial emission rate, but ethylene glycol exceeded TPM after about 100 h and continued to be the dominant VOC emitted over the long term. Even after 11 months, an ethylene glycol concentration of  $0.1 \text{ mg/m}^3$  was still being measured in the chamber air. This approximates a steady state emission rate of about  $0.1 \text{ mg/m}^2/\text{h}$ . The levels of other VOCs were near the quantification limit of the sampling and analytical methods used. Assuming a constant emission rate of  $0.1 \text{ mg/m}^2/\text{h}$ , after 1 year about 40% of the ethylene glycol will be emitted, and it will take as long as 3.5 years for all of the ethylene glycol to be released.

Although the double-exponential model indicated that the phase 2 VOC emissions should last for a long time, it failed to predict that the ethylene glycol emission can persist for more than 11 months. The discrepancy between the model predictions and the chamber data is probably due to the empirical nature of the model which oversimplifies the emission process. A physical model based on mass transfer fundamentals which take into account the characteristics of physical and chemical processes is needed to fully represent the long-term behavior of latex paint VOC emissions.

## **Conclusions**

Environmental chamber tests showed significant differences in emission rates and patterns between the VOCs released from the same latex paint applied to two different substrates—a stainless steel plate and a gypsum board. 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 in the first 100 h also changed from

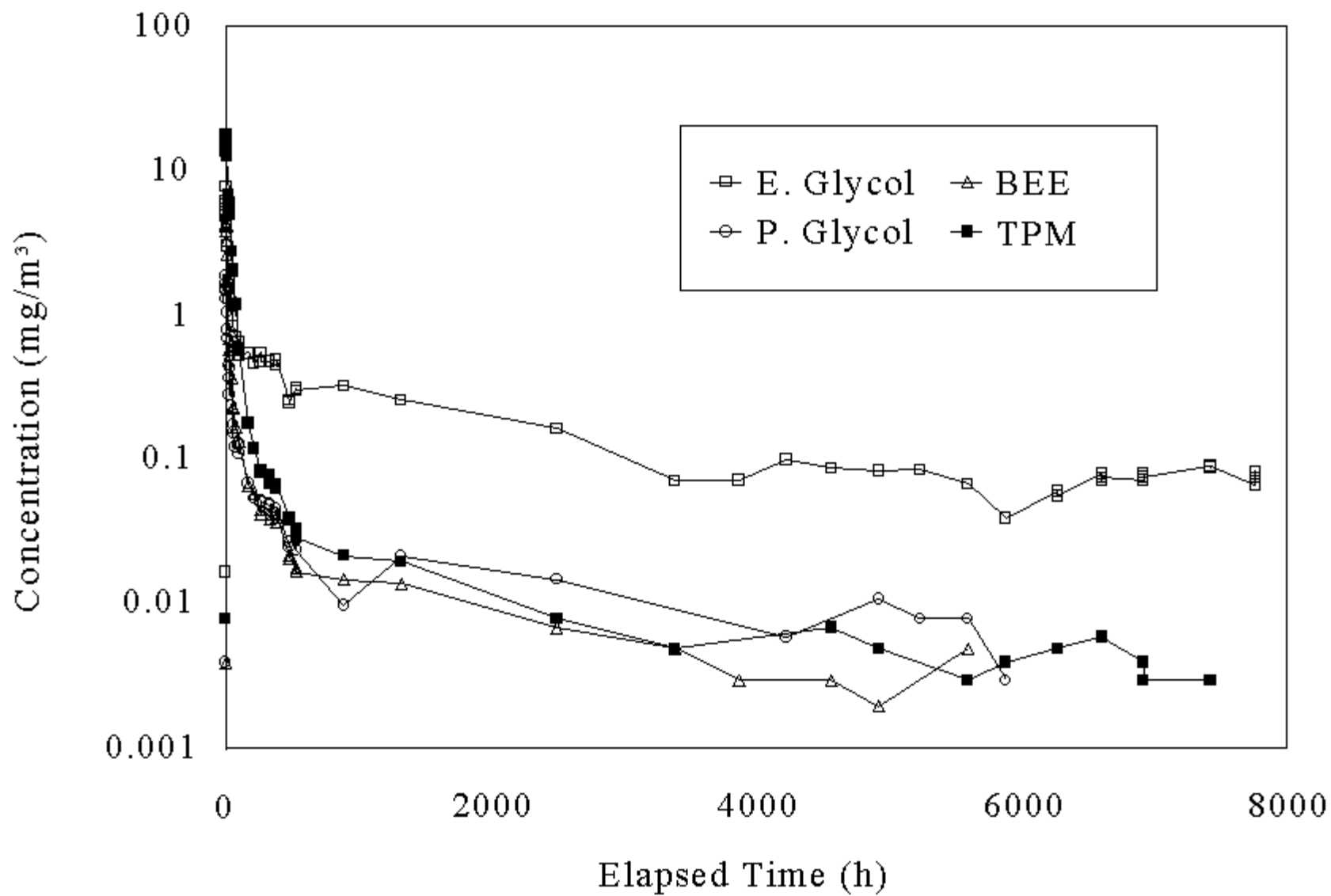


Figure 7-7. Long-term VOC emissions from painted gypsum board.

ethylene glycol to TPM 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 might 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 appeared to be controlled by the evaporation-like drying process from the painted gypsum board. The majority of the VOCs were emitted after the painted gypsum board surface was relatively dry and 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 to release all the VOCs in the paint applied to the gypsum board.

Therefore, when the objective of the test is to provide emissions data that are relevant to understanding the emissions behavior in typical indoor environments, instead of “ideal” substrates such as glass, aluminum, or stainless steel, “real” substrates such as wood and gypsum board should be used to evaluate the time-varying VOC emissions and drying mechanisms of wet products like latex paint.

## Chapter 8

### Experimental Work to Evaluate Low-VOC Paints

This chapter exemplifies the usefulness of NRMRL's paint testing practices for evaluating new paint products. It deals with a new class of paints developed and marketed on the grounds that they emit very low levels of VOCs as they dry. A standard paint testing practice provides an avenue by which environmental and public health agencies can research the properties of new products like these.

Conventional water-based latex paints use solvents and additives which contain volatile organic compounds (VOCs) to provide the following functions: binder/coalescing agent, polymer plasticizer, freeze/thaw stabilizer, defoamer, and carriers for other additives such as colorants, thickening agents, surfactants, and biocides (Turner, 1988). As the paint dries, these solvents and additives evaporate and release VOCs (Clausen et al., 1991). When the paint is applied to interior surfaces, the VOCs resulting from the drying process cause increased indoor VOC concentrations and associated indoor air pollution problems. The major VOC emissions from conventional latex paints include propylene glycol (PG), ethylene glycol (EG), 2-(2-butoxyethoxy)ethanol (BEE), and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TPM a.k.a. Texanol) (Chang et al., 1997). The elevated indoor air VOC concentrations are often related to complaints of unpleasant odors and sometimes irritant and allergic reactions by building occupants.

Considerable efforts have been made by the entire coatings industry to decrease levels of VOCs in coatings and paints (Klein, 1993; Bjorseth and Malvik, 1995). In recent years, newly developed interior architectural coatings, advertised as "low-VOC," "low-odor," or sometimes

"no-VOC" latex paints, have been commercially available. Those interior coatings are labeled as "VOC free" based on EPA Reference Method 24 (40 CFR, 1994). They are also recommended by their manufacturers as an alternative to conventional paints to reduce indoor air pollution. However, the relevance of replacing conventional latex paints with low-VOC coatings to reduce indoor air pollution has not been studied. While the off-gassing from conventional paints is a cause of indoor air pollution, no emission data from low-VOC paints are available. In addition, the VOC-containing solvents and additives are normally used to improve several important properties of conventional paints. Eliminating the VOCs in paint formulations may compromise the performance of the paint and make it improper for certain uses.

To address those issues, NRMRL evaluated four commercially available low-VOC latex paints. The purpose was to provide experimental data on the emission characteristics and the coating performance. The results can be used to assess whether those paints are suitable substitutes for conventional latex paints for preventing indoor air pollution and reducing VOC exposure. The tests conducted included bulk analyses, chamber emission tests, and performance evaluation.

## **Experimental Work**

Four commercially available low-VOC latex paints (designated as paints L-1, L-2, L-3, and L-4) and a reference paint (a commonly used conventional latex paint designated as paint 0) were acquired for the evaluation. Table 8-1 lists the characteristics of the low-VOC latex paints based on the manufacturers' specifications. EPA Method 24 was used to determine the total volatile matter content, water content, and the total VOC content of each paint. The method is the same as that used by manufacturers for labeling purposes and to support the claims about low-VOC paints. The concentrations of individual VOCs in the bulk liquid paints were determined by a GC/MS method adapted from EPA Method 311(40 CFR 1996). The paints were diluted with either acetone or acetonitrile at a rate of 1 g of the paint with 10 mL of solvent. Acetone formed an emulsion with some paints, requiring the use of acetonitrile. Samples of the diluted and centrifuged paints were analyzed by injection onto the GC column.

**Table 8-1. The Low-VOC Latex Paints Tested**

| <b>Paint</b>                | <b>L-1</b>    | <b>L-2</b>    | <b>L-3</b>      | <b>L-4</b> |
|-----------------------------|---------------|---------------|-----------------|------------|
| Color                       | Antique white | Antique white | White           | White      |
| Density, kg/L               | 1.35          | 1.33          | 1.21            | 1.25-1.31  |
| Solid content, vol. %       | 33.4          | 38            | NA <sup>a</sup> | 26-32      |
| Water content, wt. %        | 49.4          | 45.4          | 40.7            | 55.4       |
| VOCs, g/L                   | 0             | 1             | 0               | 0          |
| Coverage, m <sup>2</sup> /L | 9.8-11.1      | 9.8           | 12.3-19.7       | 9.8-11.1   |

<sup>a</sup> NA - Information not available from manufacturer-supplied data.

Emissions tests were conducted in the EPA's small chamber source characterization test facility. Each paint was applied to the top side of a glass plate (16 cm by 16 cm) by a roller. Glass plate was used as the substrate to maximize the VOC emissions to facilitate sampling and chemical analysis. The painted glass plate was weighed to ensure the amount of the paint applied was adequate before it was placed inside a 53-L electropolished stainless steel chamber with the painted side exposed to the chamber air. Each test started at the moment when the chamber door was closed. Each chamber was operated at 0.5 h<sup>-1</sup> air exchange rate, 50% relative humidity, and 23°C. A small fan was running continuously to ensure good mixing of the air inside the chamber. Air samples were collected at the exit of each chamber on Tenax tubes for analysis of VOCs and dinitrophenylhydrazine(DNPH)-treated silica gel cartridges for determination of aldehydes. The details of the test protocol and analytical procedures can be found in the literature (Chang et al., 1997; Fortmann et al., 1998).

The physical performance of the paints was evaluated by testing each paint with seven standardized methods adopted by the American Society of Testing and Materials (ASTM). The seven methods were selected based on information in the ASTM Standard Guide for Testing Latex Flat Wall Paints (ASTM 2931) and discussions with paint testing laboratories. The paint performance evaluated included specular gloss (ASTM 523), hiding power (ASTM 2805), scrub resistance (ASTM 2486), washability (ASTM 3450), sag resistance (ASTM 4400), drying time



(ASTM 1640), and yellowness index (ASTM E313). A summary description of each method is provided in Table 8-2. In addition to the four low-VOC paints, the reference paint (paint 0) was also tested as a control.

## Results and Discussion

### *Bulk Analysis*

The VOCs identified by the GC/MS analyses included EG, PG, BEE, TPM, and dipropylene glycol. Table 8-3 shows that the VOC concentrations in the liquid paints were quite low and some (expressed as BDL) were below the detection limit of 0.01 mg/g. Paint L-2 had the highest TVOC concentration (defined as the sum of the five VOCs quantified) of 3.05 mg/g, which is still more than 1 order of magnitude lower than that (45.39 mg/g) of paint 0 (a conventional latex paint) as shown in Table 8-3.

Analyses based on Method 24 (40 CFR, 1994) were also performed to estimate the VOC content of the four low-VOC latex paints. The results ranged from -1.7% to 0.8%, which indicated that Method 24 is an inaccurate method for estimating the VOC content of coatings that contain significant amounts of water and small amounts of VOC. Equation 8-1 is used by the method to calculate VOC content:

$$W_{\text{voc}} = W_{\text{vol}} - W_{\text{w}} \quad (8-1)$$

where

- $W_{\text{voc}}$  = VOC content estimated based on Method 24 (wt.%),
- $W_{\text{vol}}$  = total volatile content (wt.%), and
- $W_{\text{w}}$  = water content (wt.%).

**Table 8-2. ASTM Methods Used for Performance Testing**

| ASTM Method | Method description   |
|-------------|--|
| D523        | This test method identifies the specular gloss. The reading is made with a glossmeter at an 85° angle. The difference between 1.6 and 2 is not visible to the naked eye. The range from 4 to 6 is much more noticeable, and the range from 9 to 11 shows significant light reflecting off the surface for a flat paint.  |
| D2805       | This is an instrumental method to measure the coverage hiding power of the paint. The paint is applied to a standard chart with a wet film thickness of 1.5 mils which represents one coat of paint and a wet film thickness of 3 mils which represents two coats of paint. The paint is allowed to air dry and measurements are made. The contrast ratio is reported. Generally, a contrast ratio in the range from 0.90 to 0.95 indicates poor hiding power, and the range from 0.95 to 1.00 indicates good hiding power. Readings below 0.90 indicate very poor hiding power. |
| D2486       | This test method determines the resistance of latex flat wall paints to erosion caused by scrubbing. The paint is applied to a standard chart and allowed to dry for 7 days. The chart is then placed in a machine that scrubs the surface with a brush and an abrasive cleanser. The reported number indicates how many cycles were required before wearing through the dried paint film. The analytical laboratory that performed the tests indicated that the average number of cycles for most paints is between 250 and 500.  |
| D3450       | This test method covers the relative ease of removing soiled discolorations from the dried film of an interior coating by washing with either an abrasive or non-abrasive cleaner. The paint is applied to a standard chart and allowed to dry for 7 days. Then a dark oil stain is applied to the paint and baked on the surface overnight. The next day the stain is washed with a detergent and a sponge. The higher the percentage rating, the more of the stain that was removed by the method. Performance of the paint is evaluated relative to other paints.             |
| D4400       | This method uses a multi-notched applicator to determine the sag resistance of aqueous and non-aqueous liquid coatings at any level of sag resistance. The method used for the flat latex paint has the value of 12 as the perfect Anti-Sag Index. Values between 9 and 12 are considered good Anti-Sag Indexes. Any Index number lower than 7 is considered poor.   |
| D1640       | This method measures the time it takes for the coating to dry to touch in minutes (finger test).   |
| E313        | The Yellowness Index method compares the differences in the whiteness of the initial dry film before it is exposed to sunlight to the whiteness after it has been exposed to sunlight. The lower the initial number, the whiter the paint. The difference in the initial number and after-exposure number indicates the effect of sunlight on the film. A negative number indicates that the film has bleached in the sun, and a positive number indicates yellowing. Differences less than $\pm 0.2$ are not detectable.  |

**Table 8-3. Results of Bulk Analyses (mg/g)**

| Paint                      | 0<br>(a conventional latex paint) | L-1      | L-2       | L-3       | L-4       |
|----------------------------|-----------------------------------|----------|-----------|-----------|-----------|
| Ethylene Glycol            | 24.00±1.20 <sup>a</sup>           | 0.04±BDL | 0.59±0.01 | BDL       | BDL       |
| Propylene Glycol           | 2.32±0.19                         | 0.03±BDL | 0.09±BDL  | 0.16±0.01 | BDL       |
| Dipropylene Glycol         | BDL <sup>b</sup>                  | 0.11±BDL | 0.81±0.03 | BDL       | 0.14±0.01 |
| 2-(2-butoxy-ethoxy)ethanol | 4.98±0.25                         | 0.11±BDL | 1.51±0.01 | 0.01±BDL  | BDL       |
| TPM                        | 13.50±0.68                        | 0.03±BDL | 0.05±BDL  | BDL       | BDL       |
| TVOCs <sup>c</sup>         | 45.39±2.32                        | 0.32±BDL | 3.05±0.05 | 0.17±0.01 | 0.14±0.01 |

<sup>a</sup> Standard deviation

<sup>b</sup> Below the method detection limit estimated to be 0.01 mg/g of the paint

<sup>c</sup> Total volatile organic compounds = sum of all the volatile organic compound concentrations

For low-VOC latex paints,  $W_w$  is usually in the range of 40 to 55%, and  $W_{voc}$  could be 0.3% or less. Even if  $W_{vol}$  is absolutely accurate and precise, a 1% error of  $W_w$  can cause more than 200% error of  $W_{voc}$ . However, the within-laboratory analytical precision of  $W_w$  and  $W_v$  is expected to be 2.9 and 1.5%, respectively (40 CFR, 1994). As a result, the Method 24 data of  $W_{voc}$  scattered a wide range and often showed negative numbers. Therefore, Method 24 is not an adequate method to quantify the VOC content for those waterborne coatings.

### ***Emissions***

Very little VOC emissions were detected in the chamber air samples of the four low-VOC paints. Among the four paints, paint L-2 had the highest emissions which reflects the highest VOC content as indicated in Table 8-3. Figure 8-1 shows the TVOC concentration profile for

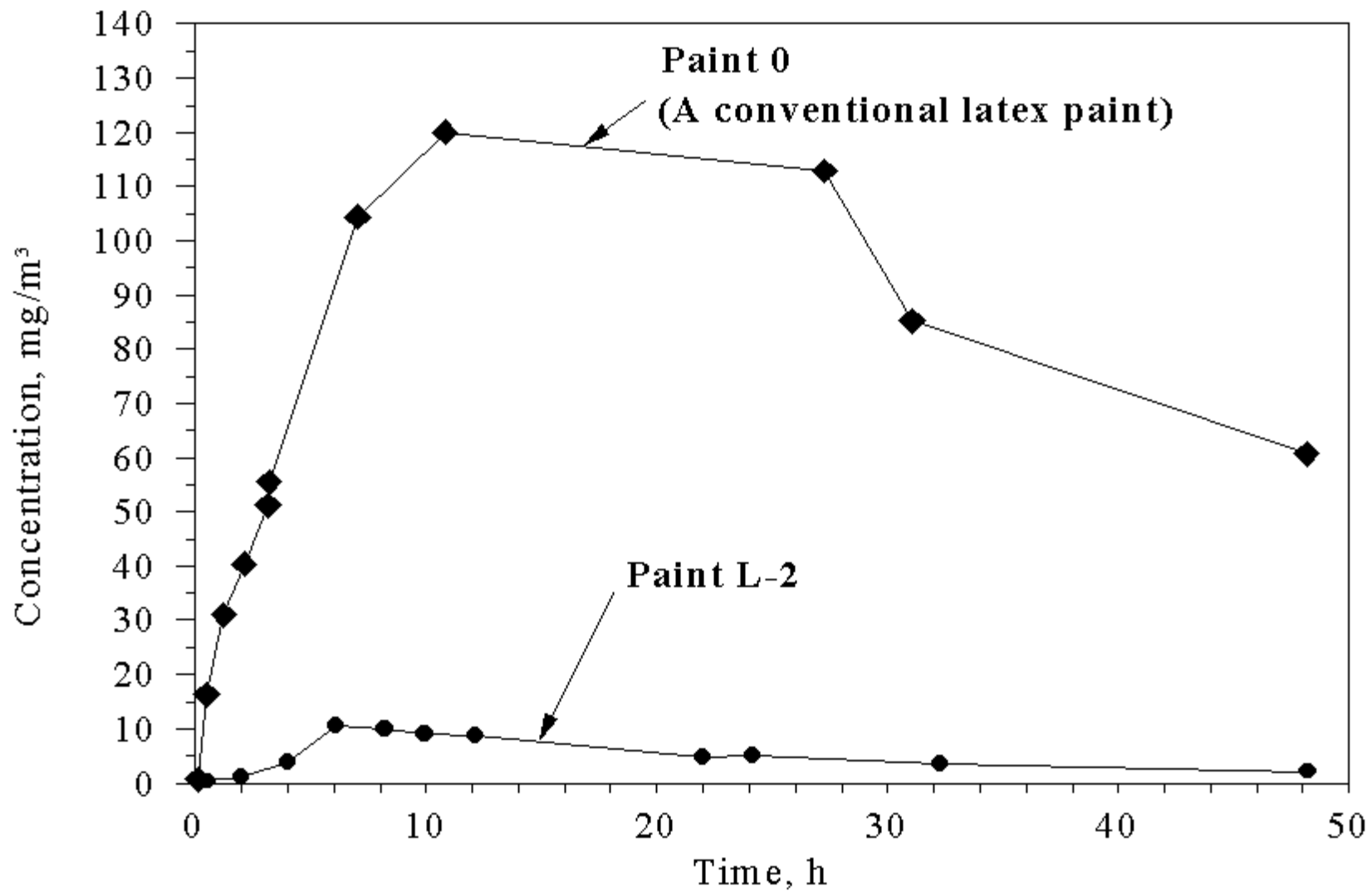


Figure 8-1. Comparison of TVOC emission profile of paint L-2 with that of paint 0 (a conventional latex paint). The method detection limit for TVOC was 0.02 mg/m<sup>3</sup>.

emissions from paint L-2. Also shown is the TVOC profile of paint 0 (a conventional latex paint). It is seen that the paint L-2 TVOC concentrations are at least 1 order of magnitude lower than that of the conventional paint.

However, significant aldehyde emissions were detected from two low-VOC latex paints (paints L-1 and L-3 as illustrated in Figures 8-2 and 8-3, respectively). The aldehyde emissions detected included formaldehyde, acetaldehyde, propanal, and benzaldehyde. Among them, the most abundant aldehyde species was formaldehyde as shown in Figures 8-2 and 8-3. The measured peak concentrations of formaldehyde were 3.15 mg/m<sup>3</sup> for paint L-1 and 5.53 mg/m<sup>3</sup> for paint L-3. The peak concentrations of the second abundant aldehyde, acetaldehyde, were 0.11 and 0.30 mg/m<sup>3</sup> for paints L-1 and L-3, respectively. In addition to the high peak concentrations, the formaldehyde emissions lasted for more than 2 days for both paints (Figures 8-2 and 8-3). The formaldehyde concentrations in the chamber air samples taken 50 h after testing were 0.011 and 0.223 mg/m<sup>3</sup> for paints L-1 and L-3, respectively. The estimated mass of formaldehyde emitted during the 50 h test period was 0.26 and 0.51 mg/g from paints L-1 and L-3, respectively.

Formaldehyde is a listed hazardous air pollutant by the Clean Air Act Amendments (CAAA, 1990). Literature data showed that formaldehyde is a primary upper respiratory tract irritant and its odor is characterized as "pungent" (AIHA, 1989). Symptoms of eye, nose, and throat irritation, such as tearing, running nose, and a burning sensation in these areas, are relatively common with formaldehyde exposure. Formaldehyde is also classified as a probable human carcinogen based on sufficient evidence in animal studies (Grindstaff et al., 1991). Formaldehyde is listed as a California Proposition 65 carcinogen and as a Toxic Air Contaminant by the California Air Resources Board (CARB) based on potential carcinogenicity.

The formaldehyde emissions from low-VOC latex paints are of special concern since those paints are promoted as the "perfect choice" for use in occupied buildings during normal business hours, without evacuating entire building sections. The newly painted room purportedly

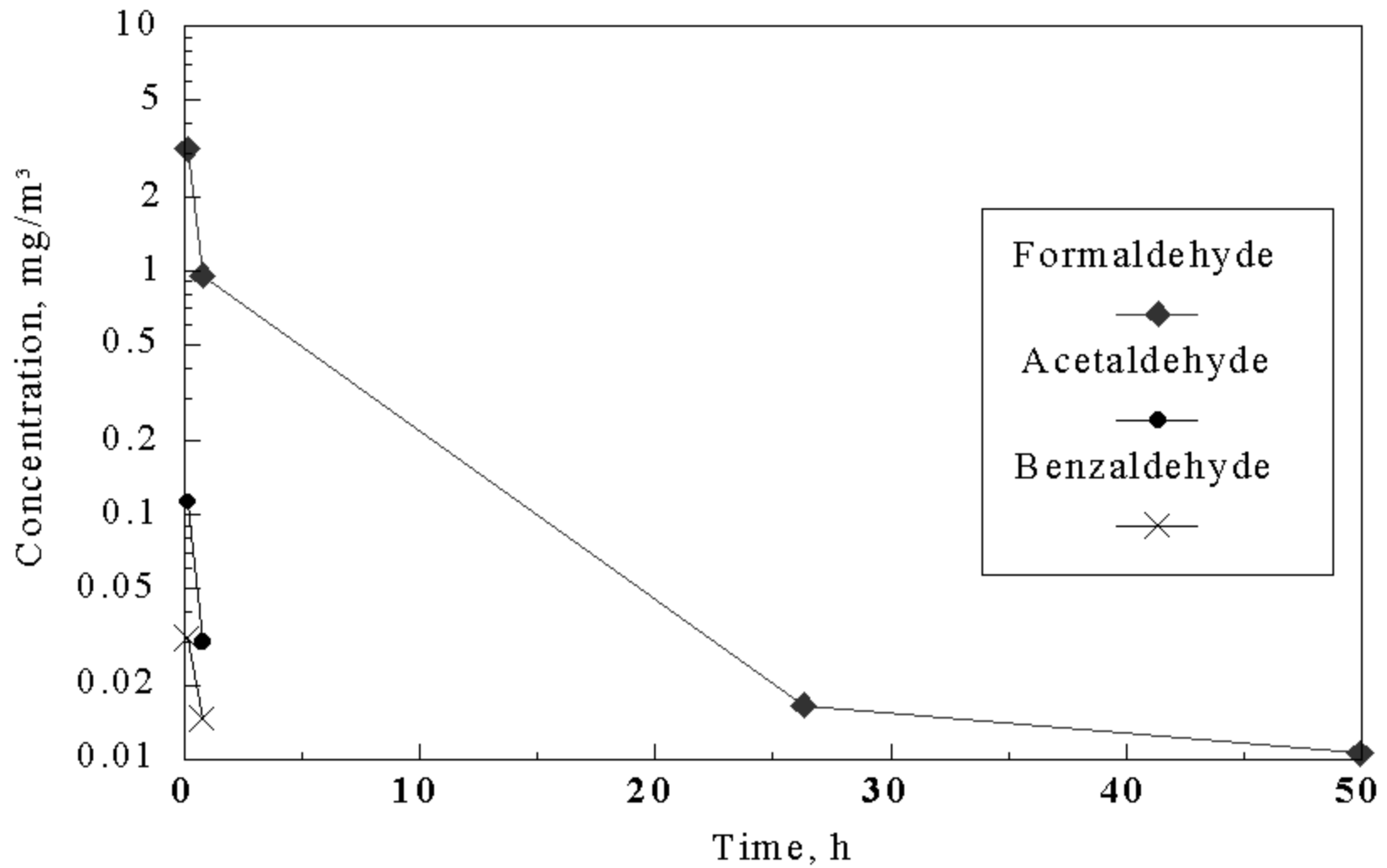


Figure 8-2. Aldehyde emission profiles of paint L-1. The method detection limits was 0.0007 mg/m<sup>3</sup> for formaldehyde and acetaldehyde, and 0.0014 mg/m<sup>3</sup> for benzaldehyde.

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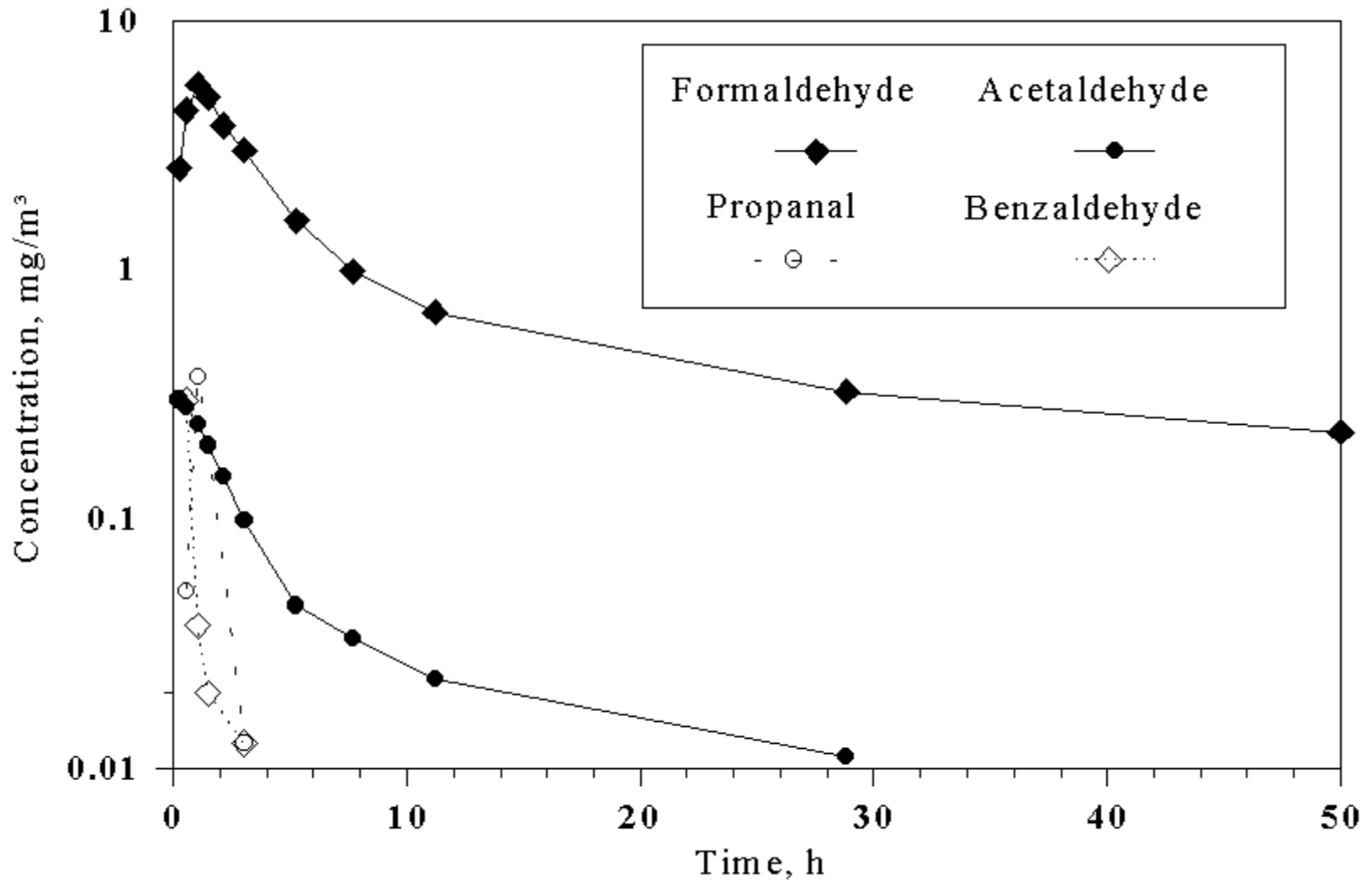


Figure 8-3. Aldehyde emission profiles of paint L-3. The method detection limit was  $0.0007 \text{ mg/m}^3$  for formaldehyde, acetaldehyde, and propanal, and  $0.0014 \text{ mg/m}^3$  for benzaldehyde.

maintain productivity. In addition, the 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 the entire building section for painting is difficult and often not desirable. However, occupants in those buildings frequently include those who are vulnerable and susceptible. When there is indoor air pollution by a potentially harmful VOC, such as formaldehyde released from the paint, the exposure potential may be high since the occupants may be located in the newly painted room and some of the normal precautions may be neglected.

### ***Performance Evaluation***

The results for performance testing are summarized in Table 8-4. It is seen that the performance characteristics of the four low-VOC latex paints varied significantly.

**Table 8-4. Results of Performance Testing**

| Paint                        | 0<br>(a conventional<br>latex paint) | L-1   | L-2   | L-3   | L-4   |
|------------------------------|--------------------------------------|-------|-------|-------|-------|
| Specular gloss               | 1.6                                  | 2     | 1.5   | 9.4   | 4.7   |
| Hiding power                 |                                      |       |       |       |       |
| Contrast ratio: 1.5 mils wet | 0.973                                | 0.968 | 0.982 | 0.928 | 0.966 |
| 3.0 mils wet                 | 0.987                                | 0.987 | 0.998 | 0.961 | 0.982 |
| Scrub resistance (cycles)    | 508                                  | 254   | 2000+ | 2000+ | 49    |
| Washability (%)              | 50                                   | 41    | 47    | 36    | 50    |
| Sag resistance               | 12                                   | 12    | 12    | 12    | 12    |
| Dry to touch (minutes)       | 12                                   | 14    | 14    | 11    | 15.5  |
| Yellowing index              | -0.01                                | -0.07 | 0.14  | -0.79 | 0.03  |



For specular gloss, the higher the value, the more light is reflecting off the surface. Table 8-4 shows that the measured values ranged from 1.5 (not visible) to 9.4 (significant light reflection) with paints 0 and L-2 at the low end. As to hiding power, the measured contrast ratios are good for all of the paints except paint L-3 at 1.5 mils wet film thickness. For scrub resistance, paints L-2 and L-3 exhibited the best performance which even exceeded that of the conventional latex paint. On the other hand, paint L-4 exhibited extremely poor scrub resistance with the number of cycles (49) far less than the typical range (250 to 500) of conventional paints. As to washability, paints 0 and L-4 scored the highest, and paint L-2 was only slightly lower. Sag-resistance was measured with a multi-notched applicator. A perfect score is 12, which was achieved with all five paints. The dry to touch time ranged from 11 to 15.5 minutes, with the fastest time exhibited by paint L-3 which had the lowest water content (Table 8-1). The inverse relationship between dry to touch time and water content was also suggested by paint L-4, which had the highest water content and exhibited the slowest time. The yellowness indices measured were relatively small and would not be considered significant.

Based on the ASTM test results, paint L-2 appeared to perform better than the other three low-VOC paints for most of the features assessed. Table 8-4 also shows that, when compared with paint 0 (the conventional latex paint used as a reference), paint L-2 also provided equivalent or superior performance on most of the categories evaluated.

## **Conclusions**

Based on the experimental data of the four paints tested, the following conclusions are drawn:

- One commercially available low-VOC latex paint (i.e., paint L-2) emitted considerably less VOCs and performed equal to or better than a conventional latex paint used as a control. However, the data also indicated that the rest of the low-VOC latex paints tested either had some inferior properties or emitted hazardous air pollutants.

- VOC content data based on Method 24 are 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.
- Chamber test data indicated that, despite having low total VOC content in the paint, emissions of individual VOCs and hazardous air pollutants (e.g., formaldehyde and acetaldehyde) can still be significant. Due to the use pattern (i.e., no full evacuation during painting and immediate re-occupation after painting) suggested by the manufacturers, the intimate exposure of sensitive occupants to those hazardous air pollutants are of special concern.
- In addition to VOC content data, consumers need emission information and performance evaluation results to assist in making purchasing decisions about low-VOC latex paints.

## Chapter 9

### Experimental Work to Characterize and Reduce Formaldehyde Emissions from Low-VOC Paint

One of the conclusions of the previous chapter was that some of the “low-VOC” latex paints that were tested actually released significant quantities of formaldehyde as they dried. This chapter provides an example of how small chamber testing methods can fit into an integrated pollution prevention (P2) effort—in this case, an effort aimed at reducing formaldehyde emissions from certain low-VOC latex paints.

Formaldehyde emissions have been detected from certain latex paints (Hansen et al., 1987). The formaldehyde emissions from low-VOC latex paints are of special concern since those paints are often used by sensitized and allergic consumers as an alternative to conventional latex paints to avoid VOC exposure. Low-VOC latex paints are also promoted for use in occupied buildings during normal business hours, without the necessity of evacuating entire sections of the building. It is claimed that the newly painted room may be put back in use almost immediately to maintain productivity. The cost of painting can also be reduced by eliminating premium pay for night or weekend painting work. As a result, low-VOC latex paints are often sold for use in occupied hospitals, extended care facilities, nursing homes, medical facilities, schools, hotels, offices, and homes where extended evacuation of the entire building section for painting is difficult and often not desirable.

Formaldehyde has been recognized as a hazardous air pollutant (CAAA, 1990), an odorous respiratory tract irritant (AIHA, 1989), and a probable carcinogen (Grindstaff et al., 1991). The World Health Organization guideline for indoor air formaldehyde concentration is 0.1 mg/m<sup>3</sup> (WHO, 1987). The California Air Resources Board recommends for homes an "action level" of 0.12 mg/m<sup>3</sup> and a "target level" of 0.06 mg/m<sup>3</sup> or lower (CARB, 1991). The U. S.

Department of Housing and Urban Development recommends that indoor formaldehyde concentrations from all sources should not exceed  $0.5 \text{ mg/m}^3$  (HUD, 1984). The California Environmental Protection Agency suggests an acute 1-h exposure concentration of  $0.17 \text{ mg/m}^3$ , based on early symptoms of eye irritation (OEHHA, 1995). Those guidelines and recommendations are established for the general population. However, occupants of buildings painted with low-VOC latex paints often include those who are vulnerable and susceptible. In case of indoor air pollution by formaldehyde released from the paint, the exposure and associated health risk will be higher than average since the occupants are located in the newly painted room and some of the normal precautions may be neglected.

To address those concerns, NRMRL evaluated four commercially available low-VOC latex paints (Chang et al., 1999), as described in Chapter 8. The results indicated that, compared with conventional latex paints, the VOC contents and emissions of those paints are considerably lower. However, formaldehyde emissions were detected from two of the four paints tested. NRMRL conducted additional studies with the low-VOC paint that had the highest formaldehyde emissions. Long-term environmental chamber tests were performed to characterize the formaldehyde emission profiles. A mathematical model was developed to interpret the chamber data. Biocide was identified and confirmed as a major source of the formaldehyde in the paint. The paint was reformulated as a pollution prevention effort to reduce formaldehyde emissions. The objective of this research is to summarize the results from the additional studies and to present the newly developed mathematical model for formaldehyde emissions.

## **Experimental Procedure**

Experiments were designed to generate formaldehyde emission data from the newly applied low-VOC latex paint as it dried for more than 350 hours under controlled experimental conditions. Tests were conducted in IEMB's small chamber source characterization facilities, along the lines of the experimental conditions described in Chapter 7.

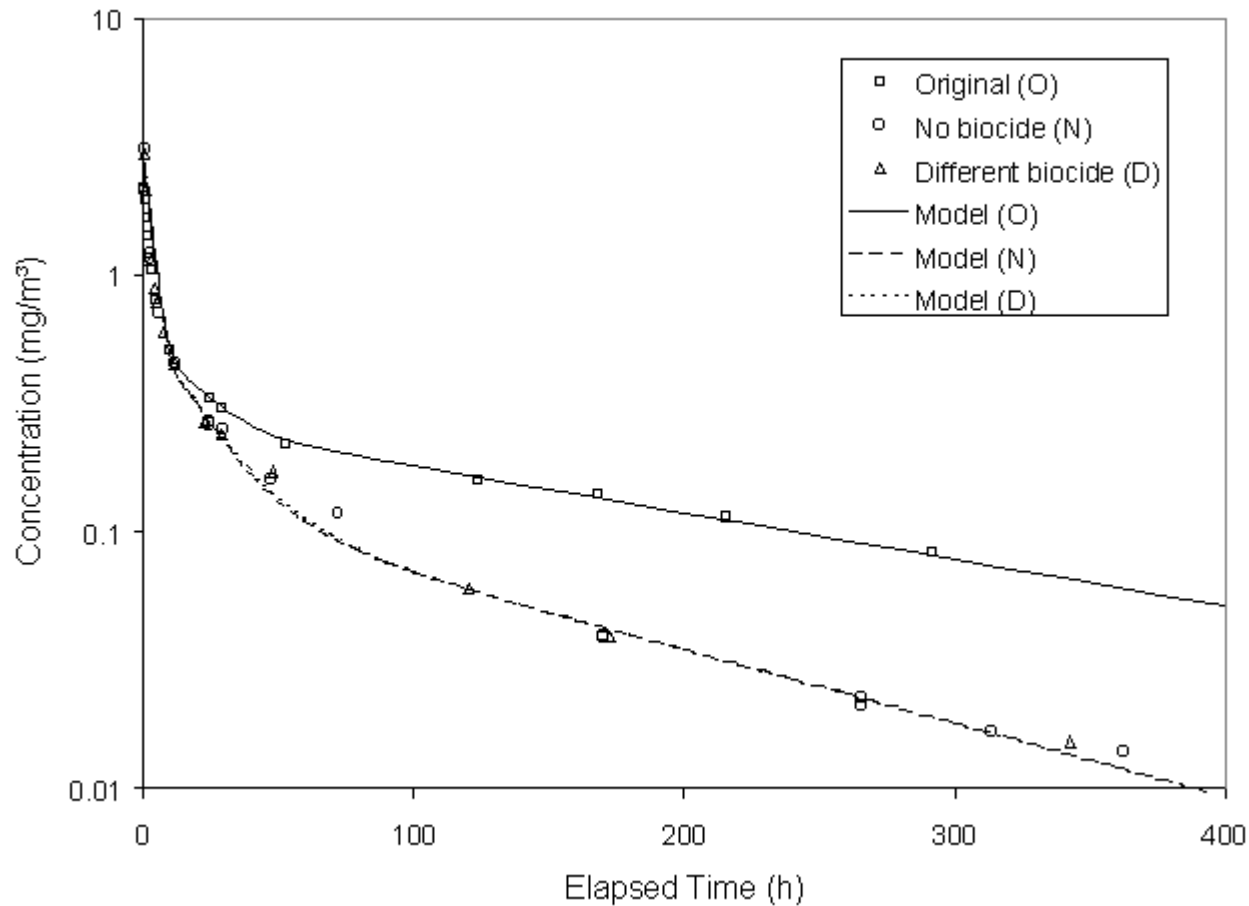
Gypsum board purchased from a local supplier of building materials was used as the substrate to provide a realistic emission profile. It was prepared, loaded with paint, and placed in the small chamber as described in Chapter 7, Experimental Work section. A typical test lasted for about 2 weeks with the clean air flow through the chamber continued at a controlled rate.

Air samples in the chamber outlet were collected based on EPA Method IP-6A (Winberry et al., 1990) using 55 to 105  $\mu\text{m}$  chromatographic-grade silica gel coated with acidified 2,4-dinitrophenylhydrazine (DNPH). Sample volumes ranged from 2 to 30 L with sample flow in the range of 200 to 400  $\text{cm}^3/\text{min}$  controlled by mass flow controllers. Each sample was extracted with 5 mL acetonitrile (ACN). Twenty-five  $\mu\text{L}$  of extract was analyzed on a Hewlett Packard 1090 high-performance liquid chromatograph (HPLC). Chromatography was performed with a C-18 reverse-phase column (4.6 x 250 mm) using a gradient program of 45% ACN to 30 minutes, then 75% ACN to 35 minutes, then 100% ACN to 41 minutes, and finished with 45% ACN to 55 minutes.

The HPLC was calibrated for formaldehyde. Quantification was performed using an external standard method with a five-point calibration based on a peak area of derivatized standards. Performance of the instrument was verified each day by analysis of a quality control check sample prior to starting the sample analysis.

## **Experimental Data**

The formaldehyde concentrations measured at the chamber exit are shown in Figure 9-1 (as squares). The first sample of the test, taken within 30 min after the start of the experiment, had the highest concentration. The formaldehyde concentrations decreased rapidly and monotonically by about 1 order of magnitude in the first 10 h of the test. Chang and Guo (1992a) suggested a fast organic emission model to interpret such results. The model assumed that a portion of the formaldehyde in the paint was emitted to the chamber air almost instantly (perhaps in a few minutes) at the start of the experiment. As a result, there was a sharp increase of



**Figure 9-1. Comparison of chamber data with model predictions. Note that model predictions for paints with no biocide and with a different biocide are not differentiable.**

formaldehyde concentration as soon as the painted gypsum board was placed inside the chamber. The first “puff” of formaldehyde emission created a relatively high initial chamber concentration, which then decayed rapidly over the initial 10-h period.

As the experiment proceeded beyond 10 h, the formaldehyde concentration decrease slowed considerably. After 100 h, the formaldehyde concentration in the chamber decayed at a very slow pace and gave a long tail to the time/concentration curve. When plotted on a semi-logarithmic scale, the tail section of the time/concentration curve became almost a straight line as shown in Figure 9-1. Chang and Guo (1992b) characterized these emissions as process controlled by the solid-phase diffusion of the organic species. The formaldehyde had to diffuse through the relatively dry and dense paint embedded in the substrate. The internal diffusion process made the emission rates low, but the emission lasted for a long time.

### **Emission Model**

It was found that the formaldehyde emissions from the paint applied to the wallboard can be represented by first-order decay in-series model as shown in Figure 9-2. The empirical model assumed that the formaldehyde in the applied paint was distributed in two layers. The top layer can be considered as the thin surface coating section of the paint. Formaldehyde was emitted from the top layer directly into the chamber air. The formaldehyde emissions from the top layer were assumed to be controlled by diffusion through the surface coating section. The bottom layer can be seen as the paint beneath the surface and embedded in the substrate (wallboard). The formaldehyde in the bottom layer had to migrate to the top layer before it was emitted. The internal diffusion in the embedded paint is the controlling mechanism of the formaldehyde migration from the bottom to the top layer.

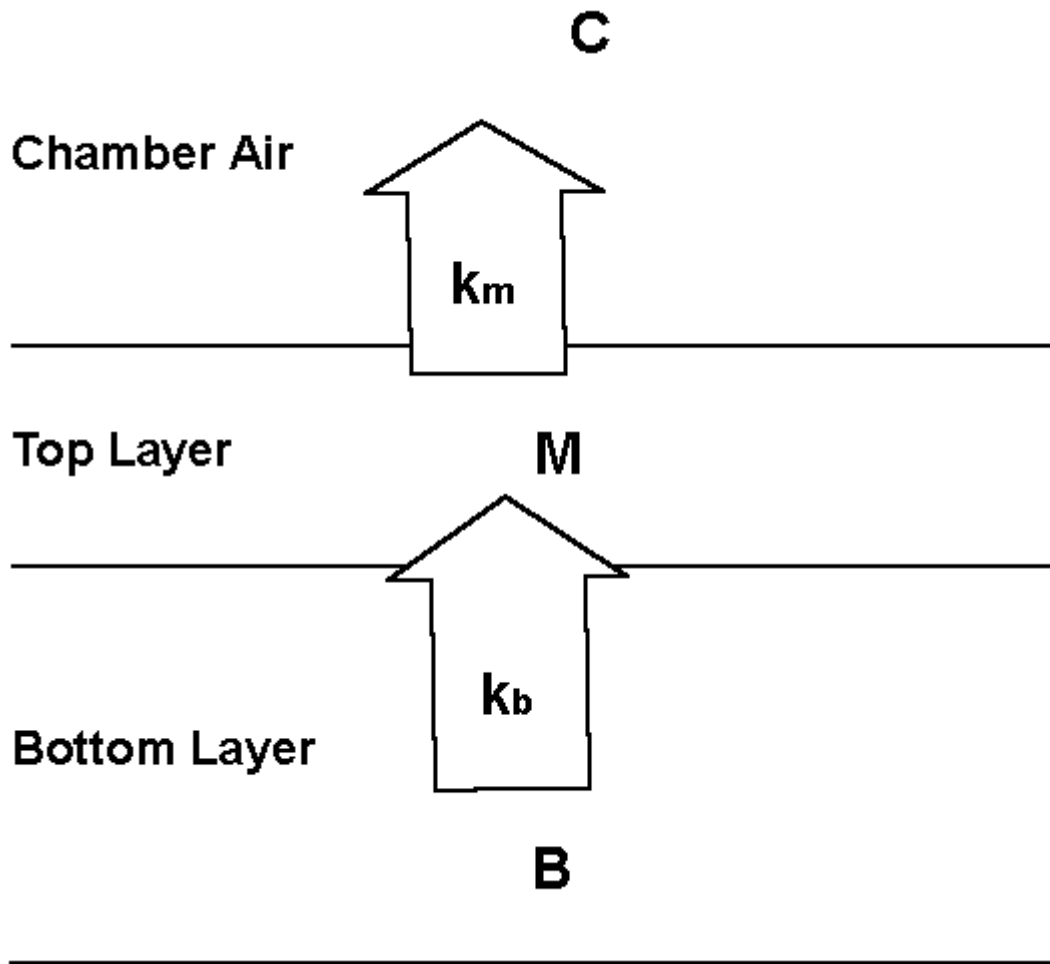


Figure 9-2 Schematic of the first-order decay in-series model.



The model also assumed that the formaldehyde emissions can be divided into three stages. First, there was an almost instant “puff”-like release of formaldehyde immediately after the paint was applied to the gypsum board. The “puff” release caused an initial peak concentration of formaldehyde,  $C_0$ , which is equivalent to the total instant formaldehyde emission divided by the chamber volume. In the second stage, the top layer formaldehyde was almost depleted, and the chamber air formaldehyde concentration decreased by more than 1 order of magnitude. The third stage formaldehyde emissions mainly came from the bottom layer and were controlled by the slow diffusion process.

With the assumption that both the formaldehyde emission and migration can be described by the first-order decay model (Clausen et al., 1991), the following mass balance equations can be written to represent the formaldehyde mass transfer between the two layers and the chamber air:

$$\frac{dB}{dt} = -k_b B \quad (9-1)$$

$$\frac{dM}{dt} = k_b B - k_m M \quad (9-2)$$

$$\frac{dC}{dt} = -N C + L k_m M \quad (9-3)$$

Initial conditions:  $C=C_0$ ,  $M=M_0$ , and  $B=B_0$  at  $t=0$ .

where

- $B$  = the amount of the formaldehyde in the bottom layer ( $\text{mg}/\text{m}^2$ ),
- $k_b$  = the first-order decay constant for formaldehyde migration from the bottom layer ( $\text{h}^{-1}$ ),
- $M$  = the amount of formaldehyde in the top layer ( $\text{mg}/\text{m}^2$ ),
- $k_m$  = the first-order decay constant for formaldehyde emission from the top layer ( $\text{h}^{-1}$ ), and
- $C$  = formaldehyde concentration in the chamber air ( $\text{mg}/\text{m}^3$ ).

Equations (9-1) to (9-3) can be solved by Laplace Transform, and the analytical solution for C is:

$$C = A_1 e^{-Nt} + A_2 e^{-k_m t} + A_3 e^{-k_b t} \quad (9-4)$$

where

$$C_0 = A_1 + A_2 + A_3 \quad (9-5)$$

$$M_0 = \frac{A_2 (N - k_m) + A_3 (N - k_b)}{L k_m} \quad (9-6)$$

$$B_0 = \frac{A_3 (N - k_b) (k_m - k_b)}{L k_m k_b} \quad (9-7)$$

In addition,

$$M = M_0 e^{-k_m t} + \frac{k_b B_0 (e^{-k_b t} - e^{-k_m t})}{k_m - k_b} \quad (9-8)$$

$$B = B_0 e^{-k_b t} \quad (9-9)$$

## Data Analysis

Of the six parameters in Equation (9-4), N is determined by the air exchange rate (0.5 h<sup>-1</sup>) used for the chamber testing, and the other five need to be estimated. Difficulties were encountered when a non-linear regression curve-fitting routine was used to estimate the values of the five parameters. However, it was found that the five unknown parameters in Equation (9-4) could be estimated by an exponential peeling procedure (Serber and Wild, 1989; Mølhave et al., 1995) for a three-compartment analysis. The procedure was based on the assumption that

$N \gg k_m \gg k_b \geq 0$ . When this assumption is valid, the first and second terms on the right-hand side of Equation (9-4) become negligible for  $t$  large, and Equation (9-4) is reduced to:

$$\ln(C) = \ln(A_3) - k_b t \quad (9-10)$$

A plot of  $\ln(C)$  against  $t$  for  $t$  large should give a straight line with intercept  $\ln(A_3)$  and slope  $-k_b$ .

The peeling procedure was initiated by the estimation of the long-term parameters,  $A_3$  and  $k_b$ , using a least-square regression method to fit Equation (9-10) to the chamber data between 100 and 300 h shown in Figure 9-1. The estimated values of  $A_3$  and  $k_b$  are listed in the second column of Table 9-1. Subsequently, the same iterative regression method was used to estimate  $A_2$  and  $k_m$  by fitting Equation (9-11) to the chamber data between 10 and 300 h. (Note that the values of  $A_3$  and  $k_b$  are already known.)

$$C = A_2 e^{-k_m t} + A_3 e^{-k_b t} \quad (9-11)$$

Finally,  $A_1$  was estimated by setting  $N=0.5$  and fitting Equation (9-4) to the entire set of chamber data shown in Figure 9-1. The estimated values of  $A_1$ ,  $A_2$ , and  $k_m$  and their standard deviations are listed in the second column of Table 9-1.

It is seen from Table 9-1 that the value of  $N$  (0.5) is considerably greater than that of  $k_m$  (0.0745) which is much greater than that of  $k_b$  (0.0042). Therefore, the assumption of the exponential peeling procedure,  $N \gg k_m \gg k_b \geq 0$ , was validated. Also, the values of  $k_m$  and  $k_b$  are in the same range (from 0.1 to 0.001  $\text{h}^{-1}$ ) as estimated before for solid-phase diffusion-controlled emissions (Chang and Guo, 1992b).

**Table 9-1. Estimated Values<sup>a</sup> of Parameters of Equation (9-4)**

| <b>Parameter</b>     | <b>Original paint</b> | <b>Without biocide</b> | <b>With a different biocide</b> |
|----------------------|-----------------------|------------------------|---------------------------------|
| $A_1, \text{mg/m}^3$ | 1.926±0.027           | 2.563±0.069            | 2.549±0.070                     |
| $A_2, \text{mg/m}^3$ | 0.513±0.021           | 0.592±0.067            | 0.602±0.086                     |
| $A_3, \text{mg/m}^3$ | 0.274±0.005           | 0.129±0.018            | 0.130±0.015                     |
| $k_m, \text{h}^{-1}$ | 0.0745±0.0031         | 0.0518±0.0062          | 0.0547±0.0081                   |
| $k_b, \text{h}^{-1}$ | 0.0042±0.0001         | 0.0066±0.0009          | 0.0066±0.0008                   |

<sup>a</sup> expressed as mean ± standard deviation

The goodness-of-fit of the model to the experimental data was evaluated based on the ASTM criteria (ASTM, 1995). The ASTM criteria (the fifth column of Table 9-2) include the slope and intercept of the best-fit line between measured and predicted values, the correlation coefficient between measured and predicted concentrations, the magnitude of prediction error relative to the measured values represented by normalized mean square error (NMSE), and the fractional bias.

The estimated values of the five goodness-of-fit criteria for the low-VOC latex paint tested are listed in the second column of Table 9-2. It is clear from Table 9-2 that all five ASTM criteria were met and the first-order decay in-series model is adequate for simulating formaldehyde emissions from the low-VOC latex paint as shown in Figure 9-1.

When all six model parameters are known, the values of  $C_o$ ,  $M_o$ , and  $B_o$  can be calculated by Equations (9-5), (9-6), and (9-7), respectively. The calculated values are shown in the second column of Table 9-3. The significance of the formaldehyde emissions from this low-VOC paint is reflected by the peak chamber concentration,  $C_o$ , of 2.71 mg/m<sup>3</sup>. This concentration is considerably higher than any of the guidelines mentioned in the beginning of the chapter.

**Table 9-2. Comparison of Quantitative Measures of Goodness of Model with ASTM Criteria (ASTM, 1995)**

|                         | Original paint | Without biocide | With a different biocide | ASTM criteria |
|-------------------------|----------------|-----------------|--------------------------|---------------|
| Slope                   | 0.998          | 0.951           | 0.998                    | 0.75 to 1.25  |
| Intercept               | 0.000377       | -0.0236         | -0.0108                  | -0.25 to 0.25 |
| Correlation coefficient | 0.999          | 0.993           | 0.996                    | > 0.9         |
| NMSE <sup>a</sup>       | 0.0015         | 0.0333          | 0.0101                   | < 0.25        |
| Fractional bias         | -0.0024        | -0.0083         | 0.0136                   | < 0.25        |

<sup>a</sup> Normalized mean square error

The total amount of formaldehyde per unit area of the applied paint can be estimated by integrating Equation (9-4) and multiplying the result by N/L. On the other hand, the total amount of formaldehyde can also be calculated as the sum of  $C_oV/A$ ,  $M_o$ , and  $B_o$ , based on the model assumptions. The term  $C_oV/A$  is equivalent to the amount of formaldehyde in the initial "puff." Table 9-3 indicates that the amount of formaldehyde emitted in the initial "puff," although resulting in the high peak concentration, accounts for only 6.8% of the total formaldehyde emitted. The majority (80.4%) of the formaldehyde emitted, according to the model, came from the bottom layer (i.e.,  $B_o$ ) via the slow solid-phase diffusion-controlled process.

**Table 9-3. Estimated Amount of Formaldehyde in the Paint Applied**

|   | Original paint | Without biocide | With a different biocide |
|---|----------------|-----------------|--------------------------|
| $C_o$ , mg/m <sup>3</sup>                     | 2.71           | 3.28            | 3.28                     |
| $M_o$ , mg/m <sup>2</sup>                     | 10.0           | 12.65           | 12.70                    |
| $B_o$ , mg/m <sup>2</sup>                     | 63.2           | 17.80           | 17.53                    |
| Total ( $C_oV/A+M_o+B_o$ ), mg/m <sup>2</sup> | 78.62          | 37.24           | 37.02                    |

Since all the parameters are known, Equations (9-8), and (9-9) can be used to estimate the amount of formaldehyde remaining in the paint which is equivalent to the sum of M and B. The results are shown in Figure 9-3. It is seen that (at  $t=350$  h)  $15.4 \text{ mg/m}^2$ , or 19.6% of the total emittable formaldehyde, was still remaining in the paint. The model predicted that it would take about 1056 h for 99% of the formaldehyde in the paint to be emitted.

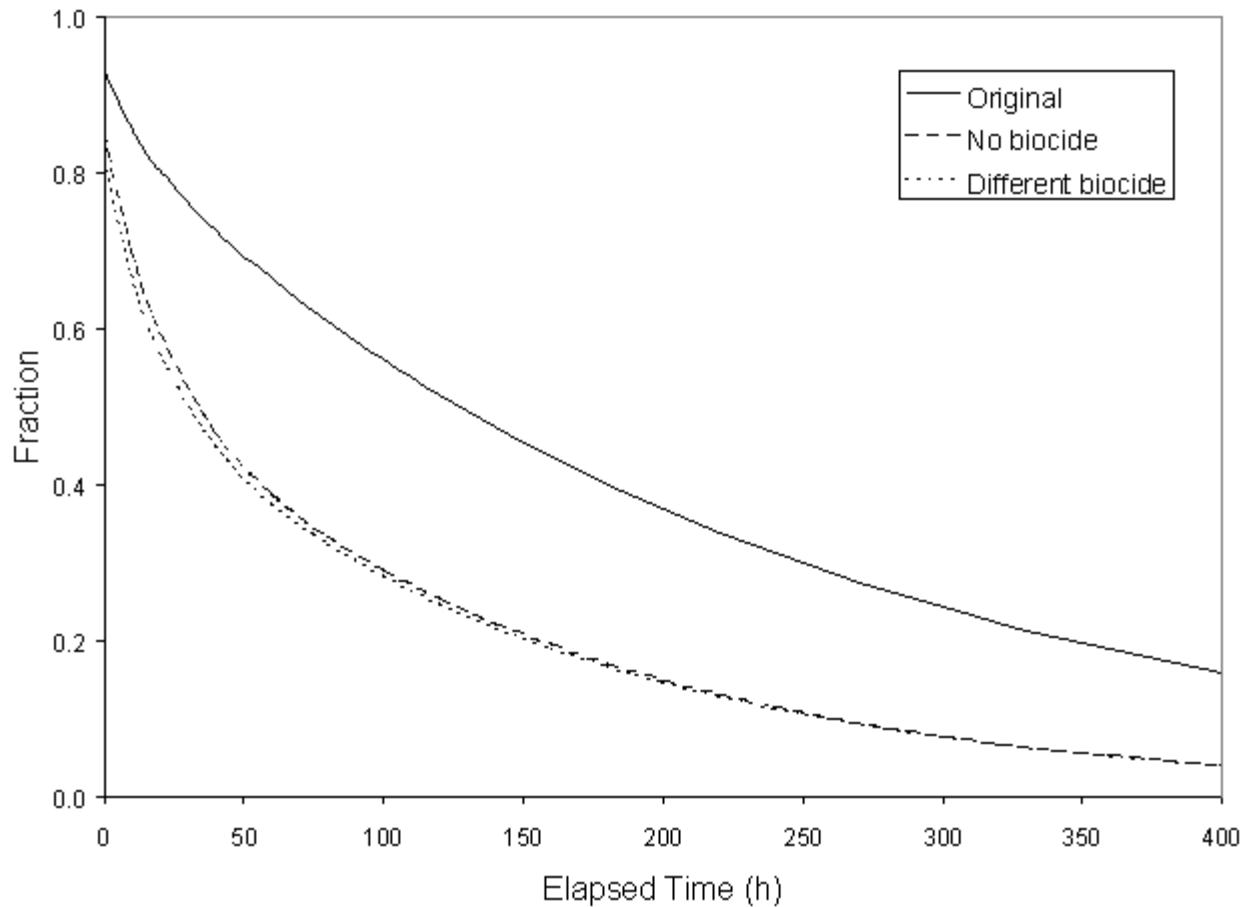
## Source Investigation

The paint manufacturer was informed about the test results, and the paint formula was reviewed. The paint manufacturer pointed out that the biocide used to preserve the paint might contain as much as 5% formaldehyde, and it was suspected that the biocide could be a major source of the formaldehyde. To confirm this hypothesis, the paint manufacturer provided a sample that contained no biocide for chamber testing.

The chamber test data with no biocide are also shown in Figure 9-1 (as circles). It is seen that the formaldehyde concentration profile followed the same pattern as the original one. But the formaldehyde concentration decreased faster and the tail section was considerably lower than that of the original paint.

The chamber concentration data with no biocide were analyzed by the first-order decay in-series model and the exponential peeling procedure. The results are listed in the third columns of Tables 9-1, 9-2, 9-3, and 9-4. Table 9-1 indicates that the assumption of the exponential peeling procedure,  $N \gg k_m \gg k_b \geq 0$ , was still valid, which confirmed that the formaldehyde was emitted in the same fashion as before. Table 9-2 shows that the first-order decay in-series model was adequate to simulate the formaldehyde emissions from the paint without biocide as illustrated by Figure 9-1. The bottom row of Table 9-4 shows that each g of the no-biocide paint contained 0.269 mg of total emittable formaldehyde which is about 56.4% less than that of the original.

Table 9-3 indicates that the decreased formaldehyde content significantly affected only the bottom-layer diffusion-controlled emissions ( $B_o$ ) which was reflected by the lower tail section of the emission profile shown in Figure 9-1. Figure 9-3 shows that (at  $t=350$  h) only  $1.93 \text{ mg/m}^2$ , or 5.4% of the total emittable formaldehyde, was still remaining in the paint without biocide. The model also predicted that it would take about 607 h for 99% of the formaldehyde to be released. Compared with the original paint, the formaldehyde in the no-biocide paint was depleted considerably faster.



**Figure 9-3. Fraction of formaldehyde remaining in the paint.**

**Table 9-4. Calculated Formaldehyde Content in Three Paints Tested**

| Test paint                            | Original paint | Without biocide | With a different biocide |
|---------------------------------------|----------------|-----------------|--------------------------|
| Paint applied, g                      | 3.26           | 3.54            | 3.43                     |
| Substrate area, m <sup>2</sup>        | 0.0256         | 0.0256          | 0.0256                   |
| Total formaldehyde, mg/m <sup>2</sup> | 78.62          | 37.24           | 37.02                    |
| Formaldehyde content of paint, mg/g   | 0.617          | 0.269           | 0.276                    |

Therefore, the chamber data confirmed that the biocide was a major source of formaldehyde in the paint. However, biocide was not the only source: other sources (e.g, additives and binders) also contributed significantly (43.6%) to the formaldehyde emissions.

### **Biocide Replacement**

In a pollution prevention effort to reduce formaldehyde emissions through reformulation, the paint manufacturer decided to replace the biocide with a new one. A sample of the reformulated paint was evaluated by a small chamber test following the same procedure as described in Chapter 7, Experimental Work section. The experimental results are also shown in Figure 9-1 as triangles. It is seen that the formaldehyde emission profile basically coincided with that of the paint without biocide. Data analysis (Tables 9-1 and 9-2) by the first-order decay in-series model and the exponential peeling procedure indicated that each g of the reformulated paint contained 0.276 mg of total emittable formaldehyde which is very similar to that (0.269 mg) of the paint without a biocide (Table 9-4). Apparently, biocide replacement eliminated a major source of formaldehyde in the paint and reduced the amount of formaldehyde emission by 55.3%. When compared with the emissions of the original paint (Table 9-3), only the third-stage long-term formaldehyde emissions were reduced by biocide replacement.



## Conclusions

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 is applied to gypsum board, the formaldehyde emissions decay very slowly after the initial peak, and the emission can last for more than a month. Certain biocides, when used as a preservative for latex paints, can be a major source of formaldehyde emissions from the paint. This particular source was verified by the significant reduction of formaldehyde emissions in the absence of the biocide.

The formaldehyde emissions from a latex paint applied to gypsum board can be characterized by a first-order decay in-series model. The semi-empirical model can be used to estimate the amount of formaldehyde emitted or remaining in the paint. It can also predict the initial peak concentration and the time of depletion. When the activity patterns of building occupants are defined, the model can further be used for exposure risk assessment. Note that the model assumed an initial, instant release of formaldehyde and can be applied only to similar cases.

The biocide-contributed formaldehyde emissions can be eliminated by paint reformulation via biocide replacement. However, when 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 exposure potential to high peak concentrations of formaldehyde still exists. Additional research is needed to identify other potential sources of formaldehyde to completely eliminate formaldehyde emissions from those paints.

## Chapter 10

### References

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## Appendix A

### A Proposed Standard Practice for Testing and Sampling of Volatile Organic Compounds (Including Carbonyl Compounds) Emitted from Paint Using Small Environmental Chambers

#### 1. Scope

1.1 This practice provides procedures for preparing test samples of alkyd primer, alkyd paint, latex primer, or latex paint applied to building materials such as gypsum wallboard, wood, or engineered wood products and procedures for sampling volatile organic compounds (VOCs) emitted from those test samples. Emissions are sampled from small environmental chambers operated under controlled conditions.

1.2 This practice describes procedures for preparation of test specimens by application of primer or paint to common building materials. Use of the procedures described in this practice for tests with other application methods or substrates may affect the results and not meet the criteria recommended in the practice.

1.3 This practice describes procedures for collection of VOCs on sorbent tubes and carbonyl compounds on silica gel treated with 2,4-dinitrophenylhydrazine (DNPH) that require analytical methods for measurement of individual organic compound and total VOC concentrations. This practice does not describe the detailed procedures of analytical methods, but refers to published methods for these analyses.

1.4 This practice describes procedures for testing and sampling VOCs emitted from paint under controlled conditions. The test conditions, when combined with analytical data, can be used to calculate emission rates. This standard practice does not recommend a method for the calculations.

1.5 Values stated in the International System of Units (SI) are to be regarded as the standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of the standard practice to establish practices for appropriate safety and health, and to determine the applicability of regulatory limitations prior to use.*

#### 2. Reference Documents

##### 2.1 *ASTM Standards*

D 16 Standard Terminology for Paint, Related Coatings, Materials, and Applications

D 355 Practice for Gas Chromatography Terms and Relationships

D 1005 Standard Test Method for Measurements of Dry Film Thickness of Organic Coatings

D 1212 Standard Test Method for Measurement of Wet Film Thickness of Organic Coatings  
Using Micrometers

- D 1356 Standard Terminology Relating to Sampling and Analysis of Atmospheres
- D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres
- D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)
- D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method
- D 5116 Guide for Small Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products
- D 5197 Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)
- D 6196 Practice for Selection of Sorbents and Pumped Sampling/Thermal Desorption Analyses Procedures for Volatile Organic Compounds in Air
- D 6345 Standard Guide for Selection of Methods for Active, Integrative Sampling of Volatile Organic Compounds in Air
- E 355 Standard Practice for Gas Chromatography Terms and Relationships
- E 741 Test Method for Determining Change in a Single Zone by Means of Tracer Gas Dilution

## 2.2 Other Referenced Documents

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Compendium Methods TO-15 and TO-17, EPA/625/R-96-010b (NTIS No. PB99-172355), (website <http://www.epa.gov/ttn/amtic/airtox.html>), U.S. EPA, Center for Environmental Research Information, Cincinnati, OH, January 1999.

## 3. Terminology

3.1 *Definitions* - For definitions and terms used in this standard practice, refer to Standard Terminology D 1356, Standard Terminology D 16, and Standard Practice E 355. For definitions and terms related to test methods using small-scale environmental chambers, refer to Standard Guide D 5116.

### 3.2 *Definitions of Terms Specific to this Standard Practice:*

3.2.1 *air changes per hour (ACH)* - the volume of clean air brought into the chamber in 1 hour divided by the chamber volume measured in identical volume units, normally expressed in air changes per hour ( $\text{h}^{-1}$ ).

3.2.2 *alkyd paint* - also referred to as oil paint, it is a paint that contains drying oil or oil varnish as the basic vehicle ingredient.

3.2.3 *chamber loading ( $\text{m}^2/\text{m}^3$ )* - the exposed surface area of the test specimen coated with paint divided by the environmental test chamber volume.

3.2.4 *clean air* - air that does not contain any individual VOC at a concentration in excess of 2  $\mu\text{g}/\text{m}^3$  and does not contain greater than 10  $\mu\text{g}/\text{m}^3$  for the sum of the VOCs measurable in the sample. The air should be conditioned to remove particulates and ozone.

3.2.5 *environmental enclosure* - a temperature controlled enclosure of sufficient size to contain the environmental test chamber(s) and allow adequate access to it to conduct the testing.

3.2.6 *environmental test chamber* - a chamber constructed of inert materials into which a material can be placed and tested to determine the VOC emission rate under controlled environmental conditions.

3.2.7 *latex paint* - a paint containing a stable aqueous dispersion of synthetic resin, produced by emulsion polymerization, as the principal constituent of the binder. Modifying resins may be present.

3.2.8 *primer* - the first of two or more coats of a paint.

3.2.9 *spreading rate* - the area covered by a unit volume of coating material, frequently expressed as square feet per gallon. It may also be referred to as *coverage* or *coverage rate* on paint container labels.

3.2.10 *test specimen* - a specimen of the paint applied to a substrate such as gypsum wallboard, wood, or engineered wood products.

3.2.11 *volatile organic compound (VOC)* - an organic compound with saturation vapor pressure greater than  $10^{-2}$  kPa at 25°C

#### **4. Summary of Standard Practice**

4.1 This practice describes procedures for testing and sampling emissions of VOCs, including formaldehyde and other carbonyl compounds, from paint applied to building materials such as gypsum wallboard, wood, and engineered wood products. Emissions tests are conducted using small environmental chambers operated in a dynamic mode with continuous flow of humidified VOC-free air through the chambers. The environmental chambers are operated at designated conditions of airflow rate, temperature, and relative humidity. The VOCs in the emissions are sampled by adsorption on an appropriate single, or multiple sorbent media that can be analyzed by thermal desorption and combined gas chromatography/mass spectrometry (GC/MS) or GC/flame ionization detection (GC/FID). Formaldehyde and other carbonyl compounds are collected on silica gel coated with DNPH reagent that can be analyzed by high performance liquid chromatography (HPLC).

4.2 This practice describes the procedures for handling and storage of paint, setup of the small environmental test chambers, preparation of test specimens, chamber performance tests, sampling and reporting.

#### **5. Significance and Use**

5.1 Latex and alkyd paints are used as coatings for walls, wooden trim, and furnishings in occupied buildings. Paint may be applied to large surface areas and may be applied repeatedly during the lifetime of a building. VOCs are emitted from paint after application to surfaces.

5.2 There is a need for data on emissions from paint. The data can be used to compare emissions from different products. The data may be used to assist manufacturers in reducing or eliminating VOC emissions from their products. The data may be used to predict concentrations of VOCs in a room or building when used with appropriate indoor air quality models.

5.3 Standard test practices and procedures are needed for the comparison of emissions data from different laboratories.

## **6. Apparatus**

6.1 This standard practice requires the use of an environmental chamber testing facility and air sample collection systems.

6.2 *Environmental Chamber Testing Facility*, consisting of an environmental test chamber, a controlled-temperature environmental enclosure, a system for supplying clean and conditioned air to the chamber, and fittings and manifolds on the chamber outlet for collection of air samples. All materials and components in contact with the test specimen or air prior to sample collection should be chemically inert and accessible for cleaning. Suitable materials include stainless steel and glass. All gaskets and flexible components should be made from chemically inert materials. General guidance for design, construction, configuration, and validation of an environmental test chamber facility is provided in ASTM Guide D 5116-97.

6.2.1 *Environmental Test Chamber*, constructed of inert materials of sufficient size to hold the test specimen. Small environmental test chambers may range in size from a few liters to 5 m<sup>3</sup>. Procedures recommended in this standard practice have been evaluated using environmental chambers with a volume of 0.053 m<sup>3</sup>. This volume is used in the standard practice for discussion and illustrative purposes. Chambers of different size and shape may be used if the standard environmental test chamber conditions can be maintained and chamber performance can be demonstrated. The chamber should be equipped with an opening large enough for loading the test specimen and for cleaning the chamber. The chamber will be equipped with a port to supply air to the chamber, an air outlet from the chamber, and ports for temperature and relative humidity probes. The chamber may be equipped with a fan to promote mixing in the chamber and to achieve the desired air velocity across the surface of the test specimen. The performance of the chamber should be evaluated prior to use to determine air-tightness, surface adsorption effects, air mixing, and air velocity at the surface of the substrate. Some of the chamber performance (i.e., air mixing and air velocity) should be evaluated with an uncoated test substrate in place. The chamber performance should be tested and demonstrated following the guidelines presented in ASTM Guide D 5116-97.

6.2.2 *Environmental Enclosure*, of sufficient size to accommodate the environmental test chamber and capable of maintaining the desired temperature within  $\pm 0.5$  °C.

6.2.3 *Clean Air Supply System*, capable of supplying a controlled flow of clean, humidified air into the test chamber, as described in ASTM Guide D 5116-97. The system should incorporate hardware for removing particles, ozone, and VOCs from the air supplied to the chamber(s). Concentrations of VOCs and aldehydes measured at the chamber inlet should not exceed  $2 \mu\text{g}/\text{m}^3$  for any single compound or  $10 \mu\text{g}/\text{m}^3$  for the sum of all measurable VOCs in the sample. The relative humidity (RH) of the air supplied to the chamber(s) should be controlled to the desired set point  $\pm 5\%$  RH. The flow rate of the air supplied to the chamber should be controlled to the desired set point  $\pm 5\%$  of the set-point airflow rate. Ideally, the chamber system will be designed such that a positive pressurization of the chamber of approximately 10 Pa relative to the environmental enclosure will be maintained and monitored at all times during the test.

6.2.4 *Environmental Measurement System*, consisting of hardware and software to measure and record the temperature, RH, and airflow rates during operation of the test system. A system for continuous recording of the data is recommended.

6.3 *Air Sampling Systems*, consisting of sorbent tubes and DNPH-silica gel cartridges, a sampling manifold, vacuum pumps, and airflow controllers/meters. Airflow controllers should control the airflow rate through the sampling system to within  $\pm 5\%$  of the specified value. All system components between the chamber and the sampling media should be constructed of chemically inert materials.

6.3.1 A glass or stainless steel manifold should be connected to the outlet of the chamber for collection of air samples. The manifold should be designed for collection of multiple samples simultaneously. The exhaust from the manifold should be vented into a laboratory fume hood or other appropriate exhaust device to prevent contamination of the air in the laboratory or environmental enclosure.

6.3.2 Vacuum pumps should be used to draw air through the sorbent tubes. The required airflow rate is a function of the type of sampler used, the size of the chamber, and the air change rate. The total airflow rate through the samplers should not exceed 50% of the flow rate from the chamber outlet. For collection of VOCs on sorbent tubes, the pump should be capable of maintaining a constant flow in the range of 10 to 200 mL/min. For collection of air samples on DNPH-silica gel cartridges, the pump should be capable of maintaining a constant flow in the range of 100 to 500 mL/min.

6.3.3 For collection of VOCs during the emissions test, tubes containing single or multiple sorbents may be used. The sorbents may be porous polymers or graphitized carbon blacks. Select an appropriate single or multi-layered sorbent tube following the procedures in ASTM Practice D 6196 and D6345, and EPA Method TO-17. Recommendations on the use of sorbent tubes from manufacturers or suppliers should be followed in selecting the sampling airflow rate and sampling period to avoid breakthrough of VOCs through the sorbent tube. The required air sampling volume at each collection time point should be determined through consideration of the safe sampling volume (SSV, see Practice D 6196) of the VOC with the lowest retention volume, concentrations to be measured, and detection limits of the analytical method.

6.3.4 For collection of VOCs during the first 10 to 20 hours following application of alkyd primer or paint, charcoal sorbents (ASTM D3687) may be used due to the high concentrations of VOCs in the chamber air.

6.3.5 For collection of formaldehyde and other carbonyl compounds, DNPH-silica gel cartridges should be used following the ASTM Method D 5197.

6.3.6 An airflow meter/controller should be used to control and measure the airflow rate during sample collection. The controller may consist of a precision flow control valve, a critical orifice, or a mass flow controller. The measurement device may consist of soap film bubble meter, calibrated high precision rotameter, or mass flow meter. A mass flow meter/controller is recommended for use during sample collection. All flow measurements should be referenced to standard temperature and pressure.

## **7. Procedures for Paint Selection, Handling, and Storage**

7.1 Procedures for selection of the paint to be tested are a function of the objectives of the tests. Paint may be procured from clients, manufacturers, distributors, or retailers. Record pertinent information upon receipt of the paint including date of acquisition, source of the paint, manufacturer, container size, lot number, and other relevant information on the label. Obtain and review the Material Safety Data Sheet (MSDS) for the paint. At least two containers of the same lot number of paint should be procured (one for testing and one to archive).

7.2 Upon receipt of the paint, it should be split into storage vials for handling and testing. The paint should be mixed in the original container on a paint shaker before the split.

7.3 Split the paint into aliquots. Special care should be taken to minimize the loss of volatile compounds during the process. Paint containers should not be left open except when required for transfer to storage vials. The size of the aliquot and storage vial is a function of the amount of paint required for the test. Vials of 40 to 60 mL volumes hold sufficient paint for GC/MS analyses of the liquid product or preparation of test specimens of 256 cm<sup>2</sup> area for chamber tests. Store paint in clean amber glass vials that can be sealed with caps that have Teflon liners. Clean vials with alkaline detergent, rinse thoroughly with deionized water, then dry before use. Individual vials of paint are used for testing to minimize losses of volatile compounds during handling and preparation of test specimens. Repeated opening of a large container of paint will result in losses of VOCs.

7.4 Pour the mixed paint into the vials, filling the vial to near the top to minimize the volume of headspace and loss of VOCs when the vial is opened. Two or more clean stainless steel balls may be placed in the vial to aid in mixing prior to use of the sample. Prepare a sufficient number of sample vials for all analyses and tests planned for the paint. Label the vials individually with a sample code and the date of preparation.

7.5 Store the vials of the paint samples and the original containers of the paint in the dark at room temperature.



7.6 Use the paint sample within the manufacturer's specified shelf-life time. VOC concentrations should be measured by GC/MS or GC/FID after extended periods of storage to verify that they have not changed during storage. Compare the concentrations of the VOCs to results from the original analyses performed immediately after the paint was obtained.

## 8. Procedures for Preparation of Test Specimens

8.1 Procure the substrate material that is appropriate for testing the emissions from the paint. The substrate should not emit any of the compounds that are to be quantified in the emissions from the paint or compounds that may interfere with quantification of the emissions from the paint. Cut the substrate material to an appropriate size (e.g., 16 by 16 cm for a loading of 0.5 m<sup>2</sup>/m<sup>3</sup> in a 0.053 m<sup>3</sup> chamber). Use an appropriate cutting device to obtain smooth edges. If necessary, sand wood substrate to provide a smooth surface.

8.2 To minimize emissions from the cut edges, seal the edges. Techniques that can be used to seal the edges include: (1) coating the edges with technical grade liquid sodium silicate, (2) wrapping with aluminum foil, or (3) mounting the substrate in a stainless steel frame that covers the exposed edges.

8.3 The substrate material should be properly stored to remain clean, dry, and structurally sound.

## 9. Procedure for Paint Application

9.1 Prior to application of paint for emissions testing, one must perform practice applications using the same type of applicator (e.g., a roller or brush) and substrate in order to develop a technique that will produce uniform and repeatable applications. The VOC emission characteristics will be influenced by the thickness of the paint applied, and care should be taken to ensure uniform paint application. If desired, wet and dry film thickness of paint applied can be determined by ASTM methods referenced in Section 2 to verify the uniformity of the application. The application should also be performed as quickly as possible to minimize VOC losses during preparation of the test specimen.

### 9.2 Paint Application Procedure

9.2.1 Determine the target mass of paint to be applied from product data sheets or the spreading rate (ft<sup>2</sup>/gal) listed on the container label. Calculate the mass of paint needed using the spreading rate (ft<sup>2</sup>/gal) and the density of the paint. The density is generally listed on product data sheets or the MSDS. The mass to be applied can be calculated as follows:

$$M_p = \left( \frac{1}{SR} \right) * (D_p) * (A) \quad (A-1)$$

Where:

$M_p$  = target mass (g) of paint to be applied,  
 $SR$  = spreading rate (cm<sup>2</sup>/mL), generally listed on container or data sheet as ft<sup>2</sup>/gal,

$D_p$  = density (g/mL) of the paint, and  
 $A$  = area of the substrate (cm<sup>2</sup>).

As an example, for paint with a spreading rate of 400 ft<sup>2</sup>/gal and a density of 1.4 g/mL, the amount of paint to be applied to a 16 by 16 cm test substrate would be 3.65 g:

$$M_p = \left[ \frac{1 \text{ gal}}{400 \text{ ft}^2} * \frac{3785 \text{ mL}}{\text{gal}} * \frac{1 \text{ ft}^2}{0.092903 \text{ m}^2} \right] * \left[ \frac{1.4 \text{ g}}{\text{mL}} \right] * \left[ 16 \text{ cm} * 16 \text{ cm} * \frac{1 \text{ m}^2}{10000 \text{ cm}^2} \right] \quad (\text{A-2})$$

9.2.2 Select a vial of paint for the test. Prepare the paint by vigorously shaking the vial for 5 minutes. Mixing must be done in the sealed vial to minimize loss of VOCs.

9.2.3 Wear cotton gloves during specimen preparation to prevent contamination by oils from the skin.

9.2.4 Weigh the substrate.

9.2.5 Pour the paint from the vial into a small, clean tray of appropriate size for the roller or brush being used for the application. Disposable trays can be made using clean aluminum foil. For a 7.6-cm wide paint roller, a tray that is 10 cm (4 in.) wide, 15 cm (6 in.) long, and 2 cm (0.75 in.) deep is appropriate.

9.2.6 Place the paint applicator into the tray and wet the surface uniformly with the paint. If a roller is used, apply the roller to the substrate starting at the center and roll outward to all edges until the surface is covered. Then rotate the substrate 90 degrees and roll back and forth across the entire surface in this direction. Use a similar application procedure if using a brush to obtain a uniform coating on the substrate surface.

9.2.7 Immediately after application, weigh the substrate with the coating and record the weight. Calculate the weight of coating applied by the difference in the weight of the substrate before and after paint application. The final weight of paint applied should be within ± 10% of the target application amount. If the weight of coating is greater than ± 10% of the target mass, adjust the application procedure (e.g., by changing the number of strokes and/or the amount of the paint in the brush) and try again with a new substrate until desirable and repeatable applications can be achieved.

9.2.8 Each paint application process, including the weight measurement and calculation, should be finished within 3 minutes.

9.2.9 If a suitable balance is not available to weigh the substrate before and after application of the paint, an alternative method can be used involving weighing of the paint and applicator. Prior to preparation of the test specimen, pour the paint in the aluminum tray. Determine the combined weight of the tray, paint, and the applicator (roller or brush). Then apply the paint to

the substrate. After the application is complete, weigh the paint tray and the applicator. Determine the amount of paint applied by calculating the weight difference.

## **10. Chamber Emissions Test Procedure**

10.1 *Preparation of the Environmental Chamber Testing System* - Prior to each test, the chambers should be cleaned and operating parameters set.

10.1.1 Clean the environmental test chamber and all internal hardware by wiping the interior surfaces with an alkaline detergent, rinsing thoroughly with deionized water, and drying with clean laboratory tissue. Solvent such as acetone or methanol and/or chamber heating can be used when necessary. Use the same procedure to clean all hardware on the chamber outlet and the sampling manifold.

10.1.2 Place the environmental test chamber in the environmental enclosure and set the enclosure temperature to the desired level. Close the chamber. Assemble the chamber outlet and manifold.

10.1.3 Adjust the water vapor concentration in the supply air to achieve the desired test conditions (e.g., 50% RH at 23 °C). For water-based paints, %RH should be recorded throughout the test because the drying paint will affect the water vapor concentration. Ideally, in those cases the water vapor concentration in the outlet air (rather than the supply) should be controlled to 50% RH. Start airflow to the chamber at the rate required for the desired air change rate (typically 0.5 or 1.0 ACH). For a 53-L chamber the airflow rate will be 442 mL/min for an ACH of 0.5 hr<sup>-1</sup>. Measure the airflow rate at the inlet and the outlet of the chamber. If the inlet and outlet flow rates differ by more than ± 5%, check for leaks.

10.1.4 Operate the empty chamber at desired test conditions for 24 hours prior to use.

10.1.5 Collect background samples from the empty chamber at the end of the 24 hours. Analyze the samples as soon as possible to ensure that the chamber background meets the criteria in Section 14.3.2 and is therefore ready for use. If the background VOC concentrations are too high, further cleaning or other measures may be required.

### *10.2 Emissions Test Procedure*

10.2.1 Place the uncoated test substrate (and holder if used) into the chamber and condition for 24 hours at the same temperature, RH, and ACH that will be used in the test.

10.2.2 At the end of the 24 hours, collect an air sample from the chamber outlet, using a sorbent tube to measure VOC background concentrations from the environmental test chamber loaded with the uncoated substrate. Collect an air sample from the chamber outlet on a DNPH-silica gel cartridge to measure background concentrations of carbonyl compounds. Analyze the chamber background samples as soon as possible after collection. Individual VOCs or carbonyl compounds that are targeted for quantification in the emissions from the paint should not be present in the samples at concentrations greater than the chamber background criteria in Section

14.3.2. The emissions from the substrate should not include any compounds that may interfere with quantification of the emissions from the paint.

10.2.3 After the substrate background levels have been determined to be acceptable, open the chamber and remove the test substrate. Maintain airflow to the chamber and close it during preparation of the test specimen to minimize contamination of the chamber with laboratory air.

10.2.4 Prepare the test specimen by applying the paint as described in Section 9. If the application is acceptable, immediately place the test specimen into the chamber and close the chamber. Record time that the chamber is closed as “Time Zero” for the start of the test. Total preparation time from chamber opening, painting, weighing, to sealing of the coated test specimen within the chamber should not exceed 5 minutes.

10.2.5 Operate the test chamber at desired conditions for a test period during which air samples are routinely collected from the chamber outlet.

## **11. Sample Collection**

11.1 Throughout the emission test, air samples will be collected from the outlet of the chamber. Samples will be collected on either charcoal media or thermal desorption sorbent tubes for VOC analyses and on DNPH-silica gel cartridges for analyses of carbonyl compounds.

11.2 Set up the vacuum pump(s) and mass flow controllers/meters for collection of sorbent tube and DNPH-silica gel cartridge samplers.

11.3 Set the flow controllers for the required airflow rates for the sorbent tube and DNPH-silica gel samplers. The required airflow rates will be a function of the emission rates for individual compounds and the volume of air sample required to obtain VOC mass on the sampler that is within the calibration range of the analytical instrument. During early stages of a test, due to the relatively high VOC concentrations, samples may need to be collected over periods of only 5 to 10 minutes at a low flow rate in order to obtain accurate sample volumes. Higher airflow rates and longer sample collection periods will be required in later stages of the test as the concentrations of VOCs decrease in the chamber air. The total sampling flow rate must be less than 50% of the airflow from the chamber (e.g., less than 221 mL/min for a 53 L chamber operated at 0.5 ACH). Set airflow rates with a sampling tube or cartridge connected to the sampling line. Sample flow rates should not exceed manufacturer’s recommendations.

11.4 Collect air samples for VOCs and carbonyl compounds at predefined intervals during the test. The duration of the test and the frequency of sample collection will be determined by the objectives of the test. A high frequency of sampling will be required if the objective of the test is to develop or evaluate source emission models. A lower frequency of sampling may be appropriate for other test objectives. If resources are available, the recommended sampling times for collection of data for model development during a 2-week test with alkyd paint are at 0.25, 0.5, 1, 1.5, 2, 4, 6, 8, 10, 12, 24, 48, 72, 96, 144, 192, 264, and 336 hours following the start of the test. Recommended sampling times during a 2-week test with latex paint are at 2, 4, 8, 12, 24, 48,

72, 96, 144, 192, 264, and 336 hours following the start of the test. After sampling, carefully seal sample tubes and record sampler flow rates and duration.

11.5 Collect duplicate air samples simultaneously at a subset of time periods. Use separate flow controllers for each sampler. Adjust total flow to be less than 50% of the chamber outlet airflow rate.

11.6 Store samples collected on sorbent media refrigerated at less than 4°C in a clean environment. Analyze samples as soon as possible after collection. Samples should be analyzed within 30 days as recommended in EPA methods referenced in Section 2. Analyses should be performed following methods referenced in Section 2 or other published methods that produce results that meet the project objectives for precision and bias.

11.7 Store samples collected on DNPH-silica gel cartridges refrigerated at less than 4°C. Analyze the samples within 30 days. Analyses should be performed following methods referenced in Section 2 or other published methods that produce results that meet the project objectives for precision and bias.

## **12. Chemical Analysis**

12.1 For VOCs collected on sorbent media for analysis by thermal desorption/GC, analyze samples following guidance in ASTM Practice D6196 and EPA Compendium Methods TO-15 and TO-17.

12.2 For VOCs collected on charcoal, follow procedures described in ASTM D3687 to extract the analytes from the charcoal media with carbon sulfide and analyze the liquid extract by GC.

12.3 For carbonyl compounds collected on DNPH-silica gel cartridges, follow procedures described in ASTM Method 5197. The Method involves extraction of the media with acetonitrile and analysis of the extract by HPLC.

## **13. Reporting Test Results**

The report should include the following information:

13.1 Test objectives - Provide a clear description of the purpose of the test.

13.2 Equipment and Methods - Provide a description of the small chamber test facility equipment, including chamber size and materials, environmental control and measurement systems, sampling and analysis equipment, and description of the test methods and protocols.

13.3 Product identification - Provide the name, specific identifiers from the manufacturer and a brief description of the product, its application, and history.

13.4 Test conditions - Provide data for the temperature, humidity, air change rate, dimensions of the test specimen, empty chamber and substrate background concentrations, mean air velocity above the surface of specimen, and mass applied.

13.5 Samples Collected – Provide a record of samples taken including sampling schedule, flow rate, volume, frequency, and type.

13.6 Quality Assurance/Quality Control Results - Describe the data quality objectives and quality control activities for the test. Provide results for quality control samples (replicates, blanks, controls).

#### **14. Quality Assurance and Quality Control**

14.1 A quality assurance and quality control (QA/QC) plan should be prepared and implemented to ensure the integrity of the measured and reported data obtained during the tests. This plan should encompass all facets of the measurement program from sample receipt to final review and issuance of reports. QA/QC activities applicable to tests to measure emissions from paint are described in ASTM Guide D 5116.

14.2 *Data Quality Objectives and Acceptance Criteria* - The QA/QC plan should be based on established data quality objectives and acceptance criteria. Recommended data quality objectives are listed in Table A-1.

##### *14.3 Quality Assurance Activities and Quality Control Samples*

14.3.1 Determine the accuracy of chamber test conditions and operating parameters (temperature and RH) by calibration of measurement devices with National Institute of Standards and Technology (NIST)-traceable primary sources. Determine the precision of the test conditions by continuous recording of the parameters. Failure to meet acceptance criteria requires immediate corrective action. Check instrument performance before and after each test by comparison of measurements with a reference device.

14.3.2 The empty chamber background concentrations of VOCs should be measured at the start of each test without the substrate in the chamber. The empty chamber background concentration shall meet the following criteria: (1) less than  $10 \mu\text{g}/\text{m}^3$  or 1/6 of the lowest concentration to be measured, whichever is lower, for TVOC, and (2) less than  $2 \mu\text{g}/\text{m}^3$  or 1/6 of the lowest concentration to be measured, whichever is lower, for individual VOCs.

14.3.3 Field blanks, consisting of sorbent tubes and DNPH silica gel cartridges that are not used for sampling, should be analyzed to verify that the tubes and cartridges have not been contaminated during handling and storage. The blanks should be stored and handled in the same manner as the samples collected during the test. The number of blanks analyzed should represent approximately 10% of the number of samples collected for each type of sampling media; a minimum of 2 blanks for each type is recommended.

14.3.4 Precision of the sampling and analysis methods should be determined by collection of replicate samples. Duplicate samples should be collected concurrently at selected time periods during the test. The number of duplicates for each type of sampling media should represent approximately 10% of the number of samples collected. Due to the limited volume of air available, duplicate samples can be collected for only one type of media during a sampling period, especially when low VOC concentrations dictate high sample volumes. Each sampling and analytical method used must have detection limits lower than the acceptable background levels stipulated in Section 14.3.2.

14.3.5 The accuracy and precision of the small chamber test method can be measured prior to start of a test program. The precision of the chamber test method, to include the combined variability of test specimen preparation, chamber operation, sampling, and analysis, can be measured by performing multiple chamber tests with the same source and substrate. Variation in test data from a single chamber and among chambers can also be established by use of standardized sources such as permeation tubes for determining organic concentrations and calculated emission rates.

Table A-1: Recommended Data Quality Objectives

| Parameter                 | Precision | Accuracy |
|---------------------------|-----------|----------|
| Chamber temperature       | ± 0.5 °C  | ± 0.5 °C |
| Chamber relative humidity | ± 5.0 %   | ± 5.0 %  |
| Airflow rate              | ± 5.0 %   | ± 5.0 %  |
| Amount of paint applied   | ± 10 %    | ± 10 %   |