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# CHARACTERIZATION OF LOW-VOC LATEX PAINTS: VOLATILE ORGANIC COMPOUND CONTENT, VOC AND ALDEHYDE EMISSIONS, AND PAINT PERFORMANCE

## FINAL REPORT

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## ABSTRACT

Commercially available latex paints, advertised as “low-odor,” “low-VOC,” or “no-VOC”, were evaluated as alternatives to conventional latex paints. The VOC content of the paints, determined by EPA Method 24, was found to be less than 0.2% by weight, substantially lower than the 2 to 10% VOC content in conventional latex paints. Analyses by GC/MS identified low levels of ethylene glycol, propylene glycol, dipropylene glycol, 2-(2-butoxyethoxy)ethanol, and Texanol in some of the paints. VOC emissions were low, consistent with the low concentrations of VOCs in the bulk paints, but elevated levels of formaldehyde were measured in the emissions from two of the paints. A peak concentration of 2.2 mg/m<sup>3</sup> of formaldehyde was measured in small chamber tests with one of the paints applied to gypsum wallboard. The total estimated emissions from the two paints applied to gypsum wallboard were 0.47 mg of formaldehyde per gram of paint and 0.15 mg/g during 14-day tests. The performance of the paints, based on results of ASTM tests, varied substantially. One of the low-VOC paints had good scrubbability, washability, and hiding power, rating higher than the other low-VOC paints and a conventional latex flat paint from the same manufacturer. The results suggest that performance of low-VOC products should be evaluated and that screening of low-VOC products might be important to identify products that have the possibility of containing formaldehyde or other volatile compounds of concern indoors.

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## 1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is conducting research and testing to characterize the emissions of volatile organic compounds (VOCs) from building materials and consumer products. Methods have been developed in the Air Pollution Prevention and Control Division (APPCD), Indoor Environment Management Branch (IEMB), to measure VOC content in liquid coatings and emissions of VOCs following application to realistic substrates. Research projects performed by the IEMB have included testing to characterize emissions from wet products such as latex paint, alkyd paint, stains and varnishes. This document reports results of a research project to characterize VOC content and emissions of VOCs and aldehydes from latex paints advertised as "low-odor" or "no-VOC" products.

## 1.1 BACKGROUND

Building materials are recognized as important sources of air contaminants indoors (Levin, 1989; Wolkoff and Nielsen, 1996; Johnston et al., 1996; and others). Although some building materials are relatively minor sources, paint may represent a significant indoor air contaminant source because of the volume of paint used and the frequency of re-application during the life of a building. Painting is frequently performed while buildings are occupied, resulting in short-term exposures to elevated levels of the most volatile compounds immediately after application, as well as long term exposure to the slower emitting, less volatile VOCs.

The U.S. EPA has performed a number of research projects to characterize emissions from alkyd and latex paints (Chang et al., 1997; Guo et al., 1996; Fortmann et al., 1998; Sparks et al., 1998). Testing has demonstrated that alkyd paints, which are typically greater than 30% by weight of organic solvents, emit high concentrations of VOCs (e.g., decane, undecane, xylenes) during a short period after application. Although VOCs from the alkyd paint can still be detected at low concentrations two weeks after application, greater than 90% of the VOCs in the paint are emitted within the first 24 hours (Fortmann, et al., 1998). Tests with latex paint have shown a dramatically different VOC emissions profile. Latex paints typically contain low concentrations (less than 5% by weight) of VOCs. The VOCs (e.g., ethylene glycol, propylene glycol, dipropylene glycol, Texanol) are emitted at a slow rate over a longer time period. In tests at APPCD, ethylene glycol could still be detected in emissions from latex paint 190 days after application to gypsum wallboard (Chang et al., 1997).

In recent years, paint manufacturers have introduced new latex paints described as "Low-Odor," "Low-VOC" and "No-VOC." Many of these paints are being marketed for use in buildings that must be occupied during painting (e.g., hospitals and other health care facilities). Use of low odor paints should

result in fewer occupant complaints during re-painting operations. Some manufacturers market their products as “no-VOC” and promote the product as a pollution prevention or “clean air” alternative.

Although the low-odor and no-VOC water-based products may have a lower content of VOCs than conventional paints, they may still contain aldehydes, glycols and other VOCs. Paints may contain VOCs due to additives or as a result of by-products of the manufacturing process. There is little data on the types or concentrations of compounds emitted from low-odor and low-VOC paints. The purpose of this research project was to gain a better understanding of the VOC composition of these paints and the emissions following application.

## 1.2 PROJECT OBJECTIVES

The objectives of the project were the following:

- Determine the VOC content of a subset of currently available latex wall paints that are marketed as low-odor, low-VOC, or no-VOC
- Conduct small chamber emissions tests to identify and quantify VOCs and aldehydes emitted from the test paints
- Evaluate the performance of low-VOC paints relative to “conventional” paints

## 1.3 PROJECT OVERVIEW

The project described in this report was a laboratory testing project to characterize VOC content, VOC emissions during curing and performance of selected low-VOC latex paints. A limited number of tests were performed with paints from four different manufacturers. Many of the tests were considered to be “range-finding” tests intended to collect an initial data set on the paints that would provide a better understanding of the volatile compounds emitted from the paint. Although quantitative measurements were made, it was beyond the scope of the project to perform extensive identification and quantification of minor constituents in the emissions from the paints.

The scope of work for the project consisted of the following tasks:

- Determine availability of low-VOC paints and identify retail sources
- Procure paints from local retail outlets or formulators; obtain material safety data sheets (MSDS') and product description sheets
- Extract each paint with an appropriate solvent and analyze by GC/MS to identify and quantify the most abundant VOCs in the bulk product
- Perform Method 24 analyses to determine volatile content, water content and VOC content
- Perform selected ASTM tests to evaluate product performance (e.g., hiding power, scrubability)

- Perform small chamber emissions tests with application of the paint to glass or gypsum wallboard
- Perform sample and data analyzes
- Perform data processing, review and compilation
- Prepare final report on the testing project

#### 1.4 SUMMARY OF THE TESTS PERFORMED

Tests were performed with a total of nine paints obtained from four manufacturers. Three of the paints were from the same manufacturer, who re-formulated the original paint during the period of the study. Most of the paints were latex flat wall paints, although a semi-gloss paint was obtained from one manufacturer. The performance characteristics of two conventional wall paints were measured for comparison to the low-VOC paints, but the VOC content and emissions from the conventional paints were not measured during this study. Small chamber tests were performed for four of the nine test paints to measure VOC emissions and for seven paints to measure aldehyde emissions. The tests performed for each paint are summarized in Table 1-1. Each paint was assigned an identification code.

Table 1-1. Summary of the Tests Performed in the Study for Each Paint

Paint ID	Manufacturer	Paint Type <sup>a</sup>	Method 24	Bulk Analysis	Chamber Emission Tests		Performance Tests
					Aldehydes	VOCs	
LVA	1	Low-VOC	X	X	X	--	X
LVB	1	Low-VOC	X	X	X	--	--
LVC	1	Low-VOC	X	X	X	X	--
LVD	2	Low-VOC	X	X	X	X	X
LVE	3	Low-VOC	X	X	X	X	X
LVF	3	Low-VOC	X	X	X	--	--
LVG	4	Low-VOC	X	X	X	X	X
LVH	4	Conventional	X	--	--	--	X
LVI	2	Conventional	--	--	--	--	X

<sup>a</sup> All paints were latex flat wall paints except paint LVF which was semi-gloss

## 2.0 SUMMARY AND CONCLUSIONS

A laboratory test project was performed to (1) characterize the content of VOCs in “low-VOC” and “low-odor” paints, (2) measure emissions of VOCs and aldehydes from the paints and (3) evaluate the performance of the paints. The project was undertaken in order to gain a better understanding of these products.

One low-VOC latex semi-gloss paint and four latex flat paints, from four manufacturers, were evaluated. The bulk paints were extracted and analyzed by gas chromatography/mass spectrometry (GC/MS) in an attempt to identify and quantify the major constituents. Analyses were also performed by EPA Method 24 to determine total volatile content, water content and VOC content. Small chamber emissions tests were performed to measure emissions from the paints applied to either glass or gypsum wallboard substrates. Samples of the emissions were collected on Tenax for GC/MS analysis of VOCs or on DNPH-silica gel for analysis of aldehydes. The performance of the paints (e.g., scrubability, hiding power) was evaluated using ASTM test methods. The following is a summary of the results and conclusions:

- The VOC content of the five low-VOC paints tested was less than 0.2 %, the minimum detection limit of the EPA Method 24 measurement. These levels are an order of magnitude less than the VOC content in a conventional latex flat paint tested in a previous project.
- Analysis of the bulk paint products by GC/MS identified ethylene glycol, propylene glycol, dipropylene glycol, 2-(2-butoxyethoxy)ethanol (BEE) and Texanol in some of the paints. Not all paints contained these compounds. One of the four latex flat wall paints contained higher VOC levels than the other three. Paint LVG contained 1.51 mg/g of BEE, 0.81 mg/g of dipropylene glycol, 0.59 mg/g of ethylene glycol and detectable levels of propylene glycol and Texanol. However, the levels were substantially lower than in a conventional latex paint tested in a previous project which contained 24 mg/g of ethylene glycol. There were relatively few other compounds detected in the bulk paints by the solvent extraction/GC/MS method and they could not be identified from the data generated with the ion trap MS.
- Formaldehyde was detected in emissions from all five of the low-VOC latex paints tested. The concentrations of formaldehyde were low for three of the paints (LVE, LVF and LVG). Paint LVA, supplied by manufacturer number 1 and paint LVD from manufacturer number 2, had elevated levels of formaldehyde in the emissions collected during dynamic small chamber tests. Paint LVA had a peak concentration of formaldehyde of 5.5 mg/m<sup>3</sup> in emissions collected during the small chamber test at 0.5 air exchanges per hour. The estimated mass of formaldehyde emitted during a 50-hour test with paint LVA applied to glass was 0.51 mg/g of paint. When the paint was applied to gypsum board the mass of formaldehyde emitted was 0.18 mg/g of paint during the first 50 hours and 0.47 mg/g for the 14 day test period. The manufacturer of the paint, upon being advised of the elevated formaldehyde concentrations, re-formulated the paint with a different biocide. Emissions from the re-formulated paint also contained formaldehyde, but at lower concentrations. The estimated mass of formaldehyde emitted from the re-formulated paint was 0.15 mg/g during the first 50 hours and 0.27 mg/g during the 14 day test period with the paint applied to gypsum board. The estimated mass of

formaldehyde emitted from paint LVD, from manufacturer number 2, when applied to glass was 0.26 mg/g for a 50 hour test period. When the paint was applied to gypsum board, the estimated mass emitted was 0.06 mg/g during the first 50 hours and 0.15 mg/g for the 14 day test period.

- Acetaldehyde was detected in the emissions from all five low-VOC paints. The peak concentrations in the emissions were low (less than 0.05 mg/m<sup>3</sup>) for three of the five paints. The two paints with the highest levels of formaldehyde in the emissions (LVA and LVD) also had the highest concentrations of acetaldehyde in the emissions. A peak concentration of 0.52 mg/m<sup>3</sup> of acetaldehyde was measured in the emissions from paint LVA applied to gypsum wallboard. The peak concentration was 0.34 mg/m<sup>3</sup> in the test with paint LVD applied to gypsum wallboard. Acetaldehyde concentrations decreased rapidly during the test. Within 8 hours after the peak concentration, acetaldehyde concentrations in the emissions decreased by an order of magnitude.
- VOC concentrations measured in the emissions were consistent with the low concentrations of VOCs measured in the bulk paints. Peak concentrations of the characteristic latex paint compounds (e.g., glycols) were typically 0.5 mg/m<sup>3</sup> or less in the small chamber tests. Concentrations decreased rapidly following application to glass or gypsum wallboard. Emissions from one of the four latex flat paints were substantially higher than from the other paints. Paint LVG, which had the highest concentrations of VOCs in the bulk paint, had peak concentrations of 4.63 mg/m<sup>3</sup> of BEE and 4.29 mg/m<sup>3</sup> of ethylene glycol in the emissions six hours after application of the paint to a glass substrate. Few VOCs, other than the target compounds, were detected in the emissions from the paints.
- The performance of the paints, based on results of ASTM tests, varied substantially. One of the low-VOC paints had high ratings for scrubability, washability and hiding power. It rated higher than the other low-VOC paints and the conventional latex flat paint from the same manufacturer.
- Results of the study have provided a better understanding of the characteristics of the low-VOC/low-odor paints currently on the market. The paints contained low concentrations of VOCs, which resulted in lower VOC emissions during use. However, paints from two manufacturers emitted formaldehyde at elevated levels. Therefore, the paints had potential for adverse impacts when used indoors. The tests also showed that performance was variable among the products and did not appear to be related to the VOC content of the product or its emissions.

### 3.0 RECOMMENDATIONS FOR FUTURE RESEARCH

The results of this study were useful for gaining a better understanding of the characteristics of the low-VOC/low-odor latex paints. Additional research on the subject may be warranted. Potential research should be considered in the following areas:

- Two low-VOC paints were identified in this project that contained elevated concentrations of formaldehyde in the emissions following application to glass and gypsum board substrates. Additional screening analyses should be performed to determine if there are other low-VOC paints that emit formaldehyde. Potential sources of formaldehyde in paints should be identified and evaluated.
- The elevated formaldehyde emissions were identified by performing small chamber emissions tests. A more cost-effective method should be identified to screen paints for potential aldehyde emissions. A method to measure aldehydes in the bulk product may be the most cost effective.
- The extraction and GC/MS method for identifying and quantifying VOCs in the bulk product was not effective for identifying minor constituents in the paint. The method should be refined in order to lower the method detection limit and improve recovery of minor constituents. The method has not been adequately developed or evaluated for identifying compounds other than the major constituents. Alternative methods should also be evaluated.
- Difficulties were encountered in the analyses of the polar compounds emitted from the latex paints. Additional method development is required to ensure accurate and precise measurements of these compounds in the bulk product and in the emissions.



## 4.0 TEST METHODS

This section describes the test methods used for the project. Included are descriptions of the methods for measuring VOC content in the bulk paints, methods for total volatile content measurements, small chamber emissions test methods and ASTM tests used to evaluate paint performance. Sampling and analysis methods used during the test program are also described.

### 4.1 PROCUREMENT OF TEST PRODUCTS

Paints were procured for testing from four U.S. paint manufacturers. Paints from three of the manufacturers were purchased at local retail outlets in the Raleigh/Durham, NC area. The fourth manufacturer was a smaller U.S. formulator who provided the products for testing.

### 4.2 METHOD 24 ANALYSES

Analyses were performed following the EPA Method 24 (U.S. EPA, 1994) for determination of total volatile matter content, water content and VOC content. The method utilizes ASTM Standard Methods and is the same as that used by manufacturers to determine VOC content.

Total volatile matter content was determined according to ASTM Standard Method D2369, a gravimetric method. Analyses were performed in duplicate, as prescribed in the method. References for this and other ASTM methods cited in this report, are included in Section 7.0.

The water content of the paint was determined according to ASTM Method D4017. Analyses were performed with a Mettler DL18 Karl Fischer Titrator. Because initial small chamber tests had demonstrated that some of the paints contained aldehydes, methanol-based reagents could not be used due to their reaction with aldehydes to form acetal and water. Therefore, analyses were performed using Hydranal Composite 5K (titrant) and Hydranal Working Medium Keto.

### 4.3 DETERMINATION OF VOC CONTENT IN THE BULK PRODUCT BY GC/MS

The predominant VOCs in the liquid paint were determined by a GC/MS analysis method used previously for alkyd and latex paints adapted from EPA Method 311 (U.S. EPA, 1996). The paints were diluted with either acetone or acetonitrile at a ratio of 1 gram of the paint with 10 mL of solvent. Acetone formed an emulsion with some paints, requiring the use of acetonitrile. The diluted paints were shaken for approximately 10 minutes, then centrifuged to remove the solids. The supernatant was analyzed by GC/MS or GC with a flame ionization detector (FID). Octanol was added as an internal standard for a subset of the

samples to assess the VOC recovery of the method. Bromofluorobenzene (BFB) was added to the samples as an internal quantitation standard for the GC/MS analyses.

During the initial phase of testing, extracts of the paints were analyzed by direct injection (1  $\mu$ L) onto the GC column. Analyses were performed with a Varian Star 3400CX Gas Chromatograph with a Varian Saturn 3 Mass Spectrometer in Electron Impact mode equipped with a capillary GC column. Operating parameters for the GC/MS system are listed in Table 4-1. Target analytes for quantitation included ethylene glycol, propylene glycol, dipropylene glycol, 2-(2-butoxyethoxy)ethanol (BEE) and Texanol, compounds previously identified in latex paint. The instrument calibration and quantitation of VOCs was performed using the relative response factor (RRF) method. Calibration standards were prepared at five levels ranging from approximately 5 to 1000 ng/ L for each target VOC. The lowest calibration standard was approximately 5 ng/ $\mu$ L, for a practical quantitation limit (PQL) of 0.05 mg/g of paint. The method detection limit (MDL) for the latex paint analytes has not been determined, but was estimated to be approximately 0.01 mg/g. Identification of the compounds targeted for quantitation and tentative identification of unknowns, was performed by use of the computerized mass spectra matching Varian software with the NIST Mass Spectra library.

Table 4-1. Operating Parameters for the Varian GC/MS System Used for Product Analysis

Parameter	Setting
GC Injector Temperature	270 °C
GC Column Type	DB-624; 0.32 mm I.D.; 1.8 $\mu$ m film thickness; 30 m nominal length
GC Temperature Program	35 °C for 5 min.; 5 °C/min. to 170 °C; 26.6 °C/min. to 250 °C; Run Time = 35 min.
Injector Type	Split (Direct injection) 40:1
Head Pressure	4 psi
Scan Rate	2 scans/sec.
Scan Range	30 - 350 m/z
Filament Delay	4.5 min.
Multiplier	2900 V

Prior to the four small chamber emissions tests to measure VOCs from the paints, additional analyses of the bulk paints were performed using a Hewlett Packard HP5890 GC/FID with an HP5970 MS. Extracts of the paints were prepared following the same procedure as described above. One  $\mu\text{L}$  aliquots of the extracts were loaded on Tenax sorbent tubes by a flash vaporization method. The samples were then analyzed by thermal desorption/GC/FID using an Entech 5100 thermal desorber and the HP5890 GC/FID. Operating parameters were as described in Table 4-2. The PQL for analysis of the bulk paints by this method was approximately 0.18 mg/g.

#### 4.4 SMALL CHAMBER EMISSION TEST METHODS

Testing was performed in the EPA APPCD Source Characterization Laboratory located in the EPA Environmental Research Center in Research Triangle Park, NC. Test methods were similar to those used previously in tests with latex and alkyd paint (Chang et al., 1997; Fortmann et al., 1998).

##### 4.4.1 Small Chambers

The small chamber emission test methods used in this project were developed by APPCD and are consistent with the methods described in the *ASTM Standard Guide for Small Scale Environmental Chamber Measurements of Organic Emissions from Indoor Materials/Products*, Designation D5116.

Table 4-2. Operating Parameters for the HP 5890 GC/FID for Analyses of Tenax Tubes

Parameter	Setting
Tube Desorption Temperature	250 °C
Tube Desorption Duration	7.5 min.
Transfer Line Temperature	150
Valve Block Temperature	150 °C
GC Column Type	30 m DB-WAX; 0.53 mm I.D.; 1 $\mu\text{m}$ film thickness
GC Temperature Program	40 °C for 5 min.; 5 °C/min. to 130 °C; 2 °C/min. to 170 °C; 10 °C/min. to 240 °C; 5 min. hold; Run Time = 51 min.
Detector	FID

The emissions tests were performed using 53-L stainless steel chambers housed in a temperature-controlled incubator. Nominal dimensions of the chambers are 51 cm (width) by 25 cm (height) by 41 cm (depth). A stainless steel plate, fitted with a Teflon-coated O-ring, is used to seal the one open side. The chambers are fitted with inlet and outlet manifolds for the air supply. The chambers are also fitted with temperature and relative humidity sensors. A small fan is operated in the chamber to ensure mixing and to obtain a nominal air speed of 10 cm/s at one cm above the substrate surface. Clean, VOC and particle-free, air was supplied to the chamber through a dedicated system consisting of an air compressor, dryer, catalytic oxidizers and particle filters. Air flow was controlled and measured with mass flow meters. The relative humidity (RH) of the air supplied to the chamber was controlled by blending dry air with humidified air from a water vapor generator. A glass sampling manifold was connected to the chamber outlet for collection of air samples. All air transfer and sampling lines were constructed of glass, stainless steel, or Teflon. A data acquisition system (DAS) continuously recorded air flow rates, temperature and RH in the chamber and RH in the inlet air. A diagram of the system is depicted in Figure 4-1. Standard operating conditions during the emissions tests are presented in Table 4-3.

#### 4.4.2 Test Substrate and Coating Preparation Methods

The substrate used in these tests was either glass plates (2.45 mm thick) or gypsum wallboard (Gold Bond Gypsum Wallboard, National Gypsum Company, 0.5 inch thick) purchased from a local retail outlet. The same lot of gypsum wallboard was used for all tests in the project. The test substrate was prepared for use by cutting to a size of 16 cm 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. A larger glass substrate was used in some of the initial tests of the project. But problems were encountered with use of larger test substrates and higher loading factors because of condensation of water in the sampling manifold. The glass plates were cleaned with laboratory detergent and dried prior to use. The edges of the gypsum wallboard test substrate were coated with liquid sodium silicate to seal the edges. The bottom of the substrate was not sealed. The test substrates were placed on the floor of the chamber during the test. The cut and sealed substrates were conditioned in the small chamber at 23 °C and 50% RH (nominal) for at least 24 hours prior to application of the paint and start of the test.

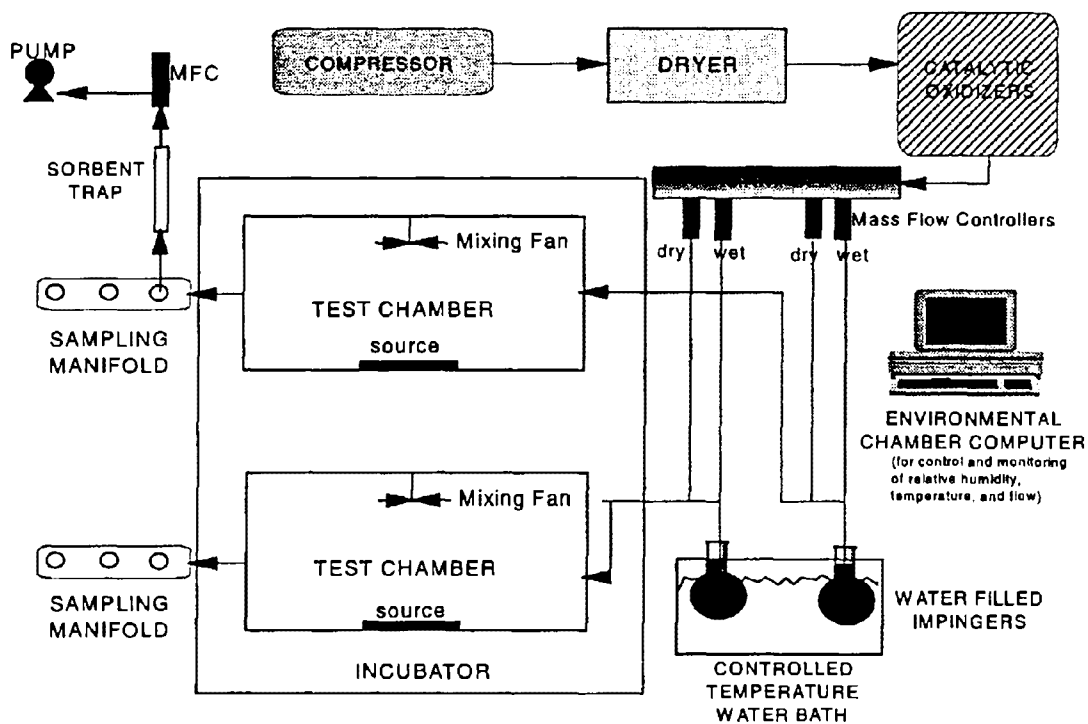


Figure 4-1. Diagram of the small emissions chamber test system

Table 4-3. Standard Operating Conditions for Small Chamber Emissions Tests

Parameter	Value
Chamber volume	53 L
Air exchange rate	0.5 h <sup>-1</sup>
Air velocity (1 cm above substrate)	10 cm/s
Relative humidity (inlet air)	50%
Temperature (in chamber)	23 °C
Loading factor	0.5 m <sup>2</sup> /m <sup>3</sup>
Substrate	Gypsum board
Application method	Paint roller

The stainless steel test chambers were cleaned with soap and water prior to use and operated for 24 hours after cleaning. Prior to opening the chamber for the start of a test, background air samples were collected, as described below.

Paint was applied to the substrate with a roller (Sherwin-Williams Company, Premium 3" Trim Roller) purchased at a local retail outlet. Paint application was performed on a laboratory bench near the chambers to facilitate weighing of the substrate and paint. The rates of application used in the tests, and resulting wet film thicknesses, were based on product label or manufacturer product data sheet specifications for coverage. Wet film thickness was not measured with a gage during the tests because (1) the gage affects the surface film characteristics and (2) it was important to get the test specimen into the chamber as quickly as possible to minimize losses of the most volatile compounds. The mass of paint applied was determined gravimetrically by weighing the substrate before and after application of the coating.

#### 4.4.3 Small Chamber Emissions Test Protocol

The protocol for each small chamber emissions test was as follows:

- Prepare chamber for testing
- Prepare substrate for testing and place in conditioning chamber at least 24 hours prior to the test
- Prior to opening the test chamber, collect Tenax and DNPH-silica gel samples to measure background concentrations of VOCs and aldehydes in the chamber with the substrate
- Remove the substrate from the small chamber
- Apply paint to the test substrate
- Determine mass applied (gravimetrically)
- Place the coated substrate into the chamber, seal the chamber and record the test start time
- Collect air samples according to test schedule
- Terminate test after 7 to 14 days, depending on schedule

The sampling schedule varied for the tests. Data from the bulk analyses by GC/MS were used to predict emissions of the target VOCs from the paints in order to develop the appropriate sampling frequency and volumes of samples to be collected.

#### 4.5 SAMPLING AND ANALYSIS METHODS

Samples were collected on Tenax sorbent tubes for analysis of VOCs and on dinitrophenylhydrazine (DNPH) treated silica gel cartridges for determination of aldehydes.

#### 4.5.1 Tenax Sorbent Sample Collection and Analysis

Air samples were collected on Tenax sorbent tubes throughout each test. The method is described in the EPA *Compendium of Methods for the Determination of Air Pollutants in Indoor Air* (Winberry et al., 1988). Detailed procedures used in the APPCD laboratories are described in the laboratory's *Facility Manual*. The commercially available Tenax sorbent tubes (T.R. Associates, Inc.) were 6 mm OD X 203 mm long, packed with 250 mg of Tenax TA (60:80 mesh). Samples were drawn through the tube using either a calibrated SampleAir pump for collection of samples of less than 0.5 L volume or with a vacuum pump and mass flow controller for sample volumes of 0.5 to 8.0 L. Sample flow rates ranged from 50 to 125 cm<sup>3</sup>/min. The sampling flow rate was set with the mass flow controller, then measured with a bubble film flow meter. The flow rate was monitored during sample collection with the mass flow meter.

The Tenax samples were analyzed by thermal desorption/GC/FID/MS using an Entech Model 5100 Thermal Desorber interfaced to the HP5890 GC described in Section 4.3. The operating parameters for analysis of VOCs collected on Tenax were the same as described previously in Table 4-2. Tenax tubes were desorbed at 250 °C and the concentrator was operated according to the recommended Entech method.

Calibration for VOCs in paint emissions was accomplished by using an average response factor method. Target analytes were identified based on retention time. Compound identification was verified in selected samples by MS. Calibration standards were prepared over a nominal range of 30 to 3000 ng/μL, with a 1 μL volume of standard loaded on the Tenax tubes used for the calibration. Standards were prepared by loading the calibration mixture containing all of the analytes onto Tenax sorbent tubes by a flash vaporization method.

#### 4.5.2 Sampling and Analysis of Carbonyl Compounds

Air samples were collected on silica gel cartridges coated with acidified 2,4-dinitrophenylhydrazine (DNPH). The method is described in the EPA *Compendium of Methods* (Winberry et al., 1988). The commercially available cartridges (Waters Sep-Pak DNPH Silica Gel Cartridge, Waters Associates, Milford, PA) contain 2.9 grams of a 55 to 105 μm chromatographic-grade silica gel. Samples of 2 to 60 L volume were collected with a vacuum pump and mass flow controller at sampling rates of 0.2 to 0.4 L/min. The sampling flow rate was set with the mass flow controller, then measured with a bubble film flow meter. The flow rate was monitored during sample collection with the mass flow meter.

Samples collected on DNPH-coated silica gel were extracted with 5 mL of acetonitrile (UV grade). An aliquot of the extract was then analyzed with a HP 590 HPLC equipped with a diode array detector and a ultraviolet/visible (UV/VIS) detector. Chromatography was performed with a C-18 reverse phase column

(4.6 x 250 mm) using a gradient program [0 - 30 min at 45 percent acetonitrile (ACN), 30 - 35 min at 75 percent, 35 - 41 min at 100 percent ACN and 41 - 55 min at 45 percent ACN].

The HPLC was calibrated for six carbonyl compounds: formaldehyde, acetaldehyde, propanal, benzaldehyde, pentanal and hexanal. The target 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. Standards were prepared at five concentration levels (between 1 and 375 ng/ $\mu$ L) and a calibration curve was generated by linear regression treatment of the concentration and chromatographic response data. The practical quantitation limit, which was based on the lowest calibration standard was 7  $\mu$ g/ $m^3$  for a nominal 30 L sample volume. The MDL would be 0.7  $\mu$ g/ $m^3$  for a nominal 30 L sample volume. Performance of the instrument was verified on each day of analysis by analysis of a calibration check sample.

#### 4.6 METHODS FOR EVALUATION OF PAINT PERFORMANCE

ASTM methods, which are listed in Section 7.0 of this report, were used to evaluate the physical performance of the low-VOC paints. The methods were selected based on information in the ASTM Standard Guide for Testing Latex Flat Wall Paints (D2931) and discussions with paint testing laboratories. Tests were selected that would evaluate the paint for practical parameters such as scrubability and washability. The methods used are described in Table 4-4. The paints were sent to an external laboratory [Paint Research Associates (Ypsilanti, MI)] for analyses. Results of tests performed with the four low-VOC paints (LVA, LVD, LVE and LVG) were compared to results for two conventional paints (LVH and LVI). The paints LVD and LVI were produced by manufacturer number 2. Paints LVG and LVH were produced by manufacturer 4, facilitating comparison of low-VOC and conventional paints produced by the same manufacturer.



Table 4-4. Summary of ASTM Methods

Method	Method Description
D523	Specular Gloss - This test method measures the specular gloss (sheen). The reading, made with a gloss meter at an 85° angle, is useful in characterizing the low angle appearance of flat paints. Most flat paints have an 85° sheen of 1 to 10. Higher values indicate more light reflecting off the surface. Flat paints with good uniformity of appearance often have lower sheen. Paints with good cleanability are often paints with higher sheen.
D2805	Hiding Power - 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 was reported. Generally, a contrast ratio in the range from 0.95 -1.0 indicates good hiding power and the range from 0.90 - 0.95 indicates poor hiding power. Readings below 0.90 indicate very poor hiding power.
D2486	Scrubbability - 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	Stain Removal (Cleanability) -This test method measures the relative ease of removing soilent 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. The reflectance of the film is measured and then a soilent consisting of carbon black dispersed in mineral oil is applied on the film. The stained panel is dried for 16 to 24 hours, then washed with a sponge and cleaner for 100 cycles. After drying the panel, the reflectance is measured again. The ratio of the reflectance is reported. Higher ratios indicate that more stain was removed. Performance of the paint is evaluated relative to other paints.
D4400	Sag Resistance - 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. Numbers between 9-12 are considered good Anti-Sag Indexes. Any Index number lower than 7 is considered poor.
D1640	Dry to Touch - This method measures the time it takes for the coating to dry to touch.
E313	Yellowness Index - The 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 between the initial number and the "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 visually observable.

## 5.0 RESULTS AND DISCUSSION

This section describes the results of analyses performed to characterize the paints. It includes a description of the paints, Method 24 measurement results, results of VOC measurements in the bulk products, results of small chamber emissions tests and characterization of paint performance by ASTM tests.

### 5.1 DESCRIPTION OF THE PRODUCTS TESTED

The initial task of the project was to collect information on the availability of paints that were advertised as “low-VOC” or “no-VOC.” Major paint formulators in the U.S. were contacted and information was requested on the availability of such paints. Based on discussions with the manufacturers, it was determined that each formulator marketed at least one type of latex paint that they labeled as either low-odor, low-VOC, or no-VOC. The terms low-VOC or no-VOC were included on some product labels and some paints were promoted as “clean air” products. But the marketing emphasis generally appeared to be on the “low-odor” characteristics of the paints. The low-odor paints were promoted as alternatives for use in occupied buildings such as hospitals and health care facilities. One paint supplier, who was not a major formulator of paints in the U.S., marketed its paints as containing “no solvents and no VOCs.” The marketing literature indicated that there would be virtually no harmful emissions into the air.

Subsequent to contacting the paint manufacturers, visits were made to local retail outlets to purchase the paints for testing. None of the low-odor, low-VOC latex paints were available in the large “do-it-yourself” home improvement supply centers in the local area. When asked about the availability of low-VOC paints, clerks at the large home improvement centers responded that (1) they didn’t know what low-VOC meant, (2) they didn’t know that low-VOC or low-odor paints were available, or (3) there was not sufficient demand for low-odor paints to warrant the shelf space and, therefore, the low-odors paints were not stocked. In order to procure products for testing, they were purchased at the manufacturer’s local retail outlets. Products from the formulator who was not a major U.S. supplier were provided by the supplier and were not purchased locally.

The product descriptions are summarized in Table 5-1. All of the paints tested were water-based (latex) paints. The paints, coded as “A” through “I”, were manufactured by four different companies,

Table 5-1. Description of the Latex Paints Tested (Based on information from MSDS, label, or product data sheets)

Latex Paint	LVA	LVB	LVC	LVD	LVE	LVF	LVG	LVH	LVI
Manufacturer	1	1	1	2	3	3	4	4	2
Color	white	white	white	antique white	white	white	antique white	dover white	white
Finish	flat	flat	flat	flat	flat	semi-gloss	flat	flat	satin flat
Density, kg/L	1.21±0.02	1.21±0.02	1.21±0.02	1.35	1.25-1.31	1.21-1.31	1.33	1.22-1.43	1.37
VOC, g/L	0	0	0	0	NA <sup>a</sup>	NA	1	60-175	250
Dry to touch (min) @ 2 °C and 50%RH	NA	NA	NA	30-60	NA	NA	60	60	NA
Dry to re-coat (min)	120	120	120	120	120	240	240	240	240
Solids, Volume %	NA	NA	NA	33.4±1	26-32	31-39	38±2	NA	24-33
Solids, Weight %	NA	NA	NA	51.0±1	NA	NA	NA	56	NA
Recommended Film Thickness: Wet (mils)	NA	NA	NA	4.0	NA	NA	4	4	NA
Dry (mils)	NA	NA	NA	1.3	NA	NA	1.5	1.4	NA
Coverage, sq. ft./ gal	500-800	500-800	500-800	400-450	400-450	400-450	400	400	400
Features	up to 2000 scrubs	up to 2000 scrubs	up to 2000 scrubs	no odor, quick dry, scrubbable	low odor, solvent-free, washable	low odor, solvent- free	low odor, low-VOC, washable	one coat, 10 years washable	high-hiding, washable

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

identified as “1” through “4.” The three paints supplied by manufacturer number 1 were basically the same but different as follows:

- LVB - same as paint LVA, but without a biocide
- LVC - paint LVA reformulated with a different biocide

The LVB and LVC paints were requested for additional testing after the elevated levels of formaldehyde were measured in emissions from paint LVA.

LVD, LVE, LVF and LVG were the four other low-odor latex paints that were tested. All of the paints tested were latex flat paints, except paint LVF which was a semi-gloss latex paint. Paints LVH and LVI were “conventional” latex paints with VOC levels of greater than 60 g/L, as indicated in the table. Emissions were not measured from LVH and LVI in this study; they were included to compare the performance of the low-VOC latex paints with conventional latex paints.

## 5.2 METHOD 24 MEASUREMENT RESULTS

As described in Section 4.0, the EPA Method 24 procedures were used to determine the total volatile content of the paints (gravimetric method), the water content (Karl Fischer determination) and VOC content (by subtraction). The results are summarized in Table 5-2. As shown in the table, the total volatile content of the paints ranged from approximately 40 to 50%. Water content was in the same range, indicating that the paints had low-VOC content. All of the low-VOC paints, except paint LVG, had VOC content of less than 0.2% as measured by Method 24. The one “conventional” paint (LVH) that was tested had a VOC content of 2.3%. The measurement of VOC content in paint LVH during this project compared well with the measurements for the same brand and type of paint performed during a previous project in 1995. As shown in the table, the precision of the gravimetric measurements of total volatile content was very good, with the relative standard deviation (RSD) for the duplicates being less than 0.4% for all nine paints. The precision of the measurement of water in the paints by the Karl Fischer method was also good, with the RSD ranging from 0.1 to 3.0%. The precision was poorest for the paints from manufacturer 3, in which case it appeared that some component in the paint interfered with the Karl Fischer reagent, making the analysis more difficult. Because VOC content is calculated by subtraction of the water content from the total volatile content by Method 24, the combined error of the two analysis methods resulted in negative values for VOC content. The results of the analyses suggest that Method 24 is not a suitable method for quantifying VOC content in low-VOC latex paints.

Table 5-2. Volatile Content, Water Content and VOC Content of the Test Paints (Weight %)

Paint	% Volatile Content (% RSD) <sup>a</sup>	% Water Content (% RSD) <sup>a</sup>	% VOC <sup>b</sup>
LVA	40.7 (0.4)	40.7 (1.2)	0.0
LVB	46.5 (0.2)	46.8 (0.8)	-0.3
LVC	50.0 (0.2)	51.7 (0.1)	-1.7
LVD	48.3 (0.1)	49.4 (0.4)	-1.1
LVE	54.3 (0.1)	55.4 (3.0)	-1.1
LVF	50.8 (0.1)	52.4 (1.8)	-1.6
LVG	46.2 (0.1)	45.4 (0.6)	0.8
LVH	43.1 (0.1)	40.8 (0.3)	2.3
LVH -1995 <sup>c</sup>	42.8 (0.1)	40.1 (0.6)	2.7

<sup>a</sup> Values reported are average of analyses of duplicate aliquots of the paint; the % relative standard deviation is presented in parentheses

<sup>b</sup> The minimum detection limit was estimated to be 0.2% based on method specification for weighing to the nearest mg for gravimetric analyses

<sup>c</sup> Data from analyses of the same brand and type of paint performed during tests in 1995

### 5.3 VOC CONTENTS IN THE PAINTS DETERMINED BY THE GC METHOD

The bulk paints were diluted with solvent, as described in Section 4.0 and analyzed by GC/MS to identify the VOCs in the products. The GC/MS was calibrated for VOCs identified in previous studies of latex paint, including ethylene glycol, propylene glycol, dipropylene glycol, 2-(2-butoxyethoxyethanol) and Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate). Quantitative results of the analyses for these compounds are presented in Table 5-3. As noted in the table, analyses of paints LVC, LVD and LVG were performed immediately prior to the chamber emission tests. Ethylene glycol was measurable at a level above the practical quantitation limit (PQL) only in paint LVG, which also contained measurable levels of dipropylene glycol and BEE. Ethylene glycol was also detected at low levels in paints LVC and LVD. Propylene glycol was detected in four of the seven low-VOC paints analyzed by the GC method. Dipropylene glycol was measurable at levels above the PQL in both paints from manufacturer number 3 (LVE and LVF) and paint LVG. It was also detected in two other paints. BEE was the most abundant of the five target VOCs in paint LVG and was detected in four of the other six low-VOC paints. None of the target VOCs were detected in paint LVB from manufacturer number 1.

Table 5-3. Concentrations of VOCs in the Low-Odor/Low-VOC Paints (mg/g)

Paint	Ethylene Glycol	Propylene Glycol	Dipropylene Glycol	2-(2-Butoxyethoxy) ethanol	Texanol
LVA	BDL <sup>a</sup>	0.16	BDL	<del>0.04</del> <sup>c</sup>	BDL
LVB	BDL	BDL	BDL	BDL	BDL
LVC <sup>b</sup>	<del>0.06</del> <sup>c</sup>	BDL	<del>0.03</del> <sup>c</sup>	<del>0.05</del> <sup>c</sup>	BDL
LVD <sup>b</sup>	<del>0.04</del> <sup>c</sup>	<del>0.03</del> <sup>c</sup>	<del>0.11</del> <sup>c</sup>	<del>0.11</del> <sup>c</sup>	<del>0.03</del> <sup>c</sup>
LVE	BDL	BDL	0.14	BDL	BDL
LVF	BDL	0.12	0.35	<del>0.02</del> <sup>c</sup>	0.14
LVG <sup>b</sup>	0.59	<del>0.09</del> <sup>c</sup>	0.81	1.51	<del>0.05</del> <sup>c</sup>
Conventional <sup>d</sup>	24.0	2.32	0.59	4.98	13.5

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

<sup>b</sup> Bulk analyses performed on HP5890 immediately prior to chamber emission tests; all other analyses performed on Varian at start of test program

<sup>c</sup> Values with strike through are above the method detection limit, but below the practical quantitation limit

<sup>d</sup> Results of bulk analyses of a conventional latex paint from manufacturer 4 performed in a previous research project (Chang et al., 1997)

Texanol was detected in only three of the seven low-VOC paints. Paint LVG had the highest total concentration of VOCs at 3.05 mg/g (0.3% VOC w/w). This level of VOCs was substantially lower than the 45 mg/g total VOCs measured in a conventional latex paint in a previous research project (Chang et al., 1997), results of which are also shown in Table 5-3.

Examination of the GC chromatograms indicated few other compounds that could be detected in the analyses of the bulk products using the solvent extraction method. Although there were some compounds detected at very low concentrations, they could not be easily identified using the Varian software and computerized mass spectra matching routine of the Varian. There was a low level of confidence ascribed to the computerized spectra matches. Additional manual spectra matching would need to be performed for identifying unknowns in the samples. In order to improve the method detection limit and improve identification of minor constituents in low-VOC paints, an alternative to the solvent extraction method would need to be used.

#### 5.4 ALDEHYDE EMISSIONS FROM THE PAINTS IN SMALL CHAMBER TESTS

Ten small chamber emissions tests were performed to measure emissions of aldehydes from the low-VOC paints. The initial tests with the paints were range-finding tests. Therefore, some of the tests were of short duration. For the paint from manufacturer number 1, a number of tests of longer duration were performed to more fully characterize the emissions of formaldehyde from the paint. Table 5-4 summarizes the test parameters for the small chamber emissions tests that were performed to measure aldehyde emissions from the low-VOC paints. As shown in the table, the duration of the tests varied from 2 days to 16 days. Generally, the tests were either 7 or 14 days. Test LVT4 was only a two-day test because the objective was to verify the results of test LVT1, during which elevated levels of formaldehyde were measured in the emissions from paint LVA.

Both glass and gypsum wallboard were used as substrates. The initial test with each paint was performed by applying the paint to glass. Glass was used as a substrate in one test with each paint to facilitate better comparison of the emissions from the different paints. Use of an inert substrate minimized background VOCs and aldehydes during the tests and potential interactions between substrate and the coating that might impact emissions. Additional tests were performed with paints LVA and LVD applied to gypsum wallboard because the two paints had elevated levels of formaldehyde in emissions during tests with the application on glass. The tests with application of LVA and LVD on gypsum were intended to demonstrate that the emissions would also occur on a realistic substrate. Tests with paints LVB and LVC, both supplied by manufacturer number 1, were performed with application on gypsum wallboard. Paint LVB was reported to be the same as paint LVA, but without biocide. Paint LVC was reported by the manufacturer to be a re-formulation of paint LVA with a different biocide.

The table includes the average and standard deviation of the temperature and relative humidity during the duration of the test. Fans used in the chamber were adjusted to obtain a nominal air velocity of 10 cm/s at 1 cm above the surface of the substrate.

The concentrations of formaldehyde, acetaldehyde, propanal, benzaldehyde, pentanal and hexanal were measured during each of the ten small chamber tests. Additionally, the chromatograms were reviewed to determine if any other non-target compounds were in the samples. Results for tests LVT2 through LVT10 are presented in Tables 5-5 through 5-13. Data are not reported for the first test, LVT1, performed with paint LVA, because the large volume samples collected during the test resulted in formaldehyde concentrations that were in excess of the method's upper limits. The test was repeated as test LVT4 on glass and a subsequent test (LVT5) was performed with paint LVA on gypsum wallboard. Both tests LVT4 and LVT5 confirmed the elevated emissions of formaldehyde from the paint.

Table 5-4. Description of the Small Chamber Emission Tests For Measurements of Aldehydes

Test Identification	LVT1	LVT2	LVT3	LVT4	LVT5
Paint Tested	LVA	LVG	LVE	LVA	LVA
Test Start Date	11/05/97	11/18/97	12/03/97	12/08/97	01/21/98
Test Duration (day)	11	7	7	2	14
Substrate Type	glass	glass	glass	glass	gypsum
Substrate Size (cm)	45.7 × 30.5	16 × 16	23 × 30.5	16 × 16	16 × 16
Coated Area (cm <sup>2</sup> )	1394	256	701	256	256
Paint Applied (g)	16.44	1.76	4.45	1.97	3.26
Application Method	roller	roller	roller	roller	roller
Air Exchange Rate (h <sup>-1</sup> )	0.51	0.49	0.52	0.50	0.50
Air Velocity (cm/s)	10	10	10	10	10
Temperature (°C)	22.5±0.15	24.4±0.04	24.1±0.09	23.1±0.03	24.3±0.06
RH (%)	48.1±13	51.5±3.9	50.8±3.4	52.8±1.8	56.1±4.3

Test Identification	LVT6	LVT7	LVT8	LVT9	LVT10
Paint Tested	LVD	LVD	LVF	LVC	LVB
Test Start Date	01/27/98	02/10/98	02/11/98	05/13/98	05/19/98
Test Duration (day)	7	16	8	14	14
Substrate Type	glass	gypsum	glass	gypsum	gypsum
Substrate Size (cm)	16 × 16	16 × 16	16 × 16	16 × 16	16 × 16
Coated Area (cm <sup>2</sup> )	256	256	256	256	256
Paint Applied (g)	1.88	2.88	1.87	3.43	3.54
Application Method	roller	roller	roller	roller	roller
Air Exchange Rate (h <sup>-1</sup> )	0.50	0.48	0.51	0.49	0.50
Air Velocity (cm/s)	10	10	10	10	10
Temperature (°C)	25.4±0.38	23.8±0.05	24.0±0.03	23.9±0.03	24.4±0.04
RH (%)	47.9±4.6	51.1±4.7	51.3±4.8	51.5±2.8	48.4±3.3



Table 5-5. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT2 with Paint LVG Applied to Glass

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-0.89 <sup>a</sup>	12.7	<del>3.76E-03</del> <sup>b</sup>	<del>6.25E-03</del>	BDL <sup>c</sup>	BDL	BDL	BDL
2.40	41.2	7.51E-02	9.82E-03	<del>4.38E-03</del>	BDL	BDL	BDL
7.57	61.2	1.35E-02	<del>2.65E-03</del>	BDL	BDL	BDL	BDL
27.58	51.8	<del>2.40E-03</del>	<del>1.35E-03</del>	BDL	BDL	BDL	BDL
52.40	63.6	<del>1.64E-03</del>	<del>1.00E-03</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-6. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT3 with Paint LVE Applied to Glass

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-1.32 <sup>a</sup>	22.4	<del>3.01E-03</del> <sup>b</sup>	<del>3.66E-03</del>	BDL <sup>c</sup>	BDL	BDL	BDL
1.68	1.7	2.79E-02	<del>9.07E-03</del>	BDL	1.39E-02	BDL	BDL
6.79	6.8	1.45E-02	<del>3.73E-03</del>	<del>1.90E-03</del>	6.76E-03	BDL	BDL
16.69	16.7	7.20E-03	<del>7.63E-04</del>	BDL	BDL	BDL	BDL
24.75	24.8	6.65E-03	<del>1.07E-03</del>	BDL	BDL	BDL	BDL
48.33	48.3	5.33E-03	<del>7.99E-04</del>	BDL	BDL	BDL	BDL
170.16	170.2	<del>2.59E-03</del>	<del>7.35E-04</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-7. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT4 with Paint LVA Applied to Glass

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-1.13 <sup>a</sup>	38.8	<del>2.37E-03</del> <sup>b</sup>	<del>9.69E-04</del>	BDL <sup>c</sup>	BDL	BDL	BDL
0.25	1.9	2.56E+00	3.01E-01	BDL	BDL	BDL	BDL
0.54	3.8	4.36E+00	2.79E-01	<del>5.16E-02</del>	<del>2.39E-02</del>	BDL	BDL
1.05	2.9	5.53E+00	2.40E-01	<del>3.73E-02</del>	<del>3.17E-02</del>	BDL	BDL
1.50	3.0	4.93E+00	1.96E-01	<del>2.00E-02</del>	BDL	BDL	BDL
2.15	3.2	3.79E+00	1.49E-01	BDL	BDL	BDL	BDL
3.05	3.8	3.02E+00	9.83E-02	<del>1.26E-02</del>	BDL	BDL	BDL
5.27	5.0	1.58E+00	4.50E-02	BDL	BDL	BDL	BDL
7.69	6.1	9.89E-01	3.32E-02	<del>8.05E-03</del>	BDL	BDL	BDL
11.22	7.4	6.76E-01	<del>2.27E-02</del>	BDL	BDL	BDL	BDL
28.85	24.9	3.24E-01	1.11E-02	BDL	BDL	BDL	BDL
50.36	54.5	2.23E-01	6.65E-03	<del>1.11E-03</del>	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-8. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT5 with Paint LVA Applied to Gypsum Wallboard

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-1.28 <sup>a</sup>	23.8	<del>7.10E-03</del> <sup>b</sup>	<del>2.36E-03</del>	BDL <sup>c</sup>	BDL	BDL	BDL
0.51	3.8	2.18E+00	5.18E-01	<del>2.09E-02</del>	<del>2.87E-02</del>	BDL	BDL
0.98	1.0	1.97E+00	5.06E-01	BDL	<del>2.90E-02</del>	BDL	BDL
1.57	1.6	1.67E+00	4.46E-01	<del>1.45E-02</del>	BDL	BDL	BDL
2.07	3.4	1.42E+00	3.81E-01	<del>1.55E-02</del>	BDL	BDL	BDL
3.27	5.8	1.05E+00	2.63E-01	<del>1.33E-02</del>	BDL	BDL	BDL
4.84	5.8	7.93E-01	1.73E-01	<del>1.10E-02</del>	BDL	BDL	BDL
7.67	5.7	3.14E-01	5.51E-02	BDL	BDL	BDL	BDL
9.77	5.7	5.08E-01	7.33E-02	BDL	BDL	BDL	BDL
25.01	7.6	3.29E-01	2.65E-02	BDL	BDL	BDL	BDL
29.29	11.8	3.02E-01	2.18E-02	BDL	BDL	BDL	BDL
52.52	18.3	2.19E-01	<del>1.03E-02</del>	BDL	BDL	BDL	BDL
123.98	24.3	1.58E-01	<del>3.25E-03</del>	BDL	BDL	BDL	BDL
168.38	15.7	1.40E-01	<del>2.86E-03</del>	BDL	BDL	BDL	BDL
215.57	23.5	1.14E-01	<del>2.64E-03</del>	BDL	BDL	BDL	BDL
291.56	23.0	8.31E-02	<del>3.03E-03</del>	BDL	BDL	BDL	BDL
339.32	46.4	<del>1.39E-03</del>	<del>7.45E-04</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-9. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT6 with Paint LVD Applied to Glass

Elapsed Time (hr)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-0.92 <sup>a</sup>	13.7	<del>5.05E-03</del> <sup>b</sup>	<del>1.99E-03</del>	BDL <sup>c</sup>	BDL	BDL	BDL
1.14	20.0	3.15E+00	1.13E-01	<del>2.00E-03</del>	3.13E-02	BDL	BDL
3.79	27.1	9.57E-01	3.01E-02	BDL	1.46E-02	BDL	BDL
26.30	64.2	1.66E-02	<del>9.32E-04</del>	BDL	BDL	BDL	BDL
49.93	75.9	1.06E-02	<del>5.18E-04</del>	BDL	BDL	BDL	BDL
193.93	144.6	2.03E-03	<del>3.15E-04</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-10. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT7 with Paint LVD Applied to Gypsum Wallboard

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-1.41 <sup>a</sup>	39.7	6.10E-03	<del>2.70E-03</del> <sup>b</sup>	BDL <sup>c</sup>	BDL	BDL	BDL
0.40	3.8	1.01E+00	3.40E-01	BDL	<del>3.64E-02</del>	BDL	BDL
1.01	3.6	8.16E-01	3.32E-01	BDL	<del>3.09E-02</del>	BDL	BDL
1.65	3.8	5.97E-01	2.60E-01	BDL	BDL	BDL	BDL
2.74	2.9	3.93E-01	1.63E-01	BDL	BDL	BDL	BDL
3.91	2.8	2.97E-01	1.15E-01	BDL	BDL	BDL	BDL
4.92	5.2	2.41E-01	6.42E-02	BDL	BDL	BDL	BDL
6.12	5.8	2.01E-01	3.88E-02	BDL	BDL	BDL	BDL
11.78	12.0	1.35E-01	<del>8.76E-03</del>	BDL	BDL	BDL	BDL
21.38	11.6	1.00E-01	<del>6.99E-03</del>	BDL	BDL	BDL	BDL
28.26	20.9	9.17E-02	<del>2.69E-03</del>	BDL	BDL	BDL	BDL
51.52	22.1	6.62E-02	<del>2.81E-03</del>	BDL	BDL	BDL	BDL
69.43	22.4	5.21E-02	<del>8.57E-03</del>	BDL	BDL	BDL	BDL
170.07	45.7	3.00E-02	<del>2.32E-03</del>	BDL	BDL	BDL	BDL
217.72	23.4	2.47E-02	<del>3.48E-03</del>	BDL	BDL	BDL	BDL
315.80	22.8	1.74E-02	<del>2.96E-03</del>	BDL	BDL	BDL	BDL
385.83	51.5	1.28E-02	<del>2.00E-03</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-11. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT8 with Paint LVF Applied to Glass

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-1.41	24.1	<del>2.95E-03</del> <sup>b</sup>	<del>2.97E-03</del>	BDL	BDL	BDL	BDL
1.12	19.1	1.26E-02	1.53E-02	BDL	3.58E-02	BDL	BDL
3.90	32.8	<del>6.03E-03</del>	7.97E-03	<del>1.61E-03</del>	2.13E-02	BDL	BDL
8.83	60.0	<del>2.46E-03</del>	<del>1.16E-03</del>	BDL	7.71E-03	BDL	BDL
24.24	48.3	<del>2.33E-03</del>	<del>8.13E-04</del>	BDL	<del>2.14E-03</del>	BDL	BDL
48.70	46.2	<del>2.21E-03</del>	<del>2.18E-03</del>	BDL	BDL	BDL	BDL
146.15	45.6	<del>2.08E-03</del>	<del>3.27E-03</del>	BDL	BDL	BDL	BDL
193.80	23.6	<del>2.81E-03</del>	<del>1.58E-03</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-12. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT9 with Paint LVC Applied to Gypsum Wallboard

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-19.48 <sup>a</sup>	27.9	<del>3.62E-03<sup>b</sup></del>	<del>3.72E-03</del>	BDL <sup>c</sup>	BDL	BDL	BDL
-1.49	26.3	<del>6.81E-03</del>	<del>4.60E-03</del>	BDL	BDL	BDL	BDL
0.41	3.5	2.95E+00	<del>4.04E-02</del>	BDL	BDL	BDL	BDL
0.93	4.3	2.16E+00	<del>3.33E-02</del>	BDL	BDL	BDL	BDL
2.74	7.7	1.15E+00	<del>1.40E-02</del>	BDL	BDL	BDL	BDL
4.29	9.9	8.89E-01	BDL	BDL	BDL	BDL	BDL
5.10	6.4	7.86E-01	BDL	BDL	BDL	BDL	BDL
7.42	10.4	6.02E-01	<del>1.17E-02</del>	BDL	BDL	BDL	BDL
11.69	15.4	4.53E-01	BDL	BDL	BDL	BDL	BDL
22.66	30.4	2.66E-01	BDL	BDL	BDL	BDL	BDL
28.99	19.5	2.41E-01	<del>2.94E-03</del>	BDL	BDL	BDL	BDL
47.77	24.1	1.72E-01	<del>2.88E-03</del>	BDL	BDL	BDL	BDL
120.42	25.7	5.96E-02	<del>4.84E-03</del>	<del>2.81E-03</del>	BDL	BDL	BDL
172.45	23.7	3.92E-02	<del>4.54E-03</del>	BDL	BDL	BDL	BDL
342.69	23.1	1.51E-02	<del>4.93E-03</del>	BDL	BDL	<del>4.34E-03</del>	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Table 5-13. Aldehyde Emissions (mg/m<sup>3</sup>) in Small Chamber Test LVT10 with Paint LVB Applied to Gypsum Wallboard

Elapsed Time (h)	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
-0.88 <sup>a</sup>	13.8	<del>6.05E-03</del> <sup>b</sup>	BDL <sup>c</sup>	BDL	BDL	BDL	BDL
0.46	4.4	3.11E+00	<del>2.33E-02</del>	BDL	BDL	BDL	BDL
1.03	4.4	2.11E+00	<del>2.75E-02</del>	BDL	BDL	BDL	BDL
2.65	13.7	1.19E+00	<del>9.84E-03</del>	BDL	BDL	BDL	BDL
6.10	13.3	7.10E-01	<del>1.39E-02</del>	<del>7.30E-03</del>	BDL	BDL	BDL
11.66	12.4	4.50E-01	<del>8.54E-03</del>	<del>6.27E-03</del>	BDL	BDL	BDL
24.74	21.0	2.65E-01	<del>6.15E-03</del>	BDL	BDL	BDL	BDL
29.89	11.2	2.49E-01	<del>7.53E-03</del>	BDL	BDL	BDL	BDL
47.55	27.1	1.59E-01	<del>5.23E-03</del>	BDL	BDL	<del>2.80E-03</del>	BDL
72.09	23.8	1.18E-01	<del>6.36E-03</del>	<del>3.94E-03</del>	BDL	<del>3.26E-03</del>	BDL
169.77	22.8	3.90E-02	<del>3.68E-03</del>	<del>5.87E-03</del>	BDL	<del>4.84E-03</del>	BDL
265.26	23.0	2.18E-02	<del>2.05E-03</del>	BDL	BDL	<del>3.11E-03</del>	BDL
313.51	31.2	1.67E-02	<del>2.67E-03</del>	BDL	BDL	<del>3.17E-03</del>	BDL
362.16	33.2	1.39E-02	<del>1.85E-03</del>	BDL	BDL	<del>3.07E-03</del>	BDL

<sup>a</sup> Chamber air background sample prior to application of the paint to the substrate

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

Formaldehyde and acetaldehyde were detected in the emissions from all paints tested in the project. However, the levels were quite low, except for paints LVA, LVB, LVC and LVD. It should be noted that the values in the tables presented with a "strike through" are concentrations that are below the practical quantitation limit (PQL) of the method, but above the minimum detection limit (MDL). The practical quantitation limit is defined based on the lowest level calibration standard and the volume of sample collected on the sorbent media. For a sample volume of 30 liters, the practical quantitation limit would be 0.007 mg/m<sup>3</sup>. The PQL varies based on the volume of the sample; the smaller the sample volume, the higher the PQL. BDL in the table indicates that the compound was below the minimum detection limit (MDL), which was determined by analysis of seven low level standards, and is three times the standard deviation of the analyses of the replicates. The MDL was approximately 0.0007 mg/m<sup>3</sup> for a 30 L sample.



Propanal and benzaldehyde were measured in some of the samples of emissions from the paints, but were rarely above the PQL. Pentanal was detected only in paint LVB, but all concentrations were below the PQL. Hexanal was not detected in the emissions from any of the paints. The aldehydes that were detected can be summarized for each paint as follows:

- Paint LVA, LVB, LVC (paints from manufacturer number 1) - elevated formaldehyde levels and detectable acetaldehyde concentrations in the emissions; propanal and pentanal detected in some samples, but always below the PQL
- Paint LVD from manufacturer 2 - elevated formaldehyde concentrations in the emissions; acetaldehyde concentrations above the PQL immediately following application; propanal and benzaldehyde detected in some samples at low levels
- Paint LVE from manufacturer 3 - low levels of formaldehyde detected; acetaldehyde detected but not above PQL
- Paint LVF from manufacturer 3 - low levels of formaldehyde and acetaldehyde detected but near or below the PQL
- Paint LVG from manufacturer 4 - low levels of formaldehyde and acetaldehyde detected immediately after application, but otherwise the concentrations were below the PQL

The emissions of formaldehyde from the paints supplied by manufacturer number 1, presented above in Tables 5-7, 5-8, 5-12 and 5-13, are depicted in Figure 5-1. The figure compares the emissions for the three types of paints during the first 50 hours following application. The highest concentrations of formaldehyde emissions were measured following application of the paint LVA to glass for which the data were presented in Table 5-7. Emissions from the paint applied to glass were higher than in the subsequent test with application to gypsum board (for which the data were presented in Table 5-8) throughout the first 50 hours of the two tests despite the fact that nearly 50% more paint was applied to the gypsum wallboard (Table 5-4). As will be described below, the total mass of formaldehyde emitted during the first hours after application of glass was substantially higher than that for the same paint applied to gypsum wallboard. The peak concentration of 2.18 mg/m<sup>3</sup> was measured in the sample collected 0.5 hour after application and was substantially lower than the peak concentration of 5.53 mg/m<sup>3</sup> measured at 1 hour when the paint was applied to glass. As shown in Figure 5-1, the emissions of formaldehyde peaked soon after application and exhibited a decay profile typical of volatile organic compounds in wet products.

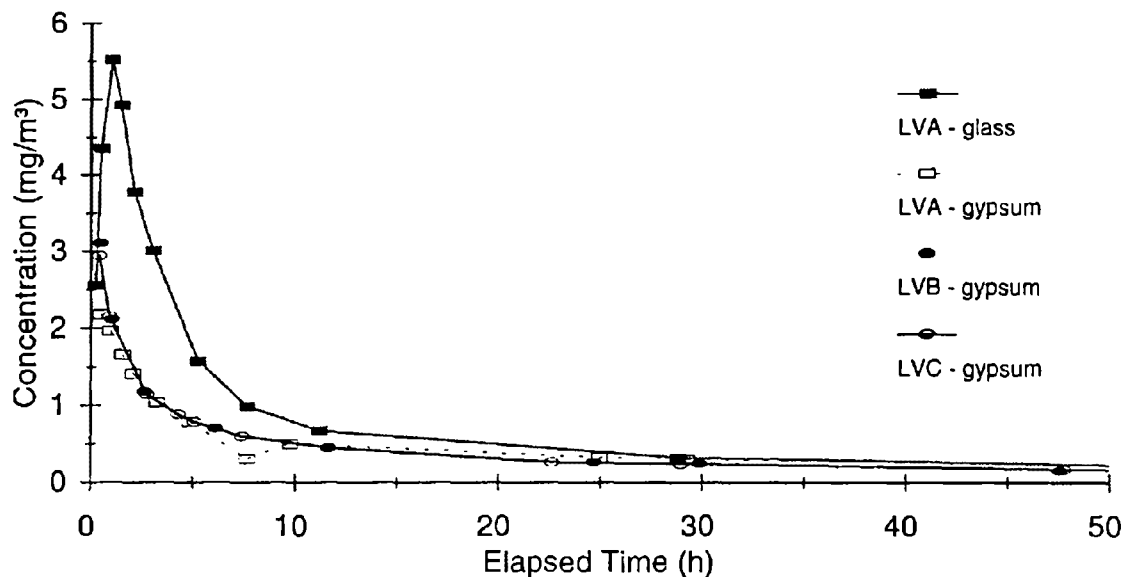


Figure 5-1. Comparison of Formaldehyde Emissions from Three Paints Supplied by Manufacturer No. 1

After determining that paint LVA emitted elevated concentrations of formaldehyde, the manufacturer was contacted to discuss the results of the tests and the possible source of the formaldehyde in the paint. The manufacturer discussed the results with the formulators of the paint and determined that the biocide used in the paint contained approximately 5% formaldehyde. Based on the amount of biocide used, the manufacturer estimated that the resulting formaldehyde concentration in the paint would be approximately 5 ppm. The manufacturer expressed concern that the paint contained formaldehyde and that the product, as formulated, was not meeting their objectives as a “non-polluting” product. The manufacturer indicated that they would identify a biocide that did not contain formaldehyde and that the product would be re-formulated. Following re-formulation, the manufacturer provided a new sample of the “no-VOC” paint for testing. At our request, they also provided a sample of paint LVA that was reported to not contain any biocide. The paints were respectively identified as LVC (re-formulated with new biocide) and LVB (LVA with no biocide). Upon receipt of the paints, small chamber tests were performed with application of the paints to gypsum wallboard. The results of the small chamber tests, presented in Tables 5-12 and 5-13, are also depicted in Figure 5-1. As the data show, there was not a substantial difference in the emissions from LVA, LVB, or LVC when applied to gypsum wallboard.

The peak concentrations of formaldehyde in the emissions were 2.18, 2.95 and 3.11 mg/m<sup>3</sup> in the three tests, with the highest concentrations measured in the test with the paint re-formulated with the new biocide. As shown in Figure 5-1, the emissions profiles were nearly identical for the three tests. It should be noted that background air samples were collected from the small chamber containing the gypsum wallboard substrate prior to each test. The concentrations of formaldehyde were detectable, but always below the PQL and were two to three orders of magnitude lower than the formaldehyde concentrations following application of the paint to the substrate. Therefore, the source of the formaldehyde does not appear to be the substrate, but rather the paint. The source of the formaldehyde in the paint has not been identified. Additional analyses of the formulation and of the bulk product would be required to determine the source.

Acetaldehyde was detected in the emissions from paint LVA. The concentrations measured in the small chamber tests peaked at 0.5 mg/m<sup>3</sup> and dropped below the PQL 52 hours after application of the paint. Acetaldehyde was also detected in tests with LVB and LVC, but the concentrations were substantially lower, being below the PQL in all samples. The reason for the differences in acetaldehyde concentrations in the three paints is not known. Acetaldehyde was not listed on the material safety data sheet (MSDS) for the biocides used in paint LVA or LVC. Although the manufacturer advised us that the only change in the formulation for LVC was to replace the biocide, the re-formulation may have affected the acetaldehyde levels in the paint.

The other paint that had elevated levels of formaldehyde in the emissions was LVD. The results of the small chamber tests are presented in Tables 5-9 and 5-10. Figure 5-2 depicts the results, comparing small chamber emission concentrations for LVD on glass and gypsum with the concentrations for LVA applied to gypsum wallboard. When applied to glass, the peak concentration of formaldehyde in the small chamber test with paint LVD was 3.15 mg/m<sup>3</sup>. Because this was the initial scouting test, only four samples were collected during the first 50 hours of the test. As shown in Figure 5-2, the concentration dropped rapidly between the 1.1 and 3.8 hour samples. As a follow-up to the test on glass, a small chamber test was performed with paint LVD applied to gypsum wallboard (Table 5-10). The peak concentration was 1.01 mg/m<sup>3</sup> and occurred at 0.4 hours after application. The concentrations dropped below 0.1 mg/m<sup>3</sup> within the first 24 hours following the application (Figure 5-2). Concentrations of formaldehyde in the emissions during the first 50 hours of the test with LVD were substantially lower than during the test with LVA on gypsum wallboard, as shown in the figure.

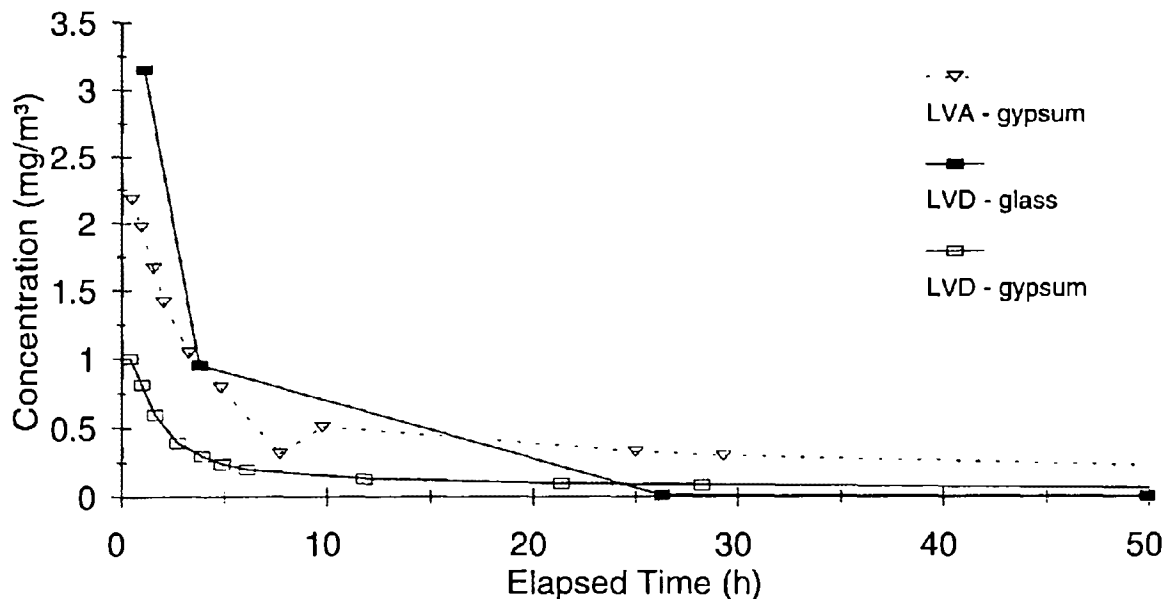


Figure 5-2. Comparison of Formaldehyde Emissions from Paints LVA and LVD in Small Chamber Tests

Acetaldehyde was also measured in the emissions from paint LVD applied to either glass or gypsum wallboard. The peak concentration was  $0.34 \text{ mg/m}^3$  at 0.4 hours following application of LVD to gypsum wallboard, but the concentration dropped quickly to below the PQL. The acetaldehyde concentrations for LVD (Table 5-10) were slightly lower than those for LVA (Table 5-8) in the small chamber emissions tests, but dropped more quickly than in the tests with LVA. It should also be noted that the amount of paint applied in test LVT5 with paint LVA was 3.26 grams compared to 2.88 grams of LVD in test LVT7.

The source of the aldehydes in paint LVD was not investigated. The manufacturer of the paint was not contacted.

In order to compare the emissions of formaldehyde from the different paints, the mass of formaldehyde emitted was estimated for the first 50 hours and also for the duration of the test by calculating the amount emitted based on the area under the time/concentration curve and the chamber air exchange rate. Results of these estimates are presented in Figures 5-3 and 5-4 and summarized in Table 5-14. The 50 hour period for integrating the mass emissions was selected because test LVT4 was only 50

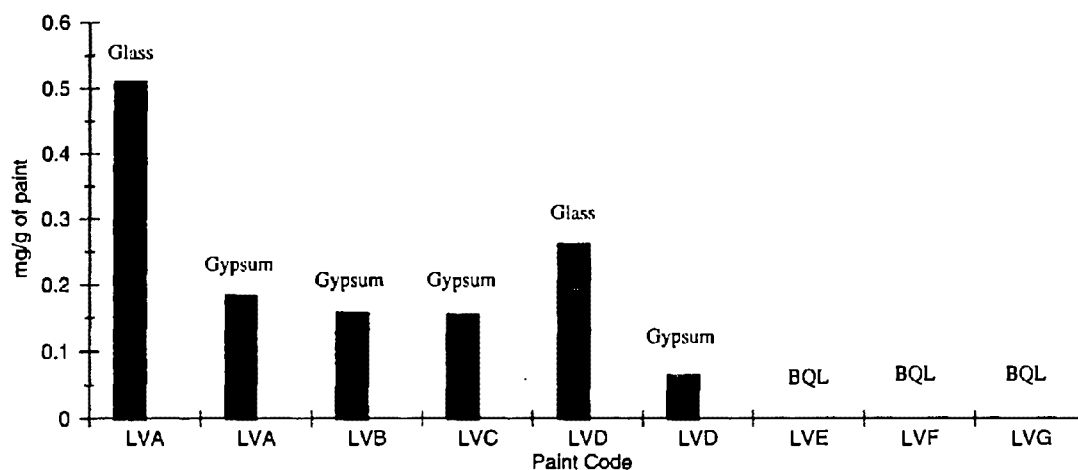


Figure 5-3. Comparison of the Mass of Formaldehyde Emitted per Gram of Paint for the First 50 Hours of Each Small Chamber Test

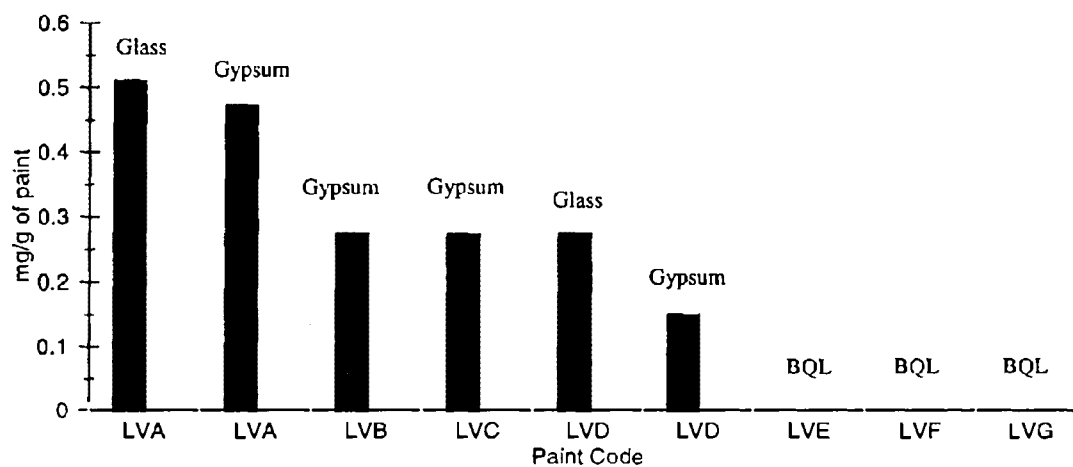


Figure 5-4. Mass of Formaldehyde Emitted from the Paints over the Duration of the Small Chamber Tests (LVA-1 = 50 hr; LVA-2, LVB and LVC = 14 days; LVD-1 = 7 Days; LVD-2 = 16 Days)

Table 5-14. Summary of the Formaldehyde Mass Emitted in the Small Chamber Emissions Tests

	LVT1	LVT2	LVT3	LVT4	LVT5
Paint tested	LVA	LVG	LVE	LVA	LVA
Substrate	Glass	Glass	Glass	Glass	Gypsum
Paint applied (g)	NC <sup>a</sup>	1.76	4.45	1.97	3.26
HCHO emitted per gram of paint (mg/g) first fifty hours	NC	BQL <sup>b</sup>	BQL	0.5102	0.1830
HCHO emitted per gram of paint (mg/g) for entire test	NC	BQL	BQL	0.5102	0.4720

	LVT6	LVT7	LVT8	LVT9	LVT10
Paint tested	LVD	LVD	LVF	LVC	LVB
Substrate	Glass	Gypsum	Glass	Gypsum	Gypsum
Paint applied (g)	1.88	2.88	1.87	3.43	3.54
HCHO emitted per gram of paint (mg/g) first fifty hours	0.2611	0.0642	BQL	0.1549	0.1570
HCHO emitted per gram of paint (mg/g) for entire test	0.2739	0.1492	BQL	0.2731	0.2739

<sup>a</sup> Not calculated because concentrations exceeded method upper limits

<sup>b</sup> Concentrations in emissions samples were below the quantitation limit in many of samples

hours in duration. In the tests with paint applied to glass, the mass of formaldehyde emitted was 0.510 mg/g of paint for LVA and 0.261 mg/g for LVD. When the paints were applied to gypsum wallboard, LVA emitted 0.183 mg/g during the first 50 hours. During the first 50 hours following application of LVD to gypsum, the emissions of formaldehyde were 0.064 mg/g, approximately one-third that of LVA. The data show that emissions were substantially lower from the paint LVD. Although manufacturer number 1 advised us that paint LVC was a paint re-formulated with a biocide that did not contain formaldehyde, the emissions of formaldehyde from LVC (0.155 mg HCHO per gram of paint) were not substantially different from LVA (0.183 mg HCHO per gram of paint) for the first 50 hours of the test. LVB, which was reported to be paint LVA without any biocide emitted 0.157 mg HCHO per gram of paint, nearly identical to LVC.

When the mass of formaldehyde emitted for the total duration of the test was compared, the differences were larger between the three paints from manufacturer number 1, as shown in Figure 5-4.

The 0.472 mg of HCHO per gram of paint emitted from paint LVA over the 14-day test was nearly twice as high as that for the re-formulated paint LVC and paint LVB, which reportedly contained no biocide. The mass of HCHO emitted per gram of paint LVA was three times higher than that for LVD over the 16-day test. The masses of HCHO emitted from the paints from manufacturers 3 and 4 were not calculated because most of the chamber concentrations were below the PQL.

## 5.5 VOC EMISSIONS FROM PAINTS IN SMALL CHAMBER TESTS

Small chamber tests were performed to measure emissions of VOCs from the low-odor/low-VOC paints from the four different paint manufacturers. Tests were performed with paints LVC, LVD, LVE and LVG, all of which were latex flat paints. The emissions were not measured from paint LVF, the only semi-gloss paint used in the study. The tests involved application of the paint on a glass substrate. Tests were 48 hours in duration. Air samples were collected on Tenax during each small chamber test and analyzed with the HP5890 GC/FID/MS to quantify the target VOCs [ethylene glycol, propylene glycol, dipropylene glycol, BEE and Texanol]. Chromatograms were also reviewed to identify non-target VOCs in the emission. Computerized mass spectra matching software was used for tentative identification of compounds not targeted for quantitation.

The test conditions and paint application data for the five tests performed to measure VOC emissions from the paints are summarized in Table 5-15.

The first test performed to measure VOC emissions was identified as test LVT11. It was a test to measure emissions of VOCs from paint LVG. After the test was started, it was determined that the concentrations of VOCs in the emissions greatly exceeded the expected emissions and that the air volumes collected on Tenax were too large. As a result, the mass of VOCs in the samples exceeded the highest calibration standard for the instrument. Although analyses were performed with a FID detector which has a wide linear range, the accuracy of the measurements can not be determined. Therefore, the test was repeated. The results of test LVT11 are not included in the data base of the study, but have been included in Appendix A to the report because the results are in good agreement with those from the second test with paint LVG.

Table 5-15. Description of Small Chamber Tests to Measure VOC Emissions

	LVT11	LVT12	LVT13	LVT14	LVT15
Paint Tested	LVG	LVD	LVE	LVC	LVG
Test Start Date	11/17/98	11/17/98	11/18/98	11/23/98	11/23/98
Test Duration (day)	2	2	2	2	2
Substrate Type	glass	glass	glass	glass	glass
Substrate Size (cm)	16 × 16	16 × 16	16 × 16	16 × 16	16 × 16
Coated Area (cm <sup>2</sup> )	256	256	256	256	256
Paint Applied (g)	2.96	2.35	2.87	3.14	3.35
Application Method	roller	roller	roller	roller	roller
Air Exchange Rate (h <sup>-1</sup> ) <sup>a</sup>	0.52	0.51	0.52	0.50	0.49
Air Velocity (cm/s) <sup>b</sup>	10	10	10	10	10
Temperature (°C) <sup>c</sup>	24.3±0.07	24.2±0.08	24.2±0.15	24.4±0.08	24.4±0.03
RH (%) <sup>c</sup>	51±1.9	48±3.0	43±8.1	51±0.9	51±0.9

<sup>a</sup> Average of starting and ending air exchange rates

<sup>b</sup> Nominal air velocity 1 cm above substrate surface

<sup>c</sup> Average ± standard deviations during the test period



#### 5.5.1 VOC Emissions from Paint LVC (Manufacturer Number 1)

Paint LVC was the re-formulated paint supplied by the smaller, independent, paint manufacturer who supplied paint LVA for the initial tests. Emissions measurements are listed in Table 5-16 and depicted in Figure 5-5. Ethylene glycol was the most abundant VOC in the emissions, with a peak concentration of 0.6 mg/m<sup>3</sup> at four hours after application to the glass substrate. Concentrations of the other VOCs targeted for quantitation were substantially lower and also peaked four hours after application. All five VOCs were measured at levels above the PQL throughout the 48 hour test.

#### 5.5.2 VOC Emissions from Paint LVD (Manufacturer Number 2)

Concentrations of VOCs measured in the emissions following application of paint LVD on glass are presented in Table 5-17 and depicted in Figure 5-6. The predominant VOC in the emissions from this paint was BEE, which peaked at 0.215 mg/m<sup>3</sup> six hours after the application. The second most abundant VOC in the emissions was Texanol. Concentrations of the VOCs in the emissions were slightly lower than in the emissions from paint LVC. Propylene glycol concentrations were below the PQL in most samples.

#### 5.5.3 VOC Emissions from Paint LVE (Manufacturer Number 3)

Concentrations of VOCs measured in the emissions following application of paint LVE are presented in Table 5-18 and depicted in Figure 5-7. The predominant VOC in the emissions from this paint was ethylene glycol, which peaked at 0.974 mg/m<sup>3</sup> four hours after the application. The second most abundant VOC in the emissions was propylene glycol, which peaked at 0.536 mg/m<sup>3</sup> at four hours. BEE, dipropylene glycol, and Texanol were detected at low levels.

#### 5.5.4 VOC Emissions from Paint LVG (Manufacturer Number 4)

Concentrations of VOCs measured in the emissions following application of paint LVG are presented in Table 5-19 and depicted in Figure 5-8. The predominant VOC in the emissions from this paint was BEE, consistent with the fact that this was the most abundant compound measured in the bulk paint. Ethylene glycol and dipropylene glycol, compounds also measurable in the paint, were the second and third most abundant VOCs in the emissions. BEE and ethylene glycol peaked six hours after paint application at 4.63 and 4.29 mg/m<sup>3</sup>, respectively. Texanol concentrations were below the PQL throughout the test, consistent with the low concentration measured in the bulk paint.

**Table 5-16. VOC Concentrations (mg/m<sup>3</sup>) in Emissions During the Small Chamber Test LVT14 with Paint LVC on Glass**

Elapsed Time (hr)	Sampling Vol. (L)	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
-1.12 <sup>a</sup>	8.50	<del>3.26E-03<sup>b</sup></del>	<del>1.32E-03</del>	<del>7.67E-03</del>	<del>4.73E-03</del>	<del>1.93E-03</del>
-1.12 <sup>c</sup>	8.18	<del>2.76E-03</del>	<del>1.53E-03</del>	<del>8.32E-03</del>	<del>3.21E-03</del>	<del>1.53E-03</del>
0.62	8.34	2.36E-02	2.79E-02	7.18E-02	3.05E-02	3.49E-02
2.18	8.09	3.35E-02	5.66E-02	4.18E-02	4.88E-02	4.42E-02
2.18	7.78	3.18E-02	4.47E-02	4.94E-02	6.69E-02	6.32E-02
4.10	8.06	5.44E-02	5.02E-01	1.80E-01	1.34E-01	5.63E-02
4.10	7.76	5.48E-02	6.93E-01	1.81E-01	1.51E-01	5.75E-02
6.10	7.74	4.30E-02	4.99E-01	1.27E-01	8.77E-02	2.47E-02
8.10	8.03	3.00E-02	3.91E-01	1.13E-01	1.27E-02	5.20E-02
10.14	8.17	4.38E-02	3.48E-01	1.08E-01	6.41E-02	4.28E-02
12.04	8.14	2.15E-02	2.99E-01	1.08E-01	7.59E-02	4.84E-02
12.04	7.84	2.30E-02	3.03E-01	1.10E-01	6.45E-02	4.21E-02
17.41	7.02	2.25E-02	2.09E-01	9.61E-02	9.17E-02	3.77E-02
24.08	8.10	2.53E-02	1.10E-01	7.53E-02	6.20E-02	2.83E-02
24.08	7.78	1.80E-02	1.25E-01	7.47E-02	4.87E-02	2.66E-02
32.13	8.23	2.68E-02	6.18E-02	6.17E-02	6.54E-02	2.12E-02
48.03	8.60	1.72E-02	2.70E-02	4.27E-02	4.94E-02	1.35E-02
48.00	7.82	1.64E-02	3.47E-02	4.85E-02	4.70E-02	1.39E-02

<sup>a</sup> Chamber background sample collected prior to start of test

<sup>b</sup> Values with strike through are below the practical quantification limit of the method

<sup>c</sup> Samples collected at the same time period are duplicates

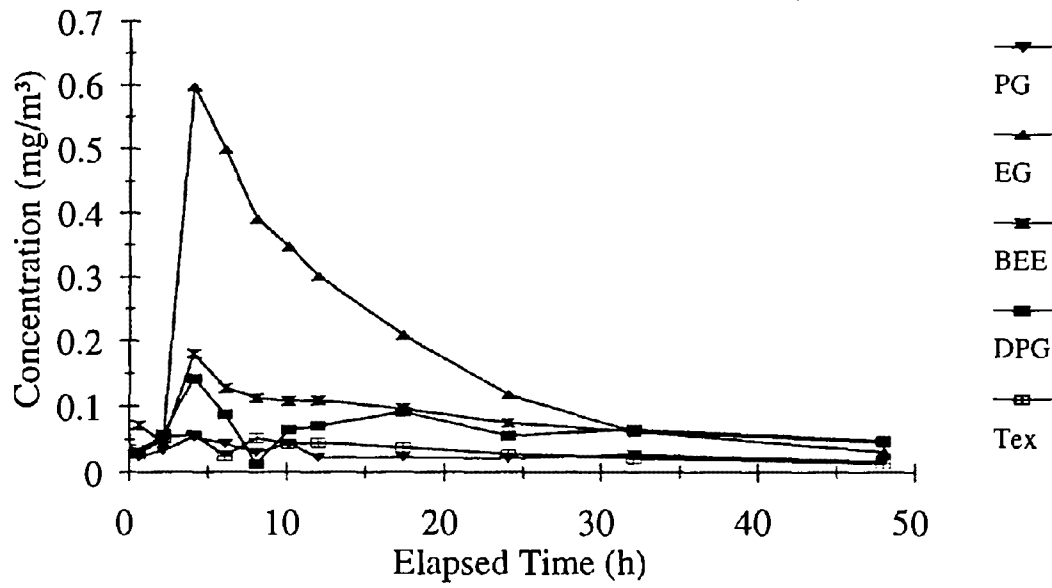


Figure 5-5. Concentrations of VOCs Measured in Emissions from Paint LVC Applied to Glass (Test LVT14)

Table 5-17. VOC Concentrations (mg/m<sup>3</sup>) in Emissions During the Small Chamber Test LVT12 with Paint LVD on Glass

Elapsed Time, (hr)	Sampling Vol. (L)	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
-2.85 <sup>a,b</sup>	7.84	<del>2.11E-04<sup>c</sup></del>	<del>1.00E-03</del>	<del>2.60E-03</del>	<del>2.80E-04</del>	<del>8.93E-04</del>
-2.85	7.70	<del>2.04E-04</del>	<del>1.00E-03</del>	<del>4.71E-03</del>	<del>1.71E-03</del>	<del>3.11E-03</del>
0.69	8.09	<del>2.99E-03</del>	<del>1.18E-02</del>	5.43E-02	1.15E-02	6.98E-02
2.17	7.83	<del>2.99E-03</del>	1.63E-02	1.81E-01	1.78E-02	8.63E-02
2.17	7.68	<del>3.10E-03</del>	2.41E-02	1.81E-01	1.83E-02	9.35E-02
4.07	7.77	2.34E-02	7.72E-02	2.12E-01	2.06E-02	9.13E-02
4.07	7.83	1.50E-02	6.06E-02	2.11E-01	1.70E-02	7.62E-02
6.04	7.77	1.79E-02	7.26E-02	2.15E-01	2.06E-02	7.54E-02
7.95	7.78	1.29E-02	6.13E-02	1.59E-01	1.72E-02	5.47E-02
10.05	8.04	<del>9.27E-03</del>	4.54E-02	2.14E-01	7.77E-02	1.41E-01
12.12	7.83	<del>9.72E-03</del>	5.08E-02	<i>1.35E+00<sup>d,e</sup></i>	<i>9.36E-01<sup>d,e</sup></i>	5.68E-02
12.12	7.95	<del>8.68E-03</del>	4.57E-02	1.40E-01	1.99E-02	5.85E-02
16.90	4.61	<del>9.84E-03</del>	5.62E-02	1.56E-01	<i>7.82E-01</i>	3.91E-02
23.97	8.15	<del>4.72E-03</del>	1.81E-02	8.03E-02	1.16E-02	2.77E-02
23.97	8.21	<del>4.64E-03</del>	1.75E-02	8.32E-02	1.29E-02	2.83E-02
32.29	7.73	<del>4.19E-03</del>	1.31E-02	6.31E-02	1.49E-02	2.24E-02
48.05	7.75	<del>4.86E-03</del>	<del>4.50E-03</del>	3.28E-02	<del>9.78E-03</del>	1.45E-02
48.05	7.61	<del>2.80E-03</del>	<del>3.80E-03</del>	3.32E-02	<del>2.61E-03</del>	<del>1.21E-02</del>

<sup>a</sup> Chamber background sample collected prior to start of test

<sup>b</sup> Samples collected at the same time period are duplicates

<sup>c</sup> Values with strike through are below the practical quantification limit of the method

<sup>d</sup> Values in italics are flagged because the concentration was above highest calibration level

<sup>e</sup> Measurement results for BEE and dipropylene glycol in this sample are inconsistent with other data, but source of error could not be determined.

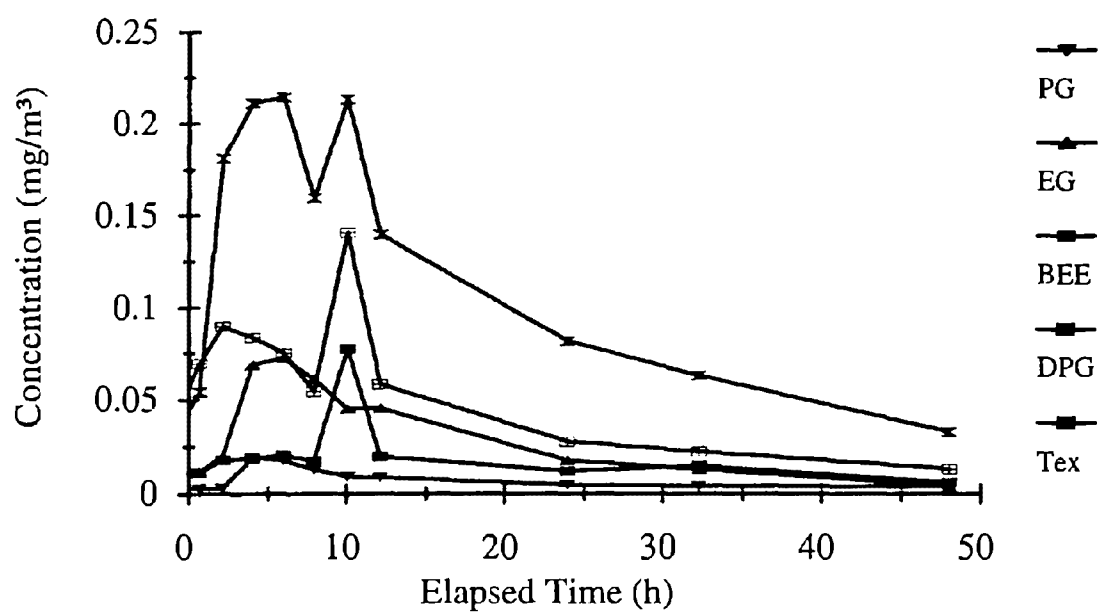


Figure 5-6. Concentrations of VOCs Measured in Emissions from Paint LVD Applied to Glass (Test LVT12)

Table 5-18. VOC Concentrations (mg/m<sup>3</sup>) in Emissions During the Small Chamber Test LVT13 with Paint LVE on Glass

Elapsed Time (hr)	Sampling Vol. (L)	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
-1.11 <sup>ab</sup>	7.73	<del>3.07E-03<sup>c</sup></del>	<del>1.63E-03</del>	<del>2.11E-03</del>	<del>3.83E-03</del>	<del>1.44E-03</del>
-1.11	7.85	<del>1.22E-03</del>	<del>2.00E-03</del>	<del>1.38E-03</del>	<del>1.76E-03</del>	<del>8.79E-04</del>
0.46	5.76	3.77E-02	3.81E-01	<del>3.66E-03</del>	<del>1.01E-02</del>	<del>1.18E-02</del>
2.76	7.65	1.87E-01	<del>4.40E-01<sup>d</sup></del>	<del>2.72E-03</del>	<del>1.12E-02</del>	2.09E-02
2.76	7.65	1.72E-01	4.22E-01	<del>2.01E-03</del>	2.30E-02	1.74E-02
3.99	7.91	<i>4.86E-01</i>	<i>8.64E-01</i>	<del>6.53E-03</del>	1.37E-02	2.56E-02
3.99	7.91	<i>5.36E-01</i>	<i>1.08E+00</i>	<del>6.56E-03</del>	<del>6.67E-03</del>	2.35E-02
6.11	7.89	2.10E-01	5.94E-01	1.62E-02	2.18E-02	3.24E-02
8.06 <sup>e</sup>	7.63	<del>3.67E-03</del>	<del>1.24E-02</del>	5.73E-02	<del>1.12E-02</del>	1.97E-02
10.06	7.59	1.45E-01	4.35E-01	1.29E-02	7.20E-02	2.01E-02
12.02	7.72	1.17E-01	3.72E-01	<del>6.80E-03</del>	7.55E-02	1.72E-02
12.02 <sup>e</sup>	NS <sup>e</sup>	NS <sup>e</sup>	NS <sup>e</sup>	NS <sup>e</sup>	NS <sup>e</sup>	NS <sup>e</sup>
17.90	6.46	8.05E-02	3.02E-01	<del>4.66E-03</del>	8.72E-02	1.56E-02
24.06	7.62	4.52E-02	2.04E-01	<del>3.62E-03</del>	7.99E-02	<del>1.14E-02</del>
24.06	7.62	4.31E-02	2.04E-01	<del>5.19E-03</del>	8.45E-02	1.29E-02
30.59	7.77	1.64E-02	9.30E-02	<del>1.85E-03</del>	4.58E-02	<del>5.84E-03</del>
48.06	8.28	<del>8.07E-03</del>	6.12E-02	<del>2.68E-03</del>	6.60E-02	<del>8.37E-03</del>
48.06	7.98	<del>7.51E-03</del>	5.36E-02	<del>2.56E-03</del>	5.77E-02	<del>7.22E-03</del>

<sup>a</sup> Chamber background sample collected prior to start of test

<sup>b</sup> Samples collected at the same time period are duplicates

<sup>c</sup> Values with strike through are below the practical quantification limit of the method

<sup>d</sup> Values in italics are flagged because the concentration was above highest calibration level

<sup>e</sup> No sample; sample lost during collection due to air flow problem

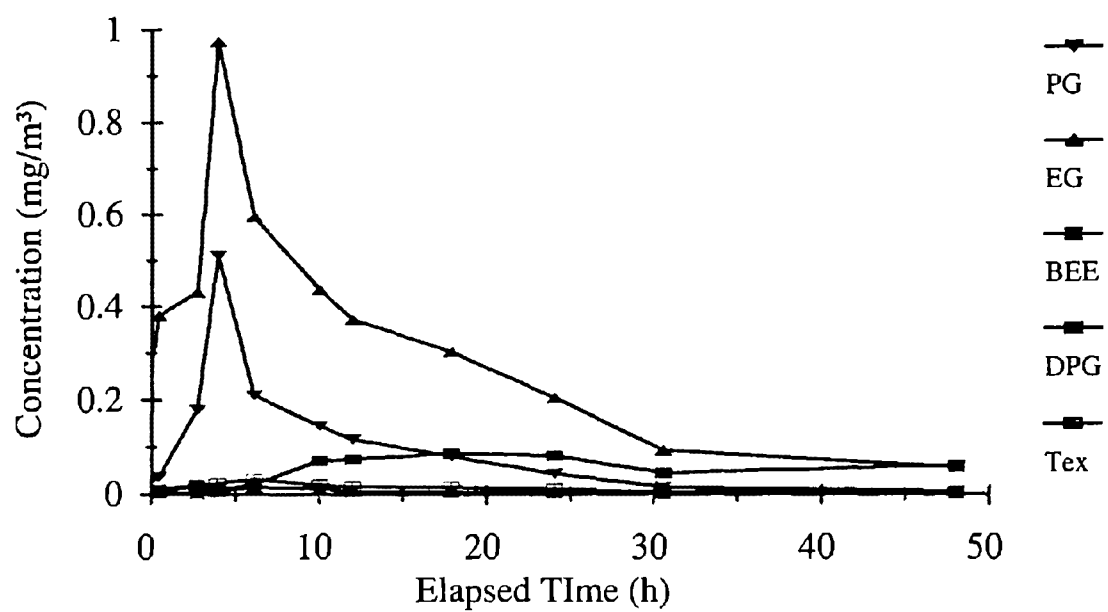


Figure 5-7. Concentrations of VOCs Measured in Emissions from Paint LVE Applied to Glass (Test LVT13)

Table 5-19. VOC Concentrations (mg/m<sup>3</sup>) in Emissions During the Small Chamber Test LVT15 with Paint LVG on Glass

Elapsed Time (hr)	Sampling Vol. (L)	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
-1.55 <sup>a,b</sup>	8.18	<del>2.75E-03<sup>c</sup></del>	<del>8.43E-04</del>	<del>1.37E-03</del>	<del>7.87E-03</del>	<del>2.69E-03</del>
-1.55	8.25	<del>2.58E-03</del>	<del>1.04E-03</del>	<del>8.73E-04</del>	<del>2.35E-03</del>	<del>1.58E-03</del>
0.53	2.85	<del>2.75E-02</del>	6.07E-02	2.12E-01	<del>3.13E-02</del>	<del>2.16E-02</del>
2.01	1.02	<del>2.08E-02</del>	<del>2.78E-02</del>	8.23E-01	<del>4.71E-02</del>	<del>4.84E-02</del>
2.01	1.01	<del>2.03E-02</del>	<del>2.78E-02</del>	9.88E-01	<del>2.77E-02</del>	<del>3.81E-02</del>
4.00	0.71	1.59E-01	4.31E-01	3.09E+00	2.66E-01	<del>7.98E-02</del>
4.00	0.70	1.50E-01	3.46E-01	3.13E+00	1.44E-01	<del>3.97E-02</del>
6.09	0.50	6.72E-01	4.29E+00	4.63E+00	1.01E+00	<del>4.32E-02</del>
8.21	0.50	5.37E-01	3.84E+00	4.54E+00	1.08E+00	<del>3.10E-02</del>
9.92	0.50	4.16E-01	3.26E+00	4.21E+00	1.10E+00	<del>3.55E-02</del>
12.07	0.50	4.15E-01	2.88E+00	4.17E+00	1.30E+00	<del>8.94E-02</del>
12.13	0.50	3.30E-01	2.81E+00	4.37E+00	1.19E+00	<del>3.05E-02</del>
21.98	1.10	1.03E-01	1.13E+00	2.20E+00	7.59E-01	<del>1.69E-02</del>
21.98	1.09	1.30E-01	1.40E+00	2.72E+00	9.46E-01	<del>2.57E-02</del>
24.08	0.50	<del>1.70E-01</del>	1.16E+00	2.64E+00	1.97E+00 <sup>d</sup>	9.52E-01
24.13	0.50	<del>1.56E-01</del>	1.34E+00	2.42E+00	9.67E-01	<del>1.56E-01</del>
32.28	0.50	<del>5.93E-02</del>	5.58E-01	1.97E+00	8.69E-01	<del>4.05E-02</del>
48.22	0.50	<del>4.38E-02</del>	2.13E-01	1.22E+00	6.68E-01	<del>2.83E-02</del>
48.22	0.50	<del>5.78E-02</del>	2.21E-01	1.17E+00	6.73E-01	<del>5.34E-02</del>

<sup>a</sup> Chamber background sample collected prior to start of test

<sup>b</sup> Samples collected at the same time period are duplicates

<sup>c</sup> Values with strike through are below the practical quantification limit of the method

<sup>d</sup> Measurement result for dipropylene glycol in this sample is inconsistent with other data, but source of error could not be determined.



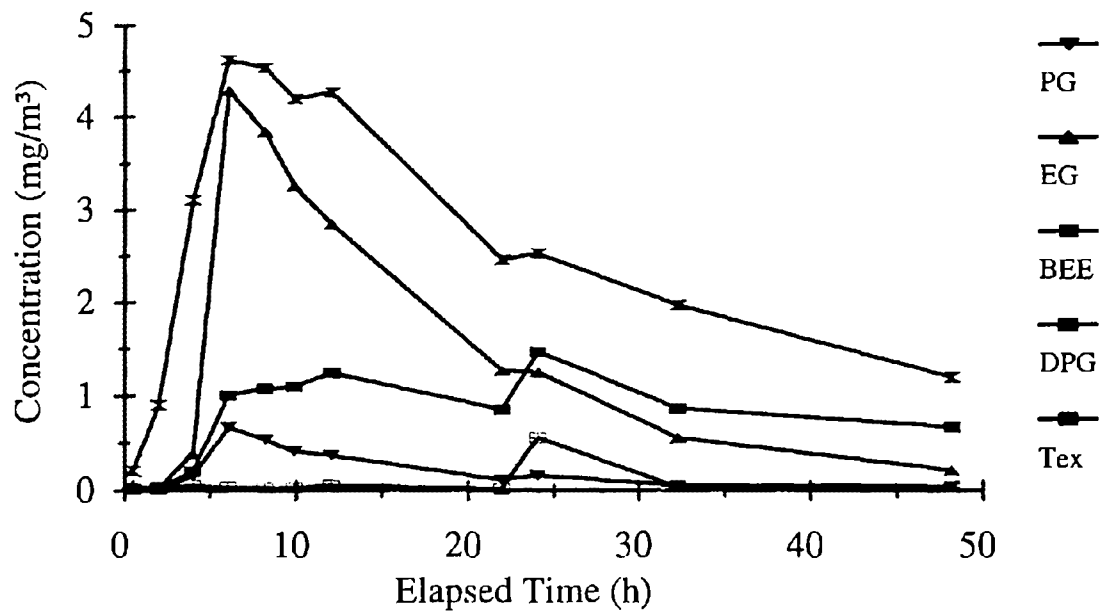


Figure 5-8. Concentrations of VOCs Measured in Emissions from Paint LVG Applied to Glass (Test LVT15)

As discussed in the introduction to Section 5.5, the first test to measure VOC concentrations was LVT11 with paint LVG. However, the mass of VOCs in the emissions exceeded the predicted amount. As a result, the mass of the VOCs on the Tenax tubes exceeded the highest calibration point for the GC. Therefore, the test was repeated as LVT15, which is reported here. The data for test LVT11 agree remarkably well with the results for LVT11 and are included in Appendix A.

#### 5.5.5 Estimated Mass of VOCs Emitted From the Paints

The measurements of VOC concentrations in Tenax samples collected during each small chamber test, in conjunction with the air flow rate through the chamber, can be used to estimate the mass of each VOC emitted during the test. The total mass (mg) of each VOC emitted during the 48 hours of the test was calculated as:

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

where  $A_c$  = the area under the time/concentration curve ( $\text{mg}/\text{m}^3\text{h}$ ) and  $Q$  = the chamber air flow rate ( $\text{m}^3\text{h}^{-1}$ ). The amount of mass of each VOC that was applied to the glass plate used as the test substrate was calculated based on the total mass of paint (g) applied to the plate, determined gravimetrically at the start of the test and the concentration (mg/g) of the VOC in the bulk paint, determined by GC analysis. The mass applied, estimated mass emitted and the calculated recovery of the applied mass are presented in Table 5-20. The % recovery could not be calculated for propylene glycol or Texanol in paint LVC because the concentrations of the VOCs in the bulk paint were below the method detection limit. The concentrations of ethylene glycol, BEE and dipropylene glycol were above the MDL, but below the PQL in paint LVC. The recoveries for these compounds ranged from 65 to 118% of the applied VOC mass.

For paint LVD, the % of the applied mass recovered in the emissions ranged from 8 to 79%. It is not clear why there was such a large variation in the calculated recoveries. However, the concentrations of the five target VOCs in the bulk paint LVD were below the method PQL. Twelve of the 16 emissions samples had propylene glycol concentrations below the PQL. The low concentrations of the compounds in the paint may affect the accuracy of the calculations because the analytical error is expected to be larger at the low concentrations.

For paint LVE, the recovery could be calculated only for dipropylene glycol because the concentrations of the other compounds were below the detection limit for the method used to measure the VOCs in the bulk paint. However, as indicated by the data in the table, although the VOCs could not be measured in the paint, they could be measured in the emissions.

Table 5-20. Percent of Applied VOC Mass Collected in the Emissions During 48-hour Small Chamber Tests

Paint		Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
LVC	Applied (mg)	NA <sup>a</sup>	0.1794 <sup>b</sup>	0.1571 <sup>b</sup>	0.0828 <sup>b</sup>	NA
	Emitted (mg)	0.0332	0.2111	0.1016	0.0827	0.0381
	% Emitted	NA	118	65	100	NA
LVD	Applied (mg)	0.0620 <sup>b</sup>	0.1001 <sup>b</sup>	0.2538 <sup>b</sup>	0.2698 <sup>b</sup>	0.0670 <sup>b</sup>
	Emitted (mg)	0.0090 <sup>c</sup>	0.0367	0.1354	0.0219	0.0530
	% Emitted	14	37	53	8	79
LVE	Applied (mg)	NA <sup>a</sup>	NA	NA	0.4018	NA
	Emitted (mg)	0.1042	0.3362	0.0065	0.0764	0.0173
	% Emitted	N/A	N/A	N/A	19	N/A
LVG	Applied (mg)	0.2961 <sup>b</sup>	1.9835	5.0421	2.7152	0.1722 <sup>b</sup>
	Emitted (mg)	0.2262	1.6756	3.2228	1.1354	0.0675
	% Emitted	76	84	64	42	39

<sup>a</sup> NA: mass in the paint was below detection limit

<sup>b</sup> Concentration in the paint was below PQL but above the MDL

<sup>c</sup> The concentration was below the PQL in 12 of 16 emissions samples during the test

Paint LVG had the highest levels of VOCs in the bulk paint. The concentrations of ethylene glycol, BEE and dipropylene glycol in the paint were measurable above the method PQL. During the chamber test with LVG, the concentrations in the Tenax samples were almost all above the PQL for these three compounds. The recoveries of the applied VOCs in the samples of emissions collected during the 2-day test ranged from 39 to 84%.

In previous tests with a conventional latex paint, Chang et al. (1997) reported greater than 89% recovery of the VOCs in paint applied to a stainless steel substrate during a 336-hour test period. In this study, the test duration was only 48 hours and the concentrations of the VOCs in the paints and the emissions were low compared those in the previous study with the conventional latex paint. Therefore, the estimates of VOC mass recovered in the emissions do not appear to be useful for evaluating the data.

#### 5.5.6 Comparison to Measurements of Emissions from a "Conventional" Latex Paint

In a previous study of the emissions of VOCs from latex paints (Guo et al., 1996), the target VOCs were measured in emissions from a conventional paint from manufacturer number 4. The ethylene glycol content in the conventional paint was 24 mg/g compared to 0.59 mg/g in the low-VOC from the same manufacturer that was tested in this study. The BEE concentration in the conventional paint was 4.98 mg/g compared to 1.51 mg/g in the low-VOC paint. The concentrations of the target VOCs in the emissions from the conventional latex paint are depicted in Figure 5-9. The data can be compared to Figure 5-8, which depicts the emissions for the low-VOC paint from the same manufacturer. In the test with the conventional latex paint, 4.1 g of paint was applied to a 16 cm X 16 cm stainless steel substrate, compared to the application of 3.35 g of the Low-VOC paint in the test described in this study. As can be seen in the figures, the ethylene glycol concentration in emissions from the low-VOC paint peaked at 3.8 mg/m<sup>3</sup> compared to the peak concentration of nearly 80 mg/m<sup>3</sup> for the conventional paint, which contained 40 times more ethylene glycol in the bulk paint. The concentrations of the other VOCs in the emissions from the low-VOC are similarly low when compared to the conventional paint and were consistent with the low-VOC content in the paint.

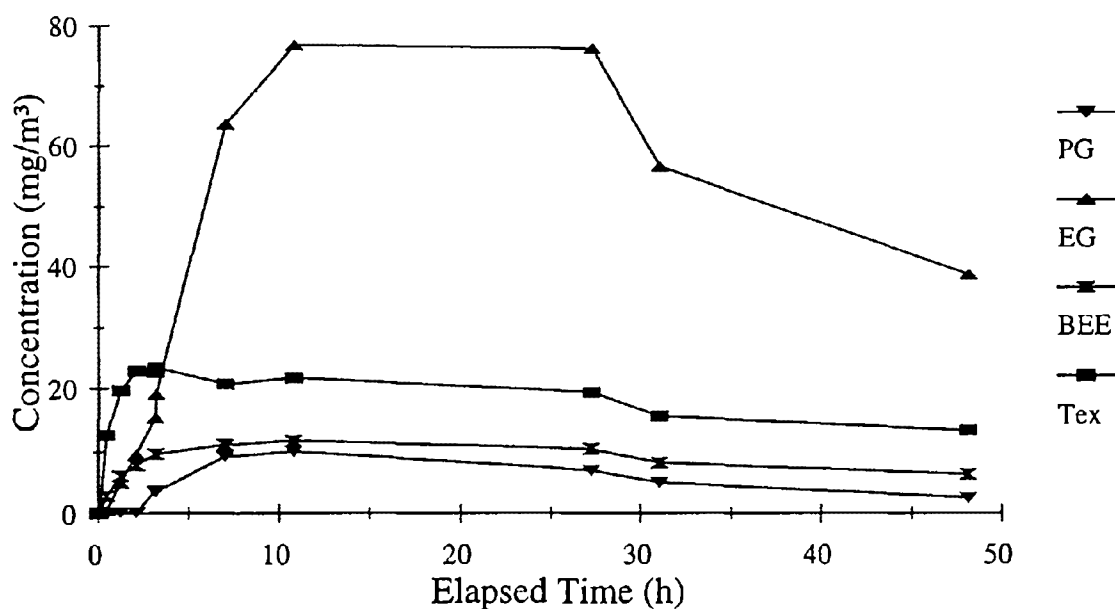


Figure 5-9. Concentrations of VOCs in Emissions Collected from a "Conventional" Paint Applied to Stainless Steel (Data from a Previous Study)

### 5.5.7 Identification of Non-Target VOCs in Emissions

As described above, five VOCs were targeted for quantification in samples of emissions collected on Tenax. These compounds were identified in the bulk paints. Chromatograms from Tenax samples collected during the small chamber emissions tests were reviewed to determine if there were other VOCs present in the samples. Few non-target VOCs were identified in the samples. The volume of sample collected on Tenax was generally less than 8 L to ensure that there was not breakthrough of the target VOCs. Some samples were less than 8 L so that the mass collected was within the calibration range of the instrument. If the objective were to identify more of the minor constituents in the emissions, a different protocol, involving collection of additional, larger volume samples, would be required.

All chromatograms were reviewed to determine if there were any unknown compounds present at high concentrations. Chromatograms for samples collected at 10 hours after paint application were reviewed in detail and the most abundant compounds were tentatively identified. There were few

compounds in the samples other than the target VOCs. The Hewlett Packard computerized mass spectra matching software was used with the NIST mass spectra library. Tentatively identified compounds are listed in Table 5-21. Only compounds with a fairly high level of confidence are reported. Quantitation was not performed for these compounds because the instrument was not calibrated for them. In general, based on area counts, the concentrations of the unknowns were similar, or lower, than the latex paint target compounds that were quantified. No additional analyses have been performed to verify the identification.

Table 5-21. Tentatively Identified VOCs in Tenax Samples Collected During Emissions Tests

Test - Paint	Compound ID	MS % Quality
LVT14 - LVC	Acetic acid	90
	2-[(2-ethylhexyl)oxy]-ethanol	91
LVT12 - LVD	Acetic acid	90
LVT13 - LVE	Limonene	91
	1-methyl-4-(1-methylethyl)-3-Cyclohexen-1-ol	93
	Linalyl propanoate	91
LVT11 - LVG	Tridecane	94
	Acetic acid	90
	2, 2-oxybis-ethanol	83

## 5.6 PERFORMANCE EVALUATION TEST RESULTS

As discussed in the previous sections, the low-VOC paints tested in this project had lower VOC content than conventional paints. With the exception of the paints that emitted formaldehyde, the VOC emissions were substantially lower from these paints than from conventional paints. If the low-VOC paints are to be considered a viable alternative to conventional paints their performance should be comparable to the conventional paints. If the paints performed poorly, reductions in VOC emissions would be offset if walls needed to be painted more frequently.

To evaluate the performance of the paints, ASTM test methods were identified that would provide an indication of the paints' performance. The methods that were selected were described previously in Table 4-4.

Results of the ASTM tests to evaluate performance are presented in Table 5-22 and summarized as follows. Tests were performed with paints LVH and LVI, conventional latex paints, for comparison to the four low-VOC paints. It should be noted that the formulation of paint LVA, for which performance tests were conducted, was reported by the manufacturer to be the same as paint LVC, for which VOC measurements were performed.

#### ASTM Method D523 - Specular Gloss

Method D523 measures the specular gloss of the paint. The higher the value the more light that is reflecting off the surface. Flat paints with good uniformity of appearance often have lower sheen. Paints with good cleanability are often paints with higher sheen. The two paints (conventional and low-VOC) from manufacturer number 4 had the lowest specular gloss. The paint LVA had the highest specular gloss. Paint LVA also had good scrubability, but its cleanability was lower than the paints from manufacturer number 4. There was no clear trend related to the differences between low-VOC and conventional paints. The low-VOC (LVG) and conventional (LVH) paints from manufacturer number 4 had nearly the same specular gloss measurement. But, the low-VOC paint from manufacturer number 2 had a lower specular gloss value than for the conventional paint.

#### ASTM Method D2805 - Hiding Power

Method D2805 measures hiding power or paint coverage. This instrumental method is used to give a contrast ratio for film thicknesses of either 1.5 or 3.0 mils. A contrast ratio of 0.95 to 1.0 indicates good hiding power. A ratio below 0.95 indicates poor hiding power. Based on the measurements, the hiding power was good for all of the paints except LVA at 1.5 mils wet film thickness. Paint LVG had the highest contrast ratio at both 1.5 and 3.0 mils and was better than the conventional paint made by the same manufacturer.

#### ASTM Method D2486 - Scrubbability

This method measures the scrubability of the paint. It is a common test used to evaluate paint performance. The manufacturer of paint LVA advertises its product as a 2000+ scrub paint. The paint did meet the manufacturer's claim, indicating a strong resistance to erosion of the surface by scrubbing. Paint LVG also reached the highest level of 2000+ cycles. The scrubability of paint LVE was poor, with only 49 cycles. LVD, the low-VOC paint from manufacturer number 2 had a higher scrubability rating than the conventional paint from the same manufacturer.

Table 5-22. Results of Measurements with ASTM Performance Tests

Paint (Manufacturer)	Test Method	LVA (1)	LVD (2)	LVI (2)	LVE (3)	LVG (4)	LVH (4)
Type of Paint (All latex flat)		No-VOC	Low-Odor	Conventional	Low-Odor	Low-Odor	Conventional
Specular Gloss (85° sheen)	523	9.4	2	5.2	4.7	1.5	1.6
Hiding Power-Contrast Ratio: 1.5 mils wet	2805	0.928	0.968	0.965	0.966	0.982	0.973
3.0 mils wet		0.961	0.987	0.979	0.982	0.998	0.987
Scrub Resistance (cycles)	2486	2000+	254	139	49	2000+	508
Cleanability (reflectance ratio)	3450	0.36	0.41	0.36	0.50	0.47	0.50
Leneta Anti-Sag (index)	4400	12.0	12.0	12.0	12.0	12.0	12.0
Set-to-touch (minutes)	1640	11	14	14	15.5	14	12
Yellowing Index	E313						
Initial		12.67	15.78	11.89	10.8	27.4	18.18
After Exposure		11.88	15.71	11.49	10.83	27.54	18.17
Difference		-0.79	-0.07	-0.40	0.03	0.14	-0.01



#### ASTM Method D3450 - Stain Removal (Cleanability)

Cleanability represents the ease with which soilants can be removed from the paint surface. The reflectance from the surface was measured prior to soiling the paint and again after cleaning with a non-abrasive cleaner. The higher the rating, the more stain that is removed. Paints LVH and LVE had the highest rating. The low-VOC paint (LVG) from manufacturer number 4 ranked only slightly lower than the conventional paint. Paint LVA had a low cleanability rating even though it had high specular gloss, as discussed above.

#### ASTM Method D4400 - Sag Resistance

Sag resistance was measured with a multi-notched applicator. A perfect score is 12, which was achieved with all six paints.

#### ASTM Method D1640 - Dry to Touch

This method measures drying time. The drying time ranged from 11 to 15.5 minutes, with the fastest drying time exhibited by paint LVA which had the lowest water content of the paints (Table 5-2). Paint LVH, a conventional paint had a drying time of 12 minutes, consistent with the fact its water content was also low (40.8%). The paint with the longest drying time, LVE, had the highest water content (Table 5-2).

#### ASTM Method E313 - Yellowness Index

The yellowness index was determined by exposing the paints to sunlight. Following an initial reading, the paint panels were inspected visually on a routine basis until a change was observed. A final reading was made and the difference calculated. A negative difference indicates a whitening or bleaching of the paint. A positive change, as occurred for paint LVG indicates yellowing. However, the differences for all the paints were relatively small and would not be considered significant based on the published precision of the method which is  $\pm 0.5$  units.

Based on the ASTM tests, paint LVG appeared to perform better than the other low-VOC paints. It also performed better than the conventional paint by the same manufacturer. Among the low-VOC paints, this was also the paint with the highest VOC content and the highest emissions of the target VOCs.

## 6.0 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance (QA) and quality control (QC) procedures implemented in this project are described in the following subsections.

### 6.1 DATA QUALITY INDICATOR GOALS

Data quality indicator goals for the laboratory are summarized in Table 6-1.

Table 6-1. Data Quality Indicator Goals for Key Measurement Parameters

Parameter	Method	Accuracy	Precision	Completeness (%) <sup>a</sup>
Temperature	RTD	± 1.0 °C	± 0.2°C	95
Relative Humidity	Thin Film Capacitance RH	± 5%	± 5% RH	95
Air Flow Rate	Soap Film Bubble Meter	± 5%	± 5%	95
Air Velocity	Anemometer	± 5% <sup>b</sup>	± 5% <sup>c</sup>	95
Paint Mass on Substrate	Gravimetric	± 0.01 g	± 5% <sup>c,d</sup>	95
VOC Concentrations	GC/FID/MS	75 - 125 %	± 25 % <sup>f</sup>	95
Aldehyde Concentrations	HPLC	80 - 120 %	± 20 % <sup>f</sup>	95

<sup>a</sup> Number of samples collected/number of samples planned

<sup>b</sup> Manufacturer's specification

<sup>c</sup> Percent Relative Standard Deviation (RSD)

<sup>d</sup> Repeatability of application to duplicate test substrates

<sup>e</sup> Calculated as percent recovery for spiked sorbent tubes

<sup>f</sup> Percent RSD for duplicates

## 6.2 SUMMARY OF DATA COMPLETENESS

Measurements of key parameters to document data quality during the study are summarized in the following sub-sections. The primary measurement parameters were concentrations of VOCs and aldehydes in the emissions collected during small chamber tests. A total of ten small chamber tests (LVT1 through LVT10) were performed to measure aldehyde emissions from the low-VOC paints. Five tests (LVT11 through LVT15) were performed to measure VOC emissions during tests with four low-VOC paints. Results from test LVT11 were not reported in this document because the VOC concentrations exceeded the calibration range of the instrument. The test was repeated and results were reported as test LVT15 for paint LVG.

Temperature, relative humidity and air flow rates into the chamber were recorded throughout each small chamber test. There were no data collection problems for the three parameters during any of the 15 tests. The data sets for temperature, relative humidity and air flow rates were 100% complete during the study.

Air velocity was not measured continuously during the tests. The air speed at 1 cm above the surface of a glass or gypsum board substrate was measured for each fan prior to placing it in service. There were no observed problems with any fans during the course of the study based on visual inspection at the start and end of each test.

Table 6-2 summarizes the number of air samples collected during the study on DNPH-silica gel or Tenax sorbents and the number of replicates, chamber background samples, field blanks and field controls.

Tests LVT1, LVT2, LVT3, LVT6 and LVT8 were scouting tests with the paint applied to glass. A minimum of four emissions samples were planned for each test. One field blank and one chamber background sample were planned for each test. There were no replicates or field controls planned for these tests. A total of six samples were planned for each test.

Test LVT4 was performed to confirm the presence of formaldehyde in the emissions from paint LVA. There were no field controls planned for the test.

Tests LVT5, LVT7, LVT9 and LVT10 were tests with paint applied to gypsum wallboard. The two-week long tests involved a minimum of 12 emissions samples, three replicates, a background sample, field blank and three spiked field controls for a total of 20 samples for each test.

For tests LVT11 through LVT15, a total of 21 samples were planned that included 11 test samples, five replicates, two chamber background samples, one field blank and two field controls per test.

Table 6-2. Number of Samples Collected During the Study

Test No.	Test Samples	Replicates	Chamber Background	Field Blanks	Field Controls	Total No. of Samples Collected/Planned
LVT1	5	0	2	1	0	8/6
LVT2	4	0	1	0	0	5/6
LVT3	6	0	1	1	0	8/6
LVT4	11	1	1	1	0	14/14
LVT5	16	4	1	1	3	25/20
LVT6	5	0	1	1	0	7/6
LVT7	12	4	1	1	3	21/20
LVT8	7	0	1	1	0	9/6
LVT9	13	3	2	1	3	22/20
LVT10	13	4	1	1	3	22/20
LVT11	11	5	2	1	2	NA*
LVT12	11	5	2	1	2	21/21
LVT13	11	4	2	1	2	20/21
LVT14	11	5	2	2	2	22/21
LVT15	11	6	2	2	2	23/21

\* Sample volumes were too large resulting in concentrations above the highest calibration point of the GC; data were not included in the data set for the study

### 6.3 DEFINITIONS

Data quality is evaluated based on instrument and method performance which is measured by analysis of quality control samples. The following are definitions of terms used in the evaluation of data quality and method performance:

- **IDL - Instrument Detection Limit** - for analyses by GC or HPLC methods, the IDL is the lowest amount of analyte mass (nanograms) that can be detected when a standard is analyzed.
- **MDL - Minimum Detection Limit** - the lowest concentration (mg/m<sup>3</sup>, µg/m<sup>3</sup>) that can be detected with the method. For sorbent sampling methods, the MDL is a function of the IDL and the volume of sample collected on the sorbent tube.
- **PQL - Practical Quantitation Limit** - the PQL is concentration measured based on the amount of mass (ng) in the lowest calibration standard. For a calibration ranging from 10 ng to 1000 ng, the PQL is based on 10 ng per sample. For a 1-liter sample and 10 ng, the PQL would be 10 ng/L (10 µg/m<sup>3</sup>).
- **BDL - Below Detection Limit** - the concentration in the sample is below the minimum detection limit.

- BQL - Below Quantitation Limit - the concentration in the sample is below the practical quantitation limit.
- ND - Not Detected
- DCC - Daily Calibration Check sample - sample, normally a mid-level calibration standard, that is analyzed each day prior to analyses of samples to verify that the instrument is performing properly. The percent recovery is calculated for the DCC and compared to criteria established for each compound in the calibration mixture.
- Field blanks - quality control samples used to determine background contamination on sampling media due to media preparation, handling, or storage.
- Replicates - quality control samples collected concurrently in duplicate or triplicate using the same method and for the same duration. Data are used to estimate the precision of the method.
- Field controls - quality control samples analyzed to estimate the accuracy of the method. Field controls are prepared by spiking the sample media with known concentrations of the target analytes. The percent recovery of the analytes is calculated.
- Chamber background samples - for small chamber emissions tests, air samples are collected from the chamber outlet to measure the background concentration of the target analytes. The measurement can be performed with the substrate in the chamber.

#### 6.4 ENVIRONMENTAL AND TEST PARAMETERS

The resistance temperature devices (RTDs) used to measure air temperatures in the small emissions chamber test facility are calibrated annually. Prior to each small chamber test, the RTD to be used in the test was collocated with a National Institute of Science and Technology (NIST) traceable mercury-in-glass thermometer. The RTD was accepted for use in the test if the reading at ambient air temperature (nominally 23 °C) was within  $\pm 1.0$  °C of the reading of the reference thermometer. The precision of the temperature control during the small chamber tests is indicated in Tables 5-4 and 5-15 which present the average  $\pm$  standard deviation of the temperature reading during the test. The standard deviation ranged from 0.03 to 0.38 °C. The criterion for precision of the temperature control to  $\pm 0.2$  °C was exceeded only in test LVT6.

The thin film capacitance RH probes were calibrated annually by use of saturated salt solutions. Calibrations were performed at 10 and 75% RH. Prior to each test, the probes were collocated with a reference probe that had been most recently calibrated. The precision of the RH control during the tests is indicated in Tables 5-4 and 5-15, which list the standard deviation of the RH readings for the tests. The standard deviation was less than  $\pm 5\%$  RH in 13 of the 15 tests. It exceeded the precision criterion for RH control of  $\pm 5\%$  RH in tests LVT1 and LVT13.

The air exchange rates were calculated based on the air flows measured with a soap film bubble meter at the start and end of each test. The measurement device is a primary reference method calibrated in the APPCD metrology laboratory.

The air velocity at 1 cm above the surface of the substrate was measured with a Bruel and Kjaer anemometer. Measurements were made prior to placing the mixing fans into service.

The data quality indicator goal for application of the paint to the substrate was accuracy of  $\pm 0.01$  g and precision of  $\pm 5\%$  for replicate applications. The accuracy of the mass application was verified by weighing the painted substrate on a calibrated balance with a resolution of 0.01 g. Tests have demonstrated that a precision of  $\pm 5\%$  can be achieved by an experienced applicator. During tests LVT1 through LVT10, the paint was applied at a rate that provided uniform coverage on the substrate based on visual observation. The rate of application varied due to the variation in the solids content of the paints. In tests LVT11 through LVT15, the goal was to apply 3.5 g of paint to the 256 cm<sup>2</sup> surface of the test substrate. The application rates, listed in Table 5-15, actually applied ranged from 67 to 96% of the target amount.

## 6.5 QUALITY CONTROL DATA FOR ALDEHYDE MEASUREMENTS

Quality control samples consisted of chamber background samples collected prior to each test, field blanks, spiked field controls and duplicates. Daily calibration check samples were run on each day of analysis.

### 6.5.1 Critical Limits

The HPLC was calibrated over a nominal range of 1.0 ng to 375 ng for each target aldehyde. The practical quantitation limit (PQL) of the instrument was defined as the lowest calibration level and was nominally 1.0 ng. For the sample dilution factor of 200 used in the DNPH-silica gel method for aldehyde measurements, the minimum amount of each aldehyde that needs to be collected on the DNPH coated silica cartridge is 200 ng. Therefore, for a 30 L volume sample, the nominal PQL would be 0.0067 mg/m<sup>3</sup>. To determine the PQL for each sample, the lowest calibration level and the sample volume are required. Sample volumes are included in the tables of this report and can be used with the lowest calibration level, nominally 1.0 ng, to calculate the PQL.

The minimum detection limit (MDL) was determined by analyzing seven DNPH cartridges spiked with a standard solution which would yield 1.5 ng of each target aldehyde on column. At three times the standard deviation, formaldehyde, acetaldehyde and propanal had an IDL of 0.1 ng and an MDL of

0.00007 mg/m<sup>3</sup> for a 30 L sample. For benzaldehyde, pentanal and hexanal, the IDL was 0.2 ng and the MDL was 0.00014 mg/m<sup>3</sup> for a 30 L sample.

#### 6.5.2 Chamber Background Measurements

Prior to each test, air samples of 12 to 53 L volume were collected on DNPH cartridges from the outlet of the small chamber to be used in the test. The substrate was in the chamber at the time. Therefore, background samples measured the VOC background due to contamination of the clean air supply, the chamber and air transfer lines and the substrate. Results of the measurements are presented in Table 6-3. Chamber background concentrations were low for all tests. Formaldehyde and acetaldehyde were detected in all chamber background samples, but were below the PQL for all but one sample that had formaldehyde at a level above the PQL. The other four target aldehydes were not measured above the MDL in any of the tests.

#### 6.5.3 Field Blanks

Field blanks consisted of DNPH coated silica gel cartridges that were not used for sample collection. The cartridges were handled and stored in the same manner as samples. Results are presented in Table 6-4.

#### 6.5.4 Results of Replicate Samples

During tests 4, 5, 7, 9 and 10, samples were collected in duplicate during each test to estimate the precision of the sampling and analysis methods. Duplicate samples were not collected in the range-finding tests (LVT1, 2, 3, 6 and 8). Results of the replicate samples collected on DNPH cartridges are presented in Table 6-5. The precision of the sampling and analysis method for formaldehyde was good with the % relative standard deviation (%RSD) being 5 or less for all but four of the 15 samples with concentrations above the PQL. Precision was also good for acetaldehyde.

#### 6.5.5 Results for Spiked Field Controls

Field controls consisted of DNPH coated silica gel cartridges spiked with standard stock solution. Controls were prepared in triplicate. One field control was analyzed within 48 hours of preparation. The other field controls were analyzed with the samples.

Table 6-3. Aldehyde Concentrations (mg/m<sup>3</sup>) in Chamber Background Air Samples

Description	Sample Vol. (L)	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
LVT1	52.8	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>
LVT2	12.7	<del>3.76E-03<sup>b</sup></del>	<del>6.25E-03</del>	BDL <sup>c</sup>	BDL	BDL	BDL
LVT3	22.4	<del>3.01E-03</del>	<del>3.66E-03</del>	BDL	BDL	BDL	BDL
LVT4	38.8	<del>2.37E-03</del>	<del>9.69E-04</del>	BDL	BDL	BDL	BDL
LVT5	23.8	<del>7.10E-03</del>	<del>2.36E-03</del>	BDL	BDL	BDL	BDL
LVT6	13.7	<del>5.05E-03</del>	<del>1.99E-03</del>	BDL	BDL	BDL	BDL
LVT7	39.7	<del>6.10E-03</del>	<del>2.70E-03</del>	BDL	BDL	BDL	BDL
LVT8	24.1	<del>2.95E-03</del>	<del>2.97E-03</del>	BDL	BDL	BDL	BDL
LVT9A	27.9	<del>3.62E-03</del>	<del>3.72E-03</del>	BDL	BDL	BDL	BDL
LVT9B	26.3	<del>6.81E-03</del>	<del>4.60E-03</del>	BDL	BDL	BDL	BDL
LVT10	13.8	<del>6.05E-03</del>	BDL	BDL	BDL	BDL	BDL
N		10	9	0	0	0	0
Minimum		2.00E-03	1.00E-03	BDL	BDL	BDL	BDL
Maximum		7.00E-03	6.00E-03	BDL	BDL	BDL	BDL
Mean		4.68E-03	3.25E-03	BDL	BDL	BDL	BDL
Std. Dev. <sup>d</sup>		1.75E-03	1.55E-03	BDL	BDL	BDL	BDL

<sup>a</sup> Results from test 1 were not reported in this document because the samples were overloaded and the concentrations generally exceeded the highest calibration level of the instrument

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the minimum detection limit

<sup>d</sup> Standard deviation



Table 6-4. Results for DNPH-Silica Gel Field Blank Measurements (ng per Sampling Cartridge)

Description	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
LVT1	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>
LVT2	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>
LVT3	<del>2.30E-01</del>	<del>1.89E-01<sup>b</sup></del>	BDL <sup>c</sup>	BDL	BDL	BDL
LVT4	<del>2.66E-01</del>	<del>2.29E-01</del>	BDL	BDL	BDL	BDL
LVT5	<del>2.47E-01</del>	<del>1.82E-01</del>	BDL	BDL	BDL	BDL
LVT6	<del>1.81E-01</del>	<del>1.55E-01</del>	BDL	BDL	BDL	BDL
LVT7	<del>2.56E-01</del>	<del>2.68E-01</del>	BDL	BDL	BDL	BDL
LVT8	<del>1.84E-01</del>	<del>3.64E-01</del>	BDL	BDL	BDL	BDL
LVT9	<del>2.10E-01</del>	<del>4.60E-01</del>	BDL	BDL	BDL	BDL
LVT10	<del>3.05E-01</del>	BDL	BDL	BDL	<del>0.39</del>	BDL
N	8	7	0	0	1	0
Minimum	<del>1.80E-01</del>	<del>1.50E-01</del>	BDL	BDL	BDL	BDL
Maximum	<del>3.00E-01</del>	<del>4.60E-01</del>	BDL	BDL	<del>0.39</del>	BDL
Mean	<del>2.35E-01</del>	<del>2.64E-01</del>	BDL	BDL	BDL	BDL
Std. Dev. <sup>d</sup>	<del>4.24E-02</del>	<del>1.11E-01</del>	BDL	BDL	BDL	BDL

<sup>a</sup> Blanks were not collected for these initial range-finding tests

<sup>b</sup> Values with strike through are below the practical quantitation limit (PQL), but above the method detection limit (MDL)

<sup>c</sup> BDL = Below the method detection limit

<sup>d</sup> Standard deviation

Table 6-5. Percent Relative Standard Deviation of Analyses of Duplicate DNPH Samples

Test	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
LVT4	13.5	7.7	-a-	-a-	-b-	-b-
LVT5	2.0	1.4	-a-	-b-	-b-	-b-
LVT5	8.2	2.5	-b-	-b-	-b-	-b-
LVT5	2.7	-a-	-b-	-b-	-b-	-b-
LVT5	-a-	-a-	-b-	-b-	-b-	-b-
LVT7	0.9	1.8	-b-	-a-	-b-	-b-
LVT7	3.0	5.8	-b-	-b-	-b-	-b-
LVT7	12.4	-a-	-b-	-b-	-b-	-b-
LVT7	1.1	-a-	-b-	-b-	-b-	-b-
LVT9	7.8	-a-	-b-	-b-	-b-	-b-
LVT9	2.3	-a-	-b-	-b-	-b-	-b-
LVT9	0.6	-a-	-b-	-b-	-a-	-b-
LVT10	3.4	-a-	-b-	-b-	-b-	-b-
LVT10	1.8	-a-	-b-	-b-	-b-	-b-
LVT10	1.6	-a-	-a-	-b-	-a-	-b-
LVT10	4.9	-a-	-b-	-b-	-a-	-b-
N	15	5	--	--	--	--
Minimum	0.6	1.4	--	--	--	--
Maximum	13.5	7.7	--	--	--	--
Mean	4.4	3.8	--	--	--	--
Median	2.7	2.5	--	--	--	--
Std. Dev. <sup>c</sup>	4.2	2.8	--	--	--	--

<sup>a</sup> One or both replicates below the PQL

<sup>b</sup> Both replicates below MDL

<sup>c</sup> Standard deviation

No field controls were prepared for range-finding tests. Controls were prepared only for tests LVT5, 7, 9 and 10, which were tests of two week duration. The controls were spiked with 200 µL standard stock solution (approximately 3000 ng of each analyte per cartridge). The percent recoveries for the controls are presented in Table 6-6. The mean recovery ranged from 99 to 108% for the six analytes and the criteria for recovery of 85 to 115% were met for all field controls.

#### **6.5.6 Daily Calibration Check Samples**

On each day of analysis, a daily calibration check (DCC) sample was analyzed to document the performance of the instrument. The recovery ranged from 90 to 110%, meeting the laboratory criteria of 85 to 115% recovery for acceptable instrument performance.

### **6.6 QUALITY CONTROL DATA FOR VOC MEASUREMENTS**

#### **6.6.1 Critical Limits**

The GC was calibrated over a nominal range of approximately 100 ng to 3000 ng for each target VOC. The practical quantitation limit (PQL) of the instrument was defined as the lowest calibration level and was nominally 100 ng. For a 0.5 L volume Tenax sample, the nominal PQL of the method would be 0.2 mg/m<sup>3</sup>. For a 8.0 L volume Tenax sample, the nominal PQL would be 0.013 mg/m<sup>3</sup>. To determine the PQL for each sample, the lowest calibration level and the sample volume are required. Sample volumes are included in the tables of this report and the lowest calibration level is nominally 100 ng. The MDL was not determined for VOC analyses. All values below the PQL are reported, but are flagged by use of a strike through in the tables.

#### **6.6.2 Chamber Background Measurements**

Prior to each test, air samples of approximately 8 L volume were collected on Tenax from the outlet of the small chamber to be used in the test. The glass substrate was in the chamber at the time. Therefore, background samples measured the VOC background due to contamination of the clean air supply, the chamber and air transfer lines and the glass substrate. Results of the measurements are presented in Table 6-7. Chamber background VOC concentrations were low for all tests.

Table 6-6. Percent Recovery for Spiked Field Controls

Test/Control ID	Formaldehyde	Acetaldehyde	Propanal	Benzaldehyde	Pentanal	Hexanal
<u>LVT5</u>						
ID6315	103	101	112	99	102	100
ID6316	102	105	110	102	103	101
ID6317	100	101	109	99	102	99
<u>LVT7</u>						
ID6431	98	98	100	95	97	95
ID6432	98	101	110	99	104	100
ID6443	103	102	112	100	103	100
<u>LVT9</u>						
ID6775	103	102	106	99	100	100
ID6776	103	105	110	100	99	100
ID6777	101	102	107	97	97	97
<u>LVT10</u>						
ID7231	101	99	106	98	99	98
ID7232	102	100	108	98	99	98
ID7233	103	104	110	100	101	100
N	12	12	12	12	12	12
Minimum	98	98	106	95	97	95
Maximum	103	105	112	102	104	101
Mean	101	102	108	99	100	99
Std. Dev. <sup>a</sup>	1.8	2.2	3.2	1.6	2.3	1.8

<sup>a</sup> Standard deviation

Table 6-7. VOC Concentrations (mg/m<sup>3</sup>) in Chamber Background Air Samples

Description	Volume (L)	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
LVT12 A	7.84	<del>4.17E-03</del>	<del>4.55E-03</del>	<del>2.55E-03</del>	<del>6.34E-03</del>	<del>2.87E-03</del>
LVT12 B	7.70	<del>2.34E-03</del>	<del>2.57E-03</del>	<del>5.99E-03</del>	<del>9.80E-03</del>	<del>2.53E-03</del>
LVT13 A	7.73	<del>3.07E-03</del>	<del>1.63E-03</del>	<del>2.11E-03</del>	<del>3.83E-03</del>	<del>1.44E-03</del>
LVT13 B	7.85	<del>1.22E-03</del>	<del>2.00E-03</del>	<del>1.38E-03</del>	<del>1.76E-03</del>	<del>8.79E-04</del>
LVT14 A	8.50	<del>3.26E-03</del>	<del>1.32E-03</del>	<del>7.67E-03</del>	<del>4.73E-03</del>	<del>1.93E-03</del>
LVT14 B	8.18	<del>2.76E-03</del>	<del>1.53E-03</del>	<del>8.32E-03</del>	<del>3.21E-03</del>	<del>1.53E-03</del>
LVT15 A	8.18	<del>2.75E-03</del>	<del>8.43E-04</del>	<del>1.37E-03</del>	<del>7.87E-03</del>	<del>2.69E-03</del>
LVT15 B	8.25	<del>2.58E-03</del>	<del>1.04E-03</del>	<del>8.73E-04</del>	<del>2.35E-03</del>	<del>1.58E-03</del>
N		8	8	8	8	8
Minimum		<del>1.22E-03</del>	<del>8.43E-04</del>	<del>8.73E-04</del>	<del>1.76E-03</del>	<del>8.79E-04</del>
Maximum		<del>4.17E-03</del>	<del>4.55E-03</del>	<del>8.32E-03</del>	<del>9.80E-03</del>	<del>2.87E-03</del>
Mean		<del>3.46E-04</del>	<del>2.42E-04</del>	<del>4.73E-04</del>	<del>6.23E-04</del>	<del>2.41E-04</del>
Std. Dev. <sup>b</sup>		<del>8.37E-04</del>	<del>1.19E-03</del>	<del>3.05E-03</del>	<del>2.81E-03</del>	<del>7.03E-04</del>

<sup>a</sup> Values with strike through are below the practical quantitation limit (PQL)<sup>b</sup> Standard deviation

### 6.6.3 Field Blanks

Field blanks consisted of Tenax tubes that were not used for sample collection. The tubes were handled and stored in the same manner as samples. Results are presented in Table 6-8. The concentration of the VOCs was below the PQL in all field blanks.

### 6.6.4 Results of Replicate Samples

Results of the analyses of duplicate samples collected on Tenax are presented in Table 6-9. The precision of the sampling and analysis method was good for all five target VOCs. The median percent relative standard deviation (%RSD) was less than 10% for all five VOCs. The data quality indicator goal (DQI) of  $\pm 25\%$  RSD was exceeded in only one sample for propylene glycol, ethylene glycol and Texanol. In two samples, the DQI goal was not met for dipropylene glycol.

### 6.6.5 Results for Spiked Field Controls

Field controls consisted of Tenax tubes spiked with a mid-level standard which contained approximately 1400 to 1700 ng per analyte. Controls were prepared in duplicate. One field control was analyzed within 48 hours of preparation. The other field control was analyzed with the rest of the samples. The percent recoveries for the controls are presented in Table 6-10. The criterion for recovery of 75 to 125% was met for all samples.

Table 6-8. Results of Field Blank Measurements (ng per tube)

Description	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) Ethanol	Dipropylene Glycol	Texanol
LVT12	<del>4.70E+00<sup>a</sup></del>	<del>1.40E+01</del>	<del>1.04E+01</del>	<del>3.27E+01</del>	<del>6.50E+00</del>
LVT13	<del>1.18E+01</del>	<del>1.25E+01</del>	<del>1.32E+01</del>	<del>6.45E+01</del>	<del>1.23E+01</del>
LVT14 F3A	<del>2.12E+01</del>	<del>1.23E+01</del>	<del>1.91E+01</del>	<del>5.47E+01</del>	<del>1.07E+01</del>
LVT14 FB3	<del>1.62E+01</del>	<del>1.53E+01</del>	<del>9.20E+00</del>	<del>1.79E+01</del>	<del>1.06E+01</del>
LVT15	<del>1.36E+01</del>	<del>1.66E+01</del>	<del>1.46E+01</del>	<del>4.10E+01</del>	<del>1.33E+01</del>
N	5	5	5	5	5
Minimum	<del>4.70E+00</del>	<del>1.23E+01</del>	<del>9.20E+00</del>	<del>1.79E+01</del>	<del>6.50E+00</del>
Maximum	<del>2.12E+01</del>	<del>1.66E+01</del>	<del>1.46E+01</del>	<del>6.45E+01</del>	<del>1.33E+01</del>
Mean	<del>1.35E+01</del>	<del>1.41E+01</del>	<del>1.33E+01</del>	<del>4.22E+01</del>	<del>1.07E+01</del>
Std. Dev. <sup>b</sup>	<del>6.06E+00</del>	<del>1.84E+00</del>	<del>3.89E+00</del>	<del>1.83E+01</del>	<del>2.60E+00</del>

<sup>a</sup> Values with strike through are below the practical quantitation limit (PQL)

<sup>b</sup> Standard deviation

Table 6-9. Percent Relative Standard Deviation Of Analyses of Duplicate Tenax Samples

Test	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
LVT12	-a-	27.4	0.0	1.9	5.6
LVT12	30.8	17.0	0.2	13.4	12.7
LVT12	-a-	7.5	-b-	-b-	2.0
LVT12	-a-	2.5	2.5	7.9	1.4
LVT12	-a-	-a-	0.9	-a-	-a-
LVT13	6.3	3.1	-a-	-a-	12.8
LVT13	-b-	-b-	-a-	-a-	5.9
LVT13	3.3	0.1	-a-	4.0	-a-
LVT13	-a-	9.4	-a-	9.5	-a-
LVT14	3.7	16.5	11.8	22.0	25.1
LVT14	0.6	22.7	0.4	8.4	1.5
LVT14	5.0	0.9	1.5	11.5	9.9
LVT14	23.6	8.5	0.5	17.0	4.4
LVT14	3.4	17.6	8.9	3.5	2.0
LVT15	-a-	-a-	12.9	-a-	-a-
LVT15	4.0	15.3	0.8	42.0	-a-
LVT15	16.1	1.6	3.3	6.7	-a-
LVT15	16.2	15.1	14.7	15.5	-a-
LVT15	-a-	10.6	6.0	48.4	-a-
LVT15	-a-	2.7	2.8	0.5	-a-
N	11	17	15	15	11
Minimum	0.6	0.1	0	0.5	1.4
Maximum	30.8	29.4	14.7	48.4	25.1
Mean	10.3	10.5	4.5	14.1	7.6
Median	5.0	9.4	2.5	9.5	5.6
Std. Dev. <sup>c</sup>	9.9	8.2	5.1	14.0	7.2

<sup>a</sup> One or both replicate below the PQL<sup>b</sup> One or both replicate above the highest calibration level<sup>c</sup> Standard deviation

Table 6-10. Percent Recovery for Spiked Tenax Field Controls

Test/Tube ID	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
<u>LVT12</u>					
FC8875	100	115	104	122	94
FC8876	104	114	103	104	103
<u>LVT13</u>					
FC8945	90	98	92	96	92
FC8946	88	100	88	91	85
<u>LVT14</u>					
FC8975	99	106	98	99	98
FC8976	103	114	104	111	103
<u>LVT15</u>					
FC8984	99	110	99	114	99
FC8982	97	107	102	102	97

#### 6.6.6 Daily Calibration Check Samples

On each day of analysis, a daily calibration check (DCC) sample was analyzed to document the performance of the instrument. All DCC samples met the criterion of 75 to 125% recovery.

#### 6.7 QUALITY CONTROL SAMPLES FOR ANALYSES OF VOCs IN PAINT

The bulk paint products were extracted with solvent and the extracts were analyzed by GC. Three paints, LVC, LVD and LVG were analyzed on the HP5890 system immediately prior to the small chamber tests. The other paints were analyzed on the Varian GC/MS at the start of the test program.

##### 6.7.1 Solvent Blanks

For the analyses of LVC, LVD and LVG, two solvent (acetone) blanks were analyzed. The results are depicted in Table 6-11. The concentrations of the target compounds were below the PQL in both blanks. Solvent blanks were not reported for the earlier analyses.



Table 6-11. Results for Analyses of Solvent Blanks (ng/μL)

Compound	Sample 1	Sample 2
Propylene glycol	<del>3.25*</del>	<del>5.48</del>
Ethylene glycol	<del>4.52</del>	<del>4.63</del>
BEE	<del>3.25</del>	<del>2.40</del>
Dipropylene glycol	<del>2.32</del>	<del>4.92</del>
Texanol	<del>2.15</del>	<del>1.03</del>

\* Values with strike through are below the PQL of the method

#### 6.7.2 Results of Analyses of Duplicate Paint Extracts

Duplicate aliquots of bulk paint were extracted and analyzed. The percent relative standard deviations for analyses of duplicate aliquots are presented in Table 6-12. The precision could not be calculated for most compounds because the concentrations were below the PQL of the method. For the samples for which the % RSD could be calculated, the precision was acceptable for all compounds, meeting the criterion for precision of  $\pm 25\%$ .

#### 6.7.3 Controls

Controls were not routinely analyzed for the paint extract samples. During the initial evaluation of the extraction and analysis method for the bulk paints, octanol was added as an internal standard to estimate extraction efficiency and recovery. Octanol was added to paints LVD, LVF and LVG prior to the extraction. Analysis was performed with the Varian GC/MS. The recoveries were 104, 103 and 103%, respectively.

Table 6-12. The Percent Relative Standard Deviation for Analyses of Duplicate Paint Extracts

Paint	Ethylene Glycol	Propylene Glycol	Dipropylene Glycol	2-(2-Butoxy-ethoxy)ethanol	Texanol
LVA	NA <sup>a</sup>	0.5	NA	NA	NA
LVB	NA	NA	NA	NA	NA
LVC	NA	NA	NA	NA	NA
LVD	NA	NA	NA	NA	NA
LVE	NA	NA	6.0	NA	NA
LVF	NA	1.4	4.9	NA	12.6
LVG	2.9	NA	1.8	1.7	NA

<sup>a</sup> NA: Could not be calculated because one or both of the duplicates was below the PQL

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## APPENDIX A

### RESULTS FOR TEST LVT11 WITH PAINT LVG

(Data are not included in the data base because the mass in the samples exceeded the highest calibration point in most cases.)

VOC Concentrations (mg/m<sup>3</sup>) in Emissions During the Small Chamber Test  
LVT11 with Paint LVG on Glass

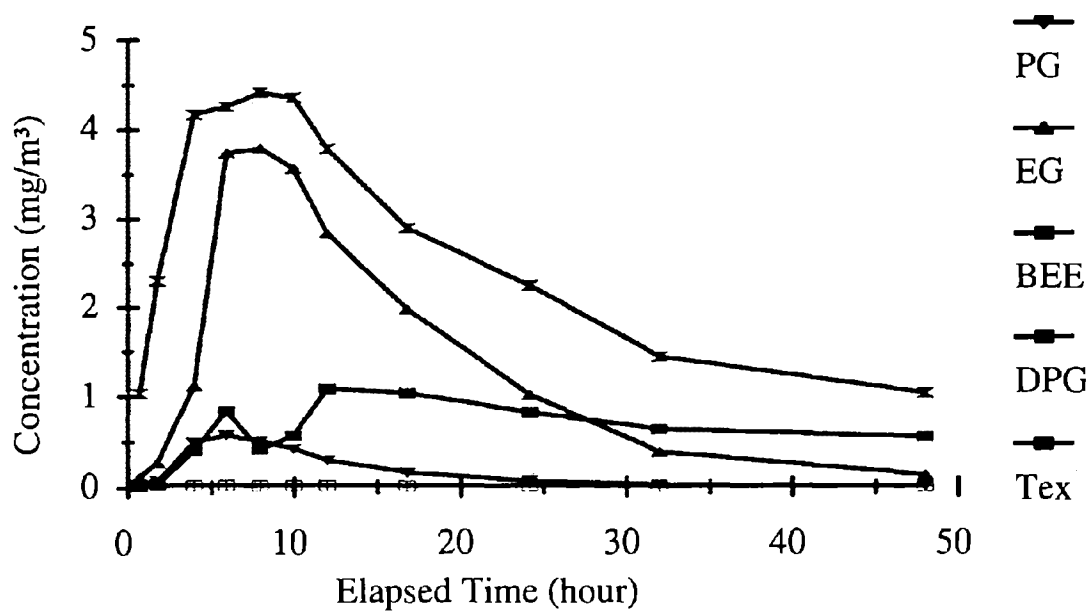
Elapsed Time (hr)	Sampling Vol. (L)	Propylene Glycol	Ethylene Glycol	2-(2-Butoxyethoxy) ethanol	Dipropylene Glycol	Texanol
-2.15 <sup>a,b</sup>	7.99	<del>2.41E-03<sup>c</sup></del>	<del>1.21E-03</del>	<del>8.01E-04</del>	<del>1.29E-03</del>	<del>1.83E-03</del>
-2.15	7.63	<del>2.37E-03</del>	<del>4.78E-03</del>	<del>1.04E-02</del>	<del>1.02E-02</del>	<del>2.19E-03</del>
0.68	7.99	4.22E-02	1.19E-01	<i>1.03E+00<sup>d</sup></i>	1.89E-02	2.27E-02
1.78	7.99	7.88E-02	2.84E-01	<i>2.38E+00</i>	4.81E-02	4.22E-02
1.78	7.63	7.72E-02	2.77E-01	<i>2.22E+00</i>	4.48E-02	2.72E-02
3.98	7.77	<i>4.98E-01</i>	<i>1.15E+00</i>	<i>4.11E+00</i>	<i>3.96E-01</i>	2.80E-02
3.98	7.64	<i>5.01E-01</i>	<i>1.09E+00</i>	<i>4.24E+00</i>	<i>4.13E-01</i>	2.73E-02
5.95	7.76	<i>5.74E-01</i>	<i>3.74E+00</i>	<i>4.26E+00</i>	<i>8.38E-01</i>	2.52E-02
7.96	7.63	<i>5.12E-01</i>	<i>3.80E+00</i>	<i>4.41E+00</i>	<i>4.27E-01</i>	2.22E-02
9.98	7.62	<i>4.24E-01</i>	<i>3.57E+00</i>	<i>4.35E+00</i>	<i>5.65E-01</i>	2.40E-02
11.99	7.78	2.96E-01	<i>2.90E+00</i>	<i>2.22E+00</i>	3.55E-02	<del>1.02E-02</del>
11.99	7.84	3.00E-01	<i>2.84E+00</i>	<i>3.79E+00</i>	<i>1.08E+00</i>	2.28E-02
16.83	6.83	1.60E-01	<i>1.97E+00</i>	<i>2.89E+00</i>	<i>1.03E+00</i>	1.87E-02
24.21	5.93	6.83E-02	<i>1.02E+00</i>	<i>2.26E+00</i>	<i>8.18E-01</i>	1.76E-02
24.21	5.84	6.67E-02	<i>1.01E+00</i>	<i>2.24E+00</i>	<i>8.17E-01</i>	<del>1.37E-02</del>
31.99	7.46	2.33E-02	3.88E-01	<i>1.44E+00</i>	<i>6.38E-01</i>	<del>1.16E-02</del>
48.02	7.62	1.23E-02	1.36E-01	<i>1.02E+00</i>	<i>5.47E-01</i>	<del>1.05E-02</del>
48.02	7.62	1.31E-02	1.31E-01	<i>1.04E+00</i>	<i>5.56E-01</i>	<del>1.15E-02</del>

<sup>a</sup> Chamber background sample collected prior to start of test

<sup>b</sup> Samples collected at the same time period are duplicates

<sup>c</sup> Values with strike through are below the practical quantification limit of the method

<sup>d</sup> Values in italics are flagged because the concentration was above highest calibration level



VOC emissions From Paint LVG During Test LVT11

NRMRL-RTP-156		TECHNICAL REPORT DATA (Please read Instructions on the reverse before comp)	
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7. AUTHOR(S) Roy Fortmann, Huei-Chen Lao, Angelita Ng, and Nancy Roache		6. PERFORMING ORGANIZATION CODE	
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16. ABSTRACT The report gives results of laboratory tests to evaluate commercially available latex paints advertised as "low-odor," "low-VOC (volatile organic compound)," or "no-VOC." Measurements were performed to quantify the total content of VOCs in the paints and to identify the predominant VOCs and aldehydes in the emissions following application to test substrates. The performance of the paints was evaluated and compared to that of commonly used conventional latex paints by American Society for Testing and Materials (ASTM) standard methods that measured parameters such as scrubability, cleanability, and hiding power. The report describes the paints that were tested, the test methods, and the experimental data. Results are presented that can be used to evaluate the low-odor/low-VOC paints as alternatives to conventional latex wall paints that contain and emit higher concentrations of VOCs.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Emission Paints Latex Organic Compounds Volatility Aldehydes		Pollution Prevention Stationary Sources	13B 14G 11C, 13C 11J 07C 20M
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