

Substrate Effects on VOC Emissions from a Latex Paint

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Abstract The effects of two substrates – a stainless steel plate and a gypsum board – on the volatile organic compound (VOC) emissions from a latex paint were evaluated by environmental chamber tests. It was found that the amount of VOCs emitted from the painted stainless steel was 2 to 10 times more than that from the painted gypsum board during the 2-week test period. The dominant chemical species emitted were also different between the two substrates. Data analysis indicated that most VOC emissions from the painted stainless steel occurred in the first 100 h via a fast, evaporation-like process. On the other hand, the majority of the gypsum board VOCs were emitted in a later stage via a slow, diffusion-controlled process. There were measurable emissions of VOCs 11 months after paint application on the gypsum board. It is suggested that, instead of the routinely used substrates such as stainless steel plates, real substrates such as wood or gypsum board should be used for the evaluation of emissions in indoor environments.

Key words Latex paint; Substrate; VOC; Emissions; Chamber; Model.

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Introduction

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

Environmental test chambers have been used to measure the VOC emission profiles under simulated indoor conditions that can be used as a basis for exposure risk assessment (ASTM, 1990). The tests involve applying the selected latex paint to a substrate and monitoring the chamber VOC concentration changes resulting from emissions of the painted substrate as a function of time. The test substrates used by most previous emission tests include stainless steel (Clausen et al., 1991; Clausen, 1993) and glass (Sheldon and Nangle, 1994). Other substrates such as aluminum pans (Stromberg and Wind, 1968; Hansen, 1974) and glass plates (Rosen and Andersson, 1990; Sullivan, 1975) were also used to study the solvent evaporation and drying mechanisms of latex paints. Those substrates have the advantage of being non-porous, non-absorbent, and easy to handle. However, latex paint is seldom applied to these substrates in real indoor environments. The surfaces most commonly painted with latex paint in the U.S. are walls and ceilings made of gypsum board. The gypsum board has a porous surface and absorbs liquid; these properties can alter the behavior of applied latex paint and change the VOC emission patterns.

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

Experimental Design and Methods

Experiments were designed to generate VOC concentration data from newly applied latex paint as it dried

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for several hundred hours under controlled experimental conditions. Tests were conducted in the EPA's small chamber source characterization facilities consisting of electropolished stainless steel chambers (Tichenor et al., 1990). The facilities allowed close control and monitoring of temperature, relative humidity, and airflow rate in the chambers. Small fans were used in the chambers to provide a velocity near (1 cm above) the test surface of 5–10 cm/s which is typical of indoor environments. The standard testing conditions were:

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

The latex paint used in this study was selected after consulting with local paint suppliers on the popularity of medium-priced paints. Sufficient paint from the same lot was purchased to conduct the small chamber tests. The purchased paint was mixed in cans and then split into 150 ml amber vials. Each vial was used for only one test.

The paint was analyzed for water content, VOCs, and density by ASTM Standard Test Methods (ASTM, 1989) and other related methods. Because the ASTM methods did not give information on the individual VOCs, these compounds were analyzed by extracting

a paint sample in acetone and analyzing the extract by gas chromatography (GC) with mass spectrometry (MS) and flame ionization detectors (FIDs). These analyses allowed the individual compounds to be identified by MS and quantified by FIDs. Paint samples were periodically analyzed by GC to assess the stability of the target compound concentrations.

The substrates evaluated were newly purchased bare stainless steel and gypsum board. The gypsum board was paper-coated with a total thickness of 1.27 cm (0.5 in) commonly used for walls and ceilings in residential and commercial buildings. The edges of the gypsum board samples were sealed with sodium silicate to minimize any adsorption of the VOCs. The latex paint was applied to the substrate specimen by a roller. It was estimated that 4.2 and 3.6 g of the paint was applied to the stainless steel and the gypsum board, respectively. The mass applied was determined using a protocol involving weighing of the substrate, the paint, and the roller before and after the application. The painted samples were placed in the chamber shortly (within 5 minutes) after the paint was applied. The test start (t=0) was established when the door to the chamber was closed. The chamber was flushed with clean air (<5 µg/m³ TVOC) before each test. A typical test lasted for about 2 weeks with the clean airflow through the chamber continuing at a controlled rate. The test duration was prolonged to more than 11 months for a long-term test.

VOCs in the chamber outlet were collected on Tenax sorbent tubes and analyzed by GC/FID. The desorp-

Table 1 Determination of Volatile Organic Compounds in the latex paint by ASTM methods (ASTM, 1989)

	Sample ID			Mean
	1	2	3	
Non-volatiles (%)	57.23%	57.16%	57.14%	57.20%
Total volatiles (Incl. water) (%)	42.77%	42.84%	42.86%	42.8%
Water content ¹	39.91%	40.31%	39.93%	40.1%
Density (g/ml)	1.41	1.42	1.43	1.42
TVOC content (mg/g)	28.6	25.3	29.3	28.0

¹ ASTM method D4017 (Karl Fischer)

Table 2 Total and individual VOCs determined by GC analysis (mg/g)

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

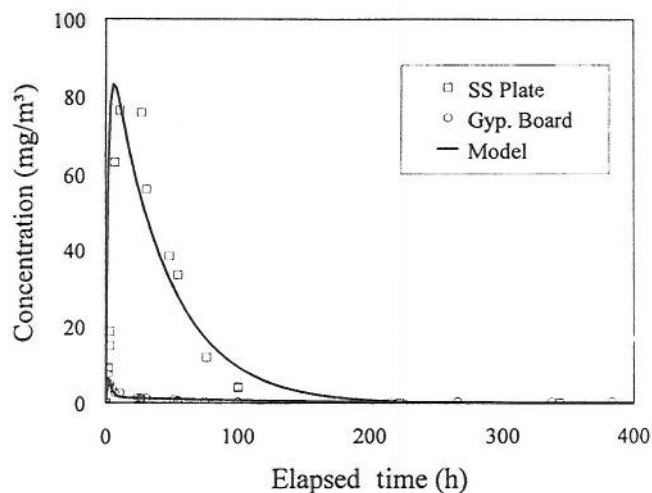


Fig. 1 Effect of substrate on ethylene glycol emissions

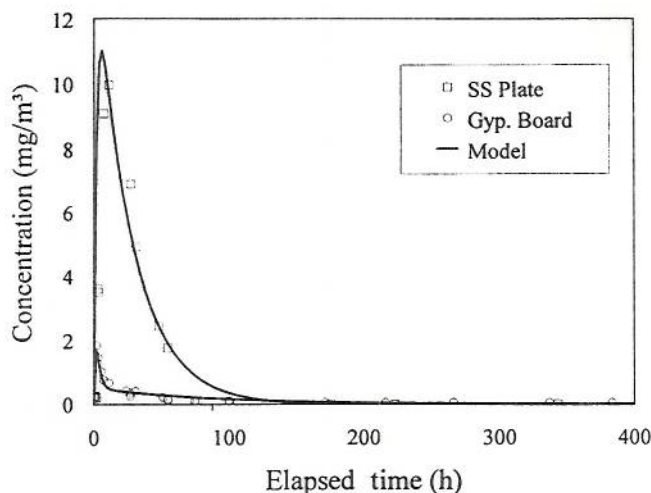


Fig. 2 Effect of substrate on propylene glycol emissions

tion unit was a combination of an Envirochem Multi-sorbent Desorber and Unacon sample concentrator. The analytical column was a J&W 30 m×0.53 mm (Megabore) DB-Wax operated at 40°C for 5 minutes and ramped at 5°C per minute to 240°C. The lower quantification limits for the target compounds were from 26 to 37 ng on GC column, which is equivalent to a chamber concentration range of 0.0026 to 0.0037 mg/m³ for 10-liter samples. Sixteen percent of the VOC samples collected were duplicates. The average relative standard deviation between duplicates was 5% to 17% for individual compounds and 9% for TVOC.

Results and Discussion

Paint Composition

Table 1 shows the paint composition obtained by ASTM methods (ASTM, 1989). Table 2 shows five major VOCs (propylene glycol, ethylene glycol, 2-(2-butoxyethoxy)ethanol, Texanol, and diethylene glycol) detected by GC analysis. The TVOC content in the bottom of each column in Table 2 is the sum of the five VOC contents in the same column. Comparison between Tables 1 and 2 indicates that the TVOC contents determined by the ASTM methods are lower than those by GC analysis. Since the ASTM TVOC was determined by the relatively small difference between total volatiles and water content, it is suspected that the results from the ASTM analysis are biased for the latex paint. Besides, the ASTM gravimetric method determining total volatiles (including water) involves heating the diluted sample in an oven at 110±5°C for 60 min. However, the boiling points (ranging from 187°C for propylene glycol to 244°C for Texanol) for

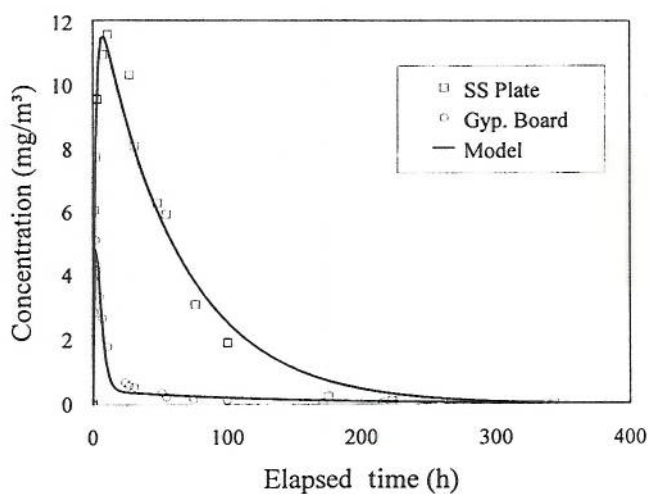


Fig. 3 Effect of substrate on 2-(2-butoxyethoxy)ethanol emissions

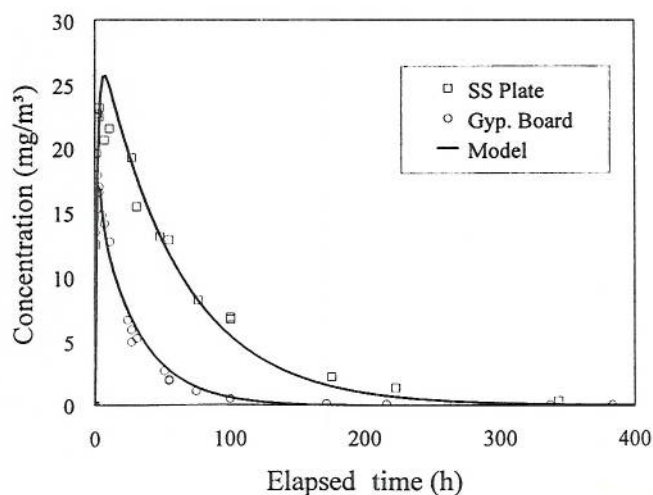


Fig. 4 Effect of substrate on Texanol emissions

Table 3 Comparison of peak concentrations measured in the environmental chambers (in mg/m³)

Compound	Stainless steel plate	Gypsum board
E. glycol	76.8	7.88
P. glycol	10.0	1.88
BEE	11.6	5.14
Texanol	23.3	18.0
TVOC	122	32.9

Table 4 Weight percentage of VOC in the latex paint emitted in the first 336-hour testing period

Compound	Stainless steel plate	Gypsum board
E. glycol	100%	9%
P. glycol	89%	17%
BEE	93%	14%
Texanol	89%	29%
TVOC	97%	20%

the VOCs in the paint are much higher than the oven temperature. It is suspected that the evaporation in the oven was incomplete at the specified temperature. Furthermore, at temperatures over 100°C, the paint polymerization is accelerated and may form a film over the residue which could significantly decrease evaporation. It is believed that the GC VOC data are more reliable than the ASTM values and will be used for mass balance calculations.

Substrate Effects on VOC Emissions

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

The differences are also reflected by the amount of each compound emitted. The amount of each VOC emitted from the latex paint in the 2-week test period

(W) was estimated by integrating the concentration curve (Colombo and De Bortoli, 1992; Guo et al., 1996):

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

where

Q=air exchange flow rate (m³/h)

C=chamber concentration of a given compound (mg/m³)

t=time (h)

n=total number of data points

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

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

where

W₀=The amount of VOC in the latex paint applied (mg).

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

Substrate Effects on Composition of VOC Emissions

When the same paint was applied to the two substrates, the compositions of VOC emissions were dra-

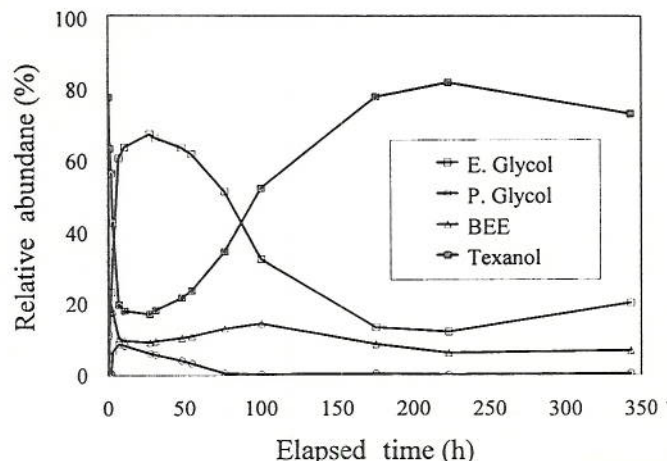


Fig. 5 VOC composition in chamber air with stainless steel substrate (relative abundance= weight percentage in TVOC)

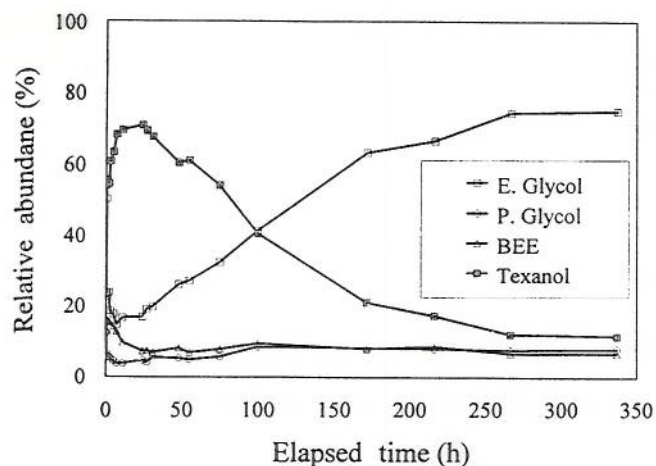


Fig. 6 VOC composition in chamber air with gypsum board substrate (relative abundance = weight percentage in TVOC)

matically different. As shown in Figure 5, when stainless steel was the substrate, ethylene glycol dominated the VOC emissions for the first 100 h and Texanol was the dominant VOC thereafter. On the other hand, when the gypsum board was the substrate, the trend was reversed. Texanol became the dominant VOC emitted for the first 100 h and ethylene glycol dominated the VOC emissions afterwards (Figure 6).

Emission Models

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

$$R(t) = R_1 + R_2 = R_{10}e^{-k_1t} + R_{20}e^{-k_2t} \quad (3)$$

where

$R(t)$ = Emission factor of a VOC ($\text{mg}/\text{m}^2/\text{h}$)

R_1 = Phase 1 emission factor ($\text{mg}/\text{m}^2/\text{h}$)

R_2 = Phase 2 emission factor ($\text{mg}/\text{m}^2/\text{h}$)

R_{10} = Phase 1 initial emission factor ($\text{mg}/\text{m}^2/\text{h}$)

k_1 = Phase 1 emission rate decay constant (h^{-1})

R_{20} = Phase 2 initial emission factor ($\text{mg}/\text{m}^2/\text{h}$)

k_2 = Phase 2 emission rate decay constant (h^{-1})

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

$$C = L \left[\frac{R_{10}(e^{-k_1t} - e^{-Nt})}{N - k_1} + \frac{R_{20}(e^{-k_2t} - e^{-Nt})}{N - k_2} \right] \quad (4)$$

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

Emission Mechanisms

Chang and Guo (1992) indicated that the double exponential model can represent a two-phase emission process. In this previous work, wood stain was applied to hardwood. The phase 1 emissions, R_1 , correspond to the period shortly after the stain was applied, while it was still relatively wet. During this phase, it appeared that VOC emissions were related to evaporation processes, characterized by relatively fast emissions. These fast emissions caused a rapid depletion of organic compounds on the surface of the wood, resulting in a rapid rise and decline of the chamber concentrations. A similar phenomenon was observed in the latex paint data for the first 50 to 100 h, as shown in Figures 1–4.

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

According to the model, R_{10}/k_1 and R_{20}/k_2 represent the total quantities of organic species emitted in phases 1 and 2, respectively. The values of those two parameters estimated from the chamber data are also listed in Table 5. It is seen that for gypsum board, the

Table 5 Summary of parameters of the double exponential model for VOC emissions from painted gypsum board

Compound	R_{10} ($\text{mg}/\text{m}^2/\text{h}$)	k_1 (h^{-1})	R_{10}/k_1 (mg/m^2)	R_{20} ($\text{mg}/\text{m}^2/\text{h}$)	k_2 (h^{-1})	R_{20}/k_2 (mg/m^2)
E. glycol	18.5	0.696	26.6	1.96	0.00694	282
P. glycol	4.78	0.724	6.60	0.561	0.0115	48.8
BEE	10.8	0.331	32.6	0.475	0.00767	61.9
Texanol	29.7	0.795	37.4	15.9	0.0317	502

Table 6 Summary of parameters of the double exponential model for VOC emissions from painted stainless steel ($R_{20}=0$)

Compound	R_{10} (mg/m ² /h)	k_1 (h ⁻¹)	R_{10}/k_1 (mg/m ²)
E. glycol	100	0.0235	4255
P. glycol	14.0	0.0368	380
BEE	13.4	0.0166	807
Texanol	30.0	0.0169	1775

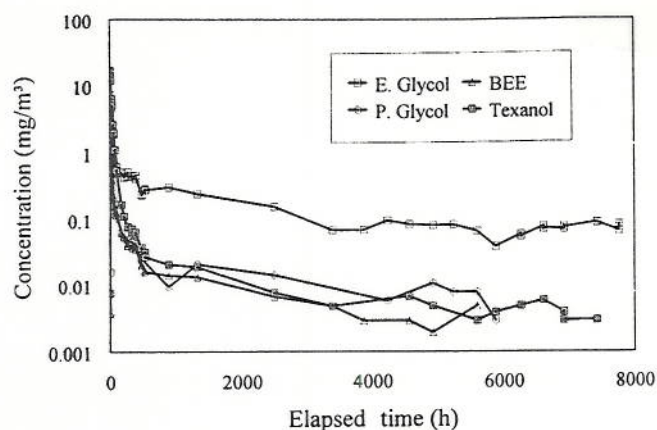
VOCs emitted in phase 2 far exceeded those in phase 1. It is likely that the majority of the latex paint VOCs penetrated into the relatively porous gypsum board and became relatively dry shortly after application. Only a small fraction of the paint VOCs stayed wet on the surface of the gypsum board, resulting in the relatively short phase 1 emissions. The rest of the VOCs applied were probably imbedded in the gypsum board and had to diffuse through the substrate to be emitted as the phase 2 emissions.

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

Long-Term Emission Data

Figure 7 shows the temporal history of the composition of the VOC emissions from a painted gypsum board over an 11-month period. As mentioned in the section "Substrate Effects on Composition of VOC Emissions", Texanol had the highest initial emission rate, but ethylene glycol exceeded Texanol after about 100 h and continued to be the dominant VOC emitted over the long term. Even after 11 months, an ethylene glycol concentration of 0.1 mg/m³ was still being measured in the chamber air. This approximates a steady-state emission rate of about 0.1 mg/m²/h. The levels of other VOCs were near the quantification limit of the sampling and analytical methods used. Assuming a constant emission rate of 0.1 mg/m²/h, after 1 year about 40% of the ethylene glycol will be emitted, and it will take as long as 3.5 years for all of the ethylene glycol to be released.

Although the double-exponential model indicated that the phase 2 VOC emissions should last for a long

**Fig. 7** Long-term VOC emissions from painted gypsum board

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

Conclusions

Environmental chamber tests showed significant differences in emission rates and patterns between the VOCs released from the same latex paint applied to two different substrates – a stainless steel plate and a gypsum board. After the first 2 weeks, over 90% of the VOCs were emitted from the paint on the stainless steel plate but less than 20% had left the gypsum board. The dominant species in the VOCs emitted also changed from ethylene glycol to Texanol when stainless steel was replaced with gypsum board. Data analysis by a double-exponential model indicated that the majority of the VOC emissions from the painted stainless steel might be simulated by an evaporation-like phenomenon with fast VOC emissions controlled by gas-phase mass transfer. On the other hand, only a small fraction of the VOCs emitted appeared to be controlled by the evaporation-like drying process from the painted gypsum board. The majority of the VOCs were emitted after the painted gypsum board surface was relatively dry and were probably dominated by a slow, solid-phase-diffusion-controlled mass transfer process. Long-term experimental data indicated that it may take as long as 3.5 years to release all the VOCs in the paint applied to the gypsum board.

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

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