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Exposure and Emission Evaluations of Methyl Ethyl Ketoxime (MEKO) in Alkyd Paints

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Abstract Small environmental chamber tests were conducted to characterize the emissions of a toxic chemical compound – methyl ethyl ketoxime (MEKO) – from three different alkyd paints. It was found that MEKO emissions occurred almost immediately after each alkyd paint was applied to a pine board. Due to the fast emission pattern, more than 90% of the MEKO emitted was released within 10 hours after painting. The peak concentrations of MEKO in chamber air correlated well with the MEKO content in the paint. Material balance showed that good recovery (more than 68%) was achieved between the MEKO applied with the paint and the MEKO emitted. The chamber data were simulated by a first order decay emission model assuming the MEKO emissions were mostly gas-phase mass transfer controlled. The model was used to predict indoor MEKO concentrations during and after painting in a test house. It was found that the predicted test house MEKO concentrations during and after the painting exceeded a suggested indoor exposure limit of 0.1 mg/m^3 for all three paints. The predicted MEKO concentrations exceeded even the lower limit of a suggested sensory irritation range of 4 to 18 mg/m^3 with two of the three paints tested. The model was also used to evaluate and demonstrate the effectiveness of risk reduction options including selection of lower MEKO paints and higher ventilation during painting.

Key words Methyl ethyl ketoxime; Alkyd; Emission; Chamber; Model.

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Introduction

Methyl ethyl ketoxime (MEKO), another name for 2-butanone oxime or ethyl methyl ketoxime [CH_3-$C(NOH)C_2H_5$, CAS Registry No. 96–29–7], is often used by paint manufacturers as an additive to interior alkyd paints (Weismantel, 1981; Turner, 1988). MEKO acts as an anti-skinning agent (or anti-oxidant) that prevents oxidative drying or skinning of the alkyd paint to improve stability in the can. Usually, the MEKO content in a paint should be less than 0.5% (Krivanek, 1982). Due to the relatively high volatility (152°C boiling point), the majority of the MEKO in the paint is expected to be released into the surrounding indoor air after painting to allow the paint to dry properly on the painted surfaces. Impacts of MEKO emissions on indoor air quality and associated exposure risk are significantly affected by source characteristics such as emission rates and patterns.

MEKO was found to be a moderate eye irritant (Krivanek, 1982). It was also the subject of a Section 4 test rule under the Toxic Substance Control Act (Federal Register, 1986). Testing conducted under the test rule (Federal Register, 1989) has evaluated a number of toxicological endpoints. MEKO demonstrated carcinogenic activity in long-term inhalation studies, causing liver tumors in both rats and mice. MEKO did not cause gene or chromosome mutations in standard genotoxicity studies. Nielsen et al. (1997) reviewed and evaluated published toxicological data on noncarcinogenic effects of MEKO. No data were found on effects in humans, and inhalation studies concordant with effects in oral studies were not available. Using a safety factor to extrapolate from animals to humans, Nielsen et al. (1997) proposed a tentative health hazard indoor air exposure limit of 0.1 mg/m^3 for MEKO and suggested a range of sensory irritation thresholds of 4 to 18 mg/m^3. Those indoor exposure threshold values were recommended to facilitate the evaluation of building materials and indoor climate.

The objectives of the research described in this paper are to characterize the MEKO emissions from alkyd

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

Experimental Method

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

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

Three commonly used alkyd paints, designated as paints 1, 2, and 3, manufactured by three major U.S. paint companies were acquired for testing. Those alkyd paints were selected after consulting with paint suppliers on the popularity of medium priced paints. In addition, a primer recommended by the paint suppliers for surface preparation for alkyd paint application was also acquired. The primer and each paint was first well-mixed in its own cans and then split into 150 mL amber vials. Each vial was used for only one test.

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

A pine board purchased from a local lumber supplier was used as the substrate to simulate the woodwork to which indoor alkyd paints would commonly be applied (Chang et al., 1997). The board was cut into 16×16 cm sections, and the exposed edges were sealed with sodium silicate solution. For each test, a sealed but unpainted section was conditioned for at least 48 h in a chamber operating under standard test conditions. One side of the conditioned board was then treated with the primer and placed horizontally inside the chamber with the treated side face up. After 48 h of drying, alkyd paint was applied to the treated side of the substrate specimen by a roller. The mass applied was determined using a protocol involving weighing of the substrate before and after the application. The painted sample was placed on the bottom of the chamber promptly (within 3 min after paint application) with the painted side exposed to the chamber air. The test start time (t=0) was established when the door to the chamber was closed. The chamber was flushed with clean air (<5 $\mu g/m^3$ total volatile organic compounds) at a constant rate (N=0.5 h^{-1}) throughout the test. The MEKO concentration in the clean air flowing into the chamber was virtually 0. Any MEKO emissions from the substrate would be reflected by the detection of MEKO in the exit air from the chamber.

Air samples at the chamber exit were collected on silica gel cartridges, 8 mm O.D.×70 mm long, consisting of two sections (150 and 75 mg) of activated silica gel (20/40 mesh). The sampling and analysis method was a modification of NIOSH Method 2010 (NIOSH, 1994). The samples were extracted with methanol and analyzed by GC/MS.

Results and Discussions

MEKO Contents

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

Chamber Emission Data

No MEKO was detected in the chamber air during the substrate conditioning and primer drying periods. The data indicated that there were no MEKO emissions from either the pine board or the primer which confirmed the bulk analysis results that the primer contained no MEKO. However, significant MEKO emissions were measured for all three alkyd paints tested. The concentration profiles (time-concentration curves)

of MEKO in the environmental chambers from paints 1, 2, and 3 are shown in Figures 1, 2, and 3, respectively. It is seen that MEKO emissions occurred immediately after painting with the chamber concentration peaking within 1 hour. Using paint 2 as an example, Figure 4 shows that more than 90% of the MEKO emitted was released in less than 10 h. The fast release of MEKO resulted in a decrease of chamber concentration by more than 2 orders of magnitude in 24 h.

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

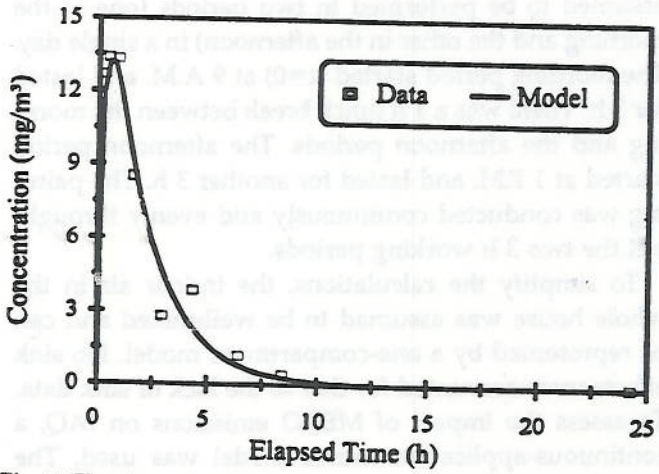

Fig. 1 Chamber concentrations resulted from the MEKO emissions from paint 1

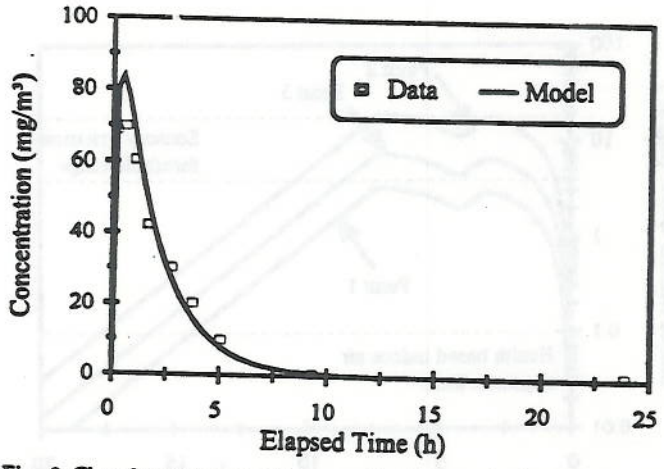

Fig. 2 Chamber concentrations resulted from the MEKO emissions from paint 2

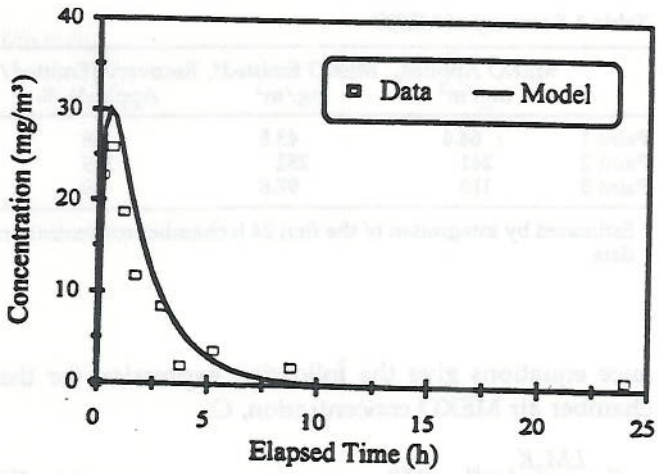

Fig. 3 Chamber concentrations resulted from the MEKO emissions from paint 3

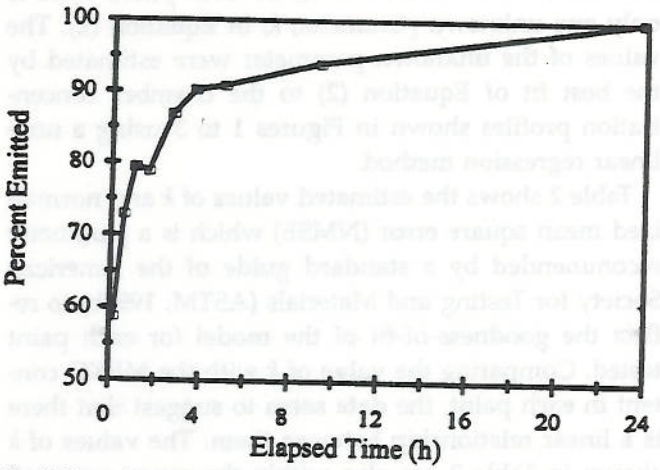

Fig. 4 Cumulative MEKO emissions for paint 2 (calculated from chamber concentration data)

MEKO Emission Model

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

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

where

R=MEKO emission factor, mg/m²/h,

M_o=initial amount of MEKO in the paint film, mg/m²,

k=first order decay rate constant, h^{-1}, and

t=time elapsed, h.

Assuming the chamber air was well-mixed, mass bal-

Table 1 Recovery of MEKO

	MEKO Applied, mg/m²	MEKO Emitted[a], mg/m²	Recovery (Emitted/Applied), %
Paint 1	64.4	43.5	68
Paint 2	241	252	105
Paint 3	110	97.8	89

[a] Estimated by integration of the first 24 h chamber concentration data

ance equations give the following expression for the chamber air MEKO concentration, C:

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

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

Table 2 shows the estimated values of k and normalized mean square error (NMSE) which is a parameter recommended by a standard guide of the American Society for Testing and Materials (ASTM, 1995b) to reflect the goodness-of-fit of the model for each paint tested. Comparing the value of k with the MEKO content in each paint, the data seem to suggest that there is a linear relationship between them. The values of k shown in Table 2 are also within the range expected for emissions controlled by the gas-phase mass transfer process (Sparks et al., 1996). The goodness-of-fit of the model was represented by NMSE which is a measure of the magnitude of prediction error relative to the predicted and measured values (ASTM, 1995b). The ASTM standard guide suggests that, considering the potential consequences of measurement uncertainties, a NMSE value of 0.25 or less can be taken as generally indicative of adequate model performance (ASTM, 1995b). Table 2 shows that the NMSE values for the three paints tested are all less than 0.25 which indicates that the first order decay model is adequate for predicting MEKO emissions.

Table 2 Estimated values of model parameter and goodness-of-fit to the chamber concentration data

	k, h^{-1}	Normalized Mean Square Error[b]	MEKO in Paint, mg/g
Paint 1	3.83±0.59[a]	0.056	0.96
Paint 2	5.19±1.20[a]	0.071	2.93
Paint 3	4.17±1.48[a]	0.219	1.34

[a] Mean±standard deviation

[b] A value of 0 indicates perfect agreement for all pairs of observed and predicted values. A value near 0.2 indicates differences of about 50%

Indoor Air Quality Impact Assessment

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

To simplify the calculations, the indoor air in the whole house was assumed to be well-mixed and can be represented by a one-compartment model. No sink effects were accounted for due to the lack of sink data. To assess the impact of MEKO emissions on IAQ, a continuous-application source model was used. The model assumed that one coat of the alkyd paint was applied to the surfaces at a constant rate. The approach

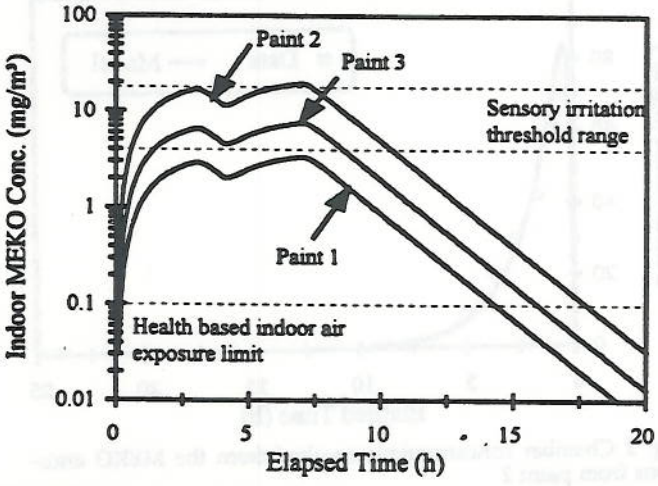

Fig. 5 Comparison of the predicted test house MEKO concentrations with the suggested indoor exposure thresholds

was to break up the application into many differential areas, and each area began emitting once the paint was applied. Evans (1996) established the mathematical models for three types of continuous-application emission sources. The analytical solution of the one-compartment model with a first order decay emission source is:

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

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

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

where

q = the paint application time of each painting period, h,
$H(t-q)$ = Heaviside operator (O'Neil, 1991),
V = volume of the test house, m^3, and
M = total amount of emittable MEKO in the applied paint during each painting period, mg.

The MEKO concentrations in the test house with an air exchange rate of 0.5 h^{-1} during and after the painting, as predicted by the model for the three alkyd paints, are shown in Figure 5. It is seen that the MEKO concentration rises sharply right after the painting started and reaches a peak at the end of the morning period. The MEKO concentration declines slightly between hours 4 and 5, which reflects the 1 h lunch break. The MEKO concentration rises again after the afternoon painting period started and reaches another peak at the end.

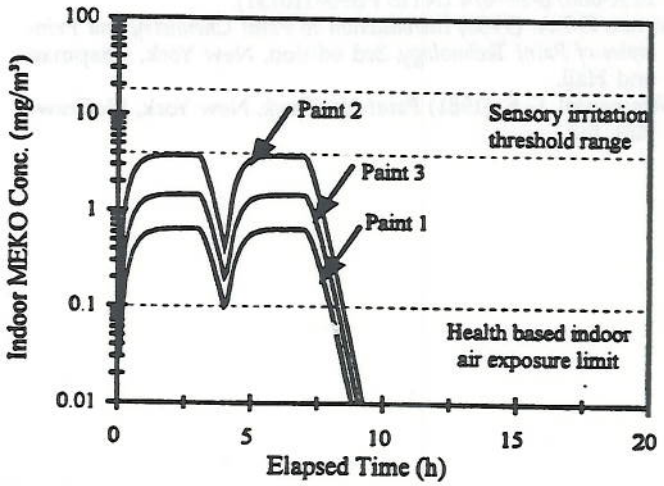

Fig. 6 Predicted test house MEKO concentrations at high (3.0 h^{-1}) air exchange rate

After all the painting is finished, the MEKO concentration decreases continuously.

Compared with the suggested indoor air exposure limit of 0.1 mg/m^3, Figure 5 shows that the test house MEKO concentration exceeded the limit for all three alkyd paints. The episode of IAQ deterioration started at the beginning of the painting and lasted for more than 7 h after the painting. The test house MEKO concentration also exceeded the lower limit of the suggested sensory irritation range when paints 2 and 3 were used.

Risk Reduction Assessment

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

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

Since Equations (3) and (4) indicate that the indoor MEKO concentration increases are proportional to the total amount of emittable MEKO in the applied paint (M), another risk reduction option can be the division of the whole paint work into several small jobs. Only a small area is painted during each paint job, and plenty of air-out time (more than 12 h) should be allowed between the jobs. For example, when paint 1 is used and the painted area is less than 1.6 m^2, the test house MEKO concentration can be maintained below 0.1 mg/m^3 at an air exchange rate of 3.0 h^{-1}. The MEKO concentration in the test house can be further reduced if the source room can be isolated from the rest of the house and high local ventilation (e.g., 3 h^{-1}) is implemented in the source room.

Conclusions

Bulk analysis showed that the MEKO content in alkyd paints can be as high as several mg/g. Material balance from the chamber tests indicated that the

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

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

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