

Characterization of Total Volatile Organic Compound Emissions from Finished Solid Wood Using an Environmental Chamber

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Abstract

Solvent-based finishes used for solid wood furniture involve exposure of workers and customers to volatile organic compounds. This study was to characterize emission parameters of total volatile organic compounds from five different types of solid wood products: urethane-coated, lacquer-coated, acrylic-coated, gloss white-painted, and matte white-painted. Emission experiments were conducted using a 10-liter environmental test chamber, and all test finished wood samples were prepared by professional furnitureworkers. Emission parameters were quantified by fitting the experimental time-dependent concentrations to the two-decaying sources model using a non linear regression method. The quantified emission rate constants of the fast-decaying phase were 5.09, 5.09, 6.84, 4.71, and 0.43 1/h for the urethane-coated, lacquer-coated, acryliccoated, gloss white-painted, and matte white-painted products, respectively, while the emission rate constants for the slow-decaying phase were 3.12×10^{-2} , 2.23×10^{-2} , 1.48×10^{-2} , 2.14×10^{-2} , and 1.2×10^{-3} 1/h, respectively. The matte white-painted wood exhibited the higher total quantities of emitted organic species than other finished wood products by 4-16 times for the fast-decaying emission and by 5-18 times for the slow-decaying emission.

Keywords: volatile organic compounds; wood finishes; emission; indoor air quality

1. Introduction

Solid wood furniture is popular in the residences of the middle- and upper-class in Thailand because of its durability and aesthetics. To embellish and protect solid wood products, wood finishing and coating are usually applied during the manufacturing process. These wood finishes include wax, shellac, lacquers, varnishes, paints, etc. (Meijer, 2001). The selection is dependent on product-utilized purposes as well as aesthetic considerations. Generally speaking, wood finishes may be classified into organic solvent-based and water-based finishes of which solvents and water are used as a carrier for other components in the coating ingredients. However, solvent-based finishes involve exposure of workers and customers to volatile organic compounds (VOCs) from the solvent residuals in the finished products, which may cause health risks or comfort problems due to unpleasant odors (Salthammer, 1999; Peng et al., 2009; Sulaiman and Mohamed, 2011). Turkulin et al. (2001) reported that the solvent-based paint and stain can penetrate more deeply into the wood surface than the waterbased coatings. The penetration of coating substances could affect the emission behaviors of organic compounds from the wood product into room air. As a result, occupants may be prone to persistent emissions of some organic airborne pollutants. However, most studies of VOC emissions from wood

finishes have been performed using typical well-defined substrates, like glass, aluminum, stainless steel (Zhu et al., 1999; Chang et al., 1997; Lee et al., 2003; Kwok et al., 2003), or common building materials, like gypsum board and plywood (Kwok et al., 2003). There is still no characterization of VOC emissions from "real" solid wood substrates being applied with varnish finishes such as finished solid hardwood furniture. This type of furniture is usually man-made by furniture-workers who perform the entire wood finishing processes, while pressed wood products are mass-produced mostly using automated systems. The solid wood finishing technique is based on the type of lumber, purpose of utilization as well as the furnitureworkers' skills and experiences. For example, the number of coating times is dependent on product quality requirements, and how well the finished wood coating appearance is. These are judged by furniture-works' experiences.

Therefore, the objective of this study was to characterize emission parameters of total VOCs (TVOC) from a variety of finished solid wood products sold on the market. The test was to provide data that are relevant for understanding the emission behaviors and persistence of the organic pollutants emitted from wood finishes in typical indoor settings. Experiments were performed on wood product specimens that were prepared by professional furniture workers

using a small-scale chamber. In addition to exposure implication, the emission parameter estimates were used to examine the impact of TVOC emissions from finished hardwood furniture in a typical room on a dynamic of room air concentrations.

2. Materials and methods

2.1. Materials

Five types of solid wood finishing were selected for emission testing based on customer-use popularity in the wood finishing market. An unfinished wood sample was also included in the comparative study. The finished wood samples included urethane-coated wood, lacquer-coated wood, acrylic-coated wood, gloss white-painted wood, and matte white-painted wood. The solid wood used for producing all test samples was obtained from the same lumber, which was Pterocarpus macrocarpus (Burma Padauk). A species of Pterocarpus is native to the southeastern Asia and it is classified into a hard wood type. Every step of the wood finishing process was performed by the professional furniture-workers at one of the wooden furniture factories in Thailand. Note that all wood samples were prepared in a circular shape with the diameter of 20.3 cm and thickness of 2.5 cm. The wood finishing processes for each products are described below.

Unfinished wood: The lumber is submerged in a wood-preservative solution. Afterward, it is dehumidified in a baking chamber for 7-10 days. The preservative is continuously being sprayed on the lumber, while baking. This treated lumber was also used for producing the other five finished wood samples.

Urethane-coated wood: After the wood surface preparation with soft chalk filler, a thinnerbased clear polyurethane finish is applied to the surface. After drying, the surface is softly polished. The process of coating and polishing is performed 4 times or until the surface appears glossy.

Lacquer-coated wood: After the wood surface preparation, shellac is applied to the surface and allowed to dry. The shellac application is done 3 times. Then, a primer lacquer sealer is brushed on the surface and left to dry. The sealer application is done 3 times. Then, the surface is softly polished until made smooth. Finally, an alkyd resin and nitrocellulose-based lacquer is sprayed on the surface 2-3 times.

Acrylic-coated wood: The wood finishing process is similar to that for the lacquer coated wood. Instead of a final application of lacquer, a thinner-based acrylic finish mixed with hardener is sprayed twice.

Gloss white-painted wood: After the wood surface preparation, shellac is applied to the surface and let

to dry. The shellac application is done 3 times. The surface is softly polished until smooth. Then, a paint primer is sprayed on the surface 2-3 times. Finally, a white-color, resin, thinnerbased paint is sprayed on the surface twice.

Matte white-painted wood: The wood finishing process is similar to that for the gloss painted wood, except that a white-color, resin, thinner-based paint mixed with matte lacquer is sprayed on the surface. After drying, the surface is polished and it is finally sprayed with a matte lacquer.

After completing the wood finishing processes, the specimens were dried in room air for a couple of days at the wood furniture factory. The finished wood samples were then wrapped with aluminum foil and packed in Ziploc bags. They were kept for use within 10 days in an environmentally controlled cabinet at 22°C and 30-50% relative humidity (RH) prior to experimentation.

2.2. Experimental system and procedure

This study followed the ASTM D 5116-06, a standard guide for determination of emissions of organic compounds from indoor materials using a small-scale environmental test chambers (ASTM, 2006). Fig. 1 shows the experimental setup consisting of a test chamber, flow system, humidifiers, and outlet gas sampling part. The 10-liter stainless steel chamber had an inner diameter of 30 cm and the lid was equipped with 0.63-cm (1/4-in.) o.d. stainless steel tube fittings (Swagelok®) for inflow and outflow. The lid was attached to the chamber body with eight C-clamps. A polyurethane o-ring was used as an air tight seal. The entire chamber inner surface was covered with a Teflon[®] sheet to minimize any sorption of emitted VOCs from the wood sample to the chamber wall. In this study, the RH and temperature was controlled at 50% and 25°C for all experiments. To achieve the desired RH inside the chamber, humidified N₂ of 100 ml/min from the humidifiers containing de-ionized (DI) water was mixed with dry N₂ of 100 ml/min before introducing into the chamber.

Prior to installation in the chamber, the bare edge and back of the wood samples were wrapped with Teflon® tape to prevent emission areas not typically exposed to bulk room air. A specific surface-to-volume ratio for the wood sample, known as the loading factor, was 3.24 m²/m³ and the chamber air exchange rate was 1.2 1/h. The experiment was started by regulating 50%-RH high purity nitrogen (N₂) into the chamber with 200 ml/min for 78 h to obtain dynamic change in the outlet concentration for emission parameter quantification using non linear regression.

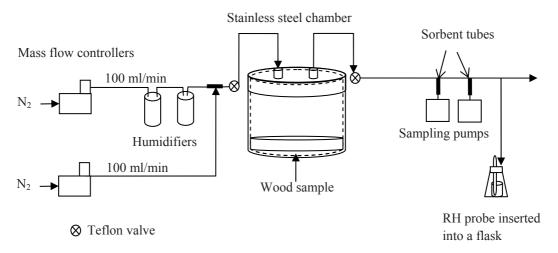


Figure 1. Experimental system

Personal sampling pumps (224-PCXR4, SKC) were used to draw gas samples to sorbent tubes at a flow rate of 80 ml/min. A glass tube, 70 mm, 7-mm o.d., containing two sections of 100/50 mg of 20/40 mesh size charcoal (SKC), was used to collect VOCs in the gas sample at the outlet. The gas sampling was conducted consecutively 8 times for each experimental trial. Duplicate samples for each sampling time were collected to assure the reliability of sampling and analytical methods.

2.3. Gas analysis

VOCs adsorbed on charcoal were desorbed with 1 ml of carbon disulfide (Merck & Co.). The vials were then sealed and horizontally shaken for 24 hours. A 1-µl aliquot was then injected on a gas chromatography-mass spectrometer (GC-MS) (Shimadzu) with helium as the carrier gas for separation in a Rtx[®]5-ms fused silica column with 0.25-µm df and 30-m length (Restek). The oven temperature was held at 33°C for 1 min, then raised to 60°C at 3°C/min and held at 60°C for 4 min, next raised to 80°C at 5°C/min and held at 80°C for 3 min. The injection temperature and the interface temperature to the MS were held at 250°C. The MS was operated in a scan mode from 10 to 300 amu. TVOC, designated in this study, was quantified by summing total ion current and calibrating with toluene as the representative species. A Four-point calibration was performed. The toluene standard solutions included 10, 20, 50, and 100 μg/ml. The gas sampling and analysis followed the NIOSH manual of analytical methods for aromatic hydrocarbons (NIOSH, 2003).

2.4. Data analysis

The emission model by Chang and Guo (1992), which was used to analyze organic emissions from

wood stain, was adopted to analyze emission data in this study because of the similarity of timedependent chamber concentration profiles. The model is described by two first-order decay sources for emissions of organic species from the emitter. A fast emission source is parameterized by EF_{10} 100 ml/min and k_1 , while a slow emission source is defined by EF_{20} and k_2 . Thus, the emission factor of a VOC from a wood finishing product is given by Equation 1:

$$EF(t) = EF_1 + EF_2 = EF_{10}e^{-k_1t} + EF_{20}e^{-k_2t}$$
 (1)

where EF(t) is the time-dependent emission factor of a VOC (mg/m²-h), EF_1 is the fast-decaying emission factor (mg/m²-h), EF_2 is the slow-decaying emission factor (mg/m²-h), E_{10} is the initial emission factor corresponding to the fast-decaying emission (mg/m²-h), E_{20} is the initial emission factor corresponding to the slow-decaying emission (mg/m²-h), k_1 is the fast-decaying emission rate constant (1/h), and k_2 is the slow-decaying emission rate constant (1/h).

Assuming that VOC sorption and chemical reactions in the chamber were negligible and the inlet gas concentration was zero, a single-compartment mass balance of the emitted VOC in the wellmixed chamber air is given by Equation 2:

$$\frac{dC(t)}{dt} = -\lambda C(t) + L * EF(t)$$
 (2)

where C(t) is the VOC concentration in the chamber bulk air (mg/m³), λ is the chamber air exchange rate (1/h), and L is the loading factor (m²/m³). Integrating the mass balance equation and assuming an initial concentration of zero gives Equation 3:

$$C(t) = L \left[\frac{EF_{10}(e^{-k_1 t} - e^{-\lambda t})}{\lambda - k_1} + \frac{EF_{20}(e^{-k_2 t} - e^{-\lambda t})}{\lambda - k_2} \right]$$
(3)

The desired parameters, EF_{10} , EF_{20} , k_I , and k_2 , were determined by fitting the experimental timedependent concentrations to Equation 3 using a non linear regression program, NLREG[®] version 6.3 (Advanced).

3. Results and discussion

3.1. Concentration profiles and emission parameter estimates

Fig. 2 shows the time-dependent TVOC concentration profiles for the unfinished wood and the other five

finished wood samples during the 78-hour test period. Note that the TVOC profiles for the finished wood samples did not exclude the background TVOC of the unfinished sample which was 1-2 orders of magnitude lower. All profiles are characterized by a sharp rise of the TVOC concentration in the chamber within the first half an hour. After the concentrations passed through a maximum level, they declined toward zero (e.g. the unfinished wood) or toward some intermediate plateau (e.g. the gloss white-painted and matte white-painted). Realistically, the concentrations should decline toward zero at the end if allowing for

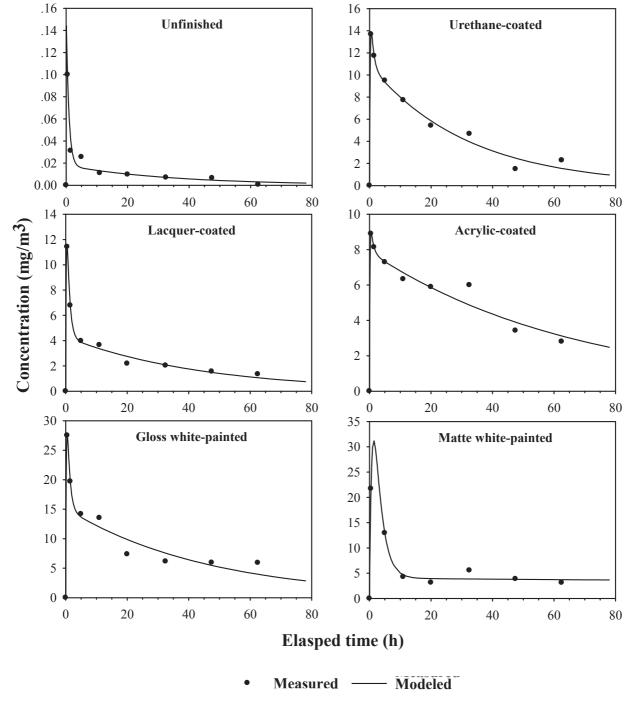


Figure 2. TVOC chamber concentration profiles of the measured and modeled data.

an emission test period to be sufficiently long because of the finite amounts of coating substrates in the finished wood samples. Fig. 2 also shows the concentration curve fits using Equation 3 with the non linear regression method

Table 1 summarizes the emission parameter estimates, EF_{10} , EF_{20} , k_1 , and k_2 as well as statistical analyses for the parameter estimates and the function being modeled. These statistical parameters are standard errors for the estimates, mean square error (MSE), R^2 (proportion of variance explained), and *Prob(F)*, which tests the overall significance of the regression model. The lowest R^2 value for any curve fitting was 0.9727. All data sets being fitted to the model yielded the Prob(F)less than 0.00025, which means there was less than 25 chances in 10,000 that all of the estimates were zero. All the test samples had the initial emission factors, EF_{10} and EF_{20} , in the same order of magnitude, except for the unfinished wood sample of which its values were 3-4 orders of magnitude lower. The extremely low emission factors are attributed to no coating application on the wood. Only oil-borne wood preservative for resistance to insects and fungus was applied during the lumber treatment process. According to the GC-MS analysis in this study, the only detectable VOC emitted from the unfinished wood was toluene since it was used as a solvent for dilution of the wood preservative.

The emission rate constants, k_1 and k_2 , for the urethane-, lacquer-, acrylic-, and gloss whitecoatings were in the same order of magnitude. The fast-decaying emission phase (k_1 and E_{10}) corresponds to the emission process of organic species existing on the surface directly exposed to the chamber air flow. This emission phase is controlled by the bulk-phase mass transport phenomena resulting from the aerodynamic and boundary layer resistances. Thus, the fast-decaying emission phase corresponds to the period shortly when the emission experiment starts with introducing

the nitrogen flow into the chamber. The characteristic times required for the fast-decaying emission sources to reduce by 63% of the initial emission values are \sim 0.2-2.3 h $(1/k_I)$ for the wood products applied with coatings, while the unfinished wood requires less than 0.03 h.

In contrast to the fast-decaying emission phase, the slow-decaying emission phase is associated with the emission process of organic species that penetrate through the thick layers of coatings and (or) through the wood structure. This emission phase is controlled by molecular diffusion from the coating layers or wood structure, resulting in low emission and slow rates. The characteristic times of TVOC for the slow-decaying emission phase require \sim 32-67 h (1/ k_2) to reduce by 63% of the initial emission values for the urethane-, lacquer-, acrylic-, and gloss white-coatings. Due to the lower emission rate constant (k_2) , the emission of the matte white-painted wood appeared to proceed more slowly to deplete the organic quantities in the finished wood than the other types of coatings. The slow-decaying emission phase (E_2) for the matte white-painted wood may be regarded as a constant emission source with an emission factor of E_{20} . It would take more than three months to reduce the TVOC emission by 95% of the initial emission value. This slow rate of TVOC emission could be resulted from the rest of the coating substrates penetrating the wood structure. Turkulin et al. (2001) examined fractured cross-sectional surfaces of wood coated with paints and stains using a scanning electron microscope (SEM). Paints and stains can penetrate in the early wood regions, but not in the cell wall. The solvent-based paint and stain appeared to penetrate deeper than the waterbased coatings. Furthermore, a number of coatings applied to the wood and the final spraying with a matte lacquer for overlay could form thick coating layers, which can act as impedance for mass transfer of VOCs to the gas phase, making the emission rate is considerably slow.

Table 1. Emission parameter estimates and statistical values

| Wood sample | Fast-decaying emission* | | Slow-decaying emission* | | MSE | R^2 | Prob(F) |
|-------------------------|-------------------------|---------------------------|-------------------------|--|-----------------------|--------|---------|
| | EF_{IQ} | k_{I} | EF_{20} | k_2 | | | |
| | (mg/m^2-h) | (1/h) | (mg/m^2-h) | (1/h) | | | |
| Unfinished [†] | 2.12×10 ⁻³ | 43.4 | 6.46×10 ⁻³ | 2.83×10 ⁻² | 4.29×10 ⁻⁵ | 0.9727 | 0.00025 |
| Urethane-coated | 22.8±13.7 | 5.09±3.43 | 3.94±0.27 | $3.12\times10^{-2}\pm4.1\times10^{-3}$ | 0.445 | 0.9875 | 0.00004 |
| Lacquer-coated | 24.3±6.35 | 5.09±1.48 | 1.56±0.11 | $2.23\times10^{-2}\pm3.5\times10^{-3}$ | 0.099 | 0.9949 | 0.00001 |
| Acrylic-coated | 18.2±34.9 | 6.84±13.1 | 2.88±0.19 | $1.48 \times 10^{-2} \pm 2.7 \times 10^{-3}$ | 0.347 | 0.9732 | 0.00024 |
| Gloss white-painted | 49.7±26.9 | 4.71±2.92 | 5.51±0.62 | $2.14\times10^{-2}\pm5.3\times10^{-3}$ | 2.990 | 0.9740 | 0.00022 |
| Matte white-painted | 18.4±1.04 | 0.43±4.5×10 ⁻² | 1.49±0.40 | 1.2×10 ⁻³ ±6.8×10 ⁻³ | 1.002 | 0.9886 | 0.00024 |

^{*} The plus and minus sign denotes the standard error of the estimate from regression analysis.

[†] Standard error was unable to compute because the covariance matrix could not be computed.

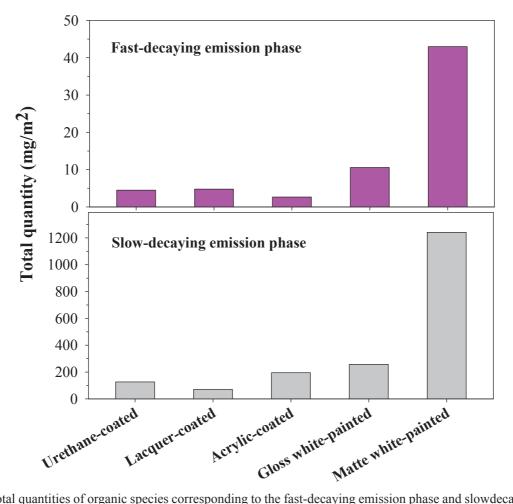


Figure 3. Total quantities of organic species corresponding to the fast-decaying emission phase and slowdecaying emission phase.

3.2. Total quantities of organic species emitted

The total quantities of organic species emitted in the fast emission phase and slow emission phase can be estimated from the model parameters, E_{10}/k_1 and E_{20}/k_2 , respectively (Chang *et al.*, 1997). The values for the five finished wood samples are comparatively depicted in Fig. 3.

The VOCs emitted in the slow-decaying emission phase were considerably greater than those in the fast-decaying emission phase for all finished wood samples. It appeared that almost all organic quantities emitted to the chamber air are attributed to the diffusion through the solid wood, making the emissions persist for a long time. The matte white-painted wood had the highest total quantity of organic species emitted in the slow emission phase. This may be explained by slow diffusion of the organic species through the wood surface. In addition to a residual coating mass of the matte-painted wood, we estimated the mass from the weight gain after applying all coating materials to the specimen and then leaving it in contact with the room air for 24 h. Note that exposure of the finished wood to room air is usually required for drying the coatings in the finishing process. The residual coating mass was found to be 344 g/m², which is approximately 6 times greater than that of the lacquer-coated wood specimen. The significantly high amount of coatings (both paint and matte lacquer for overlay) could serve as a large emission source of organic compounds continuously released into room air.

4. Conclusions

Emissions of TVOC from finished solid wood samples with five different types of coatings can be well characterized with the two first-order decay sources model using the environmental test chamber. The fast-decaying emission phase is controlled by the bulk-phase mass transport phenomena, while the slow-decaying emission phase is controlled by molecular diffusion from the coating layers or wood structure. Results indicate that different wood finishes can affect the emission rates and the total quantities of TVOC emitted. The finished wood that involves a number of coating substances, like the matte white-coated wood, appears to emit organic airborne pollutants more persistently and to contain higher quantities of organic

species emitted into room air than do other wood finishes, like the urethane, lacquer, and acrylic coatings. The persistent emission and high quantities of organic compounds emitted could be resulted from the penetration of coating materials into the wood surface and the high amount of coatings applied to the wood product. In reality, the amount of coating materials used is mainly dependent on the furniture-workers who inspect the product appearance and quality. Thus, the assessment of how emissions of wood finishes behave in typical indoor settings requires emissions data that are relevant and obtained from the finished wood products similarly constructed for sale in the market.

The dynamics of TVOC concentrations in room air over time can be modeled using Equation 3 and the parameter estimates in Table 1. The simulation results suggest that the use of ventilation may help reduce the peak concentration of indoor TVOC emitted from finished hardwood furniture to some degrees. For example, a 3.5×3 m²-dining room just recently furnished with mostly acryliccoated solid wood products having the specific surface-to-volume ratio of 0.19 m²/ m³ is predicted to have a peak concentration of emitted TVOC of 1.2 mg/m³ at the ventilation rate of 0.4 1/h. Increasing the ventilation rate to 1 1/h is expected to reduce the peak concentration by 54%. However, a means of increasing ventilation may not be effective in reducing the persistence duration of the emitted TVOC in room air because the decaying emission rate constants (k_2) are significantly less than a mean air exchange rate of typical residences of 0.68±0.63 1/h (Breen et al., 2010).

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