



## Evaluation of formaldehyde and VOCs emission factors from paints in a small chamber: The effects of preconditioning time and coating weight

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### ABSTRACT

The aims of this study were to improve the emission test method for the 20L small chamber standardized in Korea using paints and to develop an optical test method for paints. The emission factors of the total volatile organic compounds (TVOC) and formaldehyde from oil-based paints, emulsion paints and water-dispersion paints coated at 300 g/m<sup>2</sup> and cured for 24 (48) h were determined using the 20L small chamber method. The emission factors of TVOC and formaldehyde from all paints under steady state conditions were determined after 7 days with 24 (48) h of curing. The Korean standards require that paints be measured and analyzed on the third day after a test. However, the emission factors of TVOC and formaldehyde from the paints only began to stabilize 7 days after installing the samples. Until now, the emission test results have been reported mainly as concentration vs. time or emission factor vs. time profiles of TVOC and formaldehyde. The emission factors of the target volatile organic compounds (VOCs) and aldehyde types were obtained under specific test conditions according to the different coating weights. For all target volatile organic compounds and aldehyde types examined, the paint coating weight had an effect on emission.

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### 1. Introduction

Many building materials emit VOCs with the potential to affect health and comfort [1]. Over the past decade, researchers have developed a range of techniques to measure the emission of VOCs from building materials. The ASTM standard guide, which is a guideline from the Commission of the European Communities (CEC, 1992) and a European preliminary standard (ENV 13419 part 13 (CEN, 1998)), have been published. The emission test techniques for building materials are important to manufacturers, indoor air quality investigators and researchers. Such validation is important for quantifying the impact of the construction products on the indoor air quality [2]. The perforator method is one of the methods applied in the past, even though it requires a special apparatus [3]. The European particleboard association originally developed this test procedure in the late 1970s, and it was established in 1984 as the European standard EN 120. On the other hand, the desiccator method has been adopted in North America, Australia and Asia. The desiccator test was developed in the mid-1970s in Japan and stan-

dardized in the US in 1983. The Japanese industrial standard (JIS) desiccator method and similar procedures employ a closed vessel containing the test material and a water reservoir. Formaldehyde released from the material is captured in the water and the level of formaldehyde in the water is determined after a standard time interval, such as 24 h [4]. As this procedure is designed to measure the concentrations emitted from the front and back sides as well as the edges of materials, the emission behavior measured using this method is different from the emission behavior in general interior spaces.

Therefore, recent research has employed chamber methods in which air is introduced and chemical compounds emitted from the surface of materials are determined. Building and furnishing materials are important sources of VOCs and formaldehyde that contribute to indoor air pollution. A large number of VOCs and formaldehyde are emitted from flooring, wall coverings, adhesives and coating products, and have the potential to cause adverse health effects in the building occupants [5–7]. Many building products based on natural raw materials behave as secondary emission sources and generally continue to emit VOCs and formaldehyde, as opposed to synthetic building products [8]. Several small-scale chambers to measure aldehyde and VOC ERs have been proposed [9–12]. These small test chambers are often used to determine the chemical ERs from building materials [13].

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**Table 1**  
Thickness of film, density, and solid contents of paints.

Materials	Oil-based paint	Emulsion paint	Water-dispersion paint
Thickness of film ( $\mu\text{m}$ )	60	60	20
Density ( $\text{mg}/\text{m}^3$ )	1.16	1.53	10.4
Solid contents (%)	57.5	60	37

The Korean government began controlling the indoor air quality in 2004. The corresponding Ministry of Environment's law regulates the use of pollutant-emitting building materials. In renovated or completely new buildings, the levels of indoor air pollutants, particularly VOCs, emitted from construction and building materials are often several orders of magnitude higher than the VOC levels in buildings under normal use [14–17]. Furthermore, standardization of the emission test and chemical analysis has been performed by the Ministry of the Environment; the 20-L small chamber method is currently the standard method for examining the emission of VOCs and formaldehyde in Korea. The 20-L small chamber method was developed in Japan along with its performance in compliance with the ASTM [18,19], ECA reports [20–23], and ENV 13419-1 [24]. Although there are larger chambers, the 20-L chamber was used in this study because it is the standard in Korea. The air control system consisted of an air-supplying unit, a humidifier, and pumps. A 20-L small chamber was set up in a temperature-controlled climate chamber. Zero air was used for ventilation.

Until now, the emission test results have been shown mainly as concentration versus time or emission factor versus time profiles for TVOC only. This style of graph and table is too simple and cannot adequately describe the individual emission behaviors of the VOCs. Therefore, the emission factors of the target VOCs and aldehyde types under specific test conditions are shown for the different coating weights. Two problems associated with the 20-L small chamber method require improvement: (1) coating weight and (2) pre-conditioning time. The aim of this study was to improve the emission test method for paints using the 20-L small chamber and an optical test method for paints is proposed. Finally, the effects of air flow rate in the 20-L small chamber on the emission rates and the effect of changing the paint coating weight were determined.

## 2. Experimental

### 2.1. Materials

The paints evaluated to determine the VOC and formaldehyde emissions are classified mainly into oil-based and water-based paints with water-based paints being sub-categorized as emulsion or water-dispersion paints. Table 1 lists the characteristics of paints.

There are three types of commercially available paints: oil-based paints, emulsion paints and water-dispersion paints. Oil-based paints are acrylic resin paints with boiling points above  $110^\circ\text{C}$  that contain 30–40% acryl resin, 10–20% xylene, 20–30% toluene, and 20–30%  $\text{TiO}_2$ , among others. Emulsion paints generally use a binder as the solution, which is emulsified boil oil, oil banish and resin in water. The emulsion paint chosen for this study contained 1–10% acryl emulsion resin, 10–20%  $\text{TiO}_2$ , 10–20%  $\text{CaCO}_2$ , 10–20% talc, 1–10% kaolin clay, and 30–40% water. The water-dispersion paint contained 50–60% water, 30–40% water-dispersion urethane resin, 1–10% ethylene glycol monomethyl ether, and 1–10% of diethylene glycol monobutyl ether.

### 2.2. The 20-L small chamber method for collection of gas samples

Before the chamber and sealed boxes had been set-up, they were washed with water and baked out in an oven at  $260^\circ\text{C}$  to eliminate



**Fig. 1.** Examples of glass plates coated with paint.

any pollutants from the chamber itself. The 20-L small chamber was supplied with purified and humidified air at a ventilation rate of 0.5 ACH at an air-flow rate of 167 mL/min. The temperature and relative humidity (RH) inside the chamber were kept constant at  $25 \pm 1^\circ\text{C}$  and  $50 \pm 5\%$ , respectively.

The paint was applied with a brush to cleaned glass plates wrapped with aluminum foil, as shown in Fig. 1. The sample coatings applied to the glass plates were at two weights:  $300\text{ g}/\text{m}^2$  according to the regulations of the Ministry of the Environment, Korea and the weight calculated according to the recommended thickness specified by the manufacturer. The area of paint applied was  $6.32\text{ cm} \times 6.32\text{ cm}$ , which is in accordance with a loading factor of  $4.0\text{ m}^2/\text{m}^3$ . Table 2 lists the weight, area and loading factor of the individual paints applied, and Table 3 lists the pre-conditioning times of the individual paints applied. The second type of coating weight was calculated as follows:

$$\text{Coating weight (g)} = \frac{(A \times B \times C)}{(D \times 100)}$$

where, A, thickness of film of paint ( $\mu\text{m}$ ); B, area coated ( $\text{cm}^2$ ); C, density of wet materials ( $\text{g}/\text{m}^3$ ); D, solid contents (%).

The test pieces sealed with seal boxes were set in the chamber, and the air inside the chamber was sampled after 15 h. The sampling conditions were followed as author's previous work [1,6,9]. Throughout the measurements, the air temperature and relative humidity inside the test chamber were kept constant at  $25 \pm 1^\circ\text{C}$  and  $50 \pm 5\%$ , respectively, and the chamber was ventilated at  $0.5\text{ h}^{-1}$ . The sample gas was taken at 2, 4, and 12 h and at 1, 3, 5, 7, 14, 21, and 28 days after installing the samples.

**Table 2**  
Test conditions of paints applied to glass plates.

	Weight ( $\text{g}/\text{m}^2$ )		Area ( $\text{cm}^2$ )	Loading factor ( $\text{m}^2/\text{m}^3$ )
	Type 1	Type 1		
Oil-based paint	300	121	$6.32 \times 6.32$	4.0
Emulsion paint		153		
Water-dispersion paint		56		

**Table 3**  
Pre-conditioning time.

	Type 1	Type 2	Type 3
Oil-based paint	24 h	1 h	10 days
Emulsion paint	48 h		
Water-dispersion paint			

### 2.3. Emission factor

The method for calculating the emission factor (EF) is explained in ASTM D5116. Two technical terms are commonly used to describe the rate of emissions from indoor materials, EF and ER, which are related as follows:

$$ER = A(EF) \quad (1)$$

where, ER, emission rate (mg/h); A, source area (m<sup>2</sup>); EF, emission factor (mg/m<sup>2</sup>h).

Therefore, ERs can be applied to both area sources and non-area sources, whereas EFs are reported as mass/mass/time, or in the case of caulk beads, mass/length/time, when a standard bead diameter is used. In the remaining cases, only EF is used in the examples.

### 2.4. Conditions of analysis of GC/MSD and HPLC

The VOCs were analyzed using a thermal desorption system (TDS) combined with gas chromatography–mass spectrometry (GC/MS) [1,6]. In this study, TVOC was defined as the conversion of all areas of the peaks between C<sub>6</sub> and C<sub>16</sub> to concentrations using the toluene response factor. The Tenax-TA collected gas set-up was a thermal desorber system in the opposite direction, of which it collected gas and desorbed VOCs by heating. When a type of VOC was identified, mass spectrometry was performed in scan mode and the VOCs were separated by the mass spectra. Although a given VOC had an identical interval of retention time to the standard, it was classified by comparing the mass spectra. Quantitative analysis of the VOCs was accomplished with a total ion current chromatogram (TIC) using gas chromatography with mass spectrometry.

Formaldehyde and aldehyde were analyzed by high performance liquid chromatography (HPLC) [1,6]. A DNPH derivative in a 2,4-DNPH cartridge collected the air containing formaldehyde and aldehyde, which was eluted using 5.0 mL of acetonitrile, and quantitative analysis of the eluted solution was performed by HPLC.

## 3. Results and discussion

### 3.1. The effects of pre-conditioning time

Fig. 2 shows the emission factors of the TVOC in oil-based paint, emulsion paint, and water-dispersion paint coated at 300 g/m<sup>2</sup>, according to the regulations of the Ministry of Environment, Korea. The emission factors of TVOC from every paint in the earlier periods was highest for the one-hour curing condition and second highest for 24 (48)-h curing. The VOCs included in the paint, which are in the liquid phase, release and diffuse in the air as soon as the paint is applied to the surface. The paint cured for one hour still included high concentrations of TVOC and were strongly emitted, which is why the emission levels of all paints were highest for the one-hour curing condition. Because the oil-based paint was not cured in one hour, the VOCs were not separated individually at 2, 6, 12, and 24 h. The oil-based paint cured for one hour emitted mainly toluene, ethylbenzene, xylene, styrene, and 1,3,5-trimethyl benzene after 3 days.

The pre-conditioning time of paint, which is the time after the paint is applied to a surface, is classified as a 24-h curing for oil-based paint and 48-h curing for the emulsion and water-dispersion paints. Currently, for a more effective test, 10 days curing for complete curing is suggested because one hour curing is too short. Based on these results, the stability of the TVOC emission factors had no relevance to the pre-conditioning time. The TVOC emission factors with one-hour curing in all paints were higher than those with 24(48)-h curing in the earlier period. However, as observed with the 24(48)-h curing, the TVOC emission factors were stable after a minimum of 7 days. The TVOC emission factors after 10 days curing for

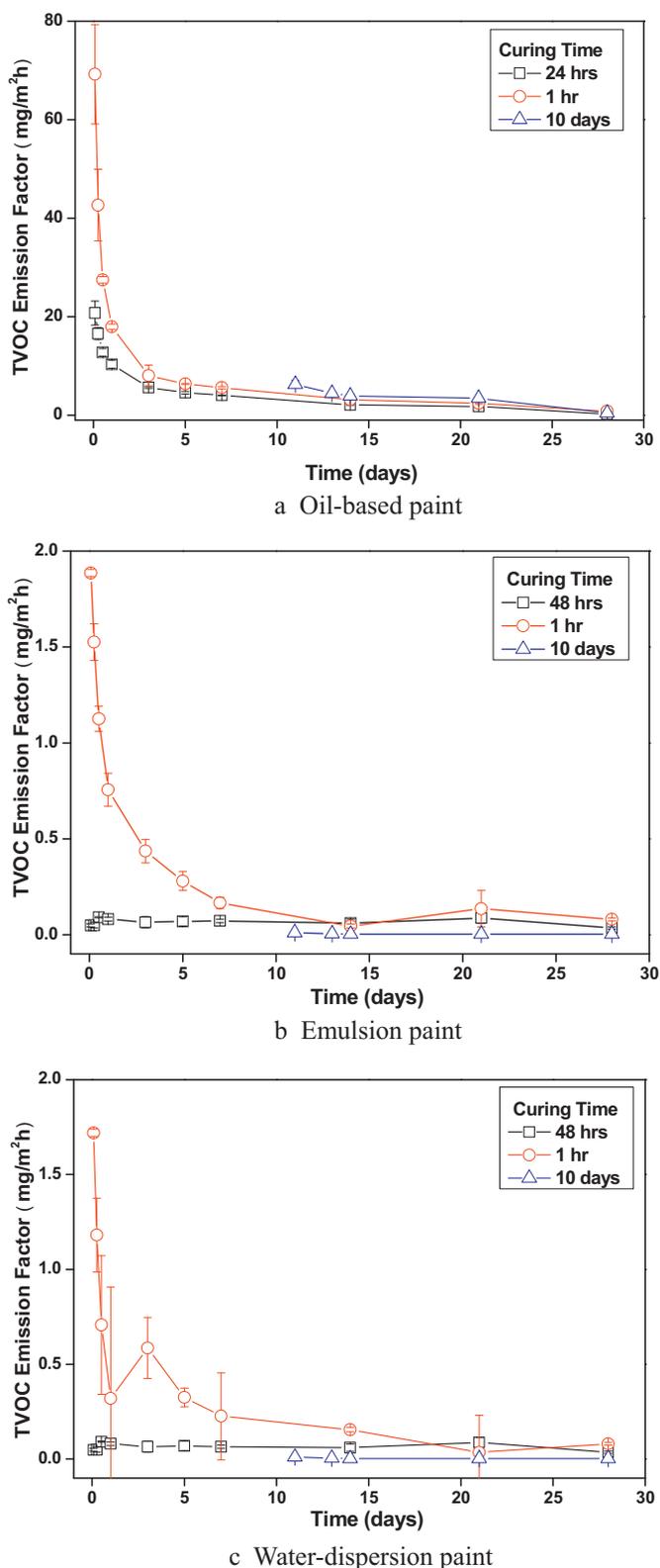
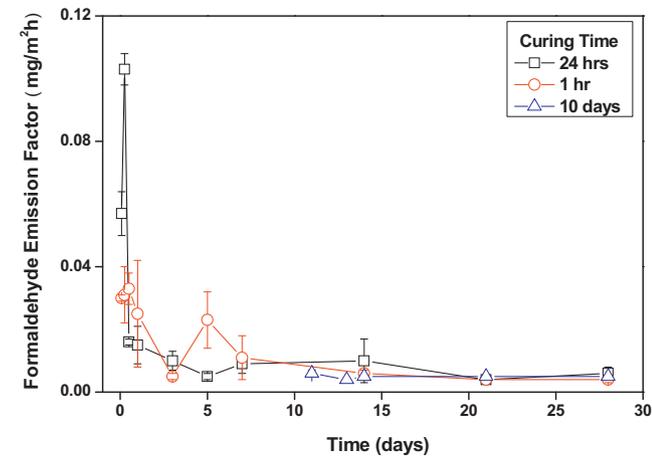


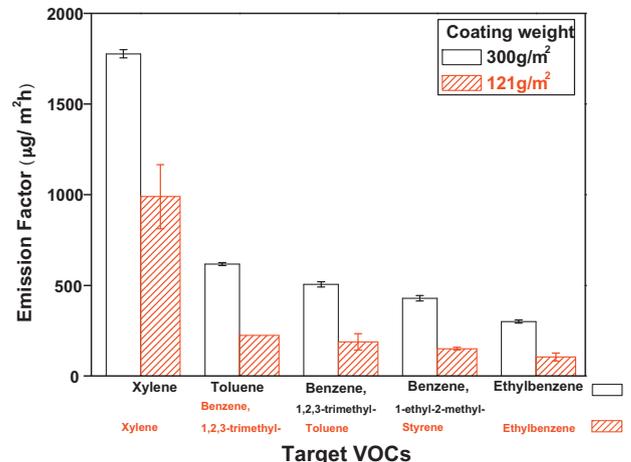
Fig. 2. Emission factors of TVOC according to the pre-conditioning time: 24(48) h, 1 h, and 10 days.

all paints were very low and similar throughout the entire test periods. Therefore, emission tests after 10 days curing are unsuitable for judge environmental paints, particularly oil-based paints.

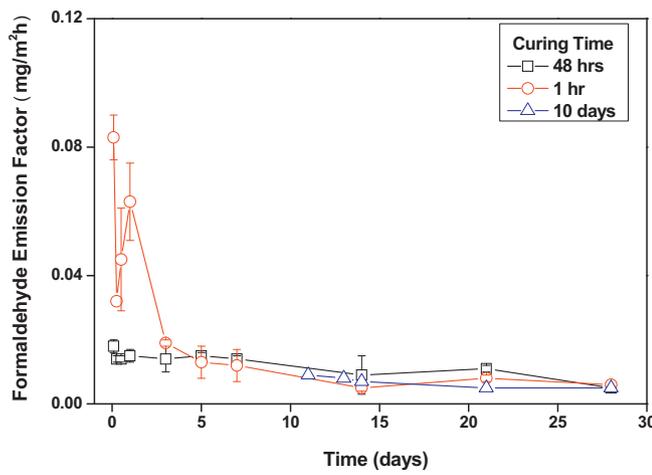
Fig. 3 shows the emission factors of formaldehyde. Oil-based paints reached a maximum emission factor after 6 h with 24 h cur-



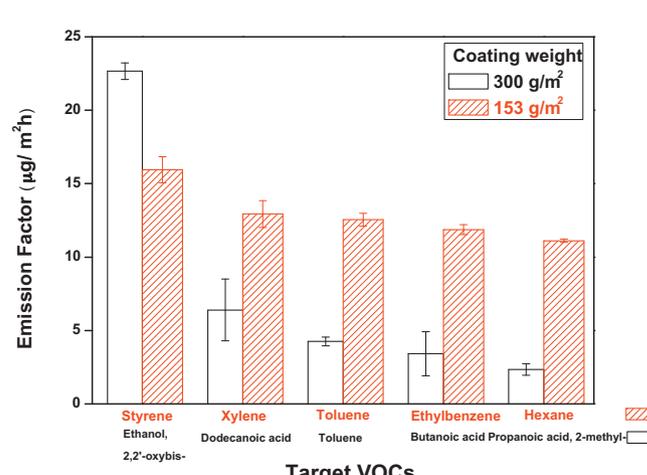
a Oil-based paint



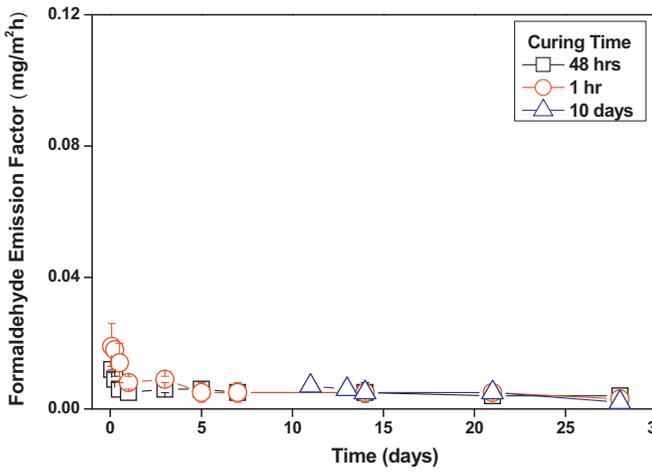
a Oil-based paint



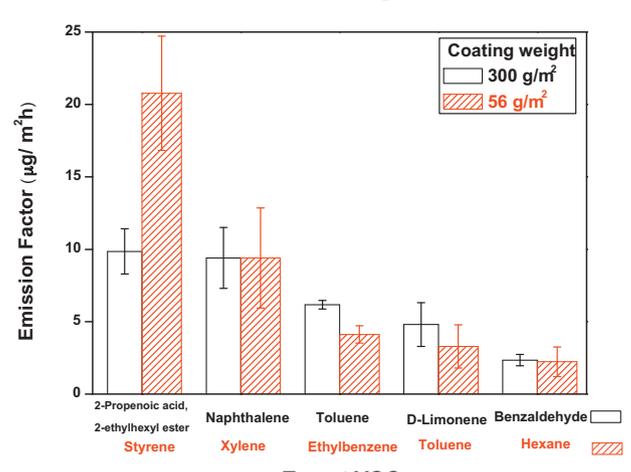
b Emulsion paint



b Emulsion paint



c Water-dispersion paint



c Water-dispersion paint

**Fig. 3.** Emission factors of formaldehyde according to the pre-conditioning time: 24(48)h, 1 h, and 10 days.

**Fig. 4.** Emission factors of the target VOCs according to the coating weight.

ing. With one-hour curing, the maximum emission factor appeared after 12 h, and the emission factor after 10 days curing was very low throughout the entire test period. In emulsion paints and water-dispersion paints, the emission factor of formaldehyde was similar and very low, with a range of 0.12–0.002 mg/m<sup>2</sup> h throughout the entire test period. The emission factor of formaldehyde also had no

connection with the pre-conditioning time. The curing time had no impact on the emission factor because these paints had no source compounds that emitted formaldehyde. The emission factor for all periods was quite low, but formaldehyde emission was stable after approximately 7 days.

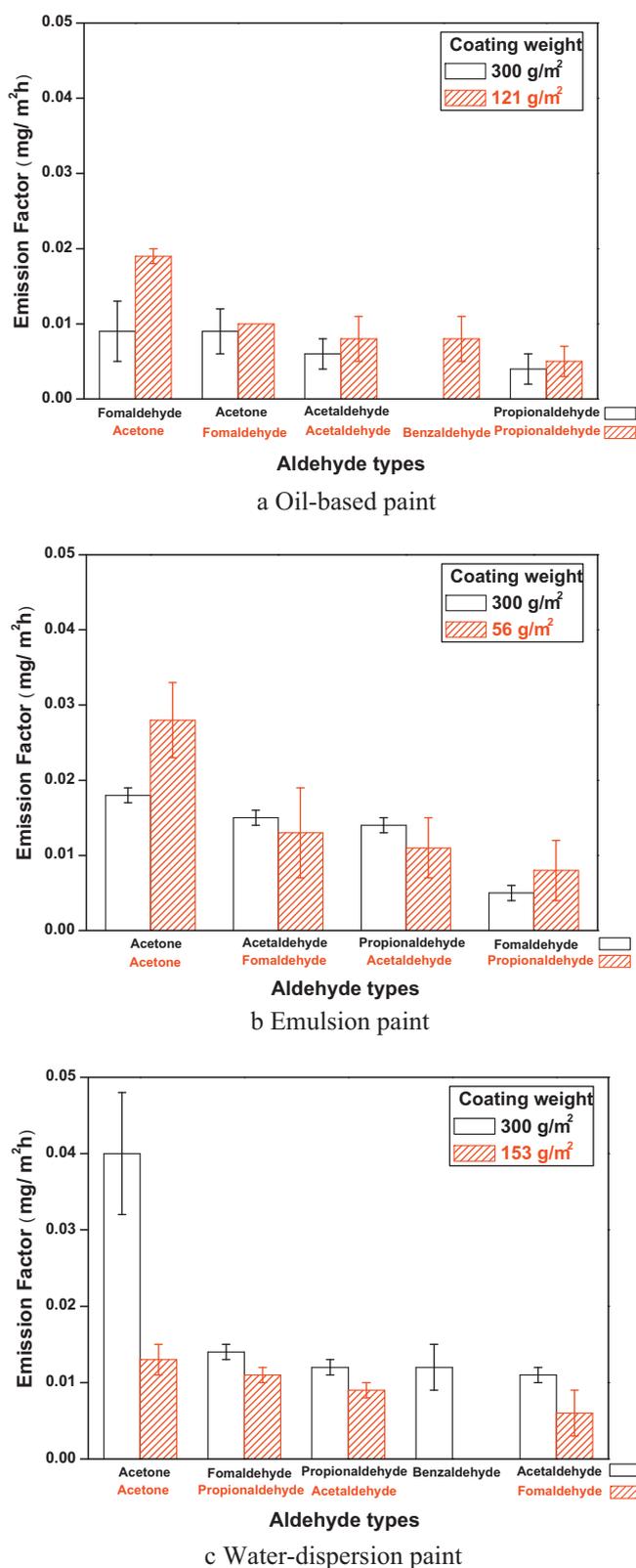


Fig. 5. Emission factors of the aldehyde types according to the coating weight.

### 3.2. Emission factor of target VOC according to coating weight

The emission factors of TVOC and formaldehyde from paint coated at 300 g/m<sup>2</sup> were markedly higher than those from all samples coated with the weight proposed by the manufacturers after 24 (48)h curing over the entire test period. The emission factor

of TVOC from all paints began to stabilize after approximately 7 days regardless of the coating weight after 24(48)h curing. The Korean standards regulate that paints be measured and analyzed 3 days after installation. However, in this study, the emission factors of TVOC from the paints began to stabilize 7 days after installing the sample. Fig. 4 shows the emission factors of the VOCs 7 days after installing the sample. All three paints (oil-based, emulsion and water-dispersion) showed different emission factor according to the coating thickness. Because the coating weight is affected by the coating thickness, optimal coating conditions for an emission test is a critical issue for liquid samples like paints. Therefore, an optimal test condition must be established for paints.

Fig. 5 presents the emission behaviors of the individual aldehyde types other than formaldehyde. These behaviors were determined for aldehyde types at coating weights of 121 g/m<sup>2</sup> and 300 g/m<sup>2</sup> in oil-based paint. The aldehyde types emitted in large quantities at both coating weights were as follows: formaldehyde, acetaldehyde, acetone, propionaldehyde and benzaldehyde. These aldehyde types were released at higher rates for the 121 g/m<sup>2</sup> coatings than the 300 g/m<sup>2</sup> coatings, except for benzaldehyde, which was emitted only at 121 g/m<sup>2</sup>. In emulsion paint, the emission behavior of the aldehyde types was determined from the coating weights of 153 g/m<sup>2</sup> and 300 g/m<sup>2</sup>. The aldehyde types emitted at large quantities at both coating weights are as follows: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde and benzaldehyde. These aldehyde types were released at higher rates at 300 g/m<sup>2</sup> than at 153 g/m<sup>2</sup>, except for acrolein and benzaldehyde. Acrolein was emitted only at 153 g/m<sup>2</sup> and benzaldehyde at 300 g/m<sup>2</sup>. In the water-dispersion paint, emission behaviors were determined for aldehyde types at coating weights of 56 g/m<sup>2</sup> and 300 g/m<sup>2</sup>. The aldehyde types emitted largely at both coating weights are as follows: formaldehyde, acetaldehyde, acetone, propionaldehyde and benzaldehyde. Other aldehyde types were released at higher rates for coatings of 121 g/m<sup>2</sup> than at 300 g/m<sup>2</sup>, except for acetone.

## 4. Conclusions

Under the 24(48)-h curing condition, the TVOC emissions for all paints were stable after a minimum of 7 days. The formaldehyde emission factor in all periods was quite low, but formaldehyde and TVOC emission was stable after approximately 7 days.

The weight of the paint coating affected the emission behavior of the target VOCs and aldehyde types; for the same paint, the main compounds emitted differed according to coating weight. In addition, the air flow rate in the chamber affected the emission behavior of the compounds according to the thickness of the paint coating.

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