

Effect of Base Board Material on the Emissions of Volatile Organic Compounds from a Natural Coating Material

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The effect of the base board on the emissions of volatile organic compounds (VOCs) from different coating materials was studied. Linseed oil, natural paint and natural wax were applied to four kinds of base board: aluminum, hardwood flooring, medium density fiber (MDF) and ceramic. These coating materials produce and emit carbonyl compounds due to aerial oxidation, and we compared such emissions when base boards of different material were used by measuring the emission rate with the small-chamber method. It was found that the base board controlled the oxidation process and, as a result, controlled VOC emissions.

Key words: Actual Measurement; Effect of Base Board; Volatile Organic Compound; Emission Rate

Introduction

The method for measuring the emission rates of VOCs from coating materials is prescribed in Section 9.3 of JIS A1901 which specifies a glass plate or an aluminum board as the base board. A standardized measurement method requires that the base board exerts no effect on the emission, and in that sense, the glass plate and the aluminum board are ideal. However, such base boards are rarely painted in reality, and the emissions are considered to vary with the other types of base board that are commonly used. The objective of this paper is to clarify the effect of base board on the emissions of the volatile organic compounds from a natural coating material.

Regarding the effect of the base board on the emissions from coating materials, Krebs et al.¹⁾ and Chang et al.²⁾ have reported that when latex paint was applied to plaster board, glycols were emitted over a long period of time due to diffusion within the plaster board. Martina et al. have reported on the effectiveness of priming as a countermeasure against the emissions of VOCs from a coating applied to furniture.³⁾ In life cycle analyses (LCA), Beetsma et al. have pointed out that the assessment of composition and painting systems should include an assessment

of the base board, from the viewpoint of maintaining the environment of the painting work.⁴⁾ After measuring VOC emissions when polyurethane paint was applied to plywood with a mizunara (Japanese oak) veneer, Sugasaki et al. have reported that the coated base board had a significant effect on emission and that this might be caused by permeation of the solvent into the base board.⁵⁾ Diaz et al. have studied the effect of base board on VOC emission after the application of oil or wax, and reported that oil and wax formed VOCs due to aerial oxidation, the base board controlled the oxidation reaction and, as a result, the base board controlled the emission of VOC.⁶⁾

Apart from the foregoing report by Diaz et al., however, there are few examples of studies comparing the difference in VOC emissions by different kinds of base board. In order to clarify the effect of the base board on emission, we applied coating materials to four kinds of base board, aluminum, hardwood flooring, MDF and ceramic, and compared the rates of emissions. Furthermore, some coating materials can readily permeate the base board and some cannot, which may produce significant discrepancies in the effect of the base board on emission. In order to monitor this effect for different coating materials, we chose natural paint and its principal ingredient, linseed oil, as coating materials that can easily permeate the base board, and chose natural wax as one that cannot.

1. Experimental

1.1 Test Samples

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The aluminum used as a base board was a metallic sheet, the hardwood flooring was pure tamo (Japanese ash), which is said to produce relatively few VOC emissions⁷⁾, the MDF board was commercially available and manufactured by Eidai Sangyo Co., and the ceramic board was "Moiss" manufactured by Mitsubishi Materials Kenzai Co. We chose the aluminum as the standard base board prescribed by JIS A1901, and the hardwood flooring and the MDF as the base boards usually painted, and the ceramic board as the representative of inorganic material boards. Each of these four samples was cut into 165 x 165mm pieces. The general physical properties correspond to some of these base boards have been published in the data book⁸⁾. We introduce the data in Table 1. Bulk specific gravity of "Moiss" is 0.6~0.9⁹⁾.

The linseed oil applied was the non-break type manufactured by Chubu Sunday Co.; the natural paint was "Kaldet" manufactured by Livos Co. (subsequently referred to as natural paint K); and the natural wax was "Healthy Wax" manufactured by Ohta Yushi Co. (subsequently referred to as natural wax A). The principal components of the ceramic board, natural paint K and natural wax A are shown in Table 2.

Table 1 Reference physical properties of the base boards in the data book⁸⁾

Material	Density (Kg/m ³)	Porosity (m ³ /m ³)	Specific heat (J/(Kg · K))
Aluminum	2700	—	800
Hard wood	650	0.47	1500
MDF	750	0.64	1880

Table 2 Principal components of Moiss ceramic board, natural paint K and natural wax A

Sample	Principal components
Moiss ceramic board	Vermiculite, calcium silicate
Natural paint K	Linseed stand oil, natural resin, flaxseed oil, orange peel oil
Natural wax A	Rice wax, perilla oil, tea tree oil

1.2 Measurement method

The small-chamber method was used according to JIS A1901 to measure the carbonyl compounds that were emitted from the coating materials when applied to each of the base boards. The small-chambers used were 20L models manufactured by Adtec Co. which were set to a temperature of 28±1°C, a humidity of 50±2% and an air exchange rate of 0.5/h (air flow rate of 167

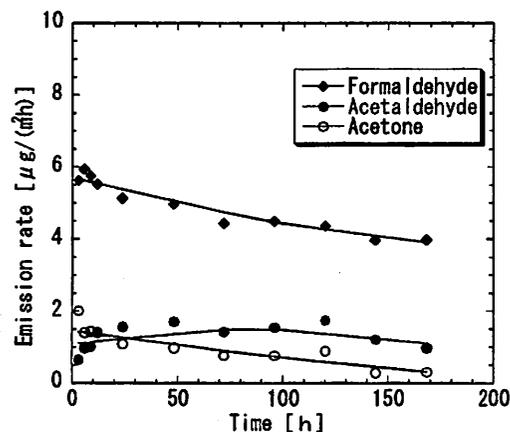


Fig. 1 Emissions of carbonyl compounds from hardwood flooring board

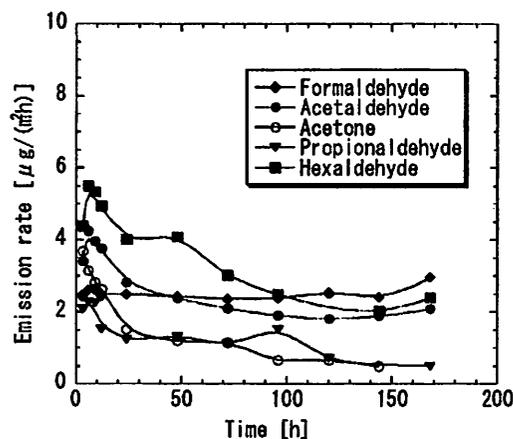


Fig. 2 Emissions of carbonyl compounds from MDF board

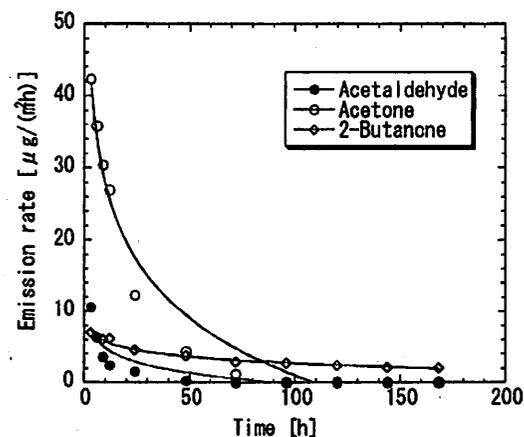


Fig. 3 Emissions of carbonyl compounds from ceramic board

mL/min). We applied 1g of each coating material to a 148 × 148mm area of a base board by a brush as speedily and uniformly as possible, and placed two painted samples with their uncoated areas covered by a sealing box into one small-chamber as speedily as possible. The peaces were set horizontally at a distance of 30 mm apart by a spacer. The loading rate in this measurement was 2.2m²/m³. We collected the carbonyl compounds in the exhaust air at predetermined times in a Sep-Pak DNPH collection cartridge manufactured by Waters Co., extracted the compounds with 5mL of acetonitrile, and analyzed them by liquid chromatography. The column used was a Crest Pak C18S (Jasco Co.) 4.6mm in diameter and 150mm long, the temperature was 40°C, detection was by a spectrophotometric sensor with a wavelength of 360nm, the eluting solvent was a 55% aqueous solution of acetonitrile a flow rate of 0.8mL/min, and the sample injection volume was 20μL.

2. Results and Discussion

2.1 Emissions from the Base Boards

The emissions of carbonyl compounds from the hardwood flooring board, MDF board and ceramic board are shown in Figs. 1 to 3. In these figures, FA, AA, AON, PA, 2BON and HA respectively represent formaldehyde, acetaldehyde, acetone, propionaldehyde, 2-butanone and hexaldehyde. In each case, the emission rate initially declined somewhat as the time progressed. Each of the base boards used in our tests was kept in the laboratory for a considerable period of time, so such a decline in emission rate was not expected. However, probably because the conditions of temperature and humidity inside the small-chambers were higher than the conditions inside the room where they had been kept, some emissions might have increased for a while. Concerning FA, each base board was of F☆☆☆☆ grade. FA and AA were emitted from the hardwood flooring, HA, FA and AA from the MDF board, and AON and 2BON from the ceramic board. Emissions of carbonyl compounds from these base board materials were therefore detected, although the quantities emitted were very low compared with those from the coating materials.

2.2 Effect of the Base Board on the Emissions from Linseed Oil

The emission rates of carbonyl compounds from linseed oil applied to the aluminum, hardwood flooring, MDF and ceramic base boards are respectively shown in Figs. 4 to 7. Fig. 4 is taken from a previous report.¹⁰⁾ PA, HA and AA, in descending order of quantity, were emitted from the linseed oil

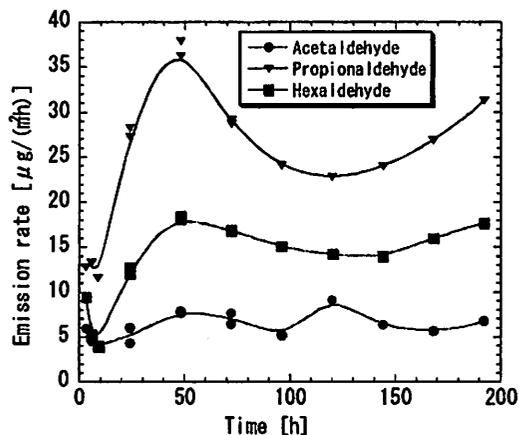


Fig. 4 Emissions of carbonyl compounds from linseed oil applied to aluminum board¹⁰⁾

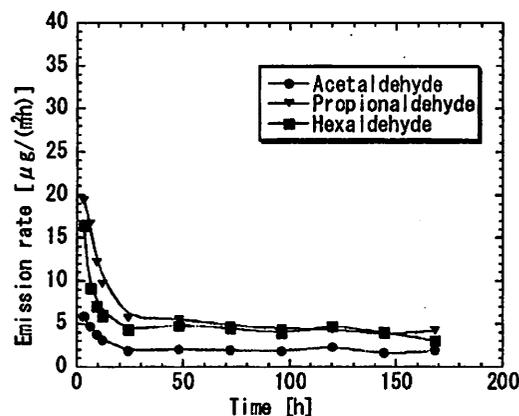


Fig. 5 Emissions of carbonyl compounds from linseed oil applied to hardwood flooring board

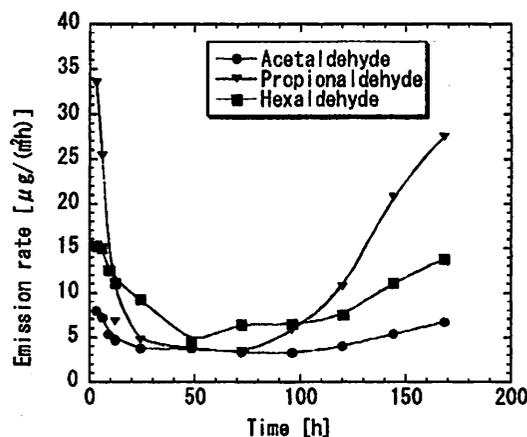


Fig. 6 Emissions of carbonyl compounds from linseed oil applied to MDF board

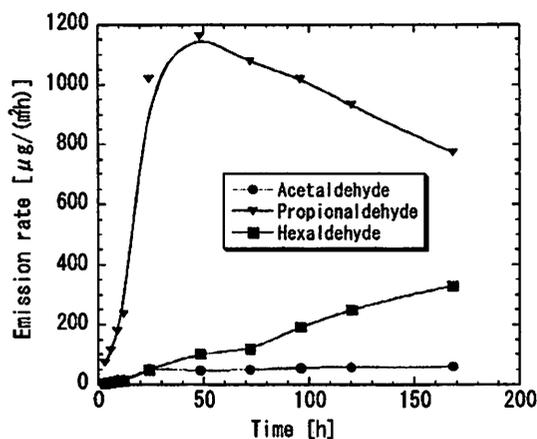


Fig. 7 Emissions of carbonyl compounds from linseed oil applied to ceramic board

coating on every base board. These aldehydes are considered to have been formed by the oxidation of specific components of the linseed oil.^{10), 11), 12)}

The emission rates of aldehydes with the aluminum base board initially increased. The initial increases of the emission rates of aldehydes may be caused by the aldehydes existing before the painting. In contrast, the emission rates of aldehydes initially decreased when the base board was hardwood flooring, and the rates remained at these reduced levels after the first day. It follows that the aerial oxidation of linseed oil was being inhibited when coated on the hardwood flooring board. This may be attributable to the restricted contact between the linseed oil and the air that resulted from linseed oil, being a liquid, deeply permeating the flooring board. As time progressed, oxidation would probably have begun and the emission rates of aldehydes would have started to increase.

In respect of the MDF board, the emission rates of aldehydes initially declined, just as they did with the hardwood flooring, but then began to increase from the fifth day. The linseed oil permeated the MDF board, as it did the hardwood flooring board, leading to the inhibition of aldehyde formation due to restricted contact between the linseed oil and air. The reason for the start of oxidation after five days may be that MDF is coarser than hardwood flooring and therefore more porous, eventually enabling better contact between linseed oil and the air. The flooring board used as the base board in our experiment corresponds to the hard wood in Table 1⁸⁾. The porosity of hard wood is lower than that of MDF.

When linseed oil was applied to the ceramic board, the aldehyde emission rates rose sharply, being a different order of magnitude from the rates with the other three base boards. In particular, the PA emission rate reached a level of 1200μ

$g/(m^2h)$ after the second day. This is presumed to have been due to the presence of catalytic components within the "Moiss" ceramic base board that accelerated the aerial oxidation of linseed oil.

2.3 Effect of the Base Board on the Emissions from Natural Paint

The emission rates of carbonyl compounds from natural paint K applied to the aluminum, hardwood flooring, MDF and ceramic base boards are respectively shown in Figs. 8 to 11. VA in these figures refers to valeraldehyde. With every base board, PA, HA, AA, VA and 2BON were emitted from natural paint K.

With the aluminum base board, there was an initial increase in the emission rates of these carbonyl compounds, particularly that of PA which increased to $1,500 \mu g/(m^2h)$, although this rate quickly decreased too, falling to $400 \mu g/(m^2h)$ after two days. The emission rates of all these carbonyl compounds subsequently continued to fall gradually.

Natural paint K applied to hardwood flooring resulted in emission rates of carbonyl compounds to initially increase, as with the aluminum base board, and then to decrease after one day. However, the emission rates with the hardwood flooring base board were lower overall than those with the aluminum base board. This may have been because natural paint K, like linseed oil, is a liquid which could permeate the hardwood flooring, limiting the aerial contact of the paint and inhibiting its oxidation. The emission rates of carbonyl compounds showed almost the same tendency when natural paint K was applied to the MDF board as those when it was applied to hardwood flooring board. This may have been because natural paint K permeated the MDF board like the hardwood flooring board, thus inhibiting contact between the paint K and the air.

When natural paint K was applied to the ceramic board, the emission rates of the carbonyl compounds initially rose sharply, as they did when linseed oil was applied. This seems to have been result of the catalytic action of a component in the ceramic board accelerating the aerial oxidation of the compounds of the natural paint K.

We next compare the results for natural paint K with those for linseed oil. Although the emission rates initially increased when each coating was applied to the aluminum board, the increases were far greater with natural paint K (Fig. 8) than with linseed oil (Fig. 4). Natural paint K is therefore considered to have been far more easily oxidized. We can reach the same conclusion when the paint was applied to the hardwood flooring and MDF base boards. The emission rates from natural paint

K initially increased (Figs. 9 and 10), while the emission rates from linseed oil initially decreased (Figs. 5 and 6). It is evident that natural paint K was more easily oxidized than linseed oil. Whereas the emission rates from linseed oil differed considerably when applied to the aluminum (Fig. 4) and ceramic board (Fig. 7), pointing clearly to the oxidation-accelerating effect of the ceramic material, the emission rates from natural paint K were almost the same between the aluminum board (Fig. 8) and the ceramic board (Fig. 11). This absence of a significant difference between the ceramic board and the aluminum board can be attributed to the fact that natural paint K was easily oxidized so that its oxidation proceeded fully from the start, even when applied to the aluminum board. Being less easily oxidized than natural paint K, linseed oil was not oxidized much when applied to the aluminum board, but is presumed to have been oxidized notably and immediately due to the catalytic effect of the ceramic material when applied to the ceramic board.

Natural paint K was thus easily oxidized, so that it might easily form a coating film, if oxidative polymerization should form such a coating film.¹²⁾ It is considered that natural paint K may be manufactured to have this characteristic, a requirement of any paint. Linseed oil that was applied to the hardwood flooring board or the MDF board permeated the base board and so the oxidation was checked, but when natural paint K was applied, oxidation occurred from the initial phase, as can be seen in Figs. 9 and 10. Natural paint K may thus quickly form a coating film, even on such base boards as the hardwood flooring board or the MDF board. Figs. 5 and 6 show that a coating film of linseed oil was formed more slowly than that of natural paint K when applied to these base boards. Linseed oil

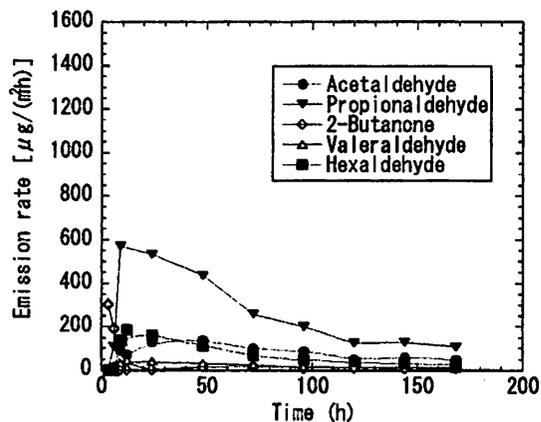


Fig. 9 Emissions of carbonyl compounds from natural paint K applied to hardwood flooring board

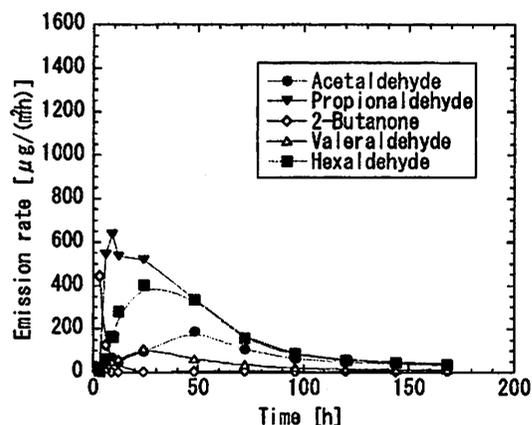


Fig. 10 Emissions of carbonyl compounds from natural paint K applied to MDF board

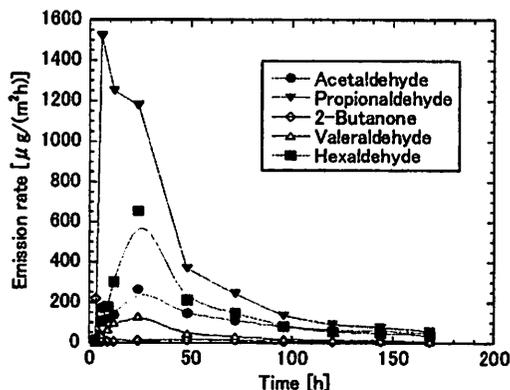


Fig. 8 Emissions of carbonyl compounds from natural paint K applied to aluminum board

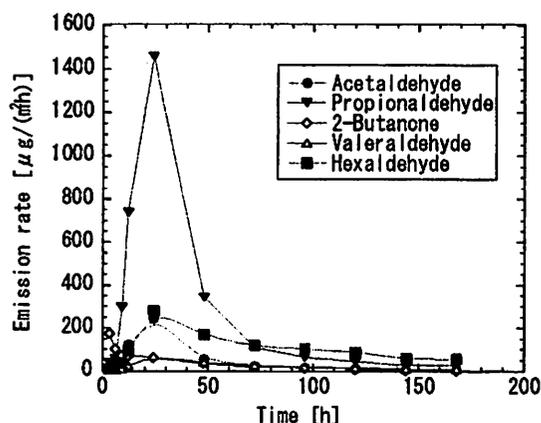


Fig. 11 Emissions of carbonyl compounds from natural paint K applied to ceramic board

contains a large amount of unsaturated fatty acids, so linseed oil should be easily oxidized. On the contrary, the oxidation of linseed oil started later than that of natural paint K, probably because the antioxidant contained in linseed oil. Linseed oil is likely to have contained more antioxidant than natural paint K, because the linseed oil used was not heat treated.

2.4 Effect of the Base Board on the Emissions from Natural Wax

The emission rates of carbonyl compounds from natural wax A applied to the aluminum, hardwood flooring, MDF and ceramic base boards are respectively shown in Figs. 12 to 15. PA, HA, AA and other compounds were emitted from natural wax A applied to all the base boards. The emission rates of these compounds initially fell, but then increased from the third day when aluminum was used as the base board, contrary to the initial increase in emission rate when linseed oil or natural paint K was applied to the aluminum board. These results indicate how natural wax A did not readily undergo aerial oxidation.

The emission rates of the foregoing carbonyl compounds initially fell when natural wax A was applied to the hardwood flooring board, just like the case with the wax applied to the aluminum board. Oxidation began after three days with the aluminum board, and began after five days with the hardwood flooring board. This difference can be attributed to the inhibiting effect on oxidation of the hardwood flooring board. Once oxidation had begun, the PA emission rate increased to a high level, because of the long period of oxidation-inhibition. When the wax was applied to the MDF board the oxidation-inhibiting effect was less than that obtained with the hardwood flooring board and similar to that obtained with the aluminum board. The emission rates when natural wax A was applied to

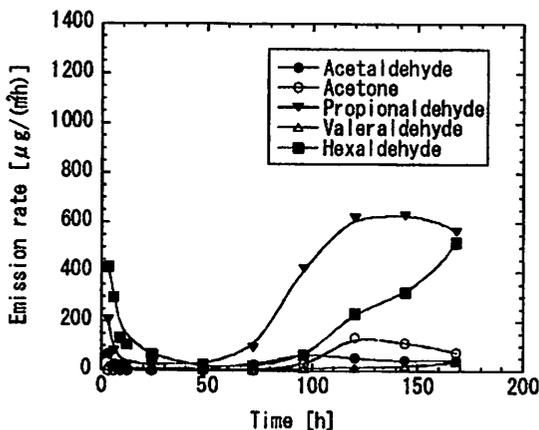


Fig. 12 Emissions of carbonyl compounds from natural wax A applied to aluminum board

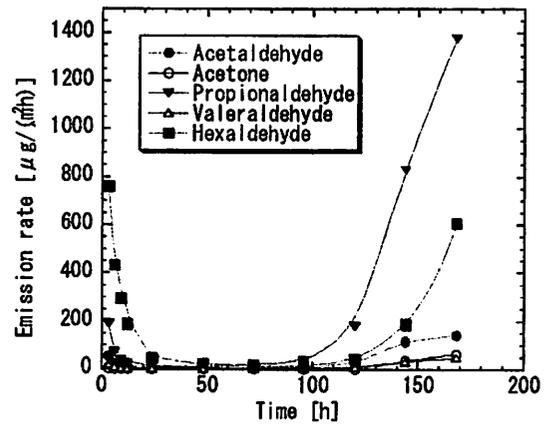


Fig. 13 Emissions of carbonyl compounds from natural wax A applied to hardwood flooring board

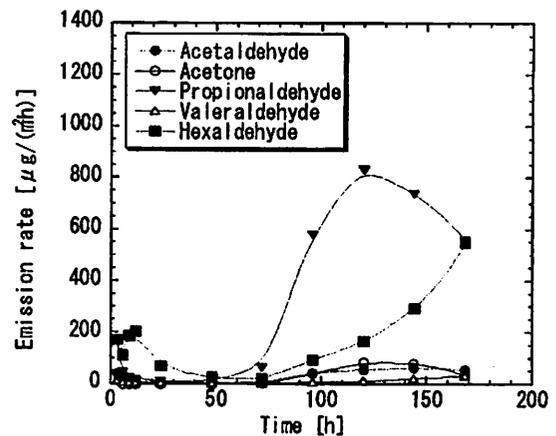


Fig. 14 Emissions of carbonyl compounds from natural wax A applied to MDF board

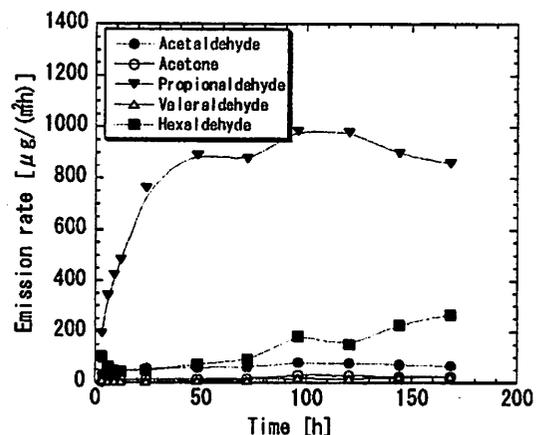


Fig. 15 Emissions of carbonyl compounds from natural wax A applied to ceramic board

the ceramic board initially increased, unlike the effect with the other three base boards, providing evidence for the oxidation-accelerating effect of the ceramic material.

We next compare the overall results for natural wax A with those for natural paint K. The emission rates of the carbonyl compounds from natural wax A initially fell, except when applied to the ceramic board, and then increased with time, whereas the emission rates from natural paint K progressively increased from the start with every base board. This shows the difference in properties between the two coatings, natural paint K being aeri ally oxidized quickly and natural wax A being aeri ally oxidized relatively slowly. This difference would have been due to the oils in wax A containing a smaller amount of unsaturated fatty acids than those in linseed oil, which was the principal component of natural paint K, so that wax A was difficult to oxidize. This difference can also be explained by the fact that a paint material must dry and quickly form a membrane, and so should be oxidized quickly, whereas wax does not need to dry quickly and so is manufactured not to be oxidized quickly under the effect of substances such as antioxidants¹⁰. Further more, wax A may not be oxidized easily, because the wax is not liquid and is not expanded easily, so that the contact between the wax and an air is restricted.

The emission rates of carbonyl compounds from each material coating the ceramic base board initially increased, slow-oxidizing natural wax A did not subsequently show any decrease, easily oxidized natural paint K showed a sharp decrease, and linseed oil was between the two. The likely reason for this is that easily oxidized substances form a membrane on their surface more quickly, and the rate-determining process of VOC emission shifts to the diffusion process of VOC through this membrane, consequently the emission rates decrease^{10, 13, 14}.

We next compare the overall results for natural wax A with those for linseed oil. The temporal changes in the emission rates from linseed oil when applied to the aluminum board (Fig. 4) are completely different from those when applied to the hardwood flooring board (Fig. 5) or the MDF board (Fig. 6). In the case of natural wax A, however, the temporal changes in the emission rates when applied to the aluminum board (Fig. 12) are similar to those when applied to the hardwood flooring board (Fig. 13) or the MDF board (Fig. 14). The reason for these results is considered that linseed oil, being a liquid, deeply permeated the hardwood flooring board or the MDF board, unlike natural wax A which is not a liquid and therefore did not permeate deeply. When linseed oil permeates these base boards,

contact between the linseed oil and the air is limited, significantly inhibiting oxidation and thereby increasing the differences of a temporal changes in emission rates. Natural wax A, on the other hand, did not permeate the base board very much, so there would not have been much difference in the temporal changes of emission rates among the base boards. Furthermore, although natural paint K is a liquid and permeated the base board, the oxidation-inhibiting effect of the hardwood flooring board (Fig. 9) and the MDF board (Fig. 10) was not apparently much different from that of the aluminum board, because the paint was easily oxidized. Even so, the oxidation of natural paint K was more significantly inhibited when applied to the hardwood flooring board (Fig. 9) or the MDF board (Fig. 10) than when applied to the aluminum board (Fig. 8).

Summary

We applied three different coating materials, linseed oil, natural paint K and natural wax A, to four different base boards of aluminum, hardwood flooring, MDF and ceramic, and studied the effect of the base board material on the emissions of carbonyl compounds from each coating material. We obtained the following conclusions:

- (1) Coating materials are oxidized by the air to produce and emit carbonyl compounds. Natural paint K is easily oxidized, natural wax A is not easily oxidized, and linseed oil lies somewhere between the two. The base board controls the rate of this oxidation process and as a result controls the emissions of VOCs.
- (2) The hardwood flooring and MDF boards inhibited this oxidation compared with aluminum board, and therefore had a greater inhibiting effect on the emissions of carbonyl compounds. This inhibition of the oxidation reaction is considered to be due to the coating material permeating the base board and consequently having limited aerial contact.
- (3) The "Moiss" ceramic base board promoted the emissions of VOCs. This effect seems to have been due to the catalytic action of a component in the ceramic board accelerating the aerial oxidation.
- (4) The greater the quantity of unsaturated fatty acids contained in the coating material, the more the emissions of VOCs from the coating material are influenced by the type of base board.
- (5) Liquid type of coating material, such as linseed oil and natural paint K, easily permeates the base board and inhibits oxidation, consequently the effect of the base

board on the emission is remarkable. Conversely, in the case of the paste type of coating material, such as natural wax A, the effect of the base board on the emission is not so remarkable.

*This paper is an edited version of the following oral presentation⁹⁾ with additional data.

Deisy Diaz, Yasuhisa Kobayashi, Toshihiro Nakai, Tatsuaki Tanaka and Kikue Kubota: Effect of the Base Board on the VOCs Emissions from the Painted Natural Sample, Conference Summary of the Society of Heating, Air-conditioning and Sanitary Engineers of Japan (Sapporo) (2005-8), pp81-84

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(Received October 1, 2007)

天然系塗布材からの揮発性有機化合物放散 に及ぼす下地の影響

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キーワード：実測・下地の影響・揮発性有機化合物・放散速度

塗布材の塗布における揮発性有機化合物の放散において、下地が放散に及ぼす影響を検討した。塗布材としては特に天然系のもを対象とした。4種類の下地、アルミ板、フローリング板、MDF板及びセラミック板に3種類の塗布材、亜麻仁油、自然塗料及び自然ワックスを塗布し、塗布材から放散したカルボニル化合物を小形チャンパー法によって測定した。下地の違いによる放散速度の経時変化の違いを比較することにより、これら下地が揮発性有機化合物の放散に及ぼす影響を調べた結果以下の結論を得た。

1) 塗布材は空気により酸化されてカルボニル化合物を生成し放散する。自然塗料Kは酸化を受けやすく、自然ワックスAは酸化を受けにくく、亜麻仁油はその中間である。下地はこの酸化反応の過程を支配し、結果的に揮発性有機化合物の放散を支配する。

2) アルミ板と比べ、フローリング板とMDF板は酸化反応を抑制し、カルボニル化合物放散を抑制する効果があった。この酸化反応の抑制は塗料のしみ込みにより空気との接触が制限されるためと考えられる。

3) セラミック板“モイス”は揮発性有機化合物の放散を促進させた。この促進はセラミック板“モイス”に含まれる成分が空気酸化を促進させる触媒作用をしているためではないかと想定される。

4) 成分中に不飽和脂肪酸（沃素価の高い油脂）を多く含む塗布材ほど揮発性有機化合物の放散は下地の影響を受け易い。

5) 亜麻仁油や自然塗料Kのような液体の塗布材では下地にしみ込み易いので、放散に及ぼす下地の影響は大きい。逆に自然ワックスAのような糊状の塗布材では放散に及ぼす下地の影響は小さい。

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(2007年10月1日原稿受付)