# Improvement of IAQ by coating of chemical adsorptive polymer: formaldehyde-adsorption characteristics of the material and evaluation in its application

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**ABSTRACT**
A coating material, composed of an adsorptive polymer by graft polymerization was developed for removing odorous substances, such as formaldehyde from gases, liquids and solids. The coating material is a water-soluble emulsion and the adsorptive polymer as main component comprises a stable substrate such as cellulose having sulfonic and amino functional groups bonded to the substrate by graft polymerization. The performance of the material was analysed by a simple method of a small glass chamber with a circulation system to evaluate the ability of both sealing and adsorption of formaldehyde. The adsorption characteristics were examined to determine the adsorption isotherm. Chemical adsorption ability of the coating material for formaldehyde was proved by the result of the adsorption isotherm test and also a desorption test in atmosphere at low pressure. It was suggested that the addition of the coating material to styrene–butadiene/methyren–acrylamide adhesive before coating is available to decrease emission of formaldehyde from the adhesive. The ability of the adsorptive coating material in field test was evaluated by TEA-dish method to measure the emission rate from each part in a new house.

**INDEX TERMS**
Adsorption of formaldehyde; Emission rate; Adhesive; Coating

## INTRODUCTION

Improvement of IAQ by coatings is required when VOCs, especially formaldehyde, concentrations in a living place cannot be decreased by using other selected materials.

The required conditions of coating material are as follows: strength of coating membrane; adsorbent of formaldehyde; easy handling by brush, roller or spray; water soluble; non-coloured; economical. The adsorptive polymer by graft polymerization in the coating material was developed by Ohkawara in 1996. The effect of formaldehyde removal from the air in buildings was firstly confirmed by Hori *et al.*

In this paper, a study was made to clarify the characteristics of formaldehyde adsorption on the coating material and the adsorption efficacy of several kinds of the functional groups, which are bonded to same substrate by graft polymerization. Further, studies were made to clarify the effect of the adsorptive polymer in case of the addition to styrene–butadiene/methyrol–acrylamide adhesive, and sealing effect of the coating material to decrease formaldehyde emission from plywood 3 months after coating.

Sealing effect test for emission control and adsorption test for removal from the air was performed by a simple method of a small glass chamber with a circulation system, and in addition, by a field test at wooden houses.

## MATERIAL AND METHODS

### Material

The adsorptive polymer in the coating material was produced by the following procedures to bond several kinds of functional groups to a substrate such as cellulose. The mixture of

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acrylate 5 wt%, glucose 3 wt%, urea 6 wt%, ethanol 5 wt%, methyl meta-acrylamide 1.5 wt%, water 84.5 wt% and cellulose powder was prepared. After a polymerization initiator was added, radiation of $^{60}Co$ was carried out for several hours in inert nitrogen atmosphere. The produced material is a clear emulsion. The material was coated by a spray or a brush and dried for 24 h or more in the room.

**Adsorption Test Methods**

A small glass chamber of 6.5 l as shown in Figure 1 (1) was used to measure the adsorption isotherms of formaldehyde of the coating material. Formaldehyde was supplied by vaporization of formalin. It was carried out with two kind methods of a filter paper in the chamber and a sampling bag. Filter paper method is as follows: Two pieces of cellulose paper filter for chemical analysis, of 9 cm diameter, were inserted in the chamber. One of them was sample of the coating material and prepared after drying for 1 day after impregnation with the emulsion solution of 1 g. Another was a formaldehyde vaporizer where a fixed amount of formalin of 36–3.6% HCHO was dropped through the wall of upper cap with a microsyringe. Stirring with a microfan and circulation with a pump promoted vaporization of formaldehyde from the filter and its contact to the coating material. After 30–60 min, the chamber was heated at 60°C for 10 min in an air bath to remove formaldehyde from the inner surface. The concentration of formaldehyde in the chamber was measured at room temperature after 30 min. The experimental room was controlled at 20–23°C, but the humidity was not controlled. In parallel, a control test with two pieces of the virgin filter was carried out. When the concentration was enough decreased, the addition of formalin was repeated.

The measurement was carried out with a detector tube for formaldehyde of 100–500 ml in sample volume or a Sep-pack DNPH cartridge HPLC method.

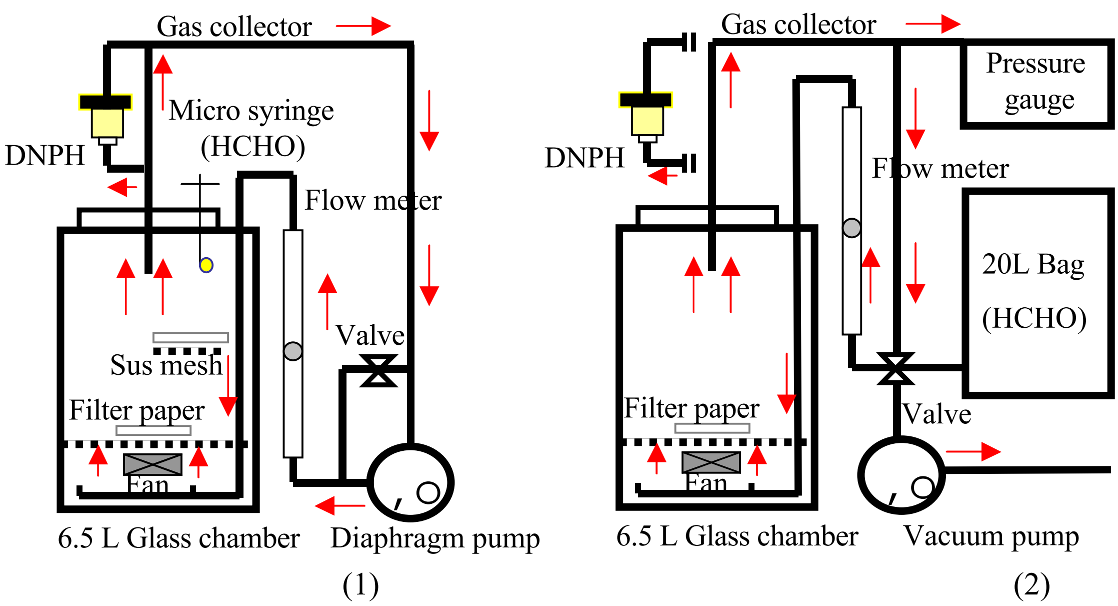


**Figure 1** Simple chamber system with a fan and a circulation pump (1) for filter vaporization method, and (2) for bag method.

The bag method is as follows: A polyester bag of 20 l was previously filled with formaldehyde of 1500–1800 ppm vaporized from bubbler filled with 36% formalin. Air in the glass chamber filled during insertion of filter paper of coating material was aspirated by a vacuum pump at 0.5 atm, and a valve was opened to introduce formaldehyde from the bag as shown in Figure 1 (2). A fan was then operated. The next procedure was the same as that of the filter paper method.

### Measurement of Emission Rate

In case of measurement of the emission rate from the styrene–butadiene/methyrol–acrylamide base adhesive, mixed with the adsorptive polymer, emission rate from a material sample was measured by a small glass chamber shown in Figure 1 and Sep-pack DNPH cartridge/HPLC method. A piece of aluminium sheet of 10 × 10 cm coated by the sample material of 1 g was inserted in the chamber and total amounts of formaldehyde emitted for 7 h was measured with the cartridge.

In the case of the emission rate measurement from plywood coated by the material, test piece of 10 × 5 cm plywood was measured by desiccator method of JIS after 1 day and 3 months, respectively.

Emission rate of formaldehyde in field: TEA-dish method developed by Hori *et al.* was applied for the measurement. It is a simple method for measurement of formaldehyde emission rate parallel to many points in field. The procedure is as follows: A filter of cellulose permeated with 10% tri-ethanol amine (TEA) is fixed on the inner surface of an aluminium dish 20 cm in diameter, which was put on surface of each part, such as ceiling and wall for 24 h.

Formaldehyde collected with the filter was determined by AHMT absorption method after abstraction to water. The concentrations of formaldehyde in fields were measured according to determination method of ISO 16000-3. The sampling was performed for 30 min after elapse of 5 h from the time when doors and windows had been shut.

## RESULTS AND DISCUSSION

### Effect of Each Functional Group on Adsorption and Comparison with the Other Coating Reagents

Adsorption efficiency of each kind of function groups comprised in the coating material was measured with a chamber shown in Figure 1 (1). Test material of 1 g was coated on a filter paper. The time course of formaldehyde concentration in the chamber for the samples is shown in Figure 2. There kinds of coating materials of the adsorptive polymers, bonded with acrylic acid and sodium *p*-styrensulfonate and *p*-styrensufonic amide, respectively, by graft polymerization were studied. The other coating reagent, adipo-dihydrazide mixed with calcium chloride and urea, was used for comparison.

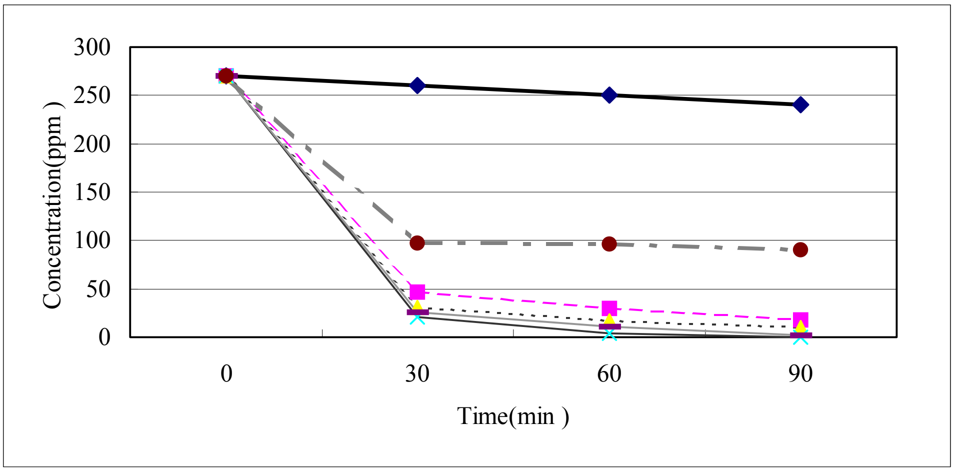


**Figure 2** Effect of different function groups and comparison with the other coating reagent. ♦ control; ● adipodihydrazide(kept for 3 months); ▪ sulfonic amide; ■ acrylic acid; × adipo-dihydrazide (fresh); ▲ sulfonate.

The colour of the sulfanilamide emulsion changed to yellow after a few days, though it was superior to the others in adsorption ability. Because of non-discoloration, acrylate type is used for the coating material. Adsorption ability of adipo-dihydrazide, having kept for 3 months in the bottle at the room temperature, was clearly decreased.

**The Adsorption Isotherms of Formaldehyde**

Figure 3 shows the relationship between concentration in equilibrium and amounts of adsorption. The amounts of adsorption were estimated by difference between equilibrium concentrations of coating material and that of control. The plot was obtained by changes in the amounts of addition of formaldehyde. The two kinds of method were used for addition of formaldehyde. Data at concentration more than 500 ppm in equilibrium were obtained only with filter vaporization. The difference in position of plot between the addition methods, however, was not found. Data show that the adsorption capacity is more than 60 mg/g in high concentrations, and at least 6 mg/g in concentrations less than 0.08 ppm. The result shows that amounts of adsorption do not extremely decrease in low concentration.

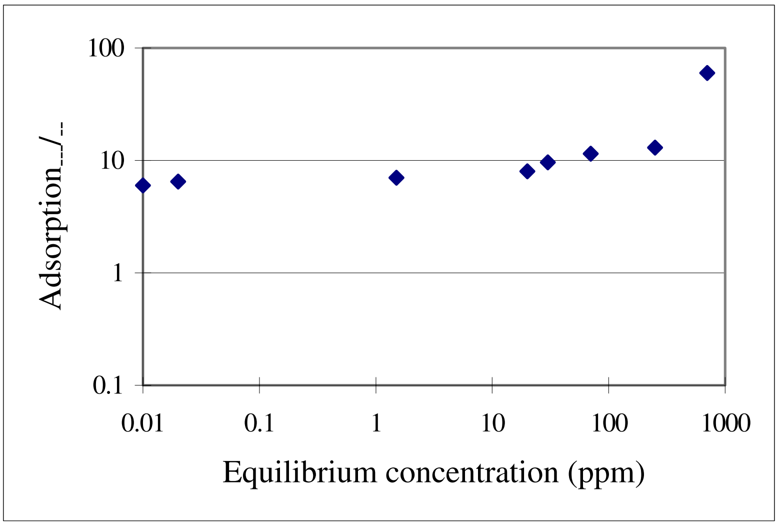


**Figure 3** Adsorption isotherm for formaldehyde of coating material by graft polymerization. The relationship between equilibrium concentration of formaldehyde and adsorption amounts.

On the other hand, the amounts of formaldehyde desorped from the formaldehyde-adsorbed material for approximately 20 min at 0.5 atmosphere and for 48 h in atmosphere, were measured with the apparatus shown in Figure 1(2) connected to a DNPH cartridge. An example data is as follows. Amount of adsorption: 24 mg prepared in the condition of five times introduction of 600 ppm; amounts of desorption: 0.63 and 0.71 µg; amounts of desorption; in control: 109 and 82 µg; blank: 0.37. It is assumed that formaldehyde detected in control and blank, respectively, comes from cellulose filter of physical adsorption and contamination of room air. The result shows that formaldehyde adsorbed in the coating material did not desorb at low pressure. Therefore, removal of formaldehyde by the coating material of emulsion prepared as shown in the section was caused by chemical adsorption.

Plywood is one of the building materials the gives out the most emission. Emission rate of formaldehyde from plywood, coated in two kinds of concentration of the coating solution was measured to evaluate sealing effect of formaldehyde after 3 months. The volume of coating material was 2 ml. The results in Table 1 show that the sealing effect continues at least for 3 months and formaldehyde was sealed even by the coating material of one-fifth dilute solution.

**Table 1** Emission rate of formaldehyde from plywood treated with the coating material after 1 day and after 3 months (with the desiccator method)

| Elapsed time after coating | Coating condition | | |
|---|---|---|---|
| | Control | 1/5 Dilution | Undiluted |
| 1 Day | 1.3 | 0.1 | 0.0 |
| 3 Months | 1.6 | 0.1 | 0.0 |

Control: 10 pieces of plywood of 5 × 10 cm, uncoated. The values are formaldehyde in mg/l of water of 300 ml in a share set in the desiccator. Formaldehyde emitted for 24 h was absorbed.

**Effect of Direct Addition on Emission Control from an Adhesive**
Styrene–butadiene/methyrol–acrylamide adhesive is used frequently as binder for materials in building construction. Emulsion of the coating material was directly added to the adhesive to control the formaldehyde emission from the adhesive. The emulsion solution of 10–50 mg was added for 1 g of the adhesive containing 47% styrene–butadiene and 1.5% methyrol acrylamide before the adhesive had been used. Figure 3 shows that ratio of emission from the adhesive of 3–5% addition case, was decreased by a factor of 1/5. The effectiveness of the addition after a long time and the relationship between addition ratios and adhesive strength would be studied to determine the best addition ratio.

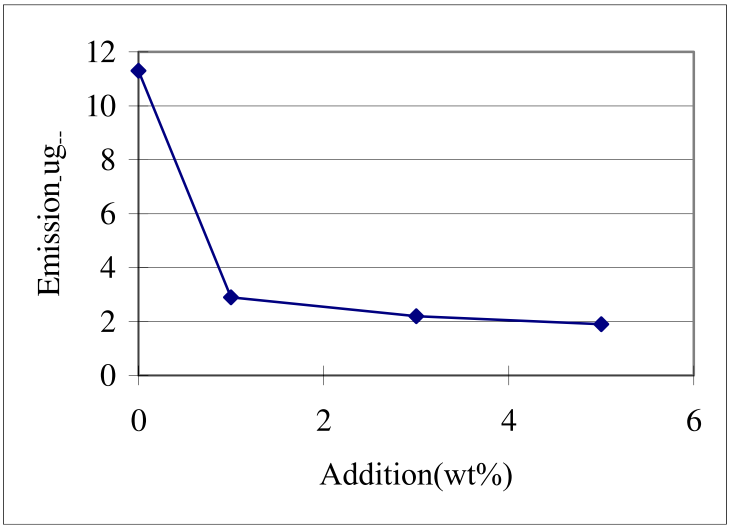


**Figure 3** The relationship between addition ratio of the material and emission amounts of formaldehyde for 7 h from the adhesive of 10 × 10 $cm^2$ in area.

**Field Test**
This coating material was applied in a new multi-family house of RC, 3LDK and 85 $m^2$ in area. The ceiling, wall and closet were treated with the coating material of 2.4 l in volume of undiluted solution and about 2 $g/m^2$ in dry weight on the surface. The floor of flooring and surface of cabinets in kitchen were not coated because of the hydrophobic nature of the surfaces. Emission rate of formaldehyde from individual parts was measured by TEA-dish method before and after coating. Emission amounts were estimated from product of emission rate of a part and area of the part. Emission rate was not measured in parts of small amounts of emission such as coated wall and ceiling. The results in Table 2 show that there is a decrease in the emission rates of the coated wall, ceiling and closet, and also that the floor heater emitted large amounts of formaldehyde from the surface.

As another example, the coating material was applied to a wooden house of 193 $m^2$. Before flooring material of 136 $m^2$ and plywood of 162 $m^2$ were used for the construction, back side of the flooring material and surface and back side of the plywood, respectively, had been treated with the coating material of 6.2 and 9.8 l. The formaldehyde concentration of room air, measured at time of just before finishing process, was 0.006 ppm, under the following conditions: room temperature, 10°C; RH, 54% and ventilation, 0.55 $h^{-1}$.

This coating material of the chemical-adsorptive polymer is valid to improve IAQ not only in new houses but also in already constructed 'sick houses'.

**Table 2** Comparison of emission rate and amounts of formaldehyde from parts before and after coating a new building

| Room | Parts | Emission rate | | | Area of part ($m^2$) | Emission amounts | |
|---|---|---|---|---|---|---|---|
| | | Before (μg/$m^2$/h) | After (μg/$m^2$/h) | Decrease (%) | | Before (μg/h) | After (μg/h) |
| Living | Wall | 1.9 | <0.5 | >73 | 42.5 | 80 | <21 |
| | Floor | 2.38 | 1.55 | 35 | 8.2 | 19.6 | 12.8 |
| | Floor (heat) | 12.3 | 7.84 | 36 | 19.3 | 237.5 | 151.4 |
| | Ceiling | 2.7 | <0.5 | >81 | 27.6 | 74.5 | <37 |
| | Closet | 14.65 | 1.23 | 92 | 0.7 | 10.5 | 0.9 |
| Private | Floor | 0.68 | 0.8 | 13 | 8.1 | 5.5 | 6.5 |
| | Wall | 2.6 | <0.5 | >80 | 26.1 | 67.6 | <13 |
| | Closet | 12.2 | <0.5 | >95 | 0.6 | 7.3 | 0 |
| Bed | Floor | 3.34 | 1.23 | 64 | 11.1 | 37 | 13.6 |
| (heating) | Wall | 1.96 | <0.5 | >76 | 30.1 | 58.9 | <30 |
| | Closet | 11.13 | 1.01 | 91 | 1.3 | 14 | 1.3 |

A part of floor area in living room was heated with a floor heater.

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