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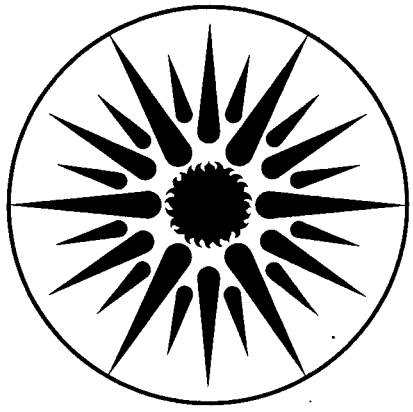

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EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM ADHESIVES WITH INDOOR APPLICATIONS

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ABSTRACT

Studies have shown that volatile organic compounds (VOC) emitted from architectural materials are potentially important indoor air pollutants in office buildings. In this study, we investigated emissions of VOC from 15 adhesives, both solvent and water based, that are used to construct and finish interiors of buildings. Adhesives were applied to an inert substrate and dried for 7 to 14 days. Vacuum extraction and cryogenic trapping of volatiles with analysis by gas chromatography/mass spectrometry were used for the qualitative and semi-quantitative determination of emissions of VOC. Emission rates of VOC were determined with a simple air exposure apparatus and collection of volatiles on charcoal adsorption tubes. Quantitative analyses were performed by gas chromatography with flame ionization detection. The major compounds emitted by the adhesives were toluene, styrene, and a variety of cyclic, branched and normal alkanes. The emission rates ranged from below the detection limit of 0.1 $\mu g\ g^{-1}\ h^{-1}$ for an individual compound for some adhesives to approximately 700 $\mu g\ g^{-1}\ h^{-1}$ of total alkanes for two water-based adhesives. The potential impacts of adhesives on indoor air quality were evaluated by applying a steady-state ventilation model which assumes well-mixed air to a hypothetical office space. The model results suggest that the two water-based adhesives are potentially important sources of indoor organic pollutants. More detailed studies of adhesives and other architectural materials are warranted to identify sources of contaminants and to develop source control strategies.

INTRODUCTION

Because cooling or heating of outdoor air used for ventilation consume a significant portion of an office building's energy budget, recent office construction practices have incorporated strategies to minimize ventilation requirements. These practices may be contributing to the growing number of non-specific health complaints by office workers that are thought to be related to poor indoor air quality. The underlying etiological agents for these complaints, as determined by the criteria of current health standards, are usually unknown. While few studies of organic contaminants in indoor air have been made in non-industrial buildings, fragmentary evidence suggests that these contaminants can be major contributors to poor indoor air quality (Berglund et al., 1982; Kreiss and Hodgson, 1983; Turiel et al., 1983). In the industrial indoor environment, exposure to elevated levels of many organic contaminants is known to have the potential to induce a variety of toxic and carcinogenic effects (American Conference of Governmental Industrial Hygienists, 1982; Peto and Schneiderman, 1981; Saffiotti and Wagner, 1976). Chronic exposure to these and similar compounds may also be occurring in non-industrial indoor environments due to the increased use of adhesives, sealants, surface-coatings and synthetic products in the construction, finishing, and furnishing of buildings. Therefore, it is important that the identities, sources, and concentrations of organic contaminants in office buildings be characterized.

Previous studies have indicated the potential of building materials to contribute to poor indoor air quality by the emission of volatile

organic compounds (VOC) (Miksch et al., 1982; Mølhave, 1982). One of these studies identified adhesives as a particularly important source of VOC in indoor air (Mølhave, 1982). Because of this, and because adhesives are suspected of causing widespread health complaints in at least one office building (Skeers-Brown, in press), we investigated the emissions of VOC from a broad range of architectural adhesives with indoor applications as part of a larger study of emissions from architectural materials (Hodgson et al., 1983).

METHODS

The 15 adhesives were selected for study based upon a broad range of applications and are formulated for bonding of carpets, vinyl floors and subfloor assemblies, and for miscellaneous architectural applications. Chemical classifications and applications for the adhesives are presented in Table 1.

In the first phase of the study, vacuum extraction with cryogenic trapping of volatile compounds was used as a screening procedure for the qualitative and semi-quantitative determination of emissions of VOC from adhesives. With this method, it was relatively easy to collect a sample of VOC in a small volume of organic solvent for direct injection into a gas chromatograph.

The vacuum-extraction apparatus consisted of a 125-ml vacuum-extraction flask, which contained the sample; a cold-finger trap cooled with liquid nitrogen; and a second cryogenic trap to prevent sample contamination by the vacuum system. The all-glass components were

connected with O-ring joints using Viton O-rings. A high-vacuum Teflon stopcock was used to isolate the cold-finger trap from the vacuum system. A second stopcock allowed the cold-finger trap to be brought to atmospheric pressure.

An adhesive sample was prepared for vacuum extraction by thinly applying wet adhesive to one side of each of three preweighed aluminum strips (1.2 X 4.7 cm). The strips were allowed to dry for 7 days at room conditions. The three strips were then reweighed, placed in a clean vacuum-extraction flask, and attached to the apparatus. The apparatus was evacuated to 0.01-0.1 Pa for two hours. At the end of the extraction period, the cold-finger trap was isolated from the vacuum system; liquid nitrogen was removed from the cold-finger trap; the system was brought to atmospheric pressure with air; the trap was opened; the cold-finger was washed with three or four 100 µL volumes of reagent grade carbon disulfide (CS_2); any acqueous layer was discarded; and the organic layer was transferred to a sample vial.

In the second phase of the study, a simple exposure apparatus was used to determine emission rates of VOC from adhesives. It consisted of a steel paint can (3.8 L) whose lid was fitted with two 6.4-mm stainless steel bulkhead fittings and an inlet tube that extended to near the bottom of the can. The test atmosphere was supplied from a cylinder of high-purity compressed air and was humidified by passing through two glass, gas-washing bottles filled with water. A critical orifice, flow-control device maintained a constant flowrate. Organic compounds were collected at the outlet of the can by a two-stage charcoal

adsorption tube.

An adhesive sample was prepared for the determination of VOC emission rates by applying adhesive to one side of a preweighed aluminum plate (10 x 10 cm) approximating the manufacturer's recommended coverage. The plate was allowed to dry for 9 to 14 days at room conditions, reweighed, and then tested for emissions.

Emission rates of VOC were determined at 23 to 25°C. Relative humidity was near 40% at 25°C. Flowrate through the chamber was 0.9 standard L m^{-1} (i.e., 14 air changes per hour). An adhesive sample was placed in a chamber and maintained at the test conditions for 1 h prior to sample collection. The sampling time was 2 h, unless more than 10% breakthrough of total VOC was detected on the second stage of the charcoal adsorption tube, in which case sampling was repeated with a 1-h period. Each adhesive was tested in duplicate.

The primary and secondary stages of the charcoal adsorption tubes were separately desorbed with CS_2 immediately after the collection of samples using the procedures recommended by the manufacturer (Supelco, Inc., 1977). To calculate emission rates, quantitative results for both sections of the charcoal sampling tubes were combined. Desorption efficiencies were assumed to be 100%; this assumption may have introduced a small negative bias into the results.

Compounds in the sample extracts were identified by gas chromatography/mass spectrometry (GC/MS); quantitative analyses are performed by gas chromatography with flame ionization detection (GC/FID).

The GC/MS system was a Finnigan MAT, Model 4023, (San Jose, CA, USA) equipped with a split/splitless syringe injector and a DB-5 fused-silica capillary column (30 m, 0.32 mm ID, 0.25 μm film thickness) from J&W Scientific, Inc. (Rancho Cordova, CA, USA). Compound identifications were made by comparing unknown spectra with spectra contained in the EPA/NIH Mass Spectral Data Base (Heller and Milne, 1978). With the exception of n-alkanes, toluene, and styrene, identifications are tentative since they were not verified by the use of standards.

The GC/FID system was a Hewlett-Packard, Model 5880A, (Palo Alto, CA, USA) equipped with a split/splitless syringe injector, and a DB-5 fused-silica capillary column (15 m, 0.32 mm ID, 1.0 μm film thickness).

RESULTS AND DISCUSSION

The results of the vacuum-extraction screening are presented in Table 2. Eight of the 15 adhesives, five of which are solvent based, continued to emit significant amounts of VOC after 7 days of drying; only trace amounts of VOC were detected in the extracts of the other adhesives. The major compounds in the extracts of the solvent-based adhesives were toluene, styrene and a variety of cyclic, branched and normal alkanes. Of these, toluene was the most abundant. A large variety of alkanes, was found in the extracts of three of the water-based adhesives. Two of the water-based adhesives, W-1 and W-2, both from the same manufacturer, emitted an almost identical complex mixture of normal and branched alkanes and cyclohexanes, indicating a common base. Two other adhesives, S-6 and W-3, emitted a mixture of higher

molecular-weight normal and branched alkanes. The similarity between S-6 and W-3 was unexpected since they are from different manufacturers and one is a solvent-based asphalt adhesive and the other a water-based natural rubber adhesive.

Emission rates of VOC were measured by the air exposure procedure for the eight adhesives determined by vacuum extraction to emit significant amounts of VOC. After drying periods of 9-14 days, only five adhesives had emission rates of individual compounds in excess of the minimum detectable value of approximately 0.1 $\mu g\ g^{-1}\ h^{-1}$ (Table 2). Three solvent-based adhesives had toluene emission rates between 0.6 and 62 $\mu g\ g^{-1}\ h^{-1}$, but no detectable amounts of other solvents were emitted by these adhesives. Two water-based adhesives, W-1 and W-2, had detectable emissions. These emitted the same complex mixture of normal and branched alkanes and cyclohexanes in the emission rate tests as they did in the vacuum-extraction screening tests. Additionally, the compounds were present in the two samples in approximately the same relative abundances indicating that emissions were far from equilibrium in both systems. Because of the complexity of the mixture from the water-based adhesive, emission rates were not determined for individual components. Instead, emission rates for total alkanes were calculated and are reported in Table 2. These emission rates ranged between 610 and 780 $\mu g\ g^{-1}\ h^{-1}$.

When an emission rate determined in this study ($\mu g\ g^{-1}\ h^{-1}$) is multiplied by the manufacturer's recommended rate of coverage ($g\ m^{-2}$) for that adhesive as listed in Table 3, an emission rate based upon surface

area to be glued is obtained ($\mu g\ m^{-2}\ h^{-1}$). These rates ranged from 0.14 to 7.4 mg $m^{-2}\ h^{-1}$ for toluene and from 140 to 180 mg $m^{-2}\ h^{-1}$ for total alkanes. Mølhave (1982) in his study of emissions for 42 commonly used building materials also found that adhesives could be significant sources of VOC. Specific emission rates for the two adhesives in his study, both water based, were 2.1 and 271 mg $m^{-2}\ h^{-1}$, in reasonable agreement with the results presented here.

MODELING

To assess the potential impacts of adhesives on indoor air quality, the emission rates determined in this study were used in a ventilation model applied to a hypothetical office space. Variations of this model, which assumes well-mixed air, have been used by others to model indoor pollutant concentrations (Traynor et al., 1982; Miksch et al., 1982; Mølhave, 1982). The model assumes that exfiltrating and indoor air have the same average pollutant concentration, and the simplified version used here ignores internal processes, such as reactive decay or adsorption on surfaces, that can increase pollutant removal rates. Furthermore, the emission rate is assumed to be independent of indoor concentration.

If it is assumed that the pollutant generation rate remains constant and that the pollutant is not present in the air entering the room (outdoor air almost always contains much less VOC than indoor air), the mass-balance equation describing a contaminant source inside a room with

well-mixed air reduces at steady-state to

$$C_{\infty} = \frac{G}{Q}$$

where C_{∞} is the concentration in the room (mg m^{-3}) which is attained as time goes to infinity; G is the pollutant generation rate (mg h^{-1}); and Q is the air infiltration and exfiltration rate ($m^3 h^{-1}$).

Guidelines established by the American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE, 1981) call for a minimum ventilation rate of 8.5 m^3 h^{-1} (5 ft^3 m^{-1}) per person in office spaces where smoking is not permitted and 34 m^3 h^{-1} (20 ft^3 m^{-1}) per person in spaces where smoking is permitted. For illustrative purposes, we have selected a hypothetical office with 100 m^2 of floor space and 7 workers. The recommended minimum ventilation rate for this office is then, either 59 or 238 m^3 h^{-1}, depending on whether smoking is permitted.

Steady-state concentrations of VOC were estimated for the hypothetical office using the manufacturers' recommended coverages for adhesives. The model results are shown in Table 3 along with Threshold Limit Values (TLVs) (American Conference of Governmental Industrial Hygienists, 1982) for toluene and representative alkanes. Because the model-dervied concentrations of alkanes produced by the water-based adhesives are a substantial fraction of the TLVs for alkanes, it appears that these adhesives have the potential to produce VOC concentrations of concern,

particularly in spaces with low ventilation rates. However, the model results must be interpreted with caution, since the adhesives would be overlaid with carpet or other coverings which would undoubtably reduce emission rates, while perhaps extending the duration of emissions. Also, it is unrealistic to assume perfect air mixing, and independence from indoor concentration.

CONCLUSION

This study of VOC emissions demonstrates the potential of adhesives to contribute to poor indoor air quality. Most notable were the high emissions of alkanes from two water-based adhesives which may be significant in certain applications. These results emphasize the need for additional studies of adhesives, in particular, and of other architectural materials, as well. A ventilation model was used to assess, on a relative basis, the potential indoor air quality impacts of carpet adhesives. Further studies in which the effects of product usage, environmental parameters and aging are determined will greatly improve the accuracy of estimates of the air quality impacts that can be made with such models. These estimates can be validated with environmental chamber studies and by measurements of VOC concentrations in office buildings where the relevant parameters are known. Combined laboratory and field studies of VOC emissions from architectural materials will also provide the organic compound identifications and the concentration ranges of these compounds that are needed for assessing potential health effects and risks to occupants. For architects and builders, these data will form an objective basis for the selection and safe utilization of

architectural materials in new or remodeled office buildings. These data are particularly essential for the realization of building energy-conservation goals since source control measures should be more cost effective than high rates of dilution ventilation for minimizing pollutant concentrations.

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Table 1. Classifications and applications of 15 adhesives investigated.

Adhesive	Chemical Base	Application
Solvent-based		
S-1	Synthetic rubber	Rigid plastic foams to walls, ceilings
S-2	Unspecified polymer	Styrene, polyurethane, cork, celotex, carpet
S-3	Synthetic rubber	Plasticized rubber, vinyl carpet
S-4	Synthetic rubber	Rigid styrene, polyurethane foam to other substrates
S-5	Synthetic rubber	Rubber, vinyl cove base to walls
S-6	Asphalt	Roof shingles, masonry cracks
S-7	Unspecified polymer	Subfloor bonding
Water-based		
W-1	Synthetic rubber	Foam backed indoor & outdoor carpet
W-2	Synthetic rubber	Foam backed indoor & outdoor carpet
W-3	Natural rubber	Foam, sponge backed indoor & outdoor carpet
W-4	Natural rubber	Vinyl, vinyl laminate, rubber backed carpet
W-5	Unspecified polymer	All types of carpet
W-6	Unspecified polymer	Vinyl, vinyl asbestos tile
W-7	Unspecified polymer	Vinyl, vinyl asbestos tile
Epoxide		
E-1	----------	Metal, glass, ceramic, plastic

Table 2. Volatile organic compounds emitted by eight adhesives. Emission rates of toluene and total alkanes are given for selected adhesives.

Adhesive	Volatile Organic Compounds	Adhesive Coverage ug cm^{-2}	Drying Time (days)	Emission Rate (ug $g^{-1}h^{-1}$)
Solvent-based				Toluene
S-1	toluene; styrene	67.0	9	0.59
S-2	low-molecular-weight alcohol?;toluene	NA		
S-3	toluene	9.3	13	62
		8.3	13	48
S-6	n-decane; n-undecane; C_{10}-C_{11} branched alkanes (9+ compounds); C_{10} cyclohexanes (4 compounds)	NA		
S-7	methyl cyclopenthane; cyclohexane; toluene	43.2	11	2.4
		65.0	11	2.6
Water-based				Total Alkanes
W-1	n-octane; n-nonane; C_8-C_9 branched alkanes (7+ compounds); methyl cyclohexane; C_8-C_9 cyclohexanes (10+ compounds)	25.4	14	740
		28.5	14	760
W-2	Same as compounds W-1	33.6	14	610
		38.2	14	780
W-3	toluene; n-nonane; n-decane; n-undecane; C_{10}-C_{11} branched alkanes (9+ compounds); C_{10} cyclohexane	NA		

NA - not applicable

Table 3. Calculated steady-state concentrations of toluene and total-alkanes producted by adhesives applied to the floor area of a 100 m^2 hypothetical office space with seven workers.

Adhesive	Recommended Coverage ($g\ m^{-2}$)	Ventilation Rate Per Occupant 34 m^3h^{-1}	8.4 m^3h^{-1}	TLV ($mg\ m^{-3}$)
		Toluene Concentration ($mg\ m^{-3}$)		
S-1	245	0.06	0.25	375
S-3	120	2.8	11	
S-7	235	0.25	1.0	
		Total Alkane Concentration ($mg\ m^{-3}$		
W-1	240	76	310	1050-1600*
W-2	225	67	270	

* Range of TLVs for n-heptane through n-nonane.

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