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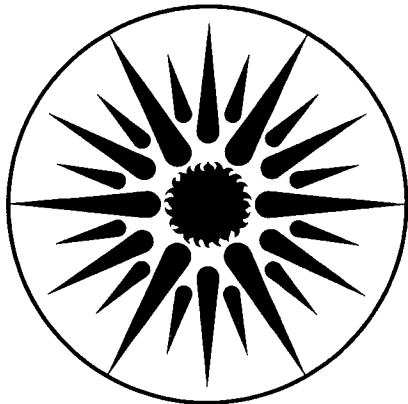
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September 1983

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EMISSIONS OF VOLATILE ORGANIC COMPOUNDS
FROM ARCHITECTURAL MATERIALS WITH INDOOR APPLICATIONS

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ABSTRACT

The objectives of this study were to (1) identify the major organic compounds emitted by some typical building construction and interior finish materials; (2) quantify emissions of organic solvents from representative adhesives that have indoor applications; and (3) evaluate methods for the rapid screening of architectural materials for organic emissions.

Organic compounds emitted by 15 building construction and interior finish materials and by 15 adhesives were identified by a vacuum-extraction screening procedure and gas chromatography/mass spectrometry. A total of 68 major compounds with molecular weights ranging from 94 to 458 were identified in the vacuum extracts of the construction and interior-finish materials. The lowest molecular-weight compounds among these were phenol, alkyl benzenes, naphthalenes and terpenes. The most frequently occurring compounds were plasticizers, dibutyl phthalate and 2,2,4-trimethyl-1,3-pentanediol di-*i*-butyrate. Toluene, styrene and a variety of cyclic and normal alkanes were identified in the vacuum extracts of the adhesives. The number of volatile compounds varied greatly among the materials: a carpet padding only emitted a single compound, while a synthetic textile wall covering emitted more than 60 compounds. Other wall and floor coverings and several adhesives also emitted relatively large numbers of compounds.

Emission rates of toluene and total alkanes from the adhesives were determined using a simple exposure apparatus. Exhaust air from the apparatus was sampled with charcoal tubes, and solvent extracts of the samples were analyzed by gas chromatography. After 9-14 days of drying,

three solvent-based adhesives had toluene emission rates ranging from 0.6 to 60 $\mu\text{g g}^{-1} \text{h}^{-1}$, and two water-based adhesives, used to glue carpets, had total alkane emission rates of 600 to 800 $\mu\text{g g}^{-1} \text{h}^{-1}$. A simple ventilation model, assuming a single, well-mixed chamber, was used to rank the potential indoor air quality impacts of the adhesives. The results demonstrated that the two water-based adhesives can be significant sources of volatile organic compounds.

INTRODUCTION

Complaints of building-associated illness in non-industrial work environments have increased in recent years. Between 1978 and 1980, the National Institute of Occupational Safety and Health conducted 115 investigations in response to some of these complaints (Kreiss and Hodgson, in press). In the majority of these building investigations, no causes other than inadequate ventilation and inadequate environmental control were found for widespread symptoms of mucous membrane irritation, headache and fatigue. However, in some investigations, the etiology was presumed to be either particulate or organic vapor emissions from building materials.

Additional investigations have been conducted by other governmental agencies and by private laboratories in response to nonspecific health complaints in buildings. Although the circumstances and results of these investigations are not generally available, several reports (Kreiss and Hodgson, in press; Berglund et al., 1982; Turiel et al., 1983) and discussions with researchers reveal that these health complaints have often occurred in new or recently remodeled buildings that had inadequate ventilation rates. It has also been observed that the number of complaints tends to decrease with time and with an increase in the fresh-air ventilation rate. While standard industrial hygiene techniques typically fail to identify the presence of specific chemical or physical agents in sufficient quantities to be classified as industrial health hazards, ambient air sampling and analytical techniques have produced some interesting results. In a new preschool building and in a new office building with health complaints, indoor air was sampled for trace organics and was shown to contain a large number of volatile organic compounds (VOC) at elevated concentrations relative to outdoor

air (Berglund et al., 1982; Turiel et al., 1982). In another new office building, several organic compounds emitted by architectural materials were identified as the probable etiological agents for widespread health complaints (Hijazi et al., 1983). These observations, taken together, suggest that emissions of organic compounds from building materials in conjunction with inadequate ventilation rates may be responsible for many cases of building associated illness.

The impact that organic emissions from building materials can have on air quality and public health is best illustrated by formaldehyde, a well-studied toxic chemical. Although, in general, it has not been found at elevated concentrations in office buildings, formaldehyde has been the cause of numerous complaints in residences (Gupta et al., 1982), where the major sources of formaldehyde are urea-formaldehyde resins in particle board, plywood, paneling and foam insulation. Formaldehyde diffuses from these products into indoor air as the products age and degrade. Whereas typical concentrations in residences are less than 0.1 parts-per-million (ppm), concentrations as high as several ppm have been measured in mobile homes. Exposures to concentrations of several ppm and less can produce short-latency illness. For example, a review by Gupta et al. (1982) showed that low-level exposure under controlled experimental conditions produced statistically significant eye, nose and throat irritant responses at 0.2 ppm which increased monotonically with dose. Other symptoms of exposure to low concentrations of formaldehyde include nausea, headache, dizziness, fatigue and skin irritation.

Formaldehyde is only one of many organic compounds emitted by architectural materials. The adhesives, sealants, surface coatings and syn-

thetic products that are used in the construction, finishing, and furnishing of buildings are major sources of solvents, monomers, plasticizers and other compounds. Previous investigations of materials that have indoor applications (Miksch et al., 1982; Molhave, 1982) have documented emissions of a large variety of organic compounds, many of which are known or suspected mucous membrane irritants.

The problem of contamination of indoor air by organic compounds emitted by architectural materials can be magnified when the amount of outside air used for ventilation in a building is reduced to achieve energy efficiency. This problem may be mitigated by source control measures for organic emissions. Ultimately these measures may prove to be more cost-effective than high rates of dilution ventilation. Some specific source control measures include selection of materials to minimize impacts on indoor air quality, isolation of unavoidable harmful products from occupants, testing and labeling of products, and use of less toxic chemicals in products (Anderson et al., 1982; Spengler and Sexton, 1983). Implementation of these preventative measures will require the concerted efforts of building designers, contractors, product manufacturers, and governmental agencies (Spengler and Sexton, 1983).

Identification and quantification of specific contaminants emitted by a wide variety of architectural materials is an important first step in the development of source control measures. In this study we attempted to (1) identify the major organic compounds emitted by some typical building construction and interior-finish materials; (2) quantify emissions of organic solvents from representative adhesives with

indoor applications; and (3) evaluate methods for rapidly screening architectural materials for organic emissions and quantifying these emissions. Adhesives were investigated in more detail than construction and finish materials since they were identified by a previous architectural material survey (Molhave, 1982) as being one of the most important sources of organic contaminants in indoor air.

METHODS

Selection of Materials

Thirty materials, selected to be representative of several major classes of construction and interior-finish materials typically used in commercial buildings, were investigated; furnishings were not included in this study. Of these, five are either structural or insulating construction materials, and ten are interior-finish materials representative of a variety of floor, wall and ceiling treatments. Descriptions of the construction and interior-finish materials are given in Table 1. The remaining 15 materials are adhesives formulated for bonding of carpets, vinyl floors, subfloor assemblies, and other miscellaneous applications. Chemical classifications and applications for the adhesives are given in Table 2.

Construction and interior-finish materials of unknown age were obtained from buildings, suppliers of building materials and a library of samples of architectural materials. Adhesives were obtained from manufacturers, distributors or contractors in unopened containers.

Sample Preparation

Construction and interior-finish materials were cut into short strips, approximately 1 cm wide, with scissors, razor blade or saw blade previously washed with acetone and hexane. Samples were weighed and then placed directly into clean vacuum-extraction flasks. The average sample weight was 9 g.

For screening by vacuum extraction, an adhesive sample was prepared by thinly applying wet adhesive to one side of each of three preweighed aluminum strips (12 mm X 47 mm) previously cleaned with acetone and hexane. The strips were allowed to dry for one week at room conditions. The three strips were then reweighed and placed into a clean vacuum-extraction flask.

For the determination of VOC emission rates, an adhesive sample was prepared by applying adhesive to one side of a preweighed aluminum plate (10 X 10 cm) previously cleaned with acetone and hexane, 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.

Vacuum-Extraction Screening Procedure

Vacuum extraction was used as a screening procedure for the qualitative determination of VOC emissions. With this method, it is relatively easy to collect a sample of the volatile organic components of an architectural material in an organic solvent for direct injection into a gas chromatograph (GC) or GC/mass spectrometer (GC/MS). Due to its simpli-

city, the screening procedure is well suited for the identification of materials that warrant further study.

The vacuum-extraction apparatus consists of a 125-ml vacuum-extraction flask, which contains 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 are connected with O-ring joints using Viton O-rings. A high-vacuum Teflon stopcock is used to isolate the cold-finger trap from the vacuum system. A second stopcock allows the cold-finger trap to be brought to atmospheric pressure. The flask and the cold-finger trap are washed with acetone and hexane, dried, and evacuated for approximately 1 h prior to use.

Extraction proceeds as follows. A sample is placed in a flask which is then attached to the apparatus. The cold-finger trap is cooled to liquid nitrogen temperature, and the system is evacuated to a typical pressure of 0.01-0.1 Pa; this pressure is maintained for 6-8 h for construction and interior-finish materials and 2 h for adhesives. At the end of the extraction period, the cold-finger trap is isolated from the vacuum system; liquid nitrogen is removed from the cold-finger trap; the system is brought to atmospheric pressure with air; the trap is opened; the cold-finger is washed with three or four 100 μ L volumes of solvent; any aqueous layer is discarded; and the organic layer is transferred to a sample vial. Nano-grade hexane is used as the solvent for construction and interior-finish materials. Reagent grade carbon disulfide (CS_2) is used for the adhesives.

Determination of VOC Emission Rates for adhesives

A simple exposure apparatus was constructed to determine emission rates of organic compounds from adhesives. It consists of a steel paint can (3.8 L) whose lid is fitted with two 6.4-mm stainless steel bulkhead fittings and an inlet tube that extends to near the bottom of the can. The test atmosphere is supplied from a cylinder of high-purity compressed air and is humidified by passing through two glass, gas-washing bottles filled with water. The apparatus is plumbed entirely with Teflon tubing. Organic compounds are collected at the outlet of the can by a two-stage charcoal adsorption tube. Periodic flowrate measurements are made with a wet test meter connected in-line between the adsorption tube and the critical-orifice flow-control device located downstream of the adsorption tube. Typically five of these exposure chambers are operated in parallel.

Emission rates of VOC were determined at room temperature which ranged between 23 and 25°C during the tests. Relative humidity in the exposure chambers was near 40% at 25°C. Flowrate through the chambers was 0.9 standard L min⁻¹ (i.e., 14 air changes per hour). Materials were placed in the chambers and maintained at these test conditions for 1 h prior to sample collection. Sampling times were 2 h unless more than 10% breakthrough of total VOC was detected on the second stage of the charcoal adsorption tubes, in which case sampling was repeated with a 1-h period. Each adhesive was tested in duplicate. Exposure chambers were initially cleaned with acetone and hexane and were cleaned between tests by heating in an oven. System blanks were below the limit of detection of the sampling method.

The primary and secondary stages of the charcoal adsorption tubes were desorbed with solvent immediately after the collection of samples using the procedures recommended by the manufacturer (Supelco, Inc., 1977). The two extracts were separately analyzed either immediately or following overnight storage at -15°C . 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.

Sample Extract Analysis

Sample extracts were first analyzed by capillary GC to determine optimal sample injection volumes for subsequent capillary GC/MS analyses. Compounds were identified by GC/MS; quantitative analyses were performed by GC.

The GC employed in this study was a Hewlett-Packard Model 5880A equipped with a flame-ionization detector (FID), an electron-capture detector (ECD), a split/splitless syringe injector, a DB5 fused-silica capillary column (15 m, 0.32 mm ID, 1.0 μm film thickness) from J&W Scientific, Inc., and a 10:1 column effluent splitter from Scientific Glassware Engineering, Inc. with 10% of the effluent going to the ECD.

The GC/MS system was a Finnigan Model 4023 equipped with a split/splitless syringe injector and a DB5 fused-silica capillary column (30 m, 0.32 mm ID, 0.25 μm film thickness). Mass spectral data for each sample were recorded and stored on magnetic disk. Compound identifications were made by comparing unknown spectra with spectra contained in the EPA/NIH Mass Spectral Data Base (Heller and Milne, 1978); identifi-

cations must be considered tentative since they were not verified by the use of standards with the exception of n-alkanes, toluene, and the di-i-butyrate which is discussed later.

RESULTS

Construction and Interior Finish Materials

The sixty-eight major compounds tentatively identified in the vacuum extracts of the construction and interior-finish materials are listed by molecular weight, which ranges from 94 to 458, in Table 3. Twice this number of major compounds were unidentified or only partially identified. (The designation "major compound" was based upon a compound's total ion-current integral.) For each sample, the integral sum of the identified and unidentified major components constitutes approximately 75% or more of the integral sum of all sample components. No compounds with retention times shorter than n-heptane were identified because they are largely obscured by the hexane solvent peak. Analyses were terminated following the retention time for n-eicosane. Many minor compounds were also identified; however, because we presumed them to be of less importance, they have not been included in the table.

The number of volatile components varies greatly among the materials (Table 4). For example, no compounds were detected in the extract of fiberglass insulation CI-1, and only one major compound, a di-i-butyrate ester, which was also present in most of the other materials, was detected in the extract of carpet padding IF-1A. At the other extreme is soft wall covering IW-2A, a synthetic textile, similar in composition and construction to a carpet, from which 60 major components were

detected, including many alkyl and aromatic compounds, suggesting that it may have been treated with a petroleum distillate solvent.

The major compounds with molecular weights less than 140 emitted by the materials were phenol, alkyl aromatic compounds, naphthalene and terpenes (Table 3). When the sample mass spectra were re-examined for other low-molecular-weight compounds which were present in low abundance and, therefore, did not meet the major-compound criteria, acetic acid, N,N-diethylformamide, 1,2,3-trimethyl benzene and an unidentified aromatic compound were found. No halogenated solvents were detected.

Based upon their total ion-current integrals, a further distinction among the major compounds in each sample was made, designating the four to six most abundant compounds. As is indicated in Table 3, 29 identified compounds were so designated among the 15 samples; eight additional most-abundant compounds remain unidentified. The identified compounds include low-molecular-weight alkyl aromatic compounds, terpenes, terpene derivatives, alkanes, a variety of higher molecular-weight aromatic compounds and plasticizers (including phthalate esters and other esters).

From Table 4, a list of the most frequently occurring major compounds was compiled (Table 5). Thirteen major compounds occurred in three or more of the material samples. All of these compounds, with the exception of phytane, are also most-abundant compounds.

The major compound most frequently occurring is dibutyl phthalate. Because of its widespread use, it may also appear as a minor system impurity and can occur in samples as a contaminant. In three of the ten samples in which it appeared (polyurethane foam insulation CI-2, vinyl

wall covering IW-1 and composition wall panel IW-3), dibutyl phthalate was one of the four to six most abundant compounds indicating that it may have been used in the manufacture of these products. The second most frequently-occurring major compound is 2,2,4-trimethyl-1,3-pentanediol di-i-butyrate, whose mass spectrum is presented in Figure 1. It is produced by Eastman Chemical Co. under the trade name Kodaflex TXIB for use as a plasticizer, primarily in surface coatings, vinyl flooring, moldings and other vinyl products. Its boiling point, 280°, is relatively low for its molecular weight of 286. In one sample, carpet padding IF-1A, the di-i-butyrate occurred in high abundance and was the only major compound. Re-examination of the mass spectra for all samples showed the compound to be distinctly present in 11 samples and possibly present in trace amounts in two others.

Adhesives

The results of the vacuum-extraction screening of the 15 adhesives are presented in Table 6. The eight adhesives listed, five of which are solvent based, continued to emit organic solvents after one week of drying; only trace amounts of solvents were detected in the extracts of the seven other adhesives. The major compounds identified in the extracts of the solvent-based adhesives are toluene, styrene and a variety of cyclic, branched and normal alkanes. Of these, toluene is the most abundant. Organic solvents, all alkanes, were found in the extracts of three of the water-based adhesives as well. Two of the water-based adhesives, W-1 and W-2, which are related products obtained from the same manufacturer, emitted an almost identical complex mixture of normal and branched alkanes and cyclohexanes. Two other adhesives, S-6 and W-

3, emitted a different mixture of higher molecular-weight normal and branched alkanes. The similarity between S-6 and W-3 is surprising since they are supplied by different manufacturers and one is a solvent-based asphalt adhesive and the other a water-based natural rubber adhesive. None of the adhesives emitted detectable quantities of halogenated solvents.

Emission rates of VOC were measured for the eight adhesives determined by vacuum extraction to have relatively high emissions. Following drying periods of 9-14 days, only five of the eight adhesives had detectable emission rates of solvents at the test conditions (Table 7). Three solvent-based adhesives had toluene emission rates between 0.6 and $62 \mu\text{g g}^{-1} \text{h}^{-1}$, but no detectable amounts of other solvents were emitted by these adhesives. The two water-based adhesives, W-1 and W-2, 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. A comparison of the GC chromatograms for the vacuum extract and the charcoal-tube air sample of adhesive W-1 is shown in Figure 2. Because of the complexity of the mixture, emission rates were not determined for individual components. Instead, emission rates as total alkanes were calculated from the sum of the peak integrals using normal alkane external standards. These emission rates ranged between 610 and $780 \mu\text{g g}^{-1} \text{h}^{-1}$ (Table 7).

DISCUSSION

Evaluation of Methods

The vacuum-extraction screening procedure was demonstrated to be suitable for estimating the potential emissions from materials of alkyl benzenes and C₇ and higher molecular-weight alkanes. As illustrated by the GC chromatograms in Figure 2, the vacuum extract of adhesive W-1 contained the same compounds in approximately the same relative abundances as the charcoal-tube air sample. Nevertheless, the method has two potential sources of negative bias which were not evaluated. First, compounds may not be quantitatively collected due to the formation of fog in the cryogenic trap. Second, polar compounds may partially partition to the aqueous phase which is almost always present.

The air-exposure apparatus which was used to determine emission rates of solvents from adhesives is nearly as simple to construct and operate as the vacuum-extraction apparatus. It has the advantage of being more versatile since it is easily adapted to the determination of the effects of sample treatment and environmental parameters on the emission rates of VOC from architectural materials. The sensitivity of the air-sampling method and the size of the adhesive samples resulted in a detectable emission rate for a single component of an adhesive of approximately $0.1 \mu\text{g g}^{-1} \text{h}^{-1}$.

Both the vacuum-extraction method and the air-sampling method employed in this study are limited in their abilities to detect low-molecular-weight compounds because of solvent-peak interferences. In addition, the solvents used may not be suitable for extracting some

polar compounds. A possible improvement to the methods would be the use of a more polar solvent, such as acetone, acetonitrile, methanol, or N,N-dimethylformamide, or a combination of solvents (e.g., see Johansen and Wendelboe, 1981; Lamb and Adin, 1983). However, a more significant improvement to the air sampling method would be the substitution of a solid sorbent/thermal desorption system for the charcoal tube/solvent desorption system. This would increase sensitivity and permit the quantification of low-molecular-weight compounds by eliminating the solvent peak (Ciccioli et al., 1976; Holzer et al., 1977; Melcher, 1983).

Comparisons with Other Studies

Molhave (1982) used test-chamber studies to determine emission rates of organic compounds for 42 materials with indoor applications including a variety of wall and floor coverings, paints, adhesives and sealants. All materials were delivered for analysis directly from factory stock. A total of 52 different compounds were chemically identified, with the majority divided among the following chemical groups: alkanes (C₆₋₁₁), alkenes (C₇₋₁₀), terpenes, alkyl benzenes (C₆₋₁₁), ketones (C₃₋₆), alcohols (C₂₋₆) and esters (C₄₋₆). Of the identified compounds, 40% are known mucous membrane irritants, 42% are suspected irritants and several are suspected carcinogens. Miksch et al. (1982) identified organic vapors emitted by 17 "new" architectural materials including floor, wall and ceiling finishes, adhesives and sealants.

A comparison of the major compounds identified in these studies with those in the present survey reveals that toluene, ethyl benzene, styrene, xylenes and normal alkanes are common to all three. The terpenes, α -pinene and limonene, and methylethyl cyclohexane are common to

the present study and the Molhave survey. The present study and the Miksch et al. survey have phenol, naphthalene, 1-methyl naphthalene, nonanal and dimethyl and trimethyl cyclohexane in common.

Most of the compounds identified in the previous surveys of emissions from new architectural materials are relatively low-molecular-weight compounds with 12 carbon atoms or less. In this study, low-molecular-weight compounds were only emitted by adhesives and by three materials believed to be relatively new: plywood CS-2, polyurethane foam insulation CI-2 and composition wall panel IW-3. The relative scarcity of low-molecular-weight volatiles may be due to several causes. First, although the date of manufacture was not known for any of the samples, at least half were presumed to be more than one year old. Aging results in the reduction and eventual loss of the more volatile components. (On the other hand, interior-finish materials with large surface areas, such as carpets and soft wall coverings, may adsorb organics from the air and would re-emit these during the extraction process.) Second, the vacuum-extraction screening procedure may not quantitatively collect low-molecular-weight compounds. These compounds might be partially lost during the solvent washing step or during sample storage. Finally, as previously noted, the solvent peak obscures compounds with short chromatographic retention times.

The large number of relatively high-molecular-weight compounds identified by the vacuum-extraction screening procedure would be expected to be present in air at low concentrations due to their low vapor pressures. Therefore, these compounds are not, in general, anticipated to constitute a contamination problem in indoor air.

Perhaps, the most significant result of the adhesive survey was the discovery that three water-based adhesives emitted relatively large amounts of organic solvents. In the case of adhesives W-1 and W-2, exceptionally large amounts of a complex mixture of alkanes were emitted. Molhave (1982) also found that water-based adhesives could be significant sources of VOC: in estimating the relative contributions of 42 architectural materials to the total equilibrium organic concentration in a hypothetical room, he found that two water-based adhesives were ranked first and third in order of importance. Based on these results, it is unwise to assume water-based products are innocuous. Rather, it is apparent that the use of some water-based adhesives could potentially result in indoor air quality problems.

The nearly ubiquitous occurrence of the di-i-butyrate ester in the materials investigated by this study is of general interest to those involved in air quality research. It has similar applications to those of phthalate esters, which have become almost universally present in the environment and even occur in ambient air at relatively remote locations (Giam et al., 1980). Due to its apparent widespread use, the compound will undoubtedly be detected in future indoor air samples and possibly in outdoor air samples as well.

Modeling

The impact of VOC emissions from architectural materials on equilibrium concentrations of organic compounds in a hypothetical office space was estimated using a simple well-mixed-tank model. Variations of this model have been used by others to model indoor pollutant concentrations (Alonzo et al., 1979; Dockery and Spengler, 1981; Traynor et al., 1982;

Miksch et al., 1982; Molhave, 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, 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, the mass-balance equation describing a contaminant source inside a well-mixed room with infiltrating and exfiltrating air reduces in steady-state to

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

where C_{∞} is the equilibrium 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).

Guidelines established by the American Society of Heating and Ventilating Engineers (ASHRAE, 1981) call for a minimum fresh-air ventilation rate of $0.14 \text{ m}^3 \text{ min}^{-1}$ ($5 \text{ ft}^3 \text{ min}^{-1}$) per person in nonsmoking office spaces and $0.56 \text{ m}^3 \text{ min}^{-1}$ ($20 \text{ ft}^3 \text{ min}^{-1}$) 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 (i.e., 14 m^2 per worker). The recommended minimum fresh-air ventilation rate for this office is then either 58 or $233 \text{ m}^3 \text{ h}^{-1}$ depending on whether smoking is permitted.

The equation for equilibrium concentration was used to evaluate the potential impacts of the adhesive products listed in Table 7 on the indoor air quality of the hypothetical office. Assuming that each adhesive would be applied to a surface equal in area to the floor area of the space using the manufacturers' recommended product coverages, equilibrium concentrations estimated from the solvent emission-rate data were calculated, as shown in Table 8. Adhesive S-3 is predicted to have the greatest impact on concentrations of toluene, and the two water-based adhesives are predicted to contribute most to concentrations of total volatile organics. The calculated equilibrium concentrations of total alkanes, particularly for the office in which smoking is not permitted, are quite high relative to typical concentrations of total volatile organics in indoor air of several ppm. However, not much reliance should be placed on the absolute values. Firstly, the emission rate data, almost certainly, do not accurately reflect emission rates under actual use conditions since the adhesives were only bonded to one surface and were tested after a short drying period. Secondly, it is unrealistic to assume an equilibrium state and perfect air mixing. Despite these shortcomings, the equilibrium equation is probably still useful for assessing on a relative basis the potential effects on indoor air quality of products with similar applications, such as the carpet adhesives S-3, W-1 and W-2. Ultimately, refinements, such as, testing combined substrate, adhesive, and bonded-material assemblages and quantifying the effects of aging and environmental parameters on emissions would greatly improve the accuracy of estimates of indoor air quality impacts.

Health Effects

Recommendations for maximum safe exposure limits to airborne toxic chemicals have been made for the work environment by the American Conference of Governmental Industrial Hygienists (ACGIH, 1983). These threshold limit values (TLV) for 8-h time-weighted-average exposures are widely accepted as guidelines and, in some cases, have the force of law. The values are intended for the industrial work place where exposures are typically restricted to a few compounds. A few of the compounds, or their parent compounds, listed in Tables 3 and 6 have occupational TLVs; the values for these compounds differ considerably, ranging from 0.1 ppm for benzoquinone to 400 ppm for methyl cyclohexane.

Although TLVs have not been determined for a large number of compounds, appropriate exposure limits for mixtures of several compounds which have similar toxicological effects can be estimated. However, there is no method to estimate safe exposure limits for a large and diverse mixture of compounds which may have additive and synergistic effects. Due to this limitation, TLVs are probably not suitable as guidelines for limiting exposures in nonindustrial work environments, such as offices, where workers may be exposed to a broad spectrum of volatile organic compounds, many of which have irritant effects.

CONCLUSION

The general lack of relevant data on health effects emphasizes the need for research on short-latency illness induced by exposure to low concentrations of volatile organics. These health effects studies should be complemented by investigations of the sources of volatile

organic contaminants in non-industrial work environments. Since architectural materials are one of the major sources, further materials research is warranted. Development of techniques for rapid screening of products for organic emissions, determination of the effects of product usage and environmental parameters on emission rates, and verification of mathematical models for indoor pollutant concentrations may ultimately lead to effective source control measures to minimize the impacts of building material emissions on indoor air quality. Implementation of these measures could then protect the health of the office work force while permitting the achievement of building energy efficiency goals.

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Table 1. Descriptions of 15 building construction and interior finish materials characterized for volatile organic compound emissions

Sample ID	Sample Description
<u>Const. Mat.</u>	
CS-1	Particle board; 3/8", subfloor
CS-2	Plywood; 3/4", fire retardant
CS-3	Cedar lumber
CI-1	Fiberglass insulation; 3-1/2", foil backed
CI-2	Polyurethane foam insulation; 3-1/2", fire retardant
<u>Int. Finish</u>	
IF-1A	Carpet padding; mixed fibers, fire retardant
IF-1B	Carpet padding; 60% polyester, 30% nylon and 4% polyolefin fibers
IF-2	Carpet; 100% nylon fiber, polypropylene and foam rubber backings
IF-3	Vinyl floor covering
IW-1	Vinyl wall covering; fabric backing
IW-2A	Soft wall covering; synthetic fiber, jute backing
IW-2B	Soft wall covering; 100% olefin or polyester fiber
IW-3	Composition wall panel; 1/4", paper face
IC-1A	Ceiling panel; mineral fiber acoustical tile, fire retardant
IC-1B	Ceiling panel; pressed fiber acoustical tile, vinyl face

Table 2. Classifications and applications of 15 adhesives investigated

Adhesive	Chemical Base	Application
<u>Solvent-based</u>		
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
<u>Water-based</u>		
W-1	Synthetic rubber	Foam backed indoor and outdoor carpet
W-2	Synthetic rubber	Foam backed indoor and outdoor carpet
W-3	Natural rubber	Foam, sponge backed indoor and 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
<u>Epoxide</u>		
E-1	---	Metal, glass, ceramic, plastic

Table 3. Major compounds emitted by building construction and interior finish materials. Tentative identifications determined by GC/MS using EPA/NIH Mass Spectral Data Bases

No.	Molecular Weight	Chemical Identification
1	94	Phenol
2	104	Styrene
3*	106	Ethyl benzene
4*	106	<u>o</u> -Xylene
5*	106	<u>m</u> -Xylene
6	128	Naphthalene
7	134	Benzene, 1-methyl-4-(1-methylethyl)-
8*	136	-Pinene
9	136	Camphene
10*	136	Limonene
11	140	2-Nonenal
12	142	Nonanal
13	142	Naphthalene, 1-methyl
14*	144	Butyl butyrate
15	146	2-Ethyl hexanol
16*	150	Thymol
17	150	Phenol, 4-(1,1-dimethylethyl)-
18	152	2-Cyclohexen-1-one, 6-methyl-3-(1-methylethyl)-
19*	154	-Terpineol
20	154	7-Oxabicyclo[2.2.1]heptane, 1-methyl-4-(1-methylethyl)-
21	156	Naphthalene, 1,4-dimethyl-
22	158	Benzene, 3-cyclohexen-1-yl-
23	164	Benzoic acid, 4-(1-methylethyl)-
24	170	2-Hydroxy biphenyl
25*	178	Benzene propanoic acid, B,B-dimethyl-
26*	180	Phenol, (1,1-dimethylethyl)-4-methoxy-
27*	182	Benzophenone
28*	186	1-Dodecanol
29	190	2-Phenyl octane
30*	192	Butanoic acid, 4-(2,5-xylyl)-
31*	194	Dimethyl phthalate
32	194	Benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl-
33	196	1,4-Benzoquinone, 2,6-bis (1,1-dimethylethyl)-
34	196	Octyl cyclohexane
35	196	Benzene, 1,2-dimethyl, 4-benzyl-
36	198	Phenyl benzoic acid
37*	198	<u>n</u> -Tetradecane
38	210	Nonyl cyclohexane
39	210	Pentadecene
40*	212	<u>n</u> -Pentadecane
41	218	<u>5</u> -Phenyl decane
42*	222	Diethyl phthalate
43	224	Decyl cyclohexane
44	226	4-Ethyl tetradecane
45	226	2-Methyl pentadecane

Table 3 (continued)

No.	Molecular Weight	Chemical Identification
46*	226	<u>n</u> -Hexadecane
47	232	5-Phenyl undecane
48	234	Phenol, 2,6- <u>bis</u> (1,1-dimethylethyl)-4-ethyl-
49	236	Indane, 1,1,3-trimethyl-3-phenyl-
50	238	Undecyl cyclohexane
51*	238	Heptadecene
52	240	2-Methyl hexadecane
53*	240	<u>n</u> -Heptadecane
54	246	Decyl xylene
55	252	Octadecene
56*	254	<u>n</u> -Octadecane
57*	268	Pristane
58*	268	<u>n</u> -Nonadecane
59	272	Thunbergene (C ₂₀ H ₃₂ branched cycloalkene)
60*	278	Dibutyl phthalate
61*	278	Di- <u>i</u> -butyl phthalate
62	282	Phytane
63	282	<u>n</u> -Eicosane
64*	286	Di- <u>i</u> -butyrate, 2,2,4-trimethyl-1,3-pentanediol
65*	290	Manoyl oxide
66*	322	2-Butoxyethyl butyl phthalate
67	444	Cyclohexasiloxane, dodecamethyl-
68*	458	Hexasiloxane, tetradecamethyl-

* Most abundant compounds

Table 4. Compounds emitted by individual building construction and interior finish materials. Numbers correspond to compounds listed in Table 3.

Sample ID	Material	Identified Compounds
CS-1	Particle board	19, 25*, 30, 42, 53, 56, 58*, 59, 60*, 62?, 63, 65?*, [+ 11 unident.]
CS-2	Plywood	7, 8*, 9, 10*, 19*, 30*, 60, [+ 5 unident.]
CS-3	Cedar	7, 16*, 18, 20, 23, 26* (2 isomers), 32, 42-I, [+ 2 unident.]
CI-1	Fiberglass insulation	None detected
CI-2	Polyurethane foam	3*, 4*, 5*, 57*, 60*, 67, [+ 13 unident.]
IF-1A	Carpet padding	64
IF-1B	Carpet padding	27, 28?*, 37*, 40*, 43?, 53*, 56, 57, 60, 62, 64*, [+ 10 unident.]
IF-2	Carpet	11, 29, 31*, 37*, 40*, 41, 47, 64*, [+ 10 unident.]
IF-3	Vinyl floor covering	15, 27*, 36, 40*, 51, 56, 64*, [+ 7 unident.]
IW-1	Vinyl floor covering	1, 27, 31*, 40, 42, 53*, 56, 57, 60*, 61*, 62, 64*, [+ 17 unident.]
IW-2A	Soft wall covering	6, 12, 13, 14*, 21?, 22, 24, 28?, 31, 34, 35, 37*, 38?, 40*, 42, 43, 44, 45?, 46, 50, 52, 53, 54, 55?, 56*, 57?, 58, 60, 64, [+ 31 unident.]
IW-2B	Soft wall covering	1, 28, 31*, 35, 37, 40, 42*, 49, 53*, 56*, 57*, 58, 60, 63, 64, [+ 13 unident.]
IW-3	Wall panel	2, 17, 31*, 33, 42, 48, 53*, 57, 60*, 64*, 66*, 68*, [+ 9 unident.]
IC-1A	Ceiling panel	40*, 46*, 57, 60, 64*, [+ 3 unident.]
IC-1B	Ceiling panel	38, 51*, 53*, 56, 60, [+ 8 unident.]

* - Most abundant compounds
 ? - Identification uncertain
 I - Impurity

Table 5. Most frequently occurring major compounds emitted by building construction and interior finish materials

No.	Frequency (No. samples)	Chemical Identification
1	10	Dibutyl phthalate
2	9	Di- <u>i</u> -butyrate, 2,2,4-trimethyl-1,3-pentanediol
3	7	<u>n</u> -Pentadecane
4	7	Diethyl phthalate
5	7	<u>n</u> -Heptadecane
6	7	<u>n</u> -Octadecane
7	7	Pristane
8	4	Dimethyl phthalate
9	4	<u>n</u> -Tetradecane
10	3	Benzophenone
11	3	<u>n</u> -Hexadecane
12	3	<u>n</u> -Nonadecane
13	3	Phytane

Table 6. Compounds emitted by adhesives

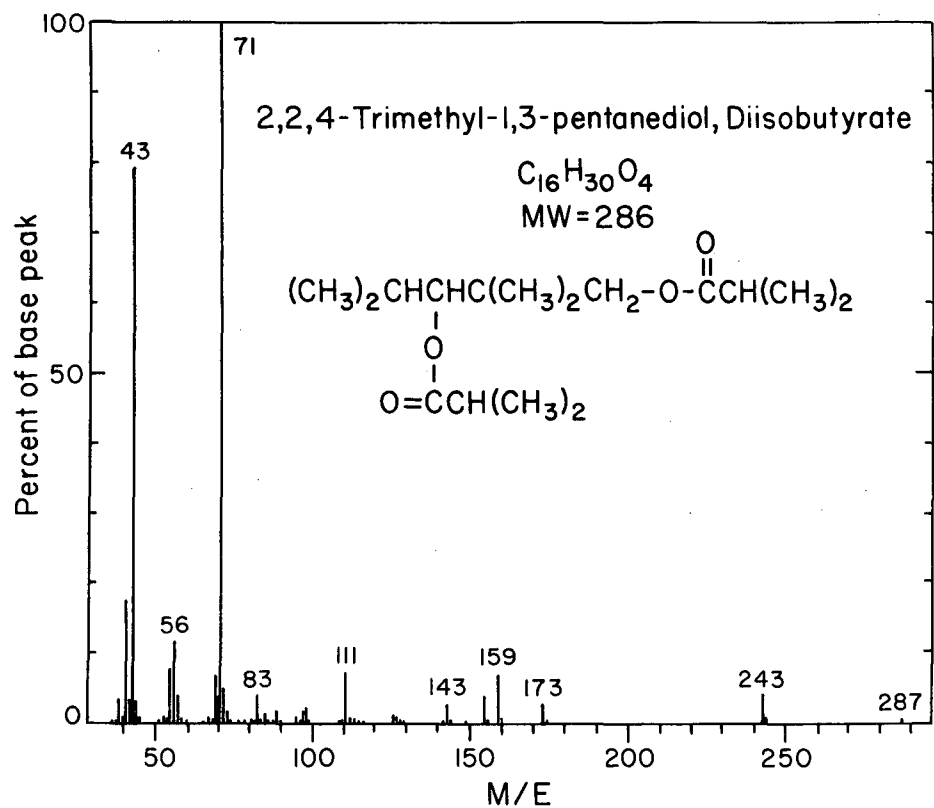
Adhesive	Chemical Identifications
S-1	Toluene; styrene
S-2	Low-molecular-weight alcohol?; toluene
S-3	Toluene
S-6	n-Decane; <u>n</u> -undecane; C ₁₀ -C ₁₁ branched alkanes (9+ compounds); C ₁₀ cyclohexanes (4 compounds)
S-7	Methyl cyclopentane; cyclohexane; toluene
W-1	<u>n</u> -Octane; <u>n</u> -nonane; C ₈ -C ₉ branched alkanes (7+ compounds); methyl cyclohexane; C ₈ -C ₉ cyclohexanes (10+ compounds)
W-2	Same compounds as W-1
W-3	Toluene; <u>n</u> -nonane; <u>n</u> -decane; <u>n</u> -undecane; C ₁₀ - C ₁₁ branched alkanes (9+ compounds); C ₁₀ cyclohexane

Table 7. Emission rates of toluene and total alkanes from five adhesives

Adhesive	Weight Adhesive (10^{-2} g cm $^{-2}$)	Drying Time (days)	Emission Rate (μ g g $^{-1}$ h $^{-1}$)
			<u>Toluene</u>
S-1	6.70	9	0.59
S-3	0.93	13	62
	0.83	13	48
S-7	4.32	11	2.4
	6.50	11	2.6
			<u>Total Alkanes</u>
W-1	2.54	14	740
	2.85	14	760
W-2	3.36	14	610
	3.82	14	780

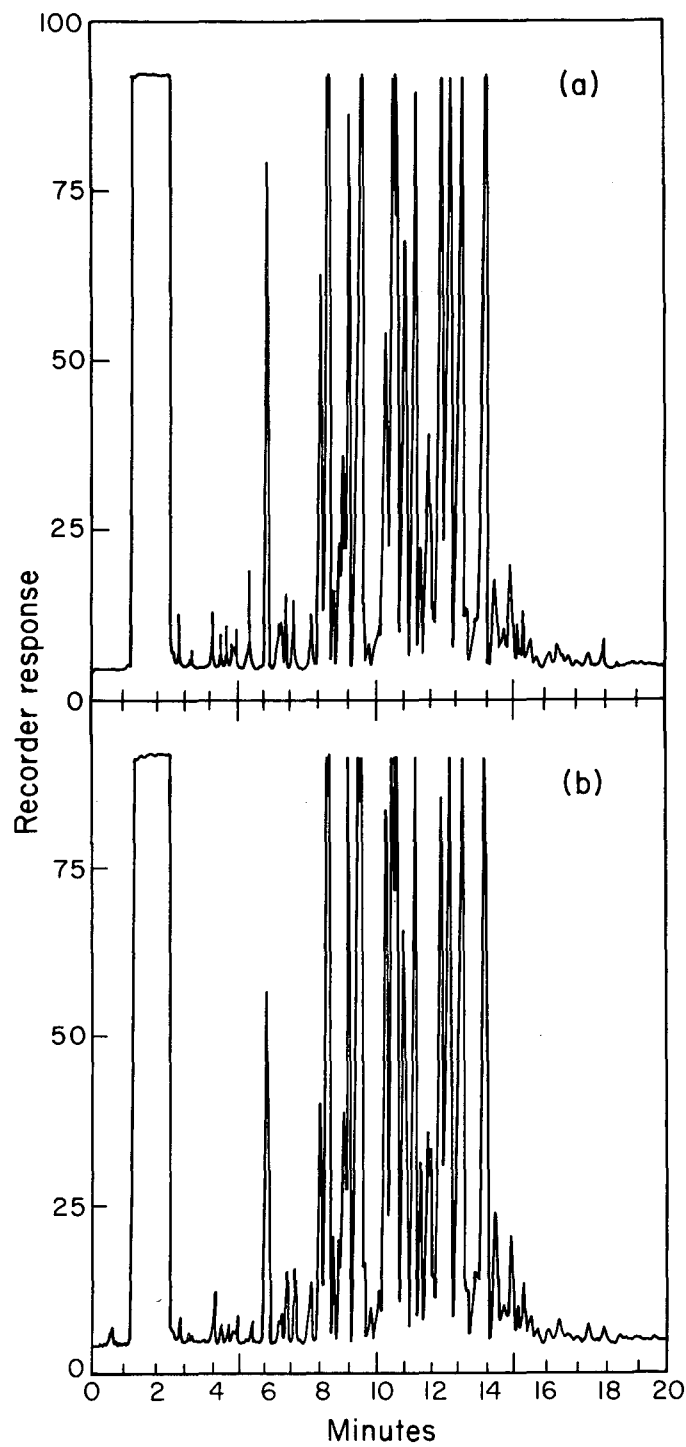
Table 8. Calculated indoor air equilibrium concentrations of toluene and total alkanes in a hypothetical office space due to emissions of these compounds by adhesives

Adhesive	Recommended Coverage (g m ⁻²)	Calculated Concentrations (mg m ⁻³)	
		Smoking	
		Permitted (233 m ³ h ⁻¹)	Not Permitted (58 m ³ h ⁻¹)
		<u>Toluene</u>	
S-1	245	0.06	0.25
S-3	120	2.8	11
S-7	235	0.25	1.0
		<u>Total Alkanes</u>	
W-1	240	76	310
W-2	225	67	270



XBL 8310-588

Figure 1. Mass spectrum of 2,2,4-Trimethyl-1,3-pentanediol, Diisobutyrate.



XBL 8310-587

Figure 2. Comparison of the GC-FID detector chromatograms of (a) the vacuum extract and, (b) the charcoal-tube air sample of adhesive W-1.

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