
An Investigation into VOC Emissions from Polyurethane Flexible Foam Mattresses

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SUMMARY

Emissions of volatile species from flexible polyurethane foam mattresses were investigated by using large scale chamber tests designed to replicate the product use as mattress cores. Various trace impurities were identified and their concentrations were measured for input into a human health and toxicity risk assessment, which has concluded that none was injurious to health. The raw materials used to make the foam were analysed to identify the source of emanations and routes to their reduction or elimination. Several analytical artefacts were identified, and some recommendations made for their avoidance. Detailed product knowledge was essential to the reliable interpretation of analytical data. A quantitative risk assessment was carried out on each of the volatiles. No evidence of any human health risk was identified from the 'worst-case' exposure model employed

INTRODUCTION

This paper describes work conducted by EUROPUR (The European Association of Flexible Polyurethane Foam Block Manufacturers) with support from many of the raw material manufacturers. It focuses on emissions from polyurethane foam mattresses in the form of Volatile Organic Compounds (VOCs) and is the second in a series of publications. The previous paper⁽¹⁾ concerned the alleged presence of toluene diamine in flexible polyurethane foam. This current paper contains a risk assessment of the detected VOCs.

General awareness to indoor air quality has increased in recent years and various test methods and standards have evolved⁽²⁻⁵⁾ to address this subject. Modern chromatographic and spectroscopic techniques can be adopted easily for the analysis of organic volatiles issuing from everyday consumer items and very detailed profiles can be assembled quickly, at relatively low cost. Such techniques are now extremely useful in developing health, safety and environmental profiles and for evaluating environmentally improved technologies.

Unfortunately, without considerable analytical experience and product knowledge, it is often possible to misinterpret such information, draw false conclusions, and overlook the significance of analytical artefacts.

The specific VOCs emitted from everyday consumer items like mattresses can obviously vary for different products and the rate of emission also varies. While there is potential for emissions from the foam fillings and covers used in furniture and mattress construction, such emanations are not unique to polyurethanes. As an example, analytical investigations of wood products by the Danish Environmental Protection Agency⁽⁶⁾ highlighted a multitude of VOCs. Rubber latex foam is reported by several authors⁽⁷⁻⁹⁾ to produce a variety of emanations. In a State of Washington programme⁽¹⁰⁾ more than 100 different products have been studied in categories such as paints, wallcoverings, carpets, furniture and construction materials.

Polyurethane foams of U.S. origin were a component of research on bed assemblies sponsored by the Sleep Products Safety Council⁽¹¹⁾ In this work 34 emanations were identified by the Research Triangle Institute from a range of bed set constructions. These emissions originated not only from the polyurethane foam layers but adhesives, fabrics and polyethylene wrapping materials also employed in the manufacture of the mattresses. Risk assessments were conducted by Versar Inc. for those species supported by adequate toxicological data. It was concluded that none posed acute inhalation or dermal health risks for normal or convalescing individuals by short-term exposure.

This publication reports on investigations into polyurethane foam as used in mattresses and some raw materials used in the production of those foams. It has not been extended to foam filled furniture but the findings are thought to be equally applicable to these consumer items.

The quality of indoor air receives more and more attention by the public, regulators and non-governmental organisations. Although many standards have been promulgated both for the workplace and outdoor air, regulatory limits for indoor “consumer” air are rarely set. There are though, two relevant examples. The first is the Danish EPA study into volatiles from wood products. However this did not present clear quantitative risk assessments and the very conservative Danish “LCI” values are difficult to reconcile in some cases with risk evaluations for occupational hygiene levels. The second example is in Germany where the Umweltbundesamt (UBA) had addressed this issue of

indoor air quality and published a “Richtwert-Konzept” (orientation values)⁽¹²⁾ Here the tolerable (RW II) and the acceptable value (RW I) for indoor air contaminants are defined as:

$$\text{RW II} = \text{NOAEL (man)}/100 \text{ or OEL}/100$$

$$\text{RW I} = \text{RW II}/10$$

Where NOAEL represents the ‘No Observed Adverse Effect Level’ and OEL is the ‘Occupational Exposure Limit’.

The factor of 100 results from several safety factors to cover the differences between workplace and permanent exposure, and to extrapolate to sensitive individuals and children. Carcinogenic and mutagenic substances or substances toxic to reproduction of EU-category 1 or 2 must not be detectable in indoor air. The EU criteria describes carcinogenic materials as: Category 1 carcinogens “substances known to be carcinogenic to man. Sufficient evidence of human exposure and development of cancer”. For category 2, “Substances which should be regarded as if they are carcinogenic to man: based on appropriate long-term animal studies and other relevant information”. In addition, following a survey of several hundred dwellings and exposure experiments with volunteers, a limit for the total amount of volatile organic compounds (TVOC) is recommended.

- TVOC 0.2 – 0.3 mg/m³: level deemed to be safe; precautionary principle.
- TVOC 1 – 3 mg/m³: level should not be exceeded in the long term.
- TVOC 10-25 mg/m³: only acceptable for short periods of time.

Such levels are questionable as the appropriate toxicological background is lacking. In addition, they may conflict with the RW I/RW II values. Nevertheless, the mixtures tested have represented the “VOC-cocktail” allegedly found in indoor air.

The human health risk assessment in this study was based on the concept of a (numerical) risk being expressed as the product of exposure and hazard. The independent analytical test laboratory Eurofins⁽¹³⁾ provided the exposure model. The hazard, expressed as a NOAEL, was derived from published occupational hygiene standards or from published literature.

EXPERIMENTAL

Analytical Protocols

Procedure for SPME VOC Collection over Raw Materials or Foams

The liquid raw materials were placed in a glass boat placed in a stainless steel tube with deactivated surfaces (Figure 1). The foam samples were placed in the tube directly.

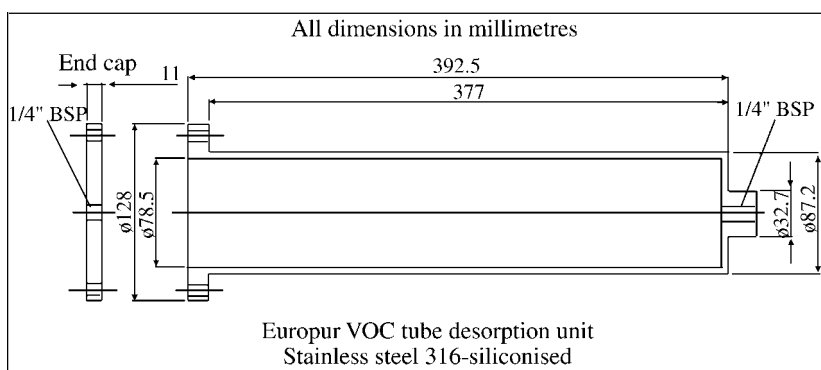


Figure 1 Europur VOC tube desorption unit

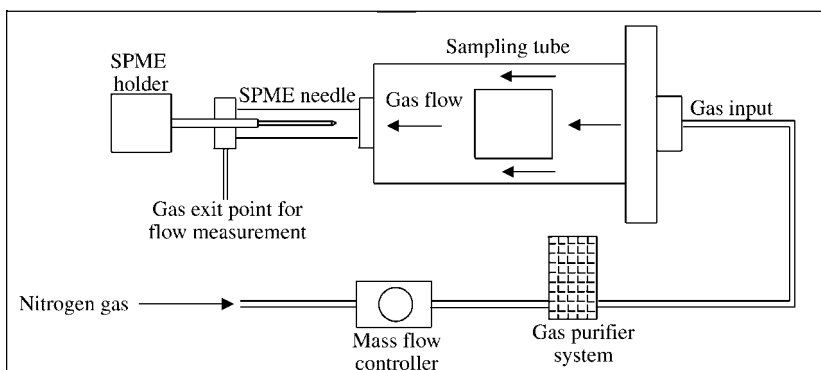


Figure 2 SPME sampling tube and needle analysis configuration

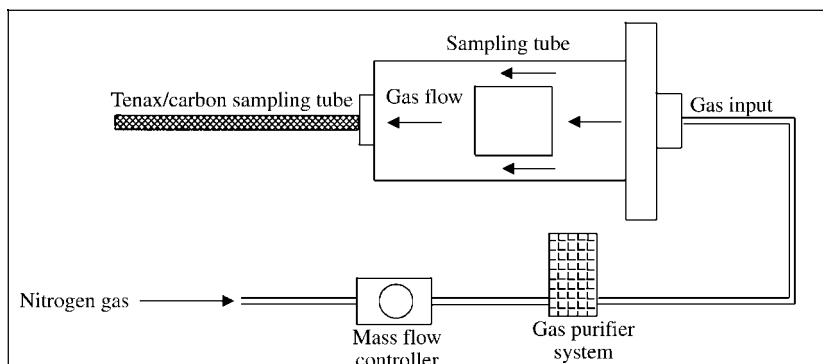


Figure 3 Tenax/carbon sampling tube analysis configuration

The SPME (solid phase micro encapsulation) needle (carboxen/polydimethyl siloxane, - Supelco #57318) was inserted through the septum and exposed for the duration of the collection period, typically two hours. After this period the needle was retracted and transferred to a gc instrument. Desorption was undertaken for 1 minute in a helium stream within the injector operating in splitless mode and held isothermally at 250°C.

Volatiles were cryofocussed with liquid nitrogen before injection onto the column. GC1, DB5 or SP2331 columns of length 60 m and internal diameter 0.25 mm have been employed, these being held for 2 minutes at 40°C and then raised to 290°C at a rate of 3°C min⁻¹ (subsequently revised to 4°C min⁻¹).

The gc analysis was conducted with a Hewlett Packard 5890 series II chromatograph fitted with split/splitless injection, and species were scanned using a Micromass Trio 2000 or 70S series mass spectrometer. Scans from m/z 20 to 550 were performed in 1-second cycles and stored data searched against NIST and Wiley spectra databases. Throughout this entire work it has always been necessary to employ extreme caution when examining computer predictions for substance identification. All results reported here have been finally accepted only after full consideration of the formulations and product under investigation.

Instrument blanks were run to confirm the absence of background contamination from SPME needles and new SPME needles were visually inspected and conditioned according to supplier's recommendations prior to running a blank test.

Between tests the sampling tube was solvent and water washed, and subjected to oven drying at 120°C followed by 4 hours purging with nitrogen at 140°C.

Procedure for Tenax Carbon Collection

This was as that for SPME, but volatiles were collected in tubes containing 50 mg Tenax TA + 20 mg carbon over a period typically of eight hours, and desorption was for a period of 2 minutes at 250°C with the injector operating in split mode.

Test Protocol for Chamber Tests on Foam Mattress Cores

Chamber tests were conducted principally at Eurofins Denmark A/S,⁽¹³⁾ by a procedure based on ISO 13419-1⁽⁴⁾. Foam mattress blanks with dimensions 200 x 100 x 12 cm were placed within a glass lined stainless steel test chamber of volume 2 or 3.2 m³. The chamber was supplied with a current of air pre-conditioned to 23°C/50% relative humidity so as to provide an exchange rate of 0.5 h⁻¹, effecting evaporation from 5 surfaces of the core foam.

The exit air from the chamber was analysed at set times selected at 5, 24, 48, 72, 120 and 160 hours. Airborne aldehydes were collected on 2,4-dinitrophenyl hydrazine (DNPH) coated silica gel, eluted with acetonitrile and analysed by HPLC using diode-array UV-detection. General VOC concentrations in the air were analysed by collection on Tenax TA or Tenax/Carboxen and desorption onto a gas chromatograph column coupled to a mass spectrometer. Calibrations were conducted by using standard solutions of analytes to determine gc response factors relative to toluene.

Supplementary tests have been conducted by LGA laboratories⁽¹⁴⁾ and the Fraunhofer Institut⁽¹⁵⁾ using minor independent procedure modifications.

Test Mattresses

A reference group of five different types of water blown, TDI-based flexible polyurethane foam were used as mattress cores. These were standard grades from constant manufacturing sources within the EUROPUR membership. All mattress sized samples were cut from within foam slabstock which had been given a one week period between manufacture and conversion. This time was considered as a typical period although in practice this can be shorter or longer depending on product demand. After cutting, the samples were wrapped and despatched to the analytical laboratories. In no case were the foams deformed permanently before testing.

Conventional Polyether

Nominal density 38 kg/m³ and hardness 180N, produced from a 3500MWt polyol.

The hardness is determined by an Indentation test carried out to 40% compression as described for example in BS4443.

High Resilience (“HR”)

Nominal density 36 kg/m³ and hardness 135N. Produced from a grafted polyol system, with a small quantity of methylene chloride as supplementary blowing agent. The foam also contained a small quantity of chlorinated phosphate flame retardant.

High Resilience FR (“HR/FR”)

Nominal density 36 kg/m³ and hardness 145N. Produced from a grafted polyol system, with a small quantity of methylene chloride as supplementary blowing agent. The foam contained a tris monochloropropyl phosphate (TMCP) flame retardant.

Combustion Modified High Resilience (“CMHR”)

Nominal density 35 kg/m³ and hardness 115N. Produced from a modified 6000 MWt polyol and blown with water only. The formulation contains TMCP and melamine flame retardants. This foam was formulated to comply with UK 1988 furniture flammability standards⁽¹⁶⁾.

Combustion Modified Polyether (“CME”)

Nominal density 33 kg/m³ and hardness 130N. Produced from 3000 MWt polyol and blown using water. The formulation contains TMCP and melamine flame retardants. This foam was also formulated to comply with UK 1988 furniture flammability standards.

Procedure for Analysing Foam Raw Materials e.g. Polyol

Polyol samples were analysed via the SPME foam protocol. The raw material was placed within the test chamber in a glass sample boat. Products tested were 3000MWt polyether triol based on propylene oxide (nominal hydroxyl value 56 mg KOH/g) and 3500MWt polyether triol based on ethylene oxide/propylene oxide (nominal hydroxyl value 48 mg KOH/g). These form the

basis of the Combustion Modified Ether foam and the Standard Ether foam reference types respectively. Samples were taken at random from bulk deliveries from various commercial manufacturing sources.

Procedure for Human Health Risk Assessment

For each of the 5 foam samples, the highest concentration recorded for each volatile, irrespective of the time the measurement was taken in the chamber, was used. Thus, for each sample, the worst-case scenario was modelled i.e. that the volatile was released at that concentration throughout the entire test period of up to 160 hours. This was never found to occur in any of the tests reported here.

As the results in Table 4 show, all volatiles for these relatively fresh foams go through a maximum, and their concentration begins to decline after about 3 days. Therefore, they do not pose a chronic hazard in indoor environments, although the risk assessment performed assumes them to be present over much longer periods of time. The flow rate of 0.5 hr^{-1} was chosen from experience to represent a typical room ventilation rate.

The NOAEL value for any substance (or substance group) used for the risk assessment was derived only where Eurofins⁽¹³⁾ reported release above the level of detection.

For each substance a full literature survey was carried out for toxicological properties. The index of choice for hazard assessment purposes was an occupational exposure limit (OEL) where one had been published. This was taken to represent the conservative NOAEL. For the purposes of these risk assessments, such values were considered preferable to NOAELs derived from published toxicological data. OELs are normally developed following extensive consultation and review by multi-disciplinary experts. Carcinogenic, mutagenic and reprotoxic properties are considered within that process. For several substances or groups of substances, no published OEL was available. In such cases, the published toxicity data was used to derive a NOAEL. Sources of published data included; TRACE (TNO-BIBRA, Carshalton, UK); NIOSH-RTECS; EU HEDSET. For four substances (chlorooctane; chloropropanol; hexanal, propylene glycol acetal and propanol, propenyloxy), it was not possible to derive a NOAEL from their inadequate toxicology.

For the purposes of exposure modelling, where the test chamber and foam block sample were scaled-up to a standard room, it was assumed that the

dimensions of the mattress would be 2 m long by 1.4 m wide by 0.15 m thick. The surface area of such a mattress would therefore be 6.62 m².

In addition, the modelling assumed that the ‘mattress’ would be able to release volatile substances from all 6 surfaces. Though unlikely in reality, this assumption added to the ‘worst case’ scenario that was intended.

Eurofins provided the conversion equation used for the risk assessment. Employing the values above, the concentration of a volatile in a standard room was derived as follows:-

$A_s:A_k$ area of sample in standard room and chamber
6.62 m² ~ 2.72 m²

$V_s:V_k$ volume of standard room and chamber
30 m³ ~ 3.2 m³

$n_s:n_k$ air change in standard room and chamber
0.5 h⁻¹ ~ 0.5 h⁻¹

$L_s:L_k$ “area specific volume flow” in standard room and chamber
 $L = A/V$

C_s calculated concentration of volatile chemical in standard room

C_k measured concentration of volatile chemical in test chamber
 $C_s = C_k \times (n_k/n_s) \times (A_s/A_k) \times (V_k/V_s)$

now; $V_s = 30 \text{ m}^3$, $V_k = 3.2 \text{ m}^3$, $n_s = 0.5 \text{ h}^{-1}$, $n_k = 0.5 \text{ h}^{-1}$

therefore; $C_s = C_k \times (1) \times (6.62/2.72) \times (3.2/30)$

therefore; $C_s = C_k \times 2.434 \times 0.107$

hence; $C_s = C_k \times 0.26$

Thus, the concentration of volatile chemical in a standard room is the product of concentration of volatile chemical in the test chamber multiplied by 0.26.

This factor was used in the calculation for each volatile to derive a ratio of the concentration in a standard room to the NOAEL.

DISCUSSION

Results of Chamber Tests on Foam Mattress Cores

Tables 1-3 list all VOCs found from the reference group of foams at the various test laboratories, without reference to sampling time. The measured concentration of most species has reduced progressively with residence time in the chamber (often to below level of detection within 24 hours) but it is apparent with the least volatile species, slow diffusion from the foam substrate results in a concentration maximum during the monitoring period.

Despite precautions taken to avoid analytical artefacts, several such substances have been identified in the various VOC analyses. Phthalate esters have frequently been detected, despite their intended absence in formulation components. It is clear that this artefact can have many origins such as indirect contact with other polymers; in extraction studies, which will form the basis of a subsequent publication, some high purity analytical reagents were found to contain traces transferred from polymeric containers.

It can readily be demonstrated that wrapping polyurethane foam directly in polyethylene foil creates high molecular weight alkane/alkene emissions as analytical artefacts. For practical reasons, however, mattress sized samples for chamber testing were wrapped in this foil. Once the sources were identified, the described artefacts need not be covered by the Risk Assessment. Problems of this nature have been identified in earlier studies involving polyurethane foams⁽¹¹⁾.

The chamber testing was carried out at the end of the project and was essentially a repetition of all the initial tests. The VOCs however were monitored after various exposure periods in the chamber. Results of this work shown in Table 4 provide peak values to be used in a comprehensive risk assessment programme. It is noteworthy that in this later series of chamber tests BHT (butylated hydroxy toluene) emissions ceased to be significant. The same trend has occurred in small-scale tests and is explained by the adoption of less volatile antioxidants by the foam industry and its raw material suppliers. Towards the end of the project, which lasted over five years, trace emissions of alternative antioxidants have sometimes appeared in small-scale headspace runs.

Several of the artefacts seen in other small-scale analysis have also appeared in the chamber series, particularly in the earlier stage of the project when the level of awareness was lower.

Table 1 VOCs found in chamber tests at Eurofins

<p>STANDARD POLYETHER Siloxanes: octamethyl cyclotetra- decamethyl tetra- decamethyl cyclopenta- + others toluene xylene TEDA dichlorobenzene alkanes, C₆-C₁₅ phthalates</p>	<p>HR FOAM Siloxanes: octamethyl tri- octamethyl cyclotetra- decamethyl tetra- decamethyl cyclopenta- dodecamethyl penta- toluene xylene hexenal styrene methylene chloride dichlorobenzene alkanes, C₆-C₁₅ dichloropropanol dichloropropane 2-ethyl hexanoic acid TMCP</p>
<p>CMHR FOAM Siloxanes: hexamethyl cyclotri- octamethyl cyclotetra- decamethyl cyclopenta- + others alkanes, C₆-C₁₅ 2-ethyl hexanoic acid TMCP</p>	<p>HR/FR FOAM Siloxanes: hexamethyl cyclotri- octamethyl tri- octamethyl cyclotetra- decamethyl tetra- decamethyl cyclopenta- dodecamethyl penta- propanal hexenal BHT toluene styrene xylene methylene chloride Alkanes, C₆-C₁₅ 2-ethyl hexanoic acid oxybis(chloropropane) dichloropropane dimethyl dioxane chloro-octane hexanal, propylene glycol acetal propanol, propenyloxy-</p>
<p>COMBUSTION MODIFIED POLYETHER Siloxanes: hexamethyl cyclotri- octamethyl tri- octamethyl cyclotetra- decamethyl tetra- decamethyl cyclopenta- dodecamethyl penta- BHT toluene xylene acetaldehyde propanal hexenal methylene chloride C3 benzenes chloropropanol tetrachloroethylene propanol, propenyloxy TEDA Alkanes, C₆-C₁₅ 2-ethyl hexanoic acid TMCP</p>	<p>HR/FR FOAM Siloxanes: hexamethyl cyclotri- octamethyl tri- octamethyl cyclotetra- decamethyl tetra- decamethyl cyclopenta- dodecamethyl penta- propanal hexenal BHT toluene styrene xylene methylene chloride Alkanes, C₆-C₁₅ 2-ethyl hexanoic acid oxybis(chloropropane) dichloropropane dimethyl dioxane chloro-octane hexanal, propylene glycol acetal propanol, propenyloxy-</p>

Table 2 VOCs found in chamber tests at LGA

<p>HR FOAM Siloxanes: octamethyl cyclotetra- decamethyl cyclopenta- BHT toluene styrene alkanes, C₆-C₁₅ N-ethyl morpholine dimethyl benzylamine oxybis(chloropropane)</p>	<p>HR/FR FOAM Siloxanes: decamethyl cyclopenta- BHT toluene alkanes, C₆-C₁₅ dimethyl benzylamine</p>
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Table 3 VOCs found in chamber tests at Fraunhofer

<p>COMBUSTION MODIFIED POLYETHER Siloxanes toluene xylene/ethyl benzene dichlorobenzene chloropropanol alkanes, C₆-C₁₅</p>	<p>STANDARD POLYETHER Siloxanes toluene alkanes, C₆-C₁₅</p>
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Tests on Raw Materials

Within the research project we have confined raw material testing to the polyols used to make two types of reference mattresses (conventional and combustion modified polyethers) but through discussion and literature have also investigated impurity profiles for other polyurethane foam raw materials.

As a general observation, polyols can display molecular weight distribution back to mono-, di-, and tri-propylene glycol and other low molecular weight oligomers together with their corresponding allylic dehydration products. The latter and a range of aldehydes, cyclic ethers and acetals have been previously reported in literature⁽¹⁷⁾. Over the period of study the majority of mainstream polyol suppliers have invested significantly in the development of so-called odour-lean polyols and there is good evidence from the tests on their materials that total VOCs and odorous species have been reduced substantially. It should be mentioned that the chamber tests were performed with raw materials

Table 4 Time dependency of VOCs found in chamber tests at Eurofins

Concentration ($\mu\text{g}/\text{m}^3$) of VOCs after time shown for individual foam types	STANDARD POLYETHER				
	24hr	48hr	72hr	120hr	160hr
BHT					
Siloxanes	689	526	501	375	413
<i>hexamethyl cyclotrisiloxane</i>					
<i>octamethyl trisiloxane</i>					
<i>octamethyl cyclotetrasiloxane</i>	24	12	9.9	5.3	2.9
<i>decamethyl tetrasiloxane</i>	380	290	280	210	230
<i>decamethyl cyclopentasiloxane</i>	55	34	31	20	20
<i>dodecamethyl pentasiloxane</i>					
<i>other</i>	230	190	180	140	160
TMCP					
methylene chloride					
propane oxybischloro					
dichloropropane					
chloropropanol					
dichlorobenzene					
chloro octane					
2-ethylhexanoic acid					
triethylene diamine	360	290	260	220	240
dimethyl dioxanes					
phthalates	1.8	1.4	2.0	1.9	2.4
alkanes $\text{C}_6 - \text{C}_{15}$	20	11	7.4	6.9	
toluene	22	8.3	4.1		
xylene					
C3 benzenes					
styrene					
propanol, propenyloxy					
propanal					
hexenal					
hexanal, propylene glycol acetal					

Table 4 Continued

Concentration ($\mu\text{g}/\text{m}^3$) of VOCs after time shown for individual foam types	CMHR				
	24hr	48hr	72hr	120hr	160hr
BHT					
Siloxanes	16	8	5	4	0
<i>hexamethyl cyclotrisiloxane</i>	4.9	1.5			
<i>octamethyl trisiloxane</i>					
<i>octamethyl cyclotetrasiloxane</i>	5.3	3.1	2.9	2.5	
<i>decamethyl tetrasiloxane</i>					
<i>decamethyl cyclopentasiloxane</i>	3.8	2.9	2.4	1.5	
<i>dodecamethyl pentasiloxane</i>					
<i>other</i>	1.7	0.9			
TMCP	1.8	1.7	2		
methylene chloride					
propane oxybischloro					
dichloropropane					
chloropropanol					
dichlorobenzene					
chloro octane					
2-ethylhexanoic acid		9.9	13	6.5	8.9
triethylene diamine					
dimethyl dioxanes					
phthalates					
alkanes $\text{C}_6 - \text{C}_{15}$	3.7	2.4	1.7		
toluene					
xylene					
C3 benzenes					
styrene					
propanol, propenyloxy					
propanal					
hexenal					
hexanal, propylene glycol acetal					

Table 4 Continued

Concentration ($\mu\text{g}/\text{m}^3$) of VOCs after time shown for individual foam types	CM ETHER				
	24hr	48hr	72hr	120hr	160hr
BHT	6.5	7.5	8.3	6.7	5.7
Siloxanes	170	183	188	128	95
<i>hexamethyl cyclotrisiloxane</i>					
<i>octamethyl trisiloxane</i>					
<i>octamethyl cyclotetrasiloxane</i>	58	43	37	16	8.5
<i>decamethyl tetrasiloxane</i>	29	68	85	70	55
<i>decamethyl cyclopentasiloxane</i>	59	50	50	28	20
<i>dodecamethyl pentasiloxane</i>	24	22	16	14	11
<i>other</i>					
TMCP	9.1	16	16	19	17
methylene chloride					
propane oxybischloro					
dichloropropane					
chloropropanol	34	30	27	15	11.0
dichlorobenzene					
chloro octane					
2-ethylhexanoic acid	28	46	48	41	33
triethylene diamine	32	10	9.4	7.5	4.8
dimethyl dioxanes					
phthalates					
alkanes $\text{C}_6 - \text{C}_{15}$	67	52	45	21	9.5
toluene	270	130	68	11	4
xylene	17	13	7.4	3.1	
C3 benzenes	4	4.1	3.8	2.2	
styrene					
propanol, propenyloxy	9	9	9	5	4
propanal					
hexenal					
hexanal, propylene glycol acetal					

Table 4 Continued

Concentration ($\mu\text{g}/\text{m}^3$) of VOCs after time shown for individual foam types	HR/FR				
	24hr	48hr	72hr	120hr	160hr
BHT					
Siloxanes	842	699	565	455	389
<i>hexamethyl cyclotrisiloxane</i>	20	10	8	6	5
<i>octamethyl trisiloxane</i>	33	13	5		
<i>octamethyl cyclotetrasiloxane</i>	160	130	97	64	44
<i>decamethyl tetrasiloxane</i>	290	250	200	160	130
<i>decamethyl cyclopentasiloxane</i>	69	56	45	35	30
<i>dodecamethyl pentasiloxane</i>	270	240	210	190	180
<i>other</i>					
TMCP					
methylene chloride	270	150		100	75
propane oxybischloro	38	31	26	21	18
dichloropropane	11	4	2.2		
chloropropanol					
dichlorobenzene					
chloro octane	67	52	43	32	26
2-ethylhexanoic acid					
triethylene diamine					
dimethyl dioxanes	12	7.2	4.9	2.4	
phthalates					
alkanes $\text{C}_6 - \text{C}_{15}$	88	64	43	33	24
toluene	7.1	3.7	2.1		
xylene					
C3 benzenes					
styrene	3.7	2.8	2.4		
propanol, propenyloxy					
propanal	42	27	23		
hexenal	76	54	42	26	20
hexanal, propylene glycol acetal	20	11	7.2		

Table 4 Continued

Concentration ($\mu\text{g}/\text{m}^3$) of VOCs after time shown for individual foam types	HR				
	24hr	48hr	72hr	120hr	160hr
BHT					
Siloxanes	645	536	444	423	327
<i>hexamethyl cyclotrisiloxane</i>					
<i>octamethyl trisiloxane</i>	60	31	6.1	2.6	
<i>octamethyl cyclotetrasiloxane</i>	71	59	41	33	20
<i>decamethyl tetrasiloxane</i>	230	210	160	160	120
<i>decamethyl cyclopentasiloxane</i>	54	26	37	37	27
<i>dodecamethyl pentasiloxane</i>	230	210	200	190	160
<i>other</i>					
TMCP	6	22	25	19	10
methylene chloride	102	106			
propane oxybischloro					
dichloropropane	6.2	3.3	2		
chloropropanol					
dichlorobenzene	2.0				
chloro octane					
2-ethylhexanoic acid	46	83	66	99	63
triethylene diamine					
dimethyl dioxanes					
phthalates					
alkanes C ₆ - C ₁₅	76	57	44	44	30
toluene	32	21	12	5.6	3.4
xylene	17	15	10	8.5	5.3
C3 benzenes					
styrene	43	42	30	29	20
propanol, propenyloxy					
propanal					
hexenal	29	26	18	17	11
hexanal, propylene glycol acetal					

available at the time before any “odour-lean” versions were available. Therefore, new foams will show somewhat lower levels of volatiles.

The earliest analyses of polyols revealed significant concentrations of siloxanes. Cross-contamination clearly had to be suspected here and precautionary measures adopted thereafter included sampling in clinically clean containers. Despite this, siloxanes continue to be seen in all polyol analyses. It has been concluded that these arise by glycolysis of the PDMS layer on the SPME needle in the presence of volatile diols⁽¹⁸⁾. Evidence for this was provided by a re-run of one polyol via the Tenax/Carbon technique. Siloxanes were then seen to be absent. There is no evidence that such a mechanism operates in foam testing; in this situation siloxanes are not artefacts.

High resilience foam polyols have not been investigated at this time, the large number of technology and sourcing permutations being a consideration. The types of emanations seen from CMHR, HR and HR/FR reference foams validate this decision.

Several chlorinated phosphate flame retardant additives were used in the reference foam formulations. Species found as trace impurities in the various foams that can originate from the various FR additives include propanol, dichloropropane, chloropropanol, hexanal, and chloroctane. It is known that thermal degradation during the exothermic foam production process can be a secondary route to some of these species.

The non-chlorinated compounds in the above group are primarily linked to polypropylene glycol impurities/side products and are therefore common to polyols. The availability of low odour additives and polyols contributes to the manufacture of odour-free foam.

The presence of methylene chloride as a VOC, whether deliberate as secondary blowing agent residue or artefact by adsorption from industrial air, can give rise to co-emanations of its trace impurities. The detection of mono- and dichlorobenzenes as emanations from foam can be traced to the use of dichlorobenzene in the distillation of TDI (toluene diisocyanate) in some manufacturing plants.

Silicone surfactants are complex proprietary blends and while the presence of dimethyl siloxane oligomers has already been stated there are indications that other organic impurities and blending agents may be detectable. These include glycols, propylene carbonate, acetic acid, propanol and toluene, although the last named is much less common in today’s materials.

We have indicated some areas where raw material and end product purity have been improved and further advances in VOC reduction are an ongoing challenge. Although foam odour is seldom a practical problem there are critical end use areas where special precautions such as additional airing can be needed. The extremely low odour threshold in air of some raw material impurities^(19,20) underwrite the importance that their concentrations in finished product are controlled at an absolute minimum.

Typical odour thresholds (ppm)	
dichloropropane	0.0058-0.25
toluene, xylene, C ₃ benzenes	0.1-0.16
styrene	0.017-0.034
hexanal	0.0067-0.016
hexenal	0.02-0.12

Human Health Risk Assessment

This study addressed whether any potential risks to human health arise from the release of volatile substances from five types of typical flexible polyurethane foam. The exposure scenario used was one of a human lying on an uncovered flexible foam mattress for eight hours per day.

Twenty two individual substances and groups of substances were subject to quantitative risk assessment. For a number of the substances, there was no published, or substantiated, OEL. In these cases, published toxicological data was the basis of a derived NOAEL.

The exposure model permitted a scaling-up of the volatile release within the test chamber to a 'standardised mattress' in a 'standardised bedroom' to give concentrations expressed in micrograms per cubic metre of air. This value was then divided by the NOAEL (where available) to arrive at a number representing the ratio between the room concentration and the NOAEL. That ratio has provided the quantitative risk assessment in this study. Results are given in Table 5.

The highest ratio obtained, for triethylene diamine (TEDA), actually revealed that the concentration was less than 1/60th of the amount that might be regarded as representing a risk to health.

There was insufficient published information to derive NOAELs for four other individual substances that were also detected (chlorooctane; hexanal,

Table 5 Calculated maximum release of volatiles

Volatile	Test chamber Highest conc ($\mu\text{g}/\text{m}^3$)	Standard room Highest conc. ($\mu\text{g}/\text{m}^3$)	NOAEL ($\mu\text{g}/\text{m}^3$)	Ratio of conc in room to NOAEL
TEDA (triethylene diamine)	360.0	93.6	6,000	1.6×10^2
Dimethyl dioxanes	12.0	3.1	300	1.0×10^2
Xylene mixed isomers	17.0	4.4	870	5.0×10^3
C3 benzenes	4.1	1.1	500	2.2×10^3
TMCP (tris monochloropropyl phosphate)	25.0	6.5	4,600	1.4×10^3
Siloxanes, total HRRR release at 24h	842	219	440,000	5.0×10^4
Toluene	270.0	70.2	191,000	3.7×10^4
Alkanes C ₆ -C ₁₅ (inc C ₁₂)	88.0	22.9	72,000	3.2×10^4
BHT	8.3	2.2	10,000	2.2×10^4
Methylene chloride	270	70.2	350,000	2.0×10^4
Propanal	42.0	10.9	71,000	1.5×10^4
bis(1 & 2-chloroisopropyl) ether	38.0	9.9	70,000	1.4×10^4
Styrene	43.0	11.2	85,000	1.3×10^4
Phthalates	2.4	0.6	5,000	1.2×10^4
Hexenal	76.0	19.8	394,000	5.0×10^5
Dichloropropane 1,2 isomer	11.0	2.9	71,000	4.0×10^5
Dichlorobenzene	2.0	0.5	300,000	0
2-ethylhexanoic acid	99.0	25.7	425,000	0
The NOAEL and ratio of the two values arranged in descending order (the lower the ratio, the greater the margin of safety)				

propylene glycol acetal and propanol, propenyloxy). The Standard Room highest concentrations were calculated as 17.4, 8.8, 5.2 and 2.3 mcg/m³ respectively. With hexanal, propylene glycol acetal and propanol, propenyloxy no published toxicity data was retrieved. However, based upon their chemical structure and the very low concentrations released, it is not considered that these materials constitutes a risk to human health, although some data exists for chlorooctane, it is insufficient to derive a NOAEL.

Based on what limited information was available and knowledge of close analogues, further work may be necessary. However, it should be noted here that chlorooctane was found in diminishing small amounts in only one of the foams tested. The foam manufacturer has taken steps to eliminate this VOC species. Tests carried out following minor reformulation for this foam grade have determined no further traces of this VOC. It may be noted however that chloroethanol has an OEL of 3.3 mg/m³ in Germany. Since toxicity is likely to be a feature of alkylation, then chloropropanol would have less alkylating potential than chloroethanol. The 3.3 mg/m³ would correspond to 3300 µg/m³. This provides a measure of reassurance that chloropropanol would not constitute a risk to health at the concentration released.

Overall this study has demonstrated that with the risk assessment methodology used, no volatile substances were released in quantities greater than one-sixtieth of that which should not cause any adverse effects in man.

The magnitude of this difference between the measured quantity released and the NOAEL nullifies any concerns about the adequacy of safety factors in the risk assessment.

Accordingly, the study demonstrated that a human, spending eight hours asleep on a new uncovered, polyurethane mattress, would not be exposed to any significant risk to their health from the small quantities of volatile substances that might be given off. This is even more true as after data from chamber tests were available raw material suppliers undertook successful effort to reduce trace-impurities.

CONCLUSIONS

- The foaming process only rarely creates emanations, but one of several routes to analytical artefacts is adsorption of extraneous species from air during processing, storage and handling.

- Species identification by computerised matching of mass spectra to library data bases can often be misleading. Considerable expertise and product knowledge is needed to support valid assignments.
- Several raw material manufacturers have invested in improvement technologies and have introduced purer products during this research.

When mattress sized foam samples were subjected to chamber testing, VOC concentrations were seen to decline sharply with time. The quantitative results have been used in a risk assessment project that used an exposure scenario of an unclothed human lying on an uncovered foam mattress for 8 hours a day. This concluded that no species was present at a concentration greater than 1/60th of its NOAEL value (No Observed Adverse Effect Level).

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