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Isocyanates in Flexible Polyurethane Foams

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Flexible polyurethane foams (PUF) are used in automobile seating, furniture, bedding, carpet pads, etc. Over 2.1 billion pounds of PUF are produced and used in the US annually (AFPF, 1999). These foams are formed by reacting a polyol with a di- or a poly-isocyanate in the presence of proper catalysts and additives. Isocyanates are of interest in occupational medicine because of their capacity to cause disease (Rosenstock and Cullen 1994). Dermal contact can provoke dermatitis with symptoms such as rash, itching, hives, and swelling of the extremities (Levy and Wegman 1988). Isocyanates are capable of producing respiratory disease at remarkably low levels of exposure (e.g. asthma, rhinitis, pneumonia, etc). Allowable concentrations in the workplace air are regulated to analogously low levels (i.e., 5 ppb for toluene diisocyanate (TDI)). PUF manufacturers have expended much time and resources in minimizing airborne exposure to isocyanates. This included shifting to the use of isocyanates with much lower volatility (e.g., methylenediphenyl diisocyanate (MDI) and prepolymers of TDI). As a result, during the past 25 years, airborne levels of isocyanates have been dramatically reduced. Yet, the development of occupational asthma remains the primary health and safety concern for isocyanate exposure. An explanation may be the recently suggested hypothesis of asthma induction through solely dermal exposure with isocyanates (Karol et al. 1981; Rattray et al. 1994; Kimber 1996; Bickis 1996; Petsonk et al. 2000).

During PUF manufacturing, an excess of isocyanate is always added above that required for stoichiometric reaction with the hydroxyl groups of polyols and water (Hugo et al. 2000; Wirpsza 1993). In spite of this and the extensive literature on the hazards of isocyanates, little has been published on the safety of PUF-containing consumer products. In several compendia covering the chemistry, manufacturing and uses of PUF, statements such as "PUF is non-toxic" are made with little or no supporting references cited (e.g., Wirpsza 1993). A limited number of studies have examined the residual isocyanates in foams produced on a small scale in the laboratory (e.g., Conte and Cossi 1981; Van Gheluwe et al. 1987) or in commercial grade factory samples (Hugo et al. 2000). The amounts of isocyanate detected in these studies were variable and depended on time, humidity, and other conditions.

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The prevalence of asthma in the overall US population has increased from 31 per 1,000 to 54 per 1,000 since the early 1980's (USDHHS 1999). This represents an increase of about 75%. Links between the use of non-feather (i.e., specifically foam) pillows, and asthma (Strachan and Carey 1995) and perennial rhinitis (Frosh et al. 1999) have been reported. These studies have raised the possibility that use of synthetic pillows may increase the chance of developing asthma or rhinitis. Considering that respiratory hypersensitivity to isocyanates might be produced by dermal as well as inhalation exposure, the examination of PUF consumer products for isocyanate seemed warranted. In addition, one of us (JE) exhibited a prompt dermatitis following use of a PUF mattress pad. Thus, we surveyed nine PUF products of varying age, type and country of manufacture using a rapid, semi-quantitative, color-indicating "wipe" test for the presence of the isocyanate group (NCO). Selected samples were also analyzed for isocyanates by high performance liquid chromatography (HPLC).

MATERIALS AND METHODS

Flexible PUF products purchased at retail outlets were tested (see Table 1 for descriptions). Non-PUF materials in upholstered furniture, bedding and carpet underlays were also tested as controls.

Colorimetric indicator wipes called Swype® (Colormetric Laboratories Inc., Des Plaines, IL) were used for detection of isocyanate groups (NCO) in the foams. These commercially prepared Swype pads change color when they come in contact with NCO. The Swype has been validated by OSHA (1997) for industrial hygiene applications as a screening tool for assessing surface contamination in a workplace or laboratory. The standard procedure involves spraying lightly with mineral oil the area to be sampled and waiting approximately 30 seconds for any isocyanate to dissolve. The surface is then wiped with a Swype pad. Color development generally occurs in 2 to 3 minutes. A pastel red-orange or pink color indicates isocyanate contamination of the surface tested. The color indication varies depending on the type and quantity of isocyanate present and the surface Swype detection limit is approximately 3-5 μg.

For the current study, the procedure was modified for testing of PUF for residual isocyanate by applying 5 drops of acetone to the Swype pad and placing it on the surface of the foam. Preliminary testing showed that leaving the pad in place for 10 min was sufficient for color development on the foam surface and or the pad. See Figure 1 for examples of Swype before and after testing a PUF sample.

For HPLC analyses (Rando et al. 1995), foam samples were cut into small pieces and shredded in an analytical mill with dry ice continually added to enhance shredding. Each finely shredded foam sample (~ 0.2 g) was weighed into a scintillation vial, and 3 mls of a 3 mg/ml MAMA reagent (9-N-methylamino-methylanthracene) in DMSO solution were added.

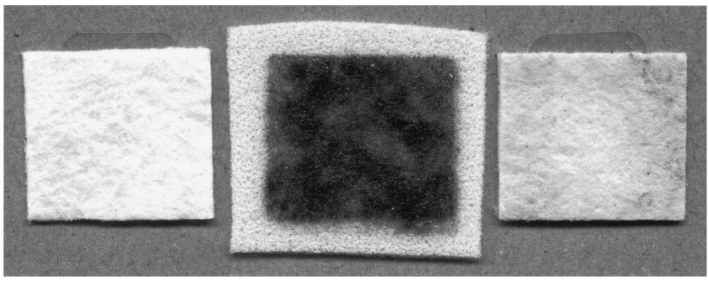

Figure 1. Swype pad before (left) and after (right) testing PUF sample (middle). An unused Swype is pale yellow in color. The PUF sample became dark red after 60 min and the Swype was colored an orange pink. Color development on the foam indicates bound/trapped isocyanate groups (NCO), whereas color on the Swype denotes free isocyanates.

Samples were filtered twice before analysis: first using a 13 mm Sweeney cassette equipped with a 13 mm Type A/E glass fiber filter followed by filtering the filtrate with a 4 mm syringe filter (0.45 μm Nylon). Samples were analyzed using the following HPLC conditions: mobile phase was 55% acetonitrile/45% water/0.08% TEA/0.16% phosphoric acid; column, a 5.0 cm X 4.6 mm, 5 μm Supelcosil LC-8-DB; flow rate 1.0 ml/min; injection volume 20 μl; run time 60 min. Detection was with fluorescence and dual-wavelength ultraviolet absorbance: fluorescence (ex = 245 nm, em = 414 nm) and two UV detectors with wavelengths set at 370mn and 245nm. TDI and total reactive isocyanate group (TRIG) were quantitated based on analysis of authentic TDI-MAMA standards. TDI was identified by retention time and response ratio. TRIG was identified by response ratio. Based on a 0.2 g sample and 3 ml extraction volume, the estimated limits of detection for 2,4-TDI, 2,6-TDI, and TRIG were 2.7 μg/g, 2.5 μg/g, and 1.3 μg/g, respectively.

RESULTS AND DISCUSSION

Table 1. lists the characteristics of the samples and response to NCO testing after 10 min and 60 min contact with a Swype pad. Non-PUF materials consistently tested negative for NCO, whereas all PUF samples exhibited a positive color development on the foam at 60 min. Six of nine PUF samples were positive at 10 min. Generally, age of foam appeared to influence the non-response at the shorter time period (i.e., the older foams were more likely to show no or minimal response at 10 min, while giving a positive at 60 min). Also note in Figure 2. that the one year old PUF (sample C) produced a positive response at 2 min. The color development on the PUF represents the presence of unreacted NCO groups "bound" into the foam polymer matrix.

In a majority of the samples, the Swype pad also developed a visible

Table 1. Results of Swype® test for NCO in polyurethane foams and similar materials.

Sample[a]	country[b]	age (yr)[c]	10 min[d]	60 min[e]	Swype[f]
mattress pad	US	1	+	+	+
mattress pad	NZ	<1	+	+	+
mattress	NZ	3	-	+	+/-
auto seat	Japan	7	+	+	+
sofa padding	US	30	+/-	+	+
carpet pad	NZ	3	+	+	+
pillow	US	15	+/-	+	-
ironing board pad	Australia	<1	+	+	+/-
child auto safety seat	Australia	0.5	+	+	+/-
latex carpet pad	NZ	8	-	-	-
latex sofa cushion	US	30	-	-	-
polyester pillow	NZ	4	-	-	-

a. all samples are flexible polyurethane foam, unless otherwise noted
b. country of manufacture
c. age of material in years
d. visible (+), faint (+/-) or no visible (-) color on material at 10 min
e. visible (+) or no visible (-) color on material at 60 min
f. visible (+), faint (+/-) or no visible (-) color on Swype at 60 min

color. This suggested the presence in the PUF of free unreacted diisocyanates (e.g., TDI, MDI, etc.). These were confirmed by solvent extraction and HPLC analysis of three samples (Table 2.). TDI monomer which is widely used in the manufacture of flexible foams, comprised between 25% and 100% of the total soluble isocyanates found. A general trend toward lower concentration in older samples was observed.

The positive Swype result and the free TDI found in the sample of 30 year-old PUF were particularly notable (Figure 2., Tables 1. and 2.). Isocyanates are considered to be highly reactive substances, even combining readily with water. "Conventional wisdom" would suggest that unreacted NCO groups would not be present in PUF consumer products. However, a study by Van Gheluwe et al. (1987) found NCO in laboratory-produced PUF 100 days after preparation using Fourier Transform Infrared Spectroscopy (FTIR) to quantitate unreacted NCO groups. The method did not distinguish between bound and free NCO. They showed there was a rapid decline in the first 10 -15 days after PUF production, followed by a slow and gradual reduction. The data produced a rate-of-decline curve which described the disappearance of NCO groups over time. In fact, setting the time at 30 years in their formula, resulted in an estimate of 5% of initial NCO groups remaining at this time point. Based on Van Gheluwe et al. (1987), it is not surprising to find NCO in PUF, even in the thirty year old foam we tested.

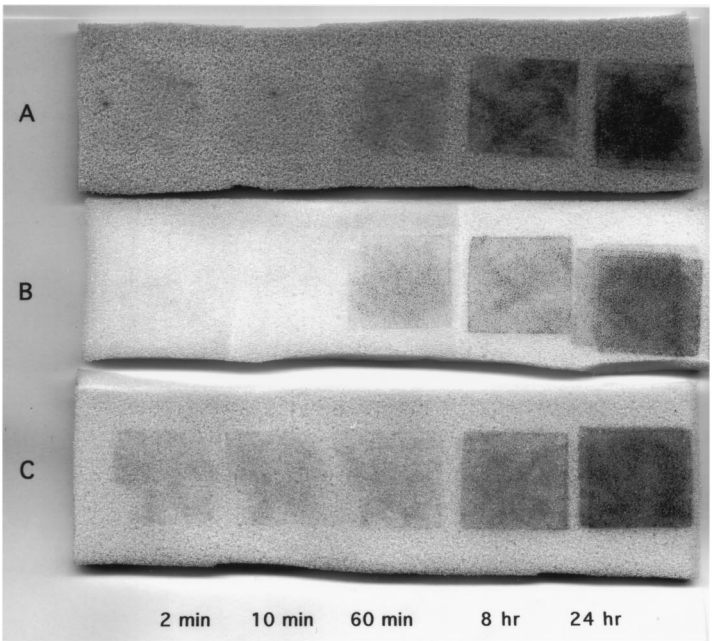

Figure 2. Results of tests for the presence of isocyanate groups (NCO) in flexible polyurethane foams. Sample A was from a 30 year-old sofa. Sample B was a 3 year-old mattress and C was a 1 year-old "egg-crate" type mattress pad. Swype pads (~1 square inch) were placed on the foams for the indicated times and then removed. The dark squares on the foams show color development occurring at each of the time points.

A more recent study (Hugo et al. 2000) raises the possibility that "trapped" isocyanate may be available to dissolve in skin oils upon dermal contact or very slowly volatilize from PUF. Hugo et al. (2000) passed TDI-containing air through PUF in a closed system and >99% of the introduced amount was retained in the foam. After a 3-day "aging" period in the closed system, <0.5% of this TDI load could be removed by passing TDI-free air through the PUF for 72 hr. No attempt was made to use solvents to extract trapped TDI from the "loaded" PUF or to determine the fate of the TDI. The color response we found on the Swype pads and the measurement of free isocyanates in PUF samples were consistent with the potential for extraction of trapped isocyanates into lipophilic skin oils and or with a slow release of trapped isocyanates.

Positive associations have been reported between the use of foam pillows and childhood asthma (Strachan and Carey 1995) and adult rhinitis (Frosh et al. 1999). Kemp et al. (1996) provided a possible explanation by showing that synthetic pillows contained more house dust mite allergen than

Table 2. Concentrations of free isocyanates in polyurethane foams.

Sample[a]	country[b]	age (yr)	TRIG[c] μg/g	2,6-TDI[d] μg/g	2,4-TDI[e] μg/g
mattress pad	US	1	19.0	ND	20.3
carpet pad	NZ	3	11.6	2.5	3.60
sofa padding	US	30	4.1	8.6	ND

a. all samples are flexible polyurethane foam
b. country of manufacture
c. total reactive isocyanate group including that from the two TDI isomers based on the weight of NCO (42 g/mole); TDI has 2 moles of NCO per mole of TDI and a molecular weight of 174 g/mole.
d. 2,6-toluene diisocyanate
e. 2,4-toluene diisocyanate

feather pillows. Exposure to mite allergen is a factor in triggering attacks of asthma in asthmatic subjects (Sporik et al. 1992). However, Strachan and Carey (1997) confirmed their earlier results by demonstrating that the association of foam pillows with current wheezing was of similar strength among children with and without skin prick reactions to Der p I, the major allergen of the house dust mite Dermatophagoides pteronyssinus. Strachan and Carey (1995) speculated that low concentrations of volatile organic compounds from foam pillows could increase mucosal permeability to inhaled allergens. The extremely low levels of airborne isocyanates that can themselves produce asthma could also be involved. Detection of bound and free isocyanates in PUF are supportive of a chemical-causation link between foam pillows and asthma/rhinitis.

An intriguing possibility is that dermal contact with PUF may be a contributing factor in the childhood asthma seen by Strachan and Carey. The first child in a family often is provided with the new crib, car seat, toys, etc. and siblings receive hand-me-downs. A higher incidence of asthma is exhibited in the first child compared to his sibling(s) (Karmaus and Botezan 2002). Our data suggests an age-related reduction in isocyanate content of PUF which is consistent with a decreasing exposure in second and later children.

Our findings are the first to demonstrate NCO in PUF-containing consumer products; in one case, 30 years post-manufacture. The discovery of free TDI in all foams tested, including bedding, suggests that safety issues related to these products still exist. Moreover, polyurethanes in various forms are used in food packaging, medical applications, insulation, adhesives, and paints that may also represent a potential for initiating immune response. The increasing incidence of asthma, especially in children, as well as its associated high costs for health services, mandate further observational and experimental investigations of these questions.

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REFERENCES

AFPF (1999) Millennium Report. Alliance for Flexible Polyurethane Foam, Arlington VA, http://www.afpf.com/millreport.pdf

Bickis U (1996) A Single Skin Contact with Toluene Diisocyanate (Tdi) Causes a One-Year Persistence of Airway Sensitization, Demonstrable in vivo and in vitro. (abstr) http://www.aiha.org/abstract/6bioderm.html

Conte A, Cossi G (1981) Gas chromatographic determination of free toluene diisocyanate in flexible urethane foams. J Chromatog 213: 162-165

Frosh AC, Sandhu G, Joyce R, Strachan DP (1999) Prevalence of rhinitis, pillow type and past and present ownership of furred pets. Clin Exp Allergy 29: 457-460

Hugo JM, Spence MW, Lickly TD (2000) The determination of the ability of polyurethane foam to release diisocyanate into air. Appl Occup Environ Hyg 15: 512-519

Karmaus W, Botezan C (2002) Does a higher number of siblings protect against the development of allergy and asthma? A review. J Epidemiol Community Health 56: 209-217

Karol MH, Hauth BA, Riley EJ, Magreni CM (1981) Dermal contact with toluene diisocyanate (TDI) produces respiratory tract hypersensitivity in guinea pigs. Toxicol Appl Pharmacol 58: 221-230

Kemp TJ, Siebers RW, Fishwick D, O'Grady GB, Fitzharris P, Crane J (1996) House dust mite allergen in pillows. Brit Med J 313: 916

Kimber I (1996) The role of the skin in the development of chemical respiratory hypersensitivity. Toxicol Lett 86: 89-92

Levy BS, Wegman DH (1988) Occupational health: recognizing and preventing work-related diseases. Second edition. Little, Brown and Co, Boston/Toronto

OSHA (1997) Technical Manual (OTM), Section II. Chapter 2. Sampling for surface contamination. Occupational Safety and Health Admin, http://www.osha-slc.gov/dts/osta/otm/otm_ii/otm_ii_2.html#ii:2_2

Petsonk EL, Wang ML, Lewis DM, Siegel PD, Husberg BJ (2000) Asthma-like symptoms in wood product plant workers exposed to methylene diphenyl diisocyanate. Chest 118: 1183-1193

Rando RJ, Poovey HG, Gibson RA (1995) Evaluation of 9-methylamino-methylanthracene as a chemical label for total reactive isocyanate group: application to isocyanate oligomers, polyurethane prepolymers, and phosgene. J Liq Chrom 18: 2743-2763

Rattray NJ, Botham PA, Hext PM, Woodcock DR, Fielding I, Dearman RJ, Kimber I (1994) Induction of respiratory hypersensitivity to

diphenylmethane-4-4'-diisocyanate (MDI) in guinea pigs. Influence route of exposure. Toxicology 88: 15-30
Rosenstock L, Cullen MR (1994) Textbook of clinical, occupational and environmental medicine. Saunders Publ, Philadelphia
Sporik R, Chapman MD, Platts-Mills TAE (1992) House dust mite exposure as a cause of asthma. Clin Exp Allergy 22: 897-906
Strachan DP, Carey IM (1995) The home environment and severe asthma in adolescence: a population based case-control study. Brit Med J 311: 1053-1056
Strachan D, Carey IM (1997) Reduced risk of wheezing in children using feather pillows is confirmed. Brit Med J 314: 518-518
USDHHS (1999) Data fact sheet: asthma statistics. US Dept of Health and Human Serv, Natl Institutes of Health, http://www.nhlbi.nih.gov/health/prof/lung/asthma/asthstat.pdf
Van Gheluwe P, Cole KC, Hébrard MJ, Leroux J (1987) Attenuated total reflectance infrared spectroscopic analysis of high index foams. J Cell Plastics 23: 73-85
Wirpsza Z (1993) Polyurethanes: chemistry, technology and applications. Ellis Horwood Publ, New York

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