Bull. Environ. Contam. Toxicol. (2005) 74:1–3

DOI: 10.1007/s00128-004-0571-1

Bulletin of Environmental Contamination and Toxicology

Letter to the Editor

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We have concerns with the techniques, interpretation and conclusions of the article "Isocyanates in Flexible Polyurethane Foams" by C.A. Krone et al. (Bull. Environ. Contam. Toxicol. 70, 328-335, 2003). Based on their tests, the authors claim that free unreacted toluene diisocyanate (TDI) was detected in a sample of polyurethane (PU) foam that was up to 30 years old. They then suggest that exposure to TDI from PU foam bedding and pillows by dermal and respiratory routes may be a cause of asthma. However, as detailed in this submission, prior work indicates that diisocyanate is bound in the foam polymer matrix and is not bioavailable. Further, the authors' alteration of the test and inconsistencies in the results raise questions about the reliability of the reported results. Therefore, the authors' speculation that there is a chemical-causation link between PU foams and childhood asthma does not appear to have adequate basis in the science.

The authors carried out tests on several aged foam samples (<0.5 to 30 years) removed from a variety of consumer products. A qualitative/semi-quantitative surface-wipe-test "screening technique," i.e., Colorimetric Swypes® (manufactured by Colormetric Laboratories Incorporated), and a liquid extraction technique were used to determine the concentration of "free diisocyanates" present in the foam samples. Our concerns with this technique and the paper's resulting conclusions include the following:

1. The authors made a change to the normal Swype® testing protocol. Five drops of acetone were applied to the Swype® and the Swype® was placed on the foam pad for 10 or 60 minutes. The normal Swype® method uses mineral oil rather than acetone. The impact of this change on the results is not known, but deserves inquiry.

2. The article reports an intense color change in the foam and a slight color change on the Swype® pad. The authors conclude the color developed in the foam is due to the bound –NCO and the slight color on the Swype® is from free TDI. Based on this, the authors state that they found free TDI in all samples tested (0.5 to 30-year-old specimens). However, several studies, described below, indicate that free TDI is not present in foams. Therefore, alternate explanations for the Swype® test results should be considered.

    - Industry evaluation has shown that PU-foam contains bound –NCO groups irreversibly attached to polymer moiety. The bound –NCO groups do not evaporate, cannot diffuse or permeate from the foam, and are not available for any biological reaction by skin contact. As noted by the Krone et

al. paper, these bound –NCO groups can cause a color change in the Swype® test.

- In a 2002 study investigating TDI levels in freshly made foams, three 37-mm-glass fiber filters coated with 1-(2-pyridyl)-piperazine reagent (OSHA Method 42 filters) were placed between two freshly-made (≈1-hour old) TDI-flexible-foam buns for 5 hours. The three filters were analyzed by HPLC using a fluorescence detector and all three filters had less than 0.1 µg of 2,4- and 2,6-TDI.

- Industry studies carried out to investigate the possible migration of chemicals from PU foam involved extensive examination of acetic acid extracts from a wide range of foam samples. If free diisocyanates had been present in the foam, they would have hydrolyzed to the corresponding amines and subsequently been identified and quantitatively measured. No such amines were detected. The level of detection (LOD) of the analytical method used was <1µg/g, well below than the LOD given by Krone et al.

- Other studies have shown that freshly manufactured TDI-based PU foam has trace amounts of unreacted free TDI, but that the free TDI rapidly disappears from the foam after manufacture (Conte A; Cossi G, J.Chrom., Vol 213, 1981, p.162-5 and Jedrzejczak K; Gaind VS, Analyst, Vol.118, 1993, 149-52). Hugo et al. (reference cited in Krone et al.) have shown that 3-day old foams do not release any TDI by passing air through the foam. Also, when TDI-laden air was passed through the foam, the TDI was not released into the air; that is, free TDI actually was captured into the foam.

3. The article only provides quantitative data for three of the foams investigated (all PU foams – no controls – no blanks). The quantitative data were generated from the analysis of liquid extracts using HPLC/external standardization. Unfortunately, the researchers were not able to confirm the identity of the reported diisocyanates and have relied on retention time and response ratio data. Lack of positive identification (for example by LCMS) of the reported diisocyanates may explain the unusual 2,4 TDI and 2,6 TDI isomer values reported where 1 of the 3 foams tested (a 1 year old foam sample) contained a relatively high amount of 2,4 TDI and no 2,6 TDI, but, in a 30 year old foam sample, the opposite was reported. The authors offer no explanation for why all the 2,6 TDI (the slower reacting of the two aforementioned isomers) would have disappeared from the one-year-

old sample but still be present in a 30-year-old sample. Unfortunately, sufficient details of the experimental procedures and methods have not been included in the paper making it impossible to judge the scientific value of the paper without further explanation by the authors.

4. The paper reports the detection limit for the Swypes® is approximately 3-5 μg, however, the highest value reported by solvent extraction/HPLC analysis is 19.0 μg/g as TRIG (NCO). If the value of 19.0 μg/g is re-calculated to show how much diisocyanate is available on the foam surface to a Swype® it is clearly below the reported limit of detection.

5. The authors suggest dermal contact with PU foam may be a route of childhood asthma (due to contact with free diisocyanate). This postulation is enormously speculative, because:

    - Respiratory sensitization requires exposures to high concentrations (Weill H; Salvaggio J; Neilson A; Butcher B; Ziskind M, Env. Health Persp. Vol 11, 1975, p101-8);
    - Dermal contact leading to respiratory sensitization is shown only in animals exposed to large doses (Karol M H; Hauth B A; Riley E J; Magreni C M, Toxicol. Appl Pharmacol. Vol 58, 1981, p221-30);
    - Skin and mattresses are separated by one or more layers of cloth; and
    - Free diisocyanate has not been adequately demonstrated by the study.

For the above reasons, we believe that the authors' postulation that there is free TDI even in old foams, which might contribute to asthma, represents no more than a speculative leap of faith derived from questionable supporting data.