IDENTIFICATION OF FLAME RETARDANTS IN POLYURETHANE FOAM COLLECTED FROM BABY PRODUCTS

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Introduction

Prior to 2004, PentaBDE was a flame retardant mixture frequently added to the polyurethane foam in consumer products (e.g. furniture). Due to concerns over the persistence, bioaccumulation, and potential toxicity of polybrominated diphenyl ethers (PBDEs) present in this commercial mixture, chemical companies voluntarily phased out the use of PentaBDE in the United States. Today, alternative types of chemical flame retardants are added to polyurethane foam to meet flammability standards for furniture. The flammability standard which primarily drives this use is California's Department of Consumer Affairs Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation Technical Bulletin 117 (TB 117). Despite the fact that TB117 is only required for residential upholstered furniture sold in the state of California, a large number of products sold elsewhere in the U.S. also comply with TB117 and therefore contain additive flame retardants. In addition to furniture, these products include baby products such as strollers, car seats, mattresses, and nursing pillows. There are currently no data available regarding the types of chemicals commonly added to foam found in baby products. This study was undertaken to determine how frequently flame retardant additives are found in specific types of baby products, identify the most common chemicals used, and determine whether the presence of a TB117 label on the product could be used as an indicator for the presence of these flame retardant chemicals in the foam.

Materials and methods

Samples of polyurethane foam from baby products were donated by volunteers who were contacted either by email listserves or via personal communications with the authors of this study and/or their colleagues. Participants were asked to remove a 3-5 cubic cm piece of foam from the product, wrap it in aluminum foil, and place it in a sealed plastic bag. For each foam sample donated, information was collected regarding the type of product, manufacturer and model, year of purchase, and if a TB 117 label was present on the product. Targeted baby products included car seats, strollers, nursing pillows, changing table pads, sleep positioners, and baby carriers that were either currently in use or used by an infant within the last few years.

In the laboratory, a small piece (1/2 cubic cm) of foam was sliced off the sample using a pre-cleaned razor blade and transferred to a test tube. Approximately 2 mL of dichloromethane was added to each tube which was then sonicated for 15 minutes. The dichloromethane was filtered through a syringe filter (0.45 μm PFTE) and transferred to an auto sampler vial. Extracts were analyzed by gas chromatography mass spectroscopy operated in both electron impact (GC/EI-MS) and negative chemical ionization modes (GC/ECNI-MS) collecting full scans. GC/EI-MS mass spectra were compared to the 2005 NIST mass spectral database to aid in the identification of peaks detected in each extract. Confirmation was also performed by comparison to authentic standards purchased from Supelco, (Bellefonte, PA), Chemservice (West Chester, PA), Sigma-Aldrich (St. Louis, MO), and Wellington Laboratories (Guelph, Ontario).

Results and discussion:

A total of 101 samples were collected and analyzed in this study. All extracts were first analyzed in GC/EI-MS mode collecting full scan spectras. Collected mass spectras were first compared to the 2005 NIST mass spectral database to identify chemicals found in greatest abundance in each extract. After a preliminary identification was made by the NIST database, authentic standards were purchased and compared to the extracts for confirmation of the chemical identity.

More than 80% of the products tested contained a known and identifiable flame retardant chemical. A majority of the flame retardants detected were chlorinated and not brominated. The flame retardant most frequently detected in these products was tris (1,3-dichloroisopropyl) phosphate (TDCPP). This chemical was positively identified in 36 samples (Table 1). Our group positively identified and measured TDCPP in a majority of furniture foam and house dust samples analyzed in a recent study[1]. The high frequency of detects for TDCPP in these baby products suggests that baby products may also be a source of TDCPP to indoor dust and the environment. This may be of concern given the higher exposure to children relative to adults for chemicals found in house dust. A recent study found that TDCPP may affect hormone levels and fertility [2].

The second most frequently detected flame retardant in the baby product foam was a mixture which contains triphenyl phosphate (TPP) and two brominated flame retardants known as 2-ethylhexyl, 2,3,4,5-tetrabromobenzoate (TBB) and bis (2-ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH). These three compounds, detected in 17 of the samples, are found in Chemtura's Firemaster ® formulations 550 and 600. These three compounds have also recently been detected in house dust samples [3]. PentaBDE was detected in four of the products, and is likely a result of its use in foam products manufactured prior to the phase out in 2004.

Two additional flame retardants detected and positively identified in samples were tris (2-chloro-2-propyl) phosphate (TCPP) and tris (2-chloroethyl) phosphate (TCEP). The latter compound, detected in 14 of the products tested, has been phased out of use in Europe and is currently listed on California's Proposition 65 list, which includes chemicals that are known carcinogens. The presence of TCEP, a known carcinogen, in baby products is a concern, particularly since TCEP was detected most often in nursing pillows. Eleven foam samples collected from nursing pillows were analyzed in this study; nine of these nursing pillows contained TCEP.

Although this study did not include random sampling, the high detection frequency of flame retardants in baby products suggests that flame retardant additives are commonly found in baby products containing polyurethane foam. This, in turn, may be a source of exposure to children given that most additive flame retardants leach out of products over time. Further research is needed to evaluate environmental and human health effects from these new use flame retardants, particularly the chlorinated organosphosphates which appear to be used in greater quantities than brominated flame retardants in foam.

References:

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2. Meeker JD, Stapleton HM. *Environ Health Perspect* 2010;118:318-323.
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Table 1. Chemicals identified in polyurethane foam collected from baby products and the frequency of their detection.

Flame Retardant	# of Detects
PentaBDE	4
TPP, TBB, and TBPH (Components of FM 550/600)	17
Tris (1,3-dichloroisopropyl) phosphate (TDCPP)	36
Tris (2-chloroethyl) phosphate (TCEP)	14
Tris (2-chloro-2-propyl) phosphate (TCPP)	15
Nothing Detected	13
Unidentified Chemicals in Foam	8