Use of Flame Retardant Chemicals in Furniture: What are the Risks?

Heather M. Stapleton, Ph.D.
Associate Professor of Environmental Chemistry
Nicholas School of the Environment
Environmental Science & Policy Division
Email: heather.stapleton@duke.edu
Outline

1. Introduction and Background
   a. What is a flame retardant (FR) and how do they work?
   b. What regulations govern the use of FRs in products?
   c. What type of products contain FRs?
   d. What type of FRs are used in consumer products?

2. Exposure to the Flame Retardants PBDEs During Early Development

3. Identification of PBDE Replacement Chemicals in Furniture
   a. In Baby Products
   b. In Residential Furniture

4. What do we know about Exposure and Effects of PBDE Replacements: Are they Better or Worse?????

5. Conclusions/ Discussion
Definition:
“A substance added or a treatment applied to a material in order to suppress, significantly reduce or delay the combustion of the material”  

_EHC:192, WHO 1997_

**Regulations That Govern the Use of FRs**

**U.S. Residential Furniture:**
- California Technical Bulletin 117

**Electronics:**
- Underwriters Laboratory Certifications for Insurance purposes (e.g. UL 746 and -94 V-2 – E&E)

**Textiles:**
- Children’s Sleepwear (CPSC)
- Seats and Drapes in Public Buildings (NFPA 701, CA TB 133)
What Type of Products are Treated with Flame Retardants in Your Home?

- Sleep Positioners
- Nursing Pillow
- Couch
- Curtains
- Car Seat
- Insulation
- Tent
- Coffee Maker
- TV
- Christmas Lights
How Do They Work?

• Most common method for retarding fire is to quench the radical species formed in the fire reaction.

Fuel + O₂ → Heat + CO₂ + H₂O

*Stop the formation of radical species

(www.bsef.com)
Flame Retardants are Classified According to Use:

**REACTIVE FRs:**
- Chemically bound to the product they are flame retarding….less likely to leach out into the environment

**ADDITIVE FRs:**
- Mixed in with the resin during extrusion process…..more likely to leach out of products over time

Examples: PentaBDE OctaBDE DecaBDE

Commercial Mixture Names
# PBDE Commercial Mixtures

<table>
<thead>
<tr>
<th>Congener (# of Br atoms)</th>
<th>% of Mixture</th>
<th>Product Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PentaBDE Commercial Mixture (DE-71; Phased out 2004)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 47 (4)</td>
<td>38.2</td>
<td></td>
</tr>
<tr>
<td>BDE 85 (5)</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>BDE 99 (5)</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>BDE 100 (5)</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>BDE 153 (6)</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>BDE 154 (6)</td>
<td>4.54</td>
<td></td>
</tr>
<tr>
<td><strong>OctaBDE Commercial Mixture (DE-79; Phased out 2004)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 153 (6)</td>
<td>8.66</td>
<td></td>
</tr>
<tr>
<td>BDE 154 (6)</td>
<td>2.68</td>
<td></td>
</tr>
<tr>
<td>BDE 183 (7)</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>BDE 196 (8)</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>BDE 197 (8)</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>BDE 207 (9)</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td><strong>DecaBDE Commercial Mixture (Saytex 102E)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 206 (9)</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>BDE 207 (9)</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>BDE 208 (9)</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>BDE 209 (10)</td>
<td>96.8</td>
<td></td>
</tr>
</tbody>
</table>

(La Guardia et al 2006)
History of PBDEs and their Phase Out

- Polybrominated diphenyl ethers (PBDEs) have chemical structures which are very similar to known cancer causing and toxic compounds: **PCBs, dioxins, furans, etc.**

- Animal and Human studies have demonstrates that PBDEs are significantly associated with changes in thyroid hormone levels (Birnbaum and Staskal, 2003; Chevrier et al. 2010; Stapleton et al. 2011)

- Human health studies have found significant associations between PBDEs in blood at birth and deficits in cognitive function and behavior (Herbstman et al 2010; Eskenazi et al 2012)

- Phased out in European Union (2002); voluntary phase out in the US (Penta- and OctaBDE- 2005; Deca-2013)
How Are We Exposed to Flame Retardants?

- Work Environment
- Diet
- Vehicles
- Our Home
- House Dust
PBDEs in Human Samples From Around the World

Total PBDE concentrations in human blood, milk and tissue (in ng/g lipid) shown as a function of sampling year.

North America
Europe
Japan

From Hites et al., 2005
Exposure studies in US adults have observed significant associations with both diet (Wu et al., 2007; Fraser et al., 2010) and dust (Johnson et al., 2010).

Exposure models suggested that infants would be receiving the highest exposure due to breast milk ingestion (Jones-Otazo et al., 2005; Schecter et al. 2003).

However, recent studies suggest that toddlers have highest exposure among all age classes due to increased exposure to house dust:
- Rose et al. (2010) reported levels in 2-5 year old children in California and found concentrations 2-50X higher than adults
- Stapleton et al (2012) toddlers (ages 1-3) serum PBDE levels significantly associated with residues measured on hands, house dust, age, and race

Several studies suggest exposure may be higher for individuals of lower SES:
- Quiros-Alcala et al. (2011) measured PBDEs in dust from low-income households; concentrations were among highest measured
- Windham et al. (2010) measured PBDEs in 6 to 8 year old girls from California and Ohio; significantly higher concentrations in CA vs Ohio; higher in blacks compared to whites
- Zota et al. (2010) wrote perspective article on PBDEs and socio-economic disparities
What Types of FRs are Being Used to Meet TB 117 Today?

• With the phase-out of PentaBDE, what type of chemical flame retardants would be most common in residential furniture?

• Will these new/alternate FRs accumulate in indoor dust and air - leading to human exposure?

• What is known about health effects for these new flame retardants?
Flame Retardants (FRs) Used to Meet California’s TB 117

- Promulgated by California Bureau of Home Furnishing and Thermal Insulation, within the Department of Consumer Affairs
- Requires 12-second open flame testing for polyurethane inside furniture
# PentaBDE Alternatives Assessment

## Table 4-1 Screening Level Toxicology and Exposure Summary

<table>
<thead>
<tr>
<th>Company</th>
<th>Chemical</th>
<th>% in Formulation</th>
<th>Human Health Effects</th>
<th>Ecotoxicity</th>
<th>Environmental</th>
<th>Potential Routes of Exposure</th>
<th>Reactive or Additive?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cancer Hazard</td>
<td>Skin Sensitizer</td>
<td>Reproductive</td>
<td>Developmental</td>
<td>Neurological</td>
</tr>
<tr>
<td>Albermarle</td>
<td>Proprietary E Tetrabromophthalate diol ester</td>
<td>L</td>
<td>L</td>
<td>L*</td>
<td>L</td>
<td>M</td>
<td>L</td>
</tr>
<tr>
<td>Albermarle</td>
<td>Proprietary B Aryl phosphate</td>
<td>L</td>
<td>L</td>
<td>M*</td>
<td>M*</td>
<td>M*</td>
<td>M</td>
</tr>
<tr>
<td>Albermarle</td>
<td>Triphenyl Phosphate CAS # 115-86-6</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>L</td>
</tr>
<tr>
<td>Amfinorm</td>
<td>FR513 Tribromoneopentyl Alcohol CAS # 36483-67-5 Firemaster 550</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Great Lakes</td>
<td>Proprietary F Halogenated anyl ester</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>L</td>
</tr>
<tr>
<td>Great Lakes</td>
<td>Proprietary G Triaryl phosphate, isopropylated</td>
<td>L</td>
<td>L</td>
<td>M*</td>
<td>M*</td>
<td>M*</td>
<td>L</td>
</tr>
<tr>
<td>Great Lakes</td>
<td>Triphenyl Phosphate CAS # 115-86-6</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>L</td>
</tr>
<tr>
<td>Great Lakes</td>
<td>Proprietary H Halogenated anyl ester</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>L</td>
<td>M</td>
</tr>
</tbody>
</table>

(Furniture Flame Retardancy Partnership V 1, EPA 2005)
Screening Consumer Products for FR Chemicals:

*Project 1- Baby Products*
*Project 2- Residential Couches*
Screening Consumer Products
Meeting CA TB 117:

**Project 1- Baby Products**
- car seats, nursing pillows, changing table pads, portable mattresses, sleep positioners, strollers, high chairs, etc
- donated by volunteers/families from in-use products

**Project 2- Residential Couches**
- only residential couches
- volunteers submitted samples had to know date and state of purchase
Analysis of the Foam Samples

Step 1. Place a small piece of foam into a test tube with dichloromethane

Step 2. Sonicate the test tube for 15 min.
**Analysis of the Foam Samples**

**Step 3.** Remove the dichloromethane, filter out the particles, and then inject the extract into a GC/MS*.

- Samples are run in full scan mode
- Signals detected are compared against a NIST mass spectral database
- For commonly known FRs we also now compare to authentic standards.

*Some sample extracts also run by LC/HRMS*
Project 1: Flame Retardants in Children’s Products

- 101 Baby products screened for flame retardant (FR) chemicals
- 80% contained a FR
- TDCPP, Firemaster 550 (FM 550), and “V6” most common FRs identified
- PentaBDE found in 5 samples
- Identified two new chlorinated organophosphate flame retardant mixtures
- Risk/exposure assessments do not consider exposure from use of these products
- Now 3 infant/juvenile products exempted from TB 117
Project 2: Flame Retardants in Couches

102 foam samples collected from residential couches in the US

Information on year of purchase, state where couch purchased, and presence of TB 117 label recorded

Samples purchased between 1985-2010

87 of 102 samples contained a FR

TDCPP, PentaBDE, and Firemaster 550 (FM 550) most common FRs identified

Identified two new organophosphate flame retardant mixtures
Flame Retardant Detection and Measurement:

- Average Concentration in foam approximately 4-5% by weight of foam (40-50 mg/g)
- Significant increase in FR applications since 2005
- Significant increase in diversity of FR chemicals in furniture since 2005
- 62% of samples without a TB 117 label still contained FRs
- California TB 117 has become a *de facto* standard for the US
TBPP Flame Retardant Mix \( (n=8) \)

Retention Time (min)

<table>
<thead>
<tr>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>7x10^7</td>
</tr>
<tr>
<td>6x10^7</td>
</tr>
<tr>
<td>5x10^7</td>
</tr>
<tr>
<td>4x10^7</td>
</tr>
<tr>
<td>3x10^7</td>
</tr>
<tr>
<td>2x10^7</td>
</tr>
<tr>
<td>10^7</td>
</tr>
</tbody>
</table>

Foam Extract Containing TBPP Mixture
Are We Exposed to These Alternate Flame Retardants and What are the Health Risks?
TDCPP was used as a FR in children’s pajamas in the 1970s.

Studies conducted at UC Berkeley discovered that TDCPP and its brominated analogue were both mutagens (likely to cause cancer). (Gold et al 1978, Blum et al 1977)

Studies conducted by the National Toxicology Program also found Increased Incidence of tumors in rats exposed to TDCPP over 2 years (NTP, 2000);

CPSC issued a 2006 report estimating that exposure to TDCPP from residential furniture was greater than acceptable daily dose (Babich, 2006)

TDCPP is ubiquitous in house dust with concentrations that are equal to or sometimes higher than PBDE levels (Stapleton et al 2009).

Major urinary metabolite detected in more than 95% of population (ongoing)
Firemaster 550 (FM 550)

- Manufactured by Chemtura
- Advertised as replacement for PentaBDE
- EPA Issued Consent Order for More Testing in 2005, but only tested effects of two brominated components
- Before 2012, no studies on health effects of FM 550 in rodents/mammals
- TPP, TBB and TBPH ubiquitous in indoor dust, levels comparable to PBDEs (Stapleton et al. 2008; 2009).....No human biomarker available yet.......
**FM 550 Reproductive Study**  
(Patisaul et al 2012)

Pregnant rats exposed to FM 550 or control from Gestational Day 6 to Postnatal Day 21

**Pregnant Dams**: collected serum, liver, brain, fat, and muscle on PND 21

- **Control**: n=3
- **Low Dose 0.3 mg/kg/day**: n=3
- **High Dose 3.0 mg/kg/day**: n=3

**Pups**: - Collected serum (limited), liver, brain, fat, and muscle from pups on PND 21, and 7 months of age  
- Assessed reproductive development, behavior and growth

NOAEL = 50 mg/kg/day (Chemtura sponsored Study)
Effects Observed from FM 550 Exposure
(Patisaul et al 2012)

• Pregnant dams had significant increase in thyroid hormone levels
• Both pregnant dams and pups accumulated FM 550 components
• Female pups born to dams in the high dose group had early onset of puberty
• All pups born to dams in the high dose group became obese (male pups 32% heavier than controls and female pups 22% heavier than controls)
• Suggests FM 550 is an endocrine disruptor
Discussion Points

- PentaBDE exposure is chronic among the US population and children receive higher exposure than adults;

- Chronic exposure to flame retardants used as replacements for PentaBDE (e.g. TDCPP, FM 550) is occurring today;

- Exposure to TDCPP may be higher than acceptable daily doses, leading to increased risks of cancer;

- Many of these newer flame retardant chemicals have properties suggestive of toxic effects, yet no studies have been conducted to evaluate potential health impacts on humans;

- Questions have been raised about purported fire safety benefits of these flame retardants at levels found in furniture meeting TB 117 standards…….
Flame Retardants Make National News

- Deceptive tactics used by chemical manufacturers to promote sales of their Products;
- Close ties between flame retardant manufacturers and tobacco companies;
- Highlights lack of proven fire safety benefits;
- Discusses issues with new flame retardants on the market
Acknowledgments

- Research funding provided by National Institute of Environmental Health Sciences and a private donation to NSOE by Fred and Alice Stanback

- Dr. Heather Patisaul (NC State), Dr Thomas F. Webster (Boston University) and Dr. Deborah Watkins (Brown University); Dr. Andreas Sjödin, (Centers for Disease Control and Prevention)

- Ms. Beth Patterson, recruiters, and the study participants