Alternatives Assessment 114 Webinar:
Flame Retardants: Framing the Issue

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* If you would like to ask a question or comment during this webinar please type your question in the Q&A box located in the control panel.
Goals

- Continuing education and dialog

- To advance the practice of alternatives assessment for informed substitution across federal, state, and local agencies through networking, sharing of experiences, development of common approaches, tools, datasets and frameworks, and creation of a community of practice.
Purpose of this call

• Addressing chemical flame retardants represents an important cross-agency chemicals management problem.
• Flame retardants serve important fire protection roles, but concerns have been raised about the environmental persistence and toxicity of many current flame retardants and their replacements.
• Restrictions on flame retardant chemicals of concern may have had the unintended consequence of their replacement by other problematic substances. In some cases, substitution has not been accompanied by careful alternatives assessments.
• Discussion has been increasing about the nature of and need for flame retardant requirements in some applications.
• This three part series will address flame retardant needs and problems, potential alternatives, how different agencies see the issue and potential solutions and possibilities for greater cross agency collaboration.
Speakers

- Alex Morgan, University of Dayton Research Institute
- Heather Stapleton, Duke University
Discussion Questions

- How do flame retardants work in general and why are they needed?
- What is the evidence of flame retardant efficacy in reducing fires?
- What are the key environmental and health concerns associated with flame retardants?
- Are benefits balanced with risks?
Webinar Discussion Instructions

• Due to the number of participants on the Webinar, all lines will be muted.

• If you wish to ask a question, please type your question in the Q&A box located in the drop down control panel at the top of the screen.

• All questions will be answered at the end of the presentations.
Fire Safety and Flame Retardant Use

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University of Dayton Research Institute
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Outline

I. The Need for Fire Protection
   - Fire Loss, Fire Risk
   - Notable Fire Events in History

II. Material Flammability
   - Combustion Science and How Matter Burns
   - Relevance to Fire Protection

III. Engineering for Fire Safety
   - Active and Passive Fire Protection Technology
   - Flame Retardant Chemistry
Fire Loss Statistics

- National Fire Prevention Association (NFPA) 2012 Fire Statistics:
  - U.S. fire departments responded to an estimated 1,375,000 fires.
    - 2,855 civilian fire fatalities, 16,500 civilian fire injuries
      - Home fires caused 2,380 (83%) of the fire deaths
    - Estimated $12,427,000,000 in direct property loss.
      - 6.6% increase compared to 2011

- Fire continues to be a problem which results in loss of life and property
US Fire Losses Since 1977

Figure 1
Estimate of Fires by Type in the United States (1977-2012)

Source: NFPA survey of fire departments (1977-2012)
What Catches Fire?

- Given enough heat and oxygen, anything carbon based will burn, as well as some metals.
  - Fuel (duh), Plastics, Wood, Composites, Textiles, Peat/Plant Matter
    - Even Diamond and Graphite under some conditions.
  - Some metals can burn very exothermically (ex – Magnesium)

- Only materials in their highest oxidation state will not combust/burn:
  - Ceramics, glass, sand, rock, minerals, concrete.
    - But – even these materials can suffer fire damage.
      - Glasses melt
      - Concrete & rock explode (Spalling)
      - Ceramics crack
Fire Risk Scenarios

◆ Anytime a flammable material could be exposed to flame, you have a fire risk scenario.

◆ Fire Safety Engineers assess risk potential for ignition, flame spread, and fire loss in these scenarios.

◆ Fire risk scenarios can be very simplistic and narrow in focus, or quite broad and complex
  ● Simple Scenario: Fire risk from electrical short circuit on a computer circuit board.
  ● Complex Scenario: Subway car catching on fire in a tunnel away from the station and with air flow through the tunnel.
Fire Risk Scenarios

- Ultimately the Fire Risk Scenario dictates what fire safety engineering approaches should be used, and what materials one should use.
  - Fire Risk Scenarios are the base upon which building codes / standards, and fire safety regulations are built.
  - Codes and standards are done in a reactive manner to fire problems as they are found.
    - Wildland-Urban Interface (habitation close to forest fire areas)
    - Tightly Packed Urban Areas (fire spread from one building to another)
    - Use of sprinklers in buildings (to allow more time to escape)
  - Fire Safety regulations are also reactive to fire problems as they are found.
    - Flame retardants in electronics (electrical fires)
    - Better fire resistance for aircraft (post-crash fires)
Notable Fire Events

- 1923 Tokyo/Yokohama Earthquake and Fires: 142,807 deaths
- 1871 Great Chicago Fire
- 1666 Great London Fire
- Station Nightclub Fire
- Mont Blanc Tunnel Fire
- Air France 2005 Crash
Modern Materials and Flammability

- Despite decrease in fire losses, as more polymers are inserted into the building environment….
  - Furniture, Mattresses
  - Carpets, Electronics, Wire & Cable
  - Wood Board Laminate
  - Consumer goods
- …catastrophic fire losses go up.

- A typical modern US room will lead to flashover conditions within 5 minutes.
  - Flashover results confirmed by UL, NIST, SwRI, and many other labs.
  - Couch is main contributor.
  - But other synthetics in rest of home still have higher heat release than older materials.
Legacy vs. Modern Room Fire Study

Comparison of Room Furnishings

Legacy Room

Time to Flashover
29:25

Modern Room

Time to Flashover
3:40

https://www.youtube.com/watch?v=mulnwTNhV6Q
Material Flammability
General Combustion Behavior

- Heat decomposes material into flammable components that can mix with oxygen and react exothermically (give off heat)
  - Fuel, oxygen, heat: Fire triangle really a cycle.
  - Fuel reacts with oxygen which gives off heat that heats up more fuel to drive more reactions.
- For carbon based materials, have to get generate small enough carbon-containing molecules which can mix with oxygen and burn.
- For metals though, small particles are not needed for burning to occur, but can accelerate the fire.

- Polymers will be our main discussion of fire behavior for this talk
- Why polymers?
  - Because they are everywhere and very useful to our society, but continue to be one of our largest areas of fire risk.
Thermoplastics melt, flow, and then decomposes to give small molecules.

- Solid to liquid to gas.

Thermosets soften, decompose to small molecules

- Solid to gas.

Small molecules mix with oxygen and combust. Radiant energy goes back to condensed phase promoting additional degradation.

Polymers and Fire Growth

◆ How the polymer decomposes and its heat release rate affect fire growth.
  ● Does it melt and flow, forming a pool of burning liquid?
  ● Does it char in place and smolder?
  ● Does it crumble / deform / delaminate with glowing coals that can ignite other nearby objects?

◆ Chemical structure of the polymer will determine if it chars or not, and in general, charring polymers do not melt & flow, and have a lower heat release rate.
  ● Lower heat release rate = lower fire risk.

◆ How the polymer behaves in a fire will determine what you do to protect against that fire risk.
Engineering for Fire Safety
Engineering Considerations

What are you trying to protect against or provide in the engineering assessment?

- Improved time to escape?
  - Time to escape from point A to point B?
  - Human factors (age, mobility)
  - Visibility issues (smoke)

- Protection of building, property, life?
  - Limit of flame spread / fire damage past ignition source
  - Corrosive gas release
  - Sub-lethal toxicity
  - Prevention of structural collapse

Many different considerations also that may have nothing to do with safety, but do affect the final design.

- Cost, manufacturing, intellectual property, aesthetics, etc.
Active and Passive Fire Protection

- Active Fire Protection is composed of items or systems which require an action to work, or are immediately active in the presence of a fire.
  - Fire suppression: Firefighters attacking a flame, extinguishers being used.
  - Water Sprinklers that activate when the room gets too hot (immediate fire suppression).
  - Fire detectors – smoke, gas alarms.
- Passive Fire Protection does not actively move to work, and typically does not put out the fire, but rather just slows it down.
  - Firewalls / doors
  - Fire protection barriers
  - Flame retardants
- Both techniques have their own pros and cons, but Passive Fire Protection tends to be the cheaper and more-often used of the two (besides alarms).
Engineering Approaches to Flame Retardancy

- Engineering approaches focus not on changing polymer chemistry, but on protection of flammable materials from ignition source/heat.
  - Fire protection barrier under fabric for aircraft seating/mass transit.
  - Metal casing around power supply/sources.
  - Intumescent paint/barriers

- Easy to implement, but, they are also easy to defeat.
  - Cut/break in barrier is weak point for fire damage/flame propagation to occur.
  - Coating falling off can lead to rapid fire growth or mechanical failure (intumescent coated steel).
Polymer Flame Retardancy

- Plastic combustion can be stopped by:
  1. Inhibit combustion at flame front.
  2. Remove heat from polymer.

- Each of these approaches can be used alone, or combined to generate flame retardancy in a polymeric material.

- Each type of flame retardant falls into a category that fits one or more of the above approaches.
General Flame Retardant Approaches

I- Gas Phase Flame Retardants (ex. Halogen, Phosphorus)
- Reduce heat in gas phase from combustion by scavenging reactive free radicals, resulting in incomplete combustion.
- Can be very effective at low loadings.
- Inherent Drawbacks: Increase in CO and smoke.

II- Endothermic Flame Retardants (ex. Metal Hydroxides, Carbonates)
- Function in Gas Phase and Condensed Phase by releasing non-flammable gases (H₂O, CO₂) which dilutes the fuel and cools the polymer.
- Tend to be very cheap in cost.
- Inherent Drawback: High loadings degrade mechanical properties.

III- Char Forming Flame Retardants (ex. Intumescents, Nanocomposites)
- Operates in Condensed Phase by preventing fuel release and providing thermal insulation for underlying polymer.
- Very robust method at providing fire safety.
- Not universally acceptable for all polymer systems, can be expensive.
What is a Flame Retardant?

- A Flame Retardant (FR) is a molecule (inorganic or organic) found to be useful for inhibiting flame growth by one of three mechanisms.

- A Flame retardant is a molecule used for a specific application, much like a drug is a molecule used to treat disease, a pigment is a molecule used to give paint a color, or a surfactant is a molecule to use as a soap.
  - FR is used to put out a fire either passively (guard against fire) or actively (extinguishing agent).
  - Some FR additives have multiple chemical applications – again application based upon chemical structure and how it interacts with fire.
    - Ex: Mg(OH)₂. In powder form can be used in antacids or can be used as flame retardant filler in wire and cable jackets.
      - But the product used for wire and cable is not the same product you eat nor can the two be used interchangeably.
Flame Retardant Design / Use Criteria

* Current flame retardant polymer solutions are tailored to the regulatory test the polymer must pass to be sold. So the molecules are designed and applied to solve the following problems:
  - Ignition Resistance
  - Flame Spread
  - Heat Output
  - Structural Integrity Under Fire and Heat
  - Smoke/Toxic Gas Output
  - Combinations of one or more of the above

* What works for one test may not (and often does not) work for another test.

* The Flame Retardant Chemist will design to the test, not universal flame retardancy / fire safety.
  - The Chemist can only design to the criteria given (fire, cost, performance, lifetime, etc.). It is impossible to design for the unforeseen criteria that may occur 10-20 years later.

* “If we knew what we were doing, it wouldn’t be called research, would it?”
  - Albert Einstein
Specific Classes of Flame Retardants
Halogenated Flame Retardants

- Halogenated FR additives cover a wide range of chemical structures.
  - Brominated FR is the most common. Chlorinated FR is used, but not as often.
    - C-Br bond just about ideal for fire applications – not too strong of a bond, not too weak.
  - Fluorine and Iodine tend not to be as effective for FR polymer additive use.
    - Fluorinated compounds inherently non-flammable (Teflon, Halon)

- Mechanism is vapor phase combustion inhibitor
  - Halogen inhibits combustion chemistry, causing flames to become unstable and extinguish.
Some Common Brominated FR Additives

- Many other structures available, including polymeric/oligomeric compounds and reactive (react into the polymer) species.
Halogenated Flame Retardants

- Halogenated FR additive benefits:
  - Very effective at lowering flammability in a wide range of polymers.
  - Provide good fire performance even after repeated recycling of polymer + FR resin.

- Halogenated FR additive drawbacks:
  - Always generate more smoke and carbon monoxide during burning.
  - Can be overwhelmed in high heat flux fires (little to no FR effectiveness).
  - Under regulatory scrutiny
    - Some structures persistent, bio-accumulative, toxic (PBT)
    - Persistence not always a drawback
      - Persistence in durable good desirable
      - Persistence in environment not desirable

- Overall an old technology (since 1930s) but proven to work.
Phosphorus Flame Retardants

- Phosphorus FR additives cover a wide range of chemical structures and can be both gas and condensed phase FR additives.
  - Wide range of chemical structures available – can be optimized for polymer and application.
    - Not as useful in as many polymers as halogen though.
  - Can work as combustion inhibitor like halogen (polymer specific)
  - Can work to help form char (polymer specific)
    - Char is more thermally stable material – will still burn, but with lower heat and intensity.

- Newer technology (1950s). A mature technology but lots of other possible chemical structures to explore and use for flame retardancy.
Common Phosphorus FR Additives

- Many other structures possible (polymers, P-N compounds, etc.) each tailored for specific needs.
Phosphorus Flame Retardants

Phosphorus FR additive benefits:
- Can be both vapor phase and condensed phase flame retardants.
- Can be very effective at lowering heat release rate at low loadings of additive.

Phosphorus FR additive drawbacks:
- Tend to generate more smoke and carbon monoxide during burning.
- Not effective in all polymers.
- Starting to be under regulatory scrutiny.
Mineral Filler Flame Retardants

- Mineral filler flame retardants cover hydroxides and carbonates.
  - Hydroxides (Al, Mg)
    - Al(OH)$_3$ releases water at a low release temperature (180-200 °C)
    - Mg(OH)$_2$ releases water at a higher release temperature (320-340 °C)
  - Carbonates (Ca, Mg)
    - Calcium carbonate (limestone) often used as a bulk filler, and since it is non-flammable it dilutes the total amount of fuel to be consumed.
    - Magnesium carbonates used in a form called “hydromagnesite” which releases a combination of water and CO$_2$ at 350 °C.
- Mineral flame retardants are often mined/refined from natural rock deposits (hence the name) but sometimes may be synthetic.
Mineral Filler Flame Retardants

- **Mineral Filler FR additive benefits:**
  - Effective at lowering heat release rate and smoke release.
  - No environmental scrutiny – perceived to be very “green” FR additives.
    - Carbon footprint to mine additives not fully studied though.

- **Mineral Filler FR additive drawbacks:**
  - Not as effective per wt% basis as other FR additives. Large loadings of material (50-80wt%) can be required to obtain FR performance in polyolefins.
  - High loadings often cause mechanical property problems which can lead to the use of polymer compatibilizers that offset some of the cost benefits of using a mineral filler in the first place.

- Depending upon what sources you believe, could be very old technology (1700s) or 20th century (1920s).
Intumescent Flame Retardants

- Intumescent FR additives are often mixtures of different additives that work together under fire conditions to form a protective barrier (carbon foam) at that “rises up in response to heat” [Intumescent]
  - Intumescent FR packages include:
    - Carbon source
      - Polymer or Polyol
    - Acid source
      - Ammonium Polyphosphate
    - Gas-blowing additive.
      - Melamine
Intumescent Flame Retardants

- Intumescent FR additive benefits:
  - Very robust fire safety and flame resistance performance.
  - One of the few systems that can use select polymer structures to actively participate in flammability reduction.

- Intumescent FR additive drawbacks:
  - Can have water pickup issues.
  - Can be expensive.
  - Can have low temperature limits that limit processing ranges.

- Intumescents are often used for applications requiring high levels of flame retardancy.
  - Building and construction, firewall/firedoor barriers, aerospace, military, wire & cable, mass transport, etc.
Polymer Nanocomposites

− Polymer nanocomposites are a new class of FR additives that work only in the condensed phase.
  − Use organically treated layered silicates (clays), carbon nanotubes/nanofibers, or other submicron particles at low loadings (1-10wt%).

− By themselves, polymer nanocomposites greatly lower the base flammability (heat release) of a material, making it easier to flame retard the polymer containing a nanocomposite structure.
  − Are effective when combined with just about all types of FR additives.
    − Exceptions do exist of course.
  − Work best when combined with other FR additives.

− As polymer nanocomposites become commercial materials – they will also be flame retardant materials at the same time due to their inherent properties.
Polymer nanocomposites lower the mass loss rate, which in turn reduces the base flammability, but additional FR is needed to lower HRR further.

PE + Clay + FR even better fire performance.

Similar behavior seen for nanocomposites made with nanofibers and nanotubes.
Polymer Nanocomposites

- Polymer nanocomposite benefits:
  - Brings balance of mechanical and flammability properties to a system.
  - Very little additive needed (no great cost increase).
  - Tend to inhibit polymer dripping / flow under fire conditions.
  - Multifunctional performance (ex: electrical conductivity from carbon nanotubes)

- Polymer nanocomposite drawbacks:
  - Difficult to set up a polymer nanocomposite structure.
  - Design of the nanocomposite requires careful design and analysis, which can bring additional R&D cost to a product.
  - Lots of unknowns with nanocomposite technology (long-term aging, EH&S, etc.)
  - New technology (1990s – maybe not proven enough for conservative fire safety principles)
Conclusions

- Fire safety in modern society still needs to be addressed.
  - Decrease in fire deaths, but continual increase in material and property losses.
  - Time to escape in some situations decreasing as more highly flammable materials are inserted into the built environment.
  - Fire safety protection measures available, but compromises must be made.
    - Active vs. Passive Fire Protection
    - Natural vs. Synthetic Materials
    - Material design requirements
      - Assumed environmental decomposition vs. De-manufacturing & recycling
  - Flame retardants an essential part of passive fire protection.
    - Have been in use since 850 BC – an old and required technology
    - Always room for improvement – as existing flame retardants are found to have problems, replace them.
Questions?
Human Exposure & Health Effects Associated with Additive Flame Retardants in Home Furnishings

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

Standards that Result in 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)
- Camping Tents (CPAI-84)
What Type of Products are Treated with Flame Retardants in Your Home?

- Couch
- Sleep Positioners
- Nursing Pillow
- Coffee Maker
- LED Lights
- Car Seat
- Curtains
- Insulation
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
PBDEs in Human Samples From Around the World

From Hites et al., 2005
How Are We Exposed to Flame Retardants?

- Work Environment
- Our Home
- House Dust
- Diet
- Vehicles
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 demonstrated 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)
**PBDEs are Thyroid Hormone Mimics**

**Thyroid Hormones**

- Triiodothyronine (T3)
- Thyroxine (T4)

**PBDE Oxidative Metabolites**

- T3-like OH-BDE
- T4-like OH-BDE
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
- Until 2005, 98% of World Market Demand for PentaBDE was in North America, primarily to meet TB 117
- Concern about persistence, bioaccumulation and potential toxicity led to phase-out in 2005
What Types of FRs are Being Used to Meet TB 117?

• 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?
# 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 Sensitivities</td>
<td>Reproductive</td>
<td>Developmental</td>
<td>Neurological</td>
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<td>Albermarle</td>
<td>SAYTEX RZ-243</td>
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<td>L'</td>
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<td></td>
<td>Proprietary B Aryl phosphate</td>
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<td>Triphenyl Phosphate CAS # 115-88-8</td>
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<td>Amert brom</td>
<td>FR513</td>
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<td>Great Lakes</td>
<td>Firemaster 550</td>
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<tr>
<td></td>
<td>Proprietary F Halogenated aryl ester</td>
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<td></td>
<td>Proprietary G Triaryl phosphate, isopropylated</td>
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<td></td>
<td>Proprietary H Halogenated aryl ester</td>
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<td>M</td>
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</tr>
</tbody>
</table>

*Ongoing studies may result in a change in this endpoint
*Persistent degradation products expected

L = Low hazard concern
M* = Moderate hazard concern
H = High hazard concern
P = Yes for pure chemical
L, M*, or H = Endpoint assigned using estimated values and professional judgment (Structure Activity Relationships)

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

*Project 1- Baby Products*
*Project 2- Residential Couches*
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.
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 chlorinated organophosphate flame retardant mixtures

Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out
Heather M. Stapleton, Smriti Sharma, Gordon Getzinger, P. Lee Ferguson, Michelle Gabriel, Thomas F. Webster, and Arlene Blum

1Nicholas School of the Environment, Duke University, Durham, North Carolina, United States
2Department of Environmental Health, Boston University School of Public Health, Boston, Massachusetts, United States
3Department of Chemistry, University of California, and Green Science Policy Institute, Berkeley, California, United States

Supporting Information
Flame Retardant Statistics Measured:

Table 1. Flame Retardant (FR) Measurements and Descriptive Statistics of Polyurethane Foam Samples (n = 102). (Values in parenthesis represent percentage of the total number of samples for that specific column)

<table>
<thead>
<tr>
<th>flame retardant</th>
<th>number of detects</th>
<th>average FR level (mg/g)</th>
<th>purchased prior to 2005&lt;sup&gt;a&lt;/sup&gt;</th>
<th>purchased 2005 or later&lt;sup&gt;a&lt;/sup&gt;</th>
<th>purchased in California&lt;sup&gt;b&lt;/sup&gt;</th>
<th>purchased outside California&lt;sup&gt;b&lt;/sup&gt;</th>
<th>yes TB 117&lt;sup&gt;c&lt;/sup&gt;</th>
<th>no TB 117&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PentaBDE</td>
<td>17</td>
<td>20.23&lt;sup&gt;d&lt;/sup&gt;</td>
<td>16 (39%)</td>
<td>1 (2%)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>7 (29%)</td>
<td>9 (12%)</td>
<td>9 (14%)</td>
<td>8 (24%)</td>
</tr>
<tr>
<td>TDCPP</td>
<td>42</td>
<td>44.87</td>
<td>10 (24%)</td>
<td>32 (52%)</td>
<td>10 (42%)</td>
<td>30 (41%)</td>
<td>33 (50%)</td>
<td>9 (26%)</td>
</tr>
<tr>
<td>FM 550</td>
<td>13</td>
<td>19.76&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2 (5%)</td>
<td>11 (18%)</td>
<td>3 (13%)</td>
<td>8 (11%)</td>
<td>12 (18%)</td>
<td>1 (3%)</td>
</tr>
<tr>
<td>V6/TCEP</td>
<td>1</td>
<td>41.77&lt;sup&gt;g&lt;/sup&gt;</td>
<td>0</td>
<td>1 (2%)</td>
<td>1 (4%)</td>
<td>0</td>
<td>1 (2%)</td>
<td>0</td>
</tr>
<tr>
<td>TBPP mix</td>
<td>8</td>
<td>7.90&lt;sup&gt;h&lt;/sup&gt;</td>
<td>0</td>
<td>8 (13%)</td>
<td>1 (4%)</td>
<td>7 (10%)</td>
<td>6 (9%)</td>
<td>1 (3%)</td>
</tr>
<tr>
<td>MPP mix</td>
<td>2</td>
<td>3.23&lt;sup&gt;i&lt;/sup&gt;</td>
<td>0</td>
<td>2 (3%)</td>
<td>0</td>
<td>2 (3%)</td>
<td>1 (2%)</td>
<td>1 (3%)</td>
</tr>
<tr>
<td>TDCPP and PentaBDE</td>
<td>2</td>
<td>22.64</td>
<td>2 (5%)</td>
<td>0</td>
<td>1 (4%)</td>
<td>1 (1%)</td>
<td>1 (2%)</td>
<td>1 (3%)</td>
</tr>
<tr>
<td>TDCPP and FM 550</td>
<td>2</td>
<td>19.06</td>
<td>0</td>
<td>2 (3%)</td>
<td>0</td>
<td>2 (3%)</td>
<td>2 (3%)</td>
<td>0</td>
</tr>
<tr>
<td>FR &lt; 0.2 mg/g</td>
<td>3&lt;sup&gt;j&lt;/sup&gt;</td>
<td>0.11</td>
<td>1 (2%)</td>
<td>2 (3%)</td>
<td>0</td>
<td>3 (4%)</td>
<td>0</td>
<td>2 (6%)</td>
</tr>
<tr>
<td>none detected</td>
<td>12</td>
<td>-</td>
<td>10 (24%)</td>
<td>2 (3%)</td>
<td>1 (4%)</td>
<td>11 (15%)</td>
<td>1 (2%)</td>
<td>11 (32%)</td>
</tr>
<tr>
<td>totals</td>
<td>102</td>
<td>41</td>
<td>61</td>
<td>24</td>
<td>73</td>
<td>66</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>

- 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
What are the Concerns about Potential Health Effects From These Flame Retardants?
PBDE Exposure

Dust and diet are known to be the greatest exposure pathway among the general population. Children are receiving significantly higher exposures through dust.

(Lorber, 2008; Rose et al. 2010; Johnson et al. 2011; Stapleton et al. 2012)

Our PBDE Exposure Study in Toddlers (Stapleton et al. 2012):

- Age, race/parental education, breast feeding history, handwipes and house dust significantly associated with serum PBDEs. (40% of variation)

- Handwipes strongest predictor of serum levels (32% of variation)
PBDE Residues on The Hands Are Predictor’s of Blood Levels in Toddlers (Stapleton et al. 2012)
## Alternate Flame Retardants Measured in House Dust 2010-2012 (ng/g; N= 81; unpublished)

<table>
<thead>
<tr>
<th>PBDE Congener</th>
<th>% Detect</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Geometric Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBB</td>
<td>100</td>
<td>6.0</td>
<td>2430</td>
<td>97</td>
</tr>
<tr>
<td>TBPn</td>
<td>100</td>
<td>83</td>
<td>20,960</td>
<td>604</td>
</tr>
<tr>
<td>TDCPP</td>
<td>100</td>
<td>621</td>
<td>13,110</td>
<td>2730</td>
</tr>
<tr>
<td>TCPP</td>
<td>97</td>
<td>&lt;217</td>
<td>67,810</td>
<td>3440</td>
</tr>
<tr>
<td>TCEP</td>
<td>97</td>
<td>&lt;20</td>
<td>6920</td>
<td>348</td>
</tr>
</tbody>
</table>

**PBDE (Stapleton et al. 2012):**

<table>
<thead>
<tr>
<th>PBDE Congener</th>
<th>% Detect</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Geometric Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE 47</td>
<td>100</td>
<td>55</td>
<td>24,720</td>
<td>870</td>
</tr>
<tr>
<td>BDE 209</td>
<td>100</td>
<td>441</td>
<td>76,130</td>
<td>2574</td>
</tr>
</tbody>
</table>
TDCPP

- 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)
- Studies conducted in my laboratory suggest TDCPP may also be a neurotoxicant with similar toxic effects observed in chlorinated organophosphate pesticides (Dishaw et al. 2011).
- Major urinary metabolite detected in more than 97% of population (ongoing)
Firemaster 550 (FM 550)

• Advertised as replacement for PentaBDE

• EPA Issues 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
**FM 550 Rodent Study**

*(Collaborative Project with H. Patisaul at NC State University)*

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

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

**Pups**: collected serum (limited), liver, brain, fat, and muscle from pups on PND 21, and 7 months of age

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

**NOAEL = 50 mg/kg/day**

*(Chemtura sponsored Study)*


**Effects Observed from FM 550 Exposure**

(Patisaul et al. 2013)

- TBB and TBPH did accumulate in female rats and their pups exposed during pregnancy and lactation; the metabolite of TBB (TBBA) accumulated more than TBB

- Significant increases in serum thyroxine were observed in dams exposed to 3 mg/kg/day; while pups displayed a suggestive decrease in thyroxine

- Effects on cardiac function were observed in male rats (increased ventricular wall thickness in heart)

- Female pups from high dose group had an early vaginal opening, were more anxious in behavioral tests, and were in persistent estrous cycle (p<0.01)

- Male pups were 32% heavier than controls at 7 months of age and female pups were 23% heavier than controls (p<0.01)

- What is the true NOAEL for FM 550? Should FM 550 or its components be considered an endocrine disruptor or chemical obesogen?
Discussion Points

• Flame retardant chemicals are present in every home and children in particular are chronically exposed to these chemicals every day.

• An average consumer has no way of determining what products contain flame retardants additives or what types of chemicals.

• Many of these PBDE alternatives have properties suggestive of toxic effects, yet no studies have been conducted to evaluate potential toxicity and impacts on human health.

• Alternative approaches such as barriers/liners that do not involve the use of chemical additives may provide the same level of fire safety without contributing to exposure and increasing risks/concerns about human health.
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)

- Duke’s Primary Care Research Consortium, recruiters, and the study participants
Discussion Questions

- How do flame retardants work in general and why are they needed?
- What is the evidence of flame retardant efficacy in reducing fires?
- What are the key environmental and health concerns associated with flame retardants?
- Are benefits balanced with risks?
Next Webinars

Alternatives Assessment 115: Identifying Safer Alternatives to Flame Retardants that are/contain Chemicals of Concern
Monday, November 4, 12-1:30pm EST
- Elizabeth Harriman, Massachusetts Toxics Use Reduction Institute,
- Emma Lavoie, US EPA, Design for Environment Branch

Alternatives Assessment 116: Challenges in Selecting Alternatives and Implementing Substitution – Cross Agency Perspectives
TBD- November 2013
- Alissa Cordner, Whitman College
- Paul Yaroshak, US Department of Defense
- Chris Weis, NIEHS (Invited)
The audio recording and slides shown during this presentation will be available at:
http://www.chemicalspolicy.org/alternativesassessment.webinarseries.php