Use of Flame Retardants to Comply with Fire Safety Requirements for Textiles

Marcelo M. Hirschler

GBH International
AATCC Flammability Symposium
September 21, 2016
Topics

- Key textile fire test methods
- Traditional approaches to meet fire safety requirements
- Scientific basis for safe use of flame retardants
- Some innovative methods for flame retardants with textiles
Textiles Typically Requiring Improved Fire Performance

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Oxygen Index (LOI)</th>
<th>Heat of Combustion (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>18-19</td>
<td>46</td>
</tr>
<tr>
<td>Nylon</td>
<td>20-21</td>
<td>33</td>
</tr>
<tr>
<td>Acrylic</td>
<td>18-19</td>
<td>27</td>
</tr>
<tr>
<td>Polyester</td>
<td>20-22</td>
<td>21</td>
</tr>
<tr>
<td>Cotton</td>
<td>17-19</td>
<td>17</td>
</tr>
<tr>
<td>Rayon</td>
<td>17-19</td>
<td>17</td>
</tr>
<tr>
<td>Wool</td>
<td>24-26</td>
<td>21</td>
</tr>
<tr>
<td>Modacrylic</td>
<td>27-31</td>
<td>24</td>
</tr>
</tbody>
</table>
Textile Applications Requiring Improved Fire Performance

- Fabrics for upholstered furniture and mattresses
- Curtains and drapes
- Carpets
- Wall coverings
- Military uniforms
- Children’s sleepwear
- Awnings/canopies/membrane structures
- Tents/sleeping bags
- Protective clothing (often use special fibers)
Fire Tests
Key Fire Test

- NFPA 701
  - Includes Test 1
  - Includes Test 2
  - Cut-off: 21 oz./yd²
  - Does not include “small scale test”
  - Widely required in codes
  - Not necessarily ideal for fire hazard
NFPA 701 Test 2

10 mm (0.4 in.)

930 mm (36.6 in.)

1190 mm (46.8 in.)

203.2 mm (8 in.)

Specimen in place for testing

Guide wires

Clips

Bottom wire supports

Pair of rods to hold vertical support wires

Pair of vertical support wires

Pair of vertical support wires

Front of cabinet is open (no door)

Pair of rods to hold vertical support wires
NFPA 701

- Vertical textile test
- Applies to virtually all textiles
- Fabrics claiming NFPA 701 compliance usually were tested to “small-scale test”, which is not in NFPA 701 and is not a valid test for fire safety
- Small-scale was taken out of NFPA 701 in 1980s
- Small-scale test is included in some textile specs (often not by name)
Fire Test for Research

- ASTM E1354: cone calorimeter
- Measures heat release (rate and amount)
- Measures ignitability
- Measures smoke release
- Heat release predicts fire hazard and large scale fire behavior
Cone Calorimeter
Larger Scale Fire Tests

- NFPA 289 (Furniture calorimeter)
- NFPA 286 (Room-corner test)
- NFPA 265 (Room-corner test)
- ASTM E84/UL 723: Steiner tunnel test
- ASTM E648: Flooring radiant panel test
- ASTM E1317/IMO surface flame spread test
ROOM/CORNER TEST STANDARDS
NFPA 286 - Basic Test Apparatus

Smoke optical density
Exhaust gases
Gas burner
Gas analysis (O₂, CO, CO₂)
Flow measurement
Exhaust hood 3 m x 3 m x 1 m
Doorway 0.8 m x 2.0 m

Applies also to NFPA 265
Fire Tests Specific to Textiles

- ASTM D6413 – Vertical flammability for uniforms
- ASTM D2859 – Carpet methenamine pill
- ASTM F2700 (Thermal Protective Performance)
- CPAI 84: Tents
- CPAI 75/ASTM F1955: Sleeping bags
- ISO 6941 and other small burner tests
European Textile Fire Tests

- BS 5852: fire test for furniture and mattresses – (fabrics and paddings) – smoldering and flaming
- EN 1021, 1 & 2: smoldering and flaming, same tests as above (ignition sources 0 and 1)
- Curtains & drapes: EN 13773, classification scheme, with tests EN 1101, 1102 & 13772
BS 5852 Furniture Fire Test

Applies to all upholstery materials
Traditional Flame Retardancy of Textiles
Flame Retardants

- Halogenated: chlorine or bromine
- Phosphorus-containing
- Inorganic, typically hydroxides
- Synergists: act together with the above
- Halogens: most efficient, gas phase action (inhibit chain reactions), often used with synergists (e.g. antimony oxide)
- Phosphorus: usually char formers, block access of oxygen
- Inorganic: needs high loadings, release water diluting vapor phase, often need silane coupling agents
Oldest Patent for Flame Retarding Textiles

- First published flame retardant patent:
  - British Patent #551, O. Wyld, 1735
- Intended for canvas, linen or paper: cellulosics
- Mixed allum, borax, vitriol or copperas
  - (Vitriol or copperas: ferrous sulfate; allum: K Al sulfate)
- Dipped the fabric or paper in the mixture, while hot
- Dried with “drying oil”
- Result was that fabric was “prevented from flaming or retaining fire”
Flame Retarding Cotton

- Montgolfier brothers coated air balloon cotton fabrics with alum to reduce fire hazard
- Gay Lussac added ammonium phosphate and borax to cotton theatre curtains in 1821
- Perkin impregnated cotton flannelette with Na stannate, ammonium sulfate and various other combinations in 1912-13
Traditional Modern Approach to Flame Retard Textiles

- Use back-coatings based primarily on brominated flame retardants (BrFRs)
- Historically decabromobiphenyl oxide and antimony oxide
- Other BrFRs are now replacing Decabromodiphenyl oxide
- BrFRs as back-coatings are effective on any textile substrate
- BrFRs Act mainly in the gas phase, whatever the fabric present
- BrFRs release active Br radicals which migrate to the front face of the fabric and act on fabric and underlying substrate
- That way, FR back-coatings on fabrics act on foams also
Figure from Richard Horrocks
Treatment Durability

- **Durable**: can sustain multiple laundering and dry-cleaning procedures without increasing flammability
- **Semi-durable**: survives water soaking or leaching but not repeated laundering
- **Non-durable**: washes off readily with water
Non Halogen Traditional Modern Approaches

- Non durable treatments for cotton and other cellulosics
  - Ammonium phosphates and polyphosphates, borax, etc.
- Non durable treatments for polyester
  - Guanidine phosphate and mixtures with sulfur compounds
- Semi durable treatments for cotton
  - Phosphorylation and addition of N compounds, back-coatings
- Durable treatments
  - THPC, THPOH, and other N & P mixtures
Other Traditional Approaches

- Topical treatments
  
  Specific finishes, e.g. for nylon (thio-urea), wool (hexafluorozirconate)

- Back-coating of carpets with metal hydroxide fillers
  
  ATH and calcium carbonate, for ASTM D2859 pill

- Melt-processable additives for polypropylene
  
  Brominated phosphate, amines

- Melt-processable additives for polyesters
  
  Phosphate esters, P& Br compounds with Antimony oxide
Br FR Back-Coatings vs. Other Traditional Approaches

- Most approaches work only with a specific type of fabric
- Many of the approaches lead to non durable or semi-durable finishes on the specific textiles
Safe Use of Flame Retardants: Science
Flame retardants of concern

- Tris(2,3-dibromopropyl) phosphate withdrawn in 1970s
- Pentabromodiphenyl oxide (pentabrom, PentaBDE) phased out in 2004
- Octabromodiphenyl oxide (octabrom, OctaBDE) no manufacture since 2005
- Decabromodiphenyl oxide (decabrom, DecaBDE) phased out in 2013

Other flame retardants being discussed include

- Tetrabromobisphenol A (TBBPA) No health effects on humans or on animals
- Used primarily in printed circuit boards and in polycarbonates
- Tris(2,3-dichloropropyl) phosphate: NO finding of human carcinogenicity
- Often confused with tris(2,3-bromopropyl) phosphate
National Research Council

- Studied various effects, including carcinogenicity and genotoxicity
- Conducted risk assessments with over-conservative baselines
- None of the 16 types of flame retardants studied were found to be problematic
Fire Fatalities

- Usually Victims Die from Inhaling Too Much Smoke of Average Toxicity
- In US, 83% Fire Fatalities Occur in Fires Leaving Room Fire Origin
- Few Victims Die if Fire Stays Small
- Few Victims Die from Burning/Heat
Scales of Toxicity

- Non-toxic
- Slightly toxic (10,000)
- Moderately toxic (2,500)
- Very toxic (1000)
- Extremely toxic (100)
- Supertoxic (10)

Categories: Poisons, Gases, Smokes

Poisons:
- Alcohol (ETHYLCERZENE: 6,250)
- Methanol (METHANOL: 428)
- Aspirin (ASPIRIN: 200)
- DDT (DDT: 130)
- Phenobarbital (PHENOBARBITAL: 27)
- Paraquat (PARAQUAT: 7)
- Nicotine (NICOTINE: 1)
- Cocaine (COCAINE: 0.5)
- Strychnine (STRYCHNINE: 0.27)
- Tiger Snake Poison (0.048)
- Oxin (0.025)
- Beaked Sea Snake Poison (0.012)

Gases:
- CO (CO: 1.400)
- CFC II (CFC II: 940)
- Chloroform (CHLOROFORM: 300)
- Ether (ETHER: 273)
- Hydrogen Chloride (HCl)
- Carbon Dioxide (CO2)
- Acrolein (ACROLEIN: 0.4)
- Phosgene (PHOSGENE: 0.17)
- Formaldehyde (0.78)

Smokes:
- PTFE (F)
- PTFE (NP)

Botulinus toxin (0.0002)

Douglas Fir (RED OAK: 0.001)

Polystyrene (POLYSTYRENE: MODACRYLIC: 10)

Horsehair (HAIR: 100,000)

Carbon (CARBON: 100,000)

Wool (WOOL: PVC: ABS: 100,000)
Fire Statistics

- Fire fatalities due to toxicity tend to have enough COHb that CO accounts for the toxicity.
- Thus, flashover fire fatalities depend mostly on CO generation alone.
- The key issue is ensuring that the fire does not become big: has low heat release.
Fire Safety

- Heat Release Rate is the Most Critical Fire Property
- Smoke Toxicity Has Very Little Effect
Flame Retardants & Heat Release

- Flame Retardants Decrease HRR, with Improvements often of > 80%
- It is Essential to Put Enough FR in the System to Improve Fire Performance
- It is Essential to Use an FR Package that is Suitable for the Polymer System
- Effective FR-substrate systems can convert materials into very low flammability products
Flame Retardants & Toxic Risk

- Flame retardants add nothing to smoke toxicity, because it is dominated by carbon monoxide.
- Halogenated dioxins and furans have a negligible toxic effect compared to toxic PAHs.
- Analytical chemistry is so advanced that flame retardants are found at levels below toxic risk.
- Finding flame retardants does not mean risk!
- The few flame retardants with toxic or other deleterious effects are out of the market.
Recent Use of Flame Retardants
Novel Use of Flame Retardants

- Back-coatings with non DecaBDE BrFRs
- Coatings with non DecaBDE BrFRs
- Reactive incorporation of new (mainly polymeric) BrFRs into the textiles
- Coatings with layer-by-layer techniques
- Coatings with intumescent materials
Typical Desirability Criteria for New Halogenated Flame Retardants

- Polymeric (or otherwise non-migrating)
- Reactive
- Durable, non-leaching
- Insoluble, non hydrolyzing
- No environmental or toxicity issues
- Reduced use of antimony oxide
- Reduced loading
- Versatility: different textiles, different use modes
Examples: Br for latex back-coatings

- ethylene-bis(pentabromophenyl) or EBP
  - Bromine content: 82%
  - Particle Size Average: 5 microns

- ethylene-bis(tetrabromophthalimide) or EBTBP
  - Bromine content: 67%
  - Particle Size Average: 3 microns
Example of back-coating formulation

<table>
<thead>
<tr>
<th>Flame Retardant Dispersion</th>
<th>FR Back-coating</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component</strong></td>
<td><strong>Wt%</strong></td>
</tr>
<tr>
<td>Flame retardant dispersion</td>
<td>25-35</td>
</tr>
<tr>
<td>EBP</td>
<td>60-70</td>
</tr>
<tr>
<td>Water</td>
<td>30-40</td>
</tr>
<tr>
<td>Dispersant</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Thickener</td>
<td>1-3</td>
</tr>
<tr>
<td>Water</td>
<td>15-20</td>
</tr>
</tbody>
</table>

- **EBP or EBTBP**
  - Very efficient flame retardants with high Br content
  - Excellent compound stability
  - Suitable for water soaking applications
  - No odor
  - Excellent color
  - Typically used with antimony trioxide (ATO) synergist
Br Polystyrene for Polyamides

- Brominated polymer (polystyrene) that is well-suited for incorporation into nylon fibers to impart improved fire performance
- Bromine content: 68%
- $T_g$: 162 °C
- Solubility in water < 0.1 wt%
- 1% wt% loss > 340 °C

This brominated polymer can be extruded just like any resin typically used for fibers (~220 °C).
Polymeric FR Based on Pentabromobenzyl Acrylate

Bromine is **chemically bound** to the Polymer Backbone

Illustrative chemical structure
New Halogenated Flame Retardants

- New materials exist that can be effective and:
  - Work on a variety of fabrics, including cotton/polyester blends
  - Work as coatings or back-coatings
  - Work as reactive additives
  - Are free of environmental/toxicity issues
  - Be durable
  - Are often polymeric
New FR for Nylon-based Fabrics

FR for 50% nylon/50% cotton, vertical tests to ASTM D6413
Flame retardants for military uniforms using new non halogen/polymeric FR systems

<table>
<thead>
<tr>
<th>Non-Halogenated Prototype</th>
<th>Polymeric Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char length: 4.5”</td>
<td>Char length: 4.8”</td>
</tr>
<tr>
<td>After flame: 0.5 secs</td>
<td>After flame: 0.5 secs</td>
</tr>
<tr>
<td>Performance maintained for &gt;50 industrial laundering cycles</td>
<td>Performance maintained for &gt;100 industrial laundering cycles</td>
</tr>
</tbody>
</table>

FR/DWR combo treatment for light weight 100% nylon (ASTM D6413)
100% nylon and polyester fabrics for outdoor applications (e.g. tents) with polymeric FRs added to provide one-step FR/DWR treatment for light-weight nylon and polyester fabrics

Char Length: 5.5”
After flame: 0 seconds
AATCC 22 Water repellency: no wetting

ASTM D6413 Typical pass/fail criteria
Char length: 6” – After flame: 2 secs
Areas with Active Research for Use of Flame Retardants

- Military uniforms: US Army and Navy now demand improved fire performance
- Mattress ticking and mattress textile barriers (often flame retarded cotton)
- Upholstered furniture fabrics and barriers
- Tents and sleeping bags
- Interior finish (including carpets) and decorations
- Blends for multiple applications
Conclusions

- Flame retardants act by decreasing the key fire property: heat release.
- Lower heat release will improve probability of passing fire tests and improve fire safety.
- Existing flame retardants are safe to use.
- New effective flame retardants exist without environmental or toxicity drawbacks.
- New safe flame retardants are being developed.
Questions?

Marcelo Hirschler
GBH International