Flame Retardant Coatings Overview

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PyroTech
What is a flame retardant?

- Something that inhibits or resists the spread of a fire
- Integrated into / with substrate (compounded)
- Coating
What is the difference between “Flame Retardant” and “Fire Retardant”? 
Flame Retardant

• Inhibit or resist the growth of a small ignition source into a larger fire.
Fire Retardant

Used to control or suppress a large, full scale fire.
Mechanisms of Flame Retardancy

- Reducing the evolved heat to below what is needed to sustain combustion
  - Inorganic and organic phosphorus-containing agents, aluminum hydroxide

- Improving the decomposition temperature
  - Inherently flame resistant fibers (e.g. aramids)

- Modifying pyrolysis process to promote char formation (barrier between flame and polymer) and decrease flammable volatiles
  - Phosphorus and nitrogen containing flame retardants

- Interfering with flame chemistry
  - Halogenated flame retardants often in synergy with antimony

- Isolating the flame from the oxygen supply
  - Halogenated flame retardants by releasing hydrogen halide
  - Hydrated flame retardants by releasing water
Flame Retardancy – How does it work?
Types of Flame Retardant

- Halogen
- Nitrogen
- Inorganic
- Phosphorus
- Intumescence
- Other
Halogen Flame Retardant Systems

- Bromine or Chlorine

- Mode of action: interruption of the radical chain mechanism of the combustion process in the gas phase
## Types and Typical Uses of Halogen Flame Retardant Systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decabromdiphenyl Ether (Deca-BDE), within the class of Polybrominated diphenyl ethers (PBDE)</td>
<td>Universally used in plastics and textiles. Banned in electronics sector (RoHS). US phase out in 2013.</td>
</tr>
<tr>
<td>Chloroparaffins</td>
<td>Liquids in thermoplastics, thermosets and elastomer.</td>
</tr>
<tr>
<td>Tetrabromobisphenol A (TBBA)</td>
<td>Printed Circuit Boards</td>
</tr>
<tr>
<td>Dedecachloropentacyclo-octadecadiene (Dechloran)</td>
<td>Polyamides</td>
</tr>
</tbody>
</table>
Nitrogen Flame Retardant Systems

• Mode of action: Nitrogen-containing flame retardants may act by the release of inert gases (ammonia, nitrogen) into the gas phase or by condensation reactions in the solid phase.
# Types and Typical Uses for Nitrogen Flame Retardant Systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine</td>
<td>Synergistic in intumescent flame retardant systems. PUR flexible foam in seating.</td>
</tr>
<tr>
<td>Melamine Cyanurate</td>
<td>Some polyamides</td>
</tr>
<tr>
<td>Melamine polyphosphate (MPP)</td>
<td>Some polyamides. Synergistic with metal phosphinates.</td>
</tr>
<tr>
<td>Melamine poly(zinc- or aluminum) phosphate</td>
<td>Cables. Synergistic with some metal phosphinates and inorganics.</td>
</tr>
<tr>
<td>Melamine-based HALS</td>
<td>Polyolefin films.</td>
</tr>
</tbody>
</table>
Inorganic Flame Retardant Systems

- Mode of action: Depending on the flame retardant, cooling of the polymer, dilution of the substrate and of the combustion gases (ATH, MOH), or formation of a charred layer, as well as synergism (ATO, AIOOH) may take place.
## Types and Typical Uses for Inorganic Flame Retardant Systems

<table>
<thead>
<tr>
<th>Metal Hydroxides</th>
<th>PVC, polyethylene, ethylene/vinyl acetate-copolymers and thermosets (decomposes 200°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Trihydrate (ATH)</td>
<td>PVC, polyethylene, ethylene/vinyl acetate-copolymers and thermosets (decomposes 200°C)</td>
</tr>
<tr>
<td>Aluminum Oxide Hydrate (AlooH)</td>
<td>Thermoplastics (decomposes 320°C)</td>
</tr>
<tr>
<td><strong>Zinc Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>Zinc Borate</td>
<td>Smoke suppressant and inhibits antiglow in thermoplastics (decomposes 415°C)</td>
</tr>
<tr>
<td>Zinc Hydroxystannate</td>
<td>Smoke suppressant for PVC, unsaturated polyesters and elastomers</td>
</tr>
</tbody>
</table>
Phosphorus Flame Retardant Systems

- Mode of action: formation of a solid charred surface layer of phosphorus compounds and in specific cases interruption of the radical chain process in the gas phase.
### Types and Typical Uses for Phosphorous Flame Retardant Systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Polyphosphate (APP)</td>
<td>Intumescent formulations, polypropylene and thermosets.</td>
</tr>
<tr>
<td>Cyclic Phosphonate Ester (CPEs) (Dialkyl alkyl phosphonates)</td>
<td>Thermoset coatings for polyester and nylon</td>
</tr>
<tr>
<td>9,10-Dihydro-9-oxa-10-phosphaphenantherene-10-oxide (DOPO)</td>
<td>Polyester fibers</td>
</tr>
<tr>
<td>Trischloropropyl Phosphate (TCCP)</td>
<td>Polyurethane flexible foams</td>
</tr>
<tr>
<td>Red Phosphorous</td>
<td>Polyamids</td>
</tr>
<tr>
<td>Resorcinol bis (diphenyl phosphate) (RDP)</td>
<td>PC/ABS blends</td>
</tr>
</tbody>
</table>
Other Flame Retardant Systems

- **Antimony trioxide (ATO)** - used as a synergist in PVC and with brominated and chlorinated flame retardants

- **Expandable graphite** – high expansion rate (100x to 300x) at 300°C

- **Nanocomposites** – Clays and organo-layered silicates. Incorporate polymer between layers in the composite.
Intumescent Flame Retardant Systems

- Coatings and compounded into polymeric systems
- +40 year old technology
- Substrates for coating: Wood, fabric backcoat, corrugate, steel, plastics
- 2K epoxy systems for petrochemical industry
- Mode of action: formation of a voluminous, insulating protective layer through carbonization and simultaneous foaming.
Intumescent Paint - Characteristics

- Mostly physical drying, thermoplastic paint systems
- High PVC
- Three main active ingredients
  - Acid donor
  - Carbon donor
  - Blowing agent
- High layer thickness (~1000 μm)
- Applied by brush or spraying
- Heat activated (250 - 300°C) insulating paint
- Swelling 40-80 times
Process of Intumescence

- Softening of the binder / polymer
- Release of an inorganic acid (Acid Donor / Charring Agent - APP) (> 300°C)

\[
\text{(NH}_4\text{PO}_3)_n \xrightarrow{>250 \degree C} (\text{HPO}_3)_n - n \text{NH}_3
\]

- Carbonization (Char Promotor – Polyalcohol)

\[
(\text{HPO}_3)_n + C_x(\text{H}_2\text{O})_m \rightarrow ["C"]_x + (\text{HPO}_3)_n x m\text{H}_2\text{O}
\]

- Gas formation by the spumific compound (Blowing Agent - Melamine)

\[
\text{H}_2\text{N} \text{N} \text{N} \text{N} \text{NH}_2 \xrightarrow{\Delta} \text{NH}_3 \xrightarrow{\text{O}_2} \text{N}_2 + \text{H}_2\text{O}
\]
Process of Intumescence

- Foaming of the mixture
- Solidification through cross-linking reactions
# Starting Point Formulation

**Part I, Grind**
- Water: 14.9
- Dispersant: 1.0
- TiO2: 6.0
- Pentraerythritol: 9.0
- Fumed Silica: 1.0
- Melamine: 7.5
- Ammonium Polyphosphate: 22.0
- Defoamer: 0.3
- Thickener, 2% water solution: 4.0

**Part II, Let down**
- PVC Emulsion: 25.0
- Coalescing Agent: 1.3
- Buffer, 10% water solution: 0.8
- Water: 8.0

**Total**

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC, %</td>
<td>68±2</td>
</tr>
<tr>
<td>Density, lb/gal</td>
<td>10.7±1</td>
</tr>
<tr>
<td>pH</td>
<td>8.2±0.2</td>
</tr>
<tr>
<td>Viscosity, mPas</td>
<td>500</td>
</tr>
</tbody>
</table>
Flame Retardant Standards
ASTM E-84 (Steiner Tunnel Test)
Standard Test Method for Surface Burning Characteristics of Building Materials

• 25’ long
• Horizontal burn
• Measure flame spread distance versus time to develop Flame Spread Index
• Class A (0 – 25), B (26 – 75), C (76 and up)
• Most commonly cited / used test
• aka UL723
ASTM E-2257
Standard Test Method for Room Fire Test of Wall and Ceiling Materials and Assemblies

- Room corner test
- Best simulation of actual flame spread conditions versus ASTM E-84
- Expensive test versus ASTM E-84
ASTM D-3806
Standard Test Method of Small-Scale Evaluation of Fire-Retardant Paints

• Small scale test for paints and coatings
• Predict results for ASTM E-84
ASTM E-119

- Time Rating Test
- 2000F flame temperature
- Test over when surface temperature of backside of substrate >100F of ambient
- 15 Minutes, 30 Minutes, 1 Hour, Etc.
- Doors, wallboard, etc.
UL 94
Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliances Testing

- 12 different classifications for three different group
- Vertical and Horizontal Tests
- V-0 hardest rating to achieve
Intumescent behavior of PP sample during UL94 vertical test
MVSS 302
Flammability of Interior Materials

• Federal standard for passenger automobiles
• Time versus distance test
• Very slow moving flame spread can pass test
NFPA 701
Standard Methods of Fire Tests for Flame Propagation of Textiles and Films

- Method 1 (Small scale)
- 1.5” flame, 12 seconds
- Pass is self-extinguish and no flaming debris
ASTM E-162 / ASTM E-662

• Combination open flame / radiant panel test
• Military Packaging
• E-662 is for smoke density
ASTM E-108
Standard Test Methods for Fire Tests of Roof Coverings

- Flame spread, burning brand, flying burning brand
- Can test for Class A, B or C rating
- Fuel source largest for Class A
- Burn through of roof deck
Flame Retardant Markets

- Electrical and Electronic Equipment
- Building and Construction
- Transportation
- Textiles
Future of FR Market

- US Demand expected to reach 938 million pounds by 2016, growth of 4.6%

- Building and Construction biggest growth area and greatest share of sales

- ATH volume estimated at 46% of US Market but higher margin brominated has greatest share of market value

- Inorganic and phosphorus will expand at the fastest rates

- Halogenated types will register subpar advances due to health and safety concern in all markets

FR Coating Market Challenges

- Majority of flame retardant business is in steel coatings for construction market and plastics masterbatch / compounding

- Must be an enforced flame retardant standard in place

  Nobody adds the cost of a flame retardant to a product because it is a “good idea”

- Niche, specialty business

  Need to target specific markets (testing costs, production capabilities) (Steel – WR Grace, RPM Carboline, International Paint)
Market Challenges

• Consultative sales approach – solution based, sample testing / qualification, bench time for application specific formulation

• No such thing as a “Universal Flame Retardant” or “Mix in Flame Retardant”

Flame retardant coating formulation drivers are flame retardant standard(s), substrate and end use.

Mix in FR’s do nothing except add more solids to a good water based latex paint that most likely already has a 0 flame spread index on cement board!
Market Challenges

- Lack of new flame retardant raw materials / additives

  Newest raw material went off patent 20 years ago (CPE)

  Nothing new (ground breaking) on the horizon

  Anything new is just a different combinations of existing technology (attaching amines to phosphates) – for the plastics compounding markets – does not apply to coatings

  Nanocomposites show promise for better / new physical characteristics in FR coatings – high cost limits development of new coatings
Market Challenges

- Environmental concerns

  Moving away from halogen flame retardant systems – some are bioaccumulation and toxic

  RoHS Directive / WEEE (EU Standard) is recognized and enforced worldwide, especially in E & E markets - bans use of PVC, antimony, shortchain chlorinated paraffins, and PBDE’s

  PDBE being phased out of production in US (Decabrom) in December 2012

  Industry moving toward phosphorus, inorganic and nitrogen based FR’s (www.PINFA.org)
Questions?
Thank you!

References:

Flame Chk, Inc.
www.flameretardants-online.com
www.pinfa.org