Flame Retardants and the Evolving Regulatory Landscape

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Product Development Engineer
Flame Retardant Products
Overview

- Background/Overview
- Thermoplastic Flammability
  - Flame Retardant Additive Chemistries and Mechanisms
- Regulatory Landscape
- Testing Standards
- FR Products meet End Applications
Definition

Materials that do not ignite readily or propagate flames under small to moderate fire exposures

- Materials are combustible
- Fire retardants reduce the intensity and spread of fire
- Reduces smoke and toxic by-products of combustion.
Goals of Flame Retardant Compounds

- Increase Resistance to Ignition
- Reduce Rate of Flame Spread
- Reduce Rate of Heat Release
- Reduce Smoke Emission

End Goal

- Meet FR Specifications
- Make the World a Safer Place!
Markets for FR Thermoplastics

- Electrical Parts
- Electronic Enclosures
- Wire and Cable
- Appliances
- Transportation
- Building and Construction
Flammability of Thermoplastics
### Thermoplastic Resin Flammability

#### Flammable
- Polyolefins
- Nylons
- Polycarbonate
- Polyesters
- Styrenics
- TPE’S

#### Inherently Flame Resistant
- Polysulfones
- Polyphenylene Sulfide
- Polyetheretherketone
- Polyetherimide
- Fluoropolymers
Challenges of Flame Retarding Plastics

Limiting Oxygen Index

- Acetal
- Cotton
- PE
- PP
- ABS
- PMMA
- SAN
- PET
- PBT
- Nylon 6/6
- PC
- PSU
- TPI
- PVDF
- PVC
- PTFE

LOI %
Flame Retardant Additives and Mechanisms
Common Types of FR Additives

- **Halogenated FR’s**
  - Brominated
  - Chlorinated

- **Halogen Free FR’s**
  - Metal hydroxides
  - Phosphorous Based
  - Melamine Based

Flame Retardant Additive Usage, 2011

- Bromine 22%
- Phosphorus 16%
- Chlorine 12%
- Inorganics 44%
- Other 6%
Halogenated technology inhibits the chemical reaction in the gas/vapor phase

Various molecules that efficiently get large amounts of free radicals to the gas phase

<table>
<thead>
<tr>
<th>Additive Type</th>
<th>Polymeric Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Higher Halogen Content</td>
<td>• Melt Blendable</td>
</tr>
<tr>
<td>• Lower Loadings</td>
<td>• Less effect on physical properties</td>
</tr>
<tr>
<td>• High Thermal Stability</td>
<td>• Enhanced Flow</td>
</tr>
</tbody>
</table>

Halogenated flame retardants are compatible in most resin systems with the exception of Acetal
Non Halogen Mechanisms

Phosphorous
- Various forms
- Contributes to the condensed phase char formation

Hydrated Minerals
- Produce water during combustion process, dilute flammable vapors
- Insulative char formation

Melamine Cyanurate
- Endothermic decomposition
- Physical removal of flame from surface

Resin Systems
- Polyolefins, Polyamides, Polyesters, Polycarbonate and alloys
- Polyolefins, Polyamides
- Polyamides, used as a synergist for other Phosphorous technologies
### Halogen vs. Halogen Free

#### Past

<table>
<thead>
<tr>
<th>Halogenated</th>
<th>Halogen Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Lower Cost</td>
<td>• Limited Availability</td>
</tr>
<tr>
<td>• Better Processing</td>
<td>• Low Smoke</td>
</tr>
<tr>
<td>• Better Efficiency</td>
<td>• Lower Toxicity</td>
</tr>
<tr>
<td>• Better Physical Properties</td>
<td>• Less Corrosive</td>
</tr>
<tr>
<td></td>
<td>• Lower Specific Gravity</td>
</tr>
<tr>
<td></td>
<td>• Niche Product</td>
</tr>
<tr>
<td>Past</td>
<td>Present</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------</td>
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<td>• Niche Product</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
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</table>
Choosing a FR System

How do we decide which FR mechanism to use?

• Resins System
• FR Specification
• Part Function
• Fillers/Additives
• Regulatory Concerns
  – Halogen, RoHS, etc
Regulatory Landscape
• **Restriction of Hazardous Substances (RoHS)**
  – EU Directive in effect as of July 2006

• **Banned Substances**
  – Lead (Pb)
  – Mercury (Hg)
  – Cadmium (Cd)
  – Hexavalent Chromium (CrVI)
  – Polybrominated Biphenyls (PBB) and Polybrominated Diphenyl Ethers (PBDE)

• **Flame Retardants and Pigments**

  Does not need to be Halogen Free!
How does RoHS compliance affect material selection?

- Drop in replacements available
- Identical Properties
  - Physical, Flow, Heat Resistance, Processability
- Cost Premium
Evolution of Halogen Free Technologies

- More “self-policing”/customer driven bans
- New FR standards
- Green Movement
- More Effective FR Chemicals
- More Economical FR Chemicals
- Increased Performance
- Competition in the Market
Halogen Restrictions

• OEM Driven Ban on Halogenated Chemicals
  – HP, DELL, IBM etc.

• Eco Labels
  – Blue Angel, White Swan, Ecolabel etc.
Impact of Halogen Free

- Resin Limitations
- Physical Properties
  - Strength/Impact
  - Flow
  - Heat Resistance
  - Resin Dependent
- Flammability
- Cost
- Reduction in Specific Gravity
### Mechanical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>RTP 205 FR</th>
<th>RTP 205 FR Halogen Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, psi</td>
<td>21000</td>
<td>19500</td>
</tr>
<tr>
<td>Tensile Modulus, psi E6</td>
<td>1.65</td>
<td>1.45</td>
</tr>
<tr>
<td>Tensile Elongation, %</td>
<td>2-4%</td>
<td>2-4%</td>
</tr>
<tr>
<td>Flexural Strength, psi</td>
<td>33000</td>
<td>31500</td>
</tr>
<tr>
<td>Flexural Modulus, psi E6</td>
<td>1.55</td>
<td>1.45</td>
</tr>
<tr>
<td>Impact Notched, ft-lb/in</td>
<td>2</td>
<td>1.8</td>
</tr>
<tr>
<td>Impact Un-notched, ft-lb/in</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>HDT @ 264 psi</td>
<td>470</td>
<td>470</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.66</td>
<td>1.41</td>
</tr>
<tr>
<td>Flammability</td>
<td>V-0 @ 1/32</td>
<td>V-0 @ 1/32</td>
</tr>
</tbody>
</table>
Property Comparison

Tensile Strength, psi

Specific Gravity

Tensile Modulus, psi

HDT @ 264 psi

Tensile Elongation, %

Impact Un-notched, ft-lb/in

RTP 205 FR

Flexural Strength, psi

RTP 205 FR Halogen Free

Impact Notched, ft-lb/in

Flexural Modulus, psi
Test Standards
Electrical and Electronics (E&E)

– Appliance, Connectors, housings, etc.

• **UL 94**
  – V, 5V, HB

• **UL 746**
  – HAI, HWI, CTI
Let's look closer at...

UL94

- Horizontal Burn (HB)
- Vertical Burn (V-0, V-1, V-2)
Classification Criterion

3.0 mm to 13.0 mm thickness  
- slower than 40 mm/minute or...
- combustion ceases prematurely

< 3.0 mm thickness  
- slower than 75 mm/minute or...
- combustion ceases prematurely

** In general most thermoplastics meet this criteria **
## UL94 VB Classification Criteria

<table>
<thead>
<tr>
<th>Classification Criteria</th>
<th>V-0</th>
<th>V-1</th>
<th>V-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of bar specimens</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Maximum flame time per specimen per flame application, sec</td>
<td>10</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Maximum total flame time 5 specimens, 2 ignitions, sec</td>
<td>50</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Specimen drips, ignites cotton</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Maximum afterglow time per specimen, sec</td>
<td>30</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Burn to holding clamp</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

**Thickness dependent ratings**
UL94 Vertical Burn Demo

Flame Retardant – V-0

Non-Flame Retardant – No Rating
FAR 25.853

• **Flammability:**
  – 15-Second Horizontal Burn
  – 12-Second Vertical Burn
  – 60-Second Vertical Burn

• **Smoke Density:**
  – $D_s@4\text{min} < 200$
  – ABD0031 or BSS 7238 or ASTM E-662

• **Ohio State University Heat Release:**
  – Calorimetry Test Measures Peak and Total Heat Release
  – <100/100, <65/65, & <55/55 are common

OEM Driven Requirements

• **Toxic Gas Emission:**
  – Varies by OEM
  – ABD0031 or BSS 7239

**Requirements vary by part size and location**
• Requirements focus on:
  – Low Smoke, Heat Release, Burn Rate, Flame Spread

• Various standard that apply:
  – UL2043, UL723/ASTM E84, ASTM E1354, NFPA 701, FM 4996, CAL TB133

• Applications
  – Wall coverings, Furniture, Plenum, Pallets, Storage systems, Roofing, Floor coverings, Ventilation
• LED Lens

• Outdoor Connector

• Overhead Speaker Unit

• Consumer Electronic Cover
Market: Consumer
Application: LED Lens Cover

Problem: UL 94 V-0, High Light Transmission, UV, Light Diffusion, RoHS Compliance

Solution: PC – Transparent, Flame retardant, Specialty pigment package

Benefit: Provided ample diffusion of high powered LED lights with a proprietary pigment technology while achieving the required flame performance
Market: Consumer

Application: Marine Connector

Problem: Strength/Impact, UV Resistance, Specialty color, UL94 V-0, F1

Solution: PC/PBT – Glass reinforced, UV stabilized, Flame retardant

Benefit: Product was able to pass the required drop impact testing and stringent UL outdoor and flammability ratings
Market: Industrial

Application: Speaker Unit

Problem: Plenum location, UL 2043, UL94 5VA, Rigidity

Solution: Polypropylene – Glass fiber reinforced, Halogen free flame retardant

Benefit: Provided structural requirements needed for function and stringent UL flame resistance
Market: E&E
Application: Wireless Access Point
Problem: Bio-Content requirements, Impact resistance, UL94 V-0, Green FR solution
Solution: PLA Alloy – Flame retardant, Impact modified
Benefit: Bio based material that meets demanding heat requirements, provides good dimensional stability and complies with the regulatory flame requirements
Designing for an FR application

- **Regulatory Landscape**
  - RoHS, Halogen Restrictions

- **Specifications**
  - UL94, FAR, ASTM, etc.

- **Part Function**
  - Performance Requirements, Application Environment, etc.

- **Economics**
  - Price is a Property
Questions?

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