Flame Retardancy of Aromatic Polyurea Spray Coatings
Presentation Content

- Presentation of Albemarle
  - Albemarle overview
  - Polymer additives business
- Introduction
  - Polyurethane, Polyurethane-urea & Polyurea spray systems
  - Materials, Equipment, Processing
- Mode of action of flame-retardants
- Flammability testing equipment and criteria
- Formulations
- Results of flammability testing
- Conclusions
Albemarle Overview

- Technology and service-based business model yields innovative solutions
- 3 business segments with strong, balanced product portfolios:
  - Polymer additives
  - Catalysts
  - Fine chemicals
- Business model is committed to product and environmental stewardship

2006 Net Sales: $2.4 billion

<table>
<thead>
<tr>
<th>Net Sales (in millions of dollars)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
</tr>
<tr>
<td>1,008</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Net Income Excluding Special Items (in millions of dollars)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
</tr>
<tr>
<td>70</td>
</tr>
</tbody>
</table>

- 39% Polymer Additives
- 35% Catalysts
- 26% Fine Chemicals
- Asia Pacific: 18%
- Europe, Middle East, Africa: 38%
- Americas: 44%
**Innovative Solution Provider**
- In 2006, Albemarle filed over 100 patents
- Currently ALB has 1,565 active patents and 1,298 pending/published patent applications

**The Flame Retardants Leader**
- Broad, Innovative Product Portfolio
  - Bromine, Mineral, Phosphorus

**Low-Cost Manufacturing**
- Bromine: plants located at low-cost brine locations (Arkansas and Jordan)
- Mineral: low capital cost in Europe; replicate China
- Phosphorus: acquire/develop regional low-cost manufacturing locations; plant to be built in China

**Polymer additives business:**
- 28% of our sales from new products
- Opened new technology center in China
- We meet customers’ needs

**2006 Net Sales $ 920**
Dollars in millions
- 74% Flame retardants
- 26% Stabilizers and curatives

**Broad Application & Product Innovation**
- Expand applications know-how into textiles and coatings
Introduction coating technologies

- Polyurethane
- Polyurethane–urea (hybrid)
- Polyurea
Two-part Polyurethane Spray Systems

- **A-side: MDI quasi-prepolymer**
  - MDI
  - Short diol (hard segment)

- **B-side: blend**
  - Long chained triol as soft-segment
  - Short diol as “chain-extender” (hard segment)

- **Slow reacting**
  - Need catalysts to get desired reactivity
Two-part Polyurethane-urea (Hybrid) Spray Systems

- **A-side: MDI quasi-prepolymer**
  - MDI
  - Long diol (soft-segment)

- **B-side: blend**
  - Long-chained triol as soft-segment
  - Aromatic diamine as chain-extender (diethyl toluenediamine, DETDA)

- Better thermal and physical properties than 1st generation coatings
  - Needs selective catalysis of –OH
Two-part Polyurea Spray Systems

                                                                                 
**A-side: MDI quasi-prepolymer**

- **MDI**
- Long-chained polyetherdiamine (soft-segment)

**B-side: blend**

- Long-chained polyetherdiamine and polyethertriamine as soft-segments
- Aromatic diamine (DETDA) as chain-extender (hard segment)

**No need for a catalyst**

- **DETDA (Ethacure 100®)** often too fast when used on its own
- **Sytem can be slowed down by adding of Ethacure® 300 or Unilink® 4200 but mechanicals are affected**

  - Ethacure® is a trademark of Albemarle
  - Unilink® is a trademark of Dorf Ketal
<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suprasec 2054</td>
<td>Low func. MDI based prep. with NCO content of 15wt%</td>
</tr>
<tr>
<td>Jeffamine D-2000</td>
<td>Amine terminated PP glycol with approx. mol. wt. of 2000</td>
</tr>
<tr>
<td>Jeffamine T-5000</td>
<td>PP oxide based triamine with approx. mol. wt. of 5000</td>
</tr>
<tr>
<td>Ethacure 100</td>
<td>Diethyl toluenediamine,</td>
</tr>
<tr>
<td>Ethacure 300</td>
<td>Dimethylthio toluenediamine</td>
</tr>
<tr>
<td>Antiblaze V490</td>
<td>Diethyl ethylphosphonate</td>
</tr>
<tr>
<td>Antiblaze TL-10-ST</td>
<td>Proprietary mixture of isomers</td>
</tr>
<tr>
<td>Antiblaze TMCP</td>
<td>Tris (2-chloro-1-methylethyl) phosphate</td>
</tr>
<tr>
<td>Saytex RB79</td>
<td>Diester/ether diol of tetrabromophthalic anhydride</td>
</tr>
<tr>
<td>Saytex RB-7970</td>
<td>Blend of Saytex 79 (70%) and Antiblaze TMCP (30%)</td>
</tr>
<tr>
<td>NcendX P-30</td>
<td>Bisphenol A bis(diphenylphosphate)</td>
</tr>
<tr>
<td>XP-7663</td>
<td>Experimental flame retardant containing Br and P</td>
</tr>
</tbody>
</table>

Suprasec® and Jeffamine® are trademarks of Huntsman

Ethacure®, Antiblaze®, Saytex® and NcendX® are trademarks of Albemarle
## Basic Formulation

<table>
<thead>
<tr>
<th>Side A</th>
<th>Parts</th>
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<tbody>
<tr>
<td>Suprasec® 2054 (MDI, 15% NCO)</td>
<td>100</td>
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<tr>
<td>A/B volume ratio = 1:1; 110 index</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Side B</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Jeffamine® D-2000</td>
<td>70.6</td>
</tr>
<tr>
<td>Ethacure® 300 (DMTDA)</td>
<td>29.4</td>
</tr>
</tbody>
</table>
MiXpac DP-400-85-1 air-operated dispenser with 200 ml tubes, 36 element static mixer
Component sides at room temperature
Postcure overnight at 80°C
Dispensing
Mode of action of FR’s

- Minerals
- Brominated
- Phosphorus
- Intumescent
Mode of Action of mineral FR’s

Gas Phase
- Oxygen
- Pyrolysis Products
- Smoke
- Decomposition
- Combustible Gases
- Heat

Solid Phase
- Solid char
- Char formation
- Heat

Chemical Reactions:

\[
2 \text{Al(OH)}_3 \xrightarrow{> 200 \degree C} \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} \\
\text{Mg(OH)}_2 \xrightarrow{> 340 \degree C} \text{MgO} + \text{H}_2\text{O}
\]

Thermal Feedback
Mode of Action of Br containing FR’s

Interruption of the radical chain mechanism of the combustion process in the gas phase

1.) Flame retardant breaks down to radicals

\[ \text{R-Br} \rightarrow \text{R} \cdot + \text{Br} \cdot \]

2.) Formation of hydrogen halides (HBr)

\[ \text{RH} + \text{Br} \cdot \rightarrow \text{HBr} + \text{R} \cdot \]

3.) Neutralisation of high energy radicals

\[ \text{HBr} + \text{H} \cdot \rightarrow \text{H}_2 + \text{Br} \cdot \]

\[ \text{HBr} + \text{OH} \cdot \rightarrow \text{H}_2\text{O} + \text{Br} \cdot \]
Mode of Action of Phosphorous FR’s

Formation of polyphosphoric acids from flame retardants

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

\[ \text{P}_{\text{red}} + \text{O}_2 \rightarrow \text{P}_4\text{O}_{10} + \text{H}_2\text{O} \rightarrow \text{(HPO}_3)_n \]

Build-up of protective coating of polyphosphoric acids and by charring

\[ \text{(HPO}_3)_n + C_x(\text{H}_2\text{O})_m \rightarrow [”C”]_x + (\text{HPO}_3)_n \cdot m\text{H}_2\text{O} \]
Mode of Action of Intumescent FR systems

Formation of foamed char on surface of polymer

Required Components
1. Acid producer (e.g. APP)
2. “C” producer (e.g. polyalcohols)
3. Gas former (e.g. Melamine)
The best rating V-0, is achieved if the mean afterflame time (of 5 specimens, after 10 applications of the flame) does not exceed 5s.

The material is classified V-1 if the mean afterflame time is < 25s.

If flaming particles ignite the cotton, the material is classified V-2.
Glow Wire Flaming Index:
• Flames or glowing of the specimen extinguish within 30s after removal of the glow-wire
• No ignition of the tissue
• No ignition of the test specimen

Glow Wire Ignition Temperature
• The temperature which is 25K (30K between 900°C and 960°C) higher than the maximum temperature of the tip of the glow-wire which does not cause ignition of a test specimen.
ISO 5660-1:1993: THE CONE CALORIMETER TEST

Total Heat Release
Total Smoke Production
Limiting Oxygen Index

A numerical index, the ‘LOI’, is defined as the minimum concentration of oxygen in oxygen – nitrogen mixture, required to just support downward burning of a vertically mounted test specimen.
DIN 4102 B2 Test

A sample will be placed in a sample holder and positioned vertically.

A small flame burner that is inclined at 45° with a flame height of 20mm will be applied to the specimens for a period of 15s.

The test is passed if the tip of the flame does not reach the reference marks at 150 mm within 20s on any sample for edge application of the flame.
### Formulations, 10php Flame-Retardant

<table>
<thead>
<tr>
<th>Formulation # 8885-7-</th>
<th>55</th>
<th>56</th>
<th>57</th>
<th>58</th>
<th>59</th>
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<tr>
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<td>Jeffamine D-2000 (php)</td>
<td>70,6</td>
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![PDA Europe logo](logo.png)
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<tr>
<td>Index</td>
<td>110</td>
<td>89</td>
<td>110</td>
<td>110</td>
<td>95</td>
</tr>
</tbody>
</table>
Strong decrease of Shore D with AB V490
Lower tensiles with FR’s, significant lower for AB V490
Similar or higher elongation with FR’s, significant lower with AB V490
FR’s increase L.O.I, except NcendX P-30
DIN 4102 B2 and UL94

- DIN 4102 B2
  - All formulations pass the B2 test criteria
  - Test is probably not severe enough to discriminate between the formulations
    - DIN 4102 B1 would be more appropriate

- UL94 VB
  - All formulations are rated V2 (Jeffamine T-5000 included in the formulations) This is due to the dripping behaviour of polyurea elastomers which ignites the cotton
    - Next trials to include anti-dripping additive
Increased GWI @ RB-7970, decreased GWI @ V490
Significant increase of GWF with FR’s except V490 & P-30
Total Heat Release

Total Heat Release (10 php)

FR’s show 10-25% reduction of THR
FR’s show 3-37% increase of TSP
Conclusions

• The addition of flame-retardants can increase the L.O.I value by more than 10%
  • Saytex RB-7970 performs best
  Ÿ Higher FR loadings are expected to increase the L.O.I index even more
• Non flame-retarded polyurea passes the DIN 4102 B2 test
  Ÿ Further evaluations are better performed according to the DIN 4102 B1 criterion with same formulations
• The temperatures increase significantly at both the GWI and GWF test in case of Saytex RB7970. Other FR’s show less performance
  • Saytex RB-7970 is best performing
• Aromatic polyurea spray formulations tend to drip. Adding flame-retardants do not change this behavior
  Ÿ Next trials to perform with anti-dripping additive
Conclusions (con’t)

- The cone calorimeter indicates that the total heat release dropped in case of flame-retarded formulations but the smoke production is higher
  - Saytex RB-7970 best performing (23% decrease THR, 3% increase TSP)
- Antiblaze V490 is a strong plasticizer and deteriorates the physical properties
  - AB V490 is not recommended for aromatic polyurea spray formulations
- NcendX P-30 shows a low flame retardancy performance which is probably due to the low phosphorus content
  - NcendX P-30 is not recommended for aromatic polyurea spray formulations
- Both in terms of physical properties and flammability performance, one can state that the best performing flame-retardants are Saytex RB7970, Antiblaze TL-10-ST and XP-7663
- Further work will be done based on specific application and local regulations
Acknowledgements

- Dominique Fasbinder,
  Senior Technologist, polymer processing & testing
- Patrick Merlin,
  Product manager Ethacures
- Jan Vijverman,
  Global bus. manager Antiblaze / Saytex flame-retardants PU/PS
Questions ???