Pushing the Boundaries of Flame Retardancy
Rome, 10th October 2019
Dr. Hung Banh
1. Common Flame Retardants in Insulation Board and Metal Panel
2. BPPO Derivatives as novel Flame Retardants - A fundamental Study-
Common Flame Retardants in ISB and MP
Polyisocyanurate Foams (PIR)
Thermally more robust than PUR foams

→ Increase of cross-linkages
→ Improved fire resistance
Flame Retardants

- Delay or even prevent ignition
- Reduce smoke
- Deter or hinder flame propagation

→ Needs to be combined with other technical safety measures of buildings
→ Increases time to escape in the event of a fire
Phosphorus-based Flame Retardants

- Mainly condensed phase mode
- Support the development of char

\[ \text{Char as a barrier for } O_2 \text{ and heat transfer} \]
Tris(2-chloroethyl) phosphate (TCPP)

- Low reactivity towards water and bases
- 9.5 wt% P
- Viscosity at 20 °C 68.5 mPas
- Reduces friability in PIR foams
- Preferred additive in rigid PU foams
- Believed to be the largest commercial phosphorus flame retardant (2015)¹

¹ Kirk-Othmer Encyclopedia of Chemical Technology, 2017 John Wiley & Sons, DOI:10.1002/0471238961.1608151923050912.a01.pub3
EU TCPP Regulation
– Estimated time-schedule–

CoRAP will start in 2020

This process starts if substance is proven to be CMR

Regulations

REACH dossier update (Lanxess, 2015)

REACH dossier update (7/2018)

RAC: harmonized classification (>2020)

TCPP on SVHC cand. (> 2021)

NTP Results public (≥2019)

TCPP ECHA decision (2020)

Valid new classification (>2021)
Triethyl phosphate (TEP)

- 17 wt% P
- Lower amount of FR necessary in formulations
- Reduces friability in PIR foams
- Viscosity $20 \degree C$ 1.7 mPas
- Viscosity depressant
- No critical classification with regard to REACH
Flammability testing standards in EU
Small Burner Test (DIN EN ISO 11925-2)

Ignitability when exposed to small flame

- Sample size
  - 250 x 90 x d mm³ (d ≤ 60 mm)
- Test conditions
  - 30 s flame treatment
  - 60 s Test
- Requirement for E-Class
  - Max Flame height ≤ 150 mm
Comparison TCPP vs. TEP

Insulation Boards based on same formulation with variation of FR

<table>
<thead>
<tr>
<th>Thickness [mm]</th>
<th>80</th>
<th>80</th>
<th>120</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR</td>
<td>TCPP</td>
<td>TEP</td>
<td>TCPP</td>
<td>TEP</td>
</tr>
<tr>
<td>P content (wt%)</td>
<td>0,43</td>
<td>0,47</td>
<td>0,43</td>
<td>0,48</td>
</tr>
<tr>
<td>Small Burner Test (11925-2) Ø Flame Height [mm]</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Class</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
</tbody>
</table>

→ Same classification in small burner test
Demands

- Reactive FR
- Polymeric FR
- Alternative FR
BPPO Derivatives as novel Flame Retardants
A fundamental Study
BPPO Derivatives as novel Flame Retardants
A fundamental Study between Covestro and IPF Dresden

Influence of the phosphorus oxidation state

Gas phase action
Solid phase action

Phosphorus oxidation state:

- + III
- + V

- Investigation of FR properties of BPPO derivatives
- Acrylate addition products not commercially available

Cone Calorimeter Test
ISO 5660-1

- Samples
  - $100 \times 100 \times d \ (\leq 50) \ mm^3$
  - In this study: $100 \times 100 \times 30 \ mm^3$
- Radiation Heat Flux: 50 kW/m$^2$
- Measurement of the Average Rate of Heat Emission
BPPO Derivatives

<table>
<thead>
<tr>
<th>FR</th>
<th>Small Burner Test DIN 4102</th>
<th>Cone Calorimeter Test DIN ISO 5660-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ø Flame Height [mm]</td>
<td>MARHE [kW/m²]</td>
</tr>
<tr>
<td>-</td>
<td>200</td>
<td>172</td>
</tr>
<tr>
<td>TEP (0.3 wt% P)</td>
<td>180</td>
<td>128</td>
</tr>
<tr>
<td>MA-BPPO/TEP (0.7/0.3 wt% P)</td>
<td>150</td>
<td>132</td>
</tr>
<tr>
<td>EA-BPPO/TEP (0.7/0.3 wt% P)</td>
<td>150</td>
<td>121</td>
</tr>
<tr>
<td>'BuA-BPPO/TEP (0.7/0.3 wt% P)</td>
<td>150</td>
<td>114</td>
</tr>
</tbody>
</table>

→ Tendency: MARHE↓ and TSR↓ with bigger side chain

Summary

• The decision on whether the use of TCPP will be regulated is postponed to 2020
• For the moment TEP is a potential substitution for TCPP in the applications Insulation Board and Metal Panel
• Fundamental studies show that BPPO derivatives can be used as flame retardants
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Unless specified to the contrary, the property values given have been established on standardized test specimens at room temperature. The figures should be regarded as typical values only and not as binding limiting values.”
Flammability testing standards in EU
Thermal attack by a single burning item (SBI) – DIN EN 13823

- Sample size
  - 2 wings
  - Short Wing: 0.5 x 1.5 m²
  - Long Wing: 1 x 1.5 m²
- Test conditions
  - 21 min flame treatment
  - 26 min Test
Flammability testing standards in EU
Classification of construction products EN 13501-1

Measured Parameters:

- FIGRA – Fire Growth Rate
- THR – Total Heat Release
- LFS - Lateral Flame Spread

<table>
<thead>
<tr>
<th>Flammability Class</th>
<th>FIGRA0,2 MJ [W/s] ≤ 120</th>
<th>THR600 [MJ] ≤ 7,5</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td></td>
<td>LFS &lt; Edge of Specimen</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>FIGRA0,2 MJ [W/s] ≤ 250</th>
</tr>
</thead>
<tbody>
<tr>
<td>THR600 [MJ] ≤ 15</td>
</tr>
<tr>
<td>LFS &lt; Edge of Specimen</td>
</tr>
</tbody>
</table>

| FIGRA0,4 MJ [W/s] ≤ 750 |

Smoke Development Class

<table>
<thead>
<tr>
<th>Smoke Development Class</th>
<th>SMOGRA</th>
<th>TSP600</th>
</tr>
</thead>
<tbody>
<tr>
<td>s₁</td>
<td>30 m²/s²</td>
<td>50 m²</td>
</tr>
<tr>
<td>s₂</td>
<td>180 m²/s²</td>
<td>200 m²</td>
</tr>
<tr>
<td>s₃</td>
<td>Not s₁ or s₂</td>
<td></td>
</tr>
</tbody>
</table>

Droplet Formation Class

<table>
<thead>
<tr>
<th>Droplet Formation Class</th>
<th>d₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>No burning droplets/particles within the first 600 s</td>
<td></td>
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</table>

| d₁ | No burning droplets/particles with an afterflame time > 10 s within the first 600 s |
|    | d₂ | Not d₀ or d₁ |

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