A New Class of Non-Halogenated Flame Retardant Polyester Film Substrates and Applications in Metallizing Environments

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Some Facts about Fire

- Over 2 million fires reported in US each year
- Direct property loss: ~0.2% GDP
- Indirect Cost: ~1% GDP
- ~4,000 people die in US each year
- ~5,000 people die in Europe
- >75% die of smoke inhalation

*Data source: EFRA - THE EUROPEAN FLAME RETARDANTS ASSOCIATION*
The Phases in the Course of a Fire

- Ignition
- Spread
- Flash over

Temperature

Full fire

> 1000°C

Time
Background-How Plastics Burn

- **Heat Source**
  - Starts degradation of plastics
  - Generates volatile components
- **Oxygen**
  - Reacts with volatile materials off-gassed from plastics
- **Fuel**
  - Replenishes volatiles for further combustion

Fire continues until at least one of the ingredients is depleted
Modes of Action of Flame Retardants

- **Physical Action**
  - Cooling: Endothermic process
  - Formation of a protective layer
  - Dilution by inert substances

- **Chemical Action**
  - Reaction in gas phase
    - Interrupt the radical process
  - Reaction in solid phase
    - Breakdown of polymer, causing pronounced flow of polymer away from the flame
    - Form a layer of carbon on the polymer surface
Types of Flame Retardants

- **Reactive Flame Retardants**: FR covalently bonded to polymer
- **Additive Flame Retardants**: added before, during or after polymerization
- **Synergist**: $1+1 > 2$ in terms of flame retardancy
Development of FR BOPET

- Novel flame retardant co-polyester
- Platy inorganic particles incorporated via compounding
- Co-extrusion
- Biaxially oriented Polyester Film: 48G –200G
- Patent pending
- Two final products presented:
  - 2-1: Clear FR film
  - 2-3: Hazy FR film with anti-dripping function
  - 0-1: Regular BOPET as control
FR-PET Relative Performance

Flame Suppressant Content

Platy Particle Content

Not Filmable-regime

Our Technology

VTM-0

VTM-2

HB-regime

Other Specs
Flammability Test Summary

- UL94
- Oxygen index (ASTM D-2863): 23-28% (regular PET ~20%)
- Smoke density (ASTM D-2843): 2.2%, (regular PET ~9.4%)
- Cone calorimeter (ASTM E1354-03): Heat and visible smoke release rates for materials and products using a oxygen consumption calorimeter
- Toxicity index, Naval engineering standard (NES) 713: 3-4
Common Flammability Test: UL94 for Thin Materials

Criteria Conditions

<table>
<thead>
<tr>
<th>Classification</th>
<th>HB</th>
<th>VTM-2</th>
<th>VTM-1</th>
<th>VTM-0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burning</td>
<td></td>
<td>Burning time ≤ 30s</td>
<td>Burning time ≤ 30s</td>
<td>Burning time ≤ 10s</td>
</tr>
</tbody>
</table>

Afterflame time for each individual specimen t1 or t2

- **VTM-0**: ≤ 10s
- **VTM-1**: ≤ 30s
- **VTM-2**: ≤ 30s

Total afterflame time for the set (t1 plus t2 for the 5 specimens) ≤ 50s

- **VTM-0**: ≤ 250s
- **VTM-1**: ≤ 250s

Afterflame plus afterglow time for each individual specimen after the second flame application (t2 + t3)

- **VTM-0**: ≤ 30s
- **VTM-1**: ≤ 60s
- **VTM-2**: ≤ 60s

Afterflame or afterglow of any specimen up to the holding clamp

- **VTM-0**: No
- **VTM-1**: No
- **VTM-2**: No

Cotton indicator ignited by flaming particles or drips

- **VTM-0**: No
- **VTM-1**: No
- **VTM-2**: Yes
UL94 Test of Metallized PET Film: Regular and FR PET Film

Regular PET, metallized
Fail (HB)

FR PET, metallized
VTM0
## UL94 Test Summary

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness</th>
<th>0-1 Regular PET</th>
<th>2-1 Clear FR PET</th>
<th>2-3 Hazy FR PET</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biax base film</td>
<td>1 mil</td>
<td>HB</td>
<td>HB* (-VTM0)</td>
<td>VTM2 (-VTM0)</td>
<td>Shrink up to 125 mm mark</td>
</tr>
<tr>
<td>Metallized biax film</td>
<td>1 mil</td>
<td>HB</td>
<td>VTM2 (-VTM0)</td>
<td>VTM0</td>
<td>Metallizing prevents shrinking and dripping</td>
</tr>
<tr>
<td>Amorphous film</td>
<td>12 mil</td>
<td>HB</td>
<td>VTM0</td>
<td>VTM0</td>
<td></td>
</tr>
</tbody>
</table>

*For thin film, UL94 test is a difficult measurement not because of burning, but because of heat induced shrinkage to 125mm. UL94 does not take this into account.*
Limited Oxygen Index: ASTM D2869-95

- Minimum oxygen concentration to support candle-like combustion of plastics
- Sample rolled to form a cylinder
- Sample burned consistently for a period of 180s or a linear distance of 80 mm at lowest oxygen obtainable
- Air has ~20.8% oxygen, O\textsubscript{2}
- LOI results:
  - 0-1: 20.0%
  - 2-1: 28.0%
  - 2-3: 23.0%
Cone Calorimeter Test: ASTM E 1354-03

- Specimen (100mmx100mm) mounted into a holder and placed horizontally below a cone shaped radiant heat source emitting a specified heat flux (50 kW/m²)
- A spark source located 13mm above the specimen surface to promote ignition

- Information from cone calorimeter test
  - Rate of heat release
  - Mass loss rate
  - Time to sustained flaming
  - Smoke obscuration
Heat Release Rate of 92G Polyester Film
## Cone Calorimeter Test: ASTM E 1354-03

<table>
<thead>
<tr>
<th>Sample</th>
<th>0-1</th>
<th>2-1</th>
<th>2-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combined Specimen Thickness (6 sheets) (mm)</td>
<td>0.20</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>Combined Initial Mass (g)</td>
<td>2.20</td>
<td>2.11</td>
<td>2.11</td>
</tr>
<tr>
<td>Final Mass (g)</td>
<td>0.03</td>
<td>0.53</td>
<td>0.00</td>
</tr>
<tr>
<td>Total Mass Loss (kg/m²)</td>
<td>0.22</td>
<td>0.16</td>
<td>0.21</td>
</tr>
<tr>
<td>Peak Mass Loss Rate (g/s.m²)</td>
<td>21.07</td>
<td>17.26</td>
<td>17.76</td>
</tr>
<tr>
<td>Average Mass Loss Rate (g/s.m²)</td>
<td>4.48</td>
<td>10.84</td>
<td>1.64</td>
</tr>
<tr>
<td>Time to Ignition (s)</td>
<td>27</td>
<td>31</td>
<td>34</td>
</tr>
<tr>
<td>Time to Flame-out (s)</td>
<td>55</td>
<td>72</td>
<td>104</td>
</tr>
<tr>
<td>Time of Peak Rate of Heat Release (s)</td>
<td>45</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>Peak Rate of Heat Release (kW/m²)</td>
<td>167.2</td>
<td>134.3</td>
<td>139.9</td>
</tr>
<tr>
<td>Average Rate of Heat Release (kW/m²)</td>
<td>88.7</td>
<td>54.0</td>
<td>42.1</td>
</tr>
<tr>
<td>Total Heat Release (kW/m²)</td>
<td>2.47</td>
<td>2.19</td>
<td>2.49</td>
</tr>
</tbody>
</table>
Toxicity Results per Naval Engineering Standard (NES) 713

<table>
<thead>
<tr>
<th>GAS</th>
<th>Lethal limit (ppm) 30 min</th>
<th>A2-1</th>
<th>A2-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Film Thickness</td>
<td></td>
<td>186μ</td>
<td>302μ</td>
</tr>
<tr>
<td>PHOSGENE</td>
<td>25</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NH₃</td>
<td>750</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SO₂</td>
<td>400</td>
<td>32.1</td>
<td>40.0</td>
</tr>
<tr>
<td>HCN</td>
<td>150</td>
<td>3.2</td>
<td>4.0</td>
</tr>
<tr>
<td>CO</td>
<td>4,000</td>
<td>7,459.3</td>
<td>11,996.3</td>
</tr>
<tr>
<td>H₂S</td>
<td>750</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>100,000</td>
<td>106,726.2</td>
<td>80,923.3</td>
</tr>
<tr>
<td>HCl</td>
<td>500</td>
<td>1.9</td>
<td>0.8</td>
</tr>
<tr>
<td>FORMALDEHYDE</td>
<td>500</td>
<td>21.2</td>
<td>20.0</td>
</tr>
<tr>
<td>PHENOL</td>
<td>250</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>ACRYLONITRILE</td>
<td>400</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NOₓ</td>
<td>250</td>
<td>3.2</td>
<td>4.0</td>
</tr>
<tr>
<td>HF</td>
<td>100</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Toxicity Index | 3.1 | 4.0 |

- **Most important**: Toxicity Index: 3-4
- **Navy requirement**: ≤ 5
- **Typical vinyl**: 11-13
FR BOPET Film Flame Retardant Mechanism

- Mainly in the solid phase with some in gas phase
- Char formation to form an insulating layer
  - Char formation via dehydration of polymer and platy particles

TPA’s FR Film

- Resin → Heat
  - IV. Radiation
- Volatile gas → Combustion
  - II. Oxidation
- Polymer → Char
  - III. Exothermic Reaction
  - Shielding
A Typical Application Example

**Original Structure**

- 48-142 G Regular BOPET
- Adhesive layer: halogenated FR
- Substrate

**New Structure with Same FR Properties**

- 48G FR BOPET Film
- Regular thinner adhesive layer
- Substrate

(More Effective: FR is in outer layer)
Summary

- TPA has produced a highly innovative non-halogenated flame retardant PET Film suitable for metallizing applications
  - Patent pending
  - Novel P-based copolyester resin as the “flame suppressant”
  - Platy inorganic particles to reduce tendency of PET film to flow or drip under burning conditions
  - Clear or semi-gloss version
- Film available in sheet or small roll form: 48G to 200G.
- *We are working with our customers to meet the relevant FR specifications for their applications*

‘TORAY’
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