Discussion

- Flame Retardant Mechanisms
- What to consider when choosing a flame retardant.
- Phosphorus Chemistry
- What Valtris has to offer
Fire Triangle: Oxygen Chemical Reaction

Reaction between oxygen and fuel that is triggered by a heat source or ignition.
PVC resin itself is not flammable.

- However, plasticizers and other additives act as fuel.
- High plasticizer content means high flammability.
- During combustion, plasticizers volatilize and increase flammability.
How do Flame Retardents work?

Flame Retardants are compounds, which when added to materials during or after manufacture, inhibit or suppress the combustion process.

1. Increase ignition temperature and time to ignition.
   - Prevent the fire from starting.
2. Decrease the rate of combustion, resulting in lower heat release.
   - Allows occupants time to escape.
3. Reduce the rate of fire spread to avoid flash over.
   - Increase response time.
Flame Retardant Mechanisms

➢ By Cooling – through an endothermic reaction releasing bound water of hydration which cools the volatile components.
  • Examples: Alumina Trihydrate and Magnesium Hydroxide

\[
2 \text{Al(OH)}_3 \xrightarrow{\Delta -298 \text{ kJ/mole}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}
\]

Aluminium Trihydrate (ATH) breaks down around 200°C to aluminium oxide in an endothermic reaction with the release of water vapor.

As a result of the endotherm, the polymer is cooled, therefore fewer pyrolysis products are formed.

The aluminium oxide, together with the charring products formed on the substrate, acts as an insulating protective layer.

The water vapor liberated has a diluting effect in the gas phase and forms an oxygen displacing protective layer.
Flame Retardant Mechanisms

➢ **Free Radical Method** – free radical scavengers interfere with the formation of combustible gases during or released in the decomposition of the polymer.

- Examples: Halogen based flame retardants and antimony oxide
Flame Retardant Mechanisms

➢ **Free Radical Method – Antimony Oxide**

➢ Antimony trioxide reacts with the HCl evolved from burning PVC to form antimony oxychlorides which then decompose to form antimony trichloride.

➢ The antimony trichloride formed is believed to enter the gas phase during combustion, therefore introducing a source of chlorine radicals directly into the flame.
Flame Retardant Mechanisms

➢ **Altering Melt Behavior** – increase melt flow so as that the PVC product literally drips away from the fuel source.

  • Example: Organic Peroxides

➢ **Gas Dilution** – form inert gases which dilute the combustible gases. This lowers and disperses the fuel available for ignition

  • Example: Melamine Cyanurate
Flame Retardant Mechanisms

➢ **Formation of Protective Layer** – combustible gases generated during the decomposition of thermoplastics can be shielded by forming a solid barrier or protective gas blanket, more commonly known as char.

- Example: Phosphorus Flame Retardants

![Chemical reaction diagram](image)
What to consider when choosing a flame retardant?
What are you looking for in a Flame Retardant?

We reviewed the mechanisms of various flame retardants.

The next challenge is how to formulate a product that meets the specific performance requirements of your application while adding flame retardancy.

What is your main objective?

• Flame Retardancy?
• Smoke Suppression
• A combination of both?
• Are you looking to pass a certain specification?
What are you looking for in a Flame Retardant?

Flame retardant materials can be:

- Solids
- Liquids
- Plasticizers
- Halogen
- Non-halogen

- Specific performance requirements
  - Low temperature flexibility
  - Dielectric properties
  - UV resistance
  - Limiting Oxygen Index
  - Long Term Heat Stability

These attributes need to be considered when formulating your product.

Many formulations use more than one flame retardant.
Non-Halogenated Phosphate Ester Flame Retardants
Phosphate Ester Flame Retardants form a layer of char, or a protective barrier that then excludes oxygen and heat transfer, stopping the flame from spreading.

Phosphate Esters are put into three categories:

- Triaryl Phosphate Esters
- Alkyl Aryl Phosphate Esters
- Trialkyl Phosphate Esters
Non-Halogenated - Phosphate Esters Flame Retardants

- **Tri alkyl**
  - Low smoke
  - High flame

- **Alkyl Aryl**

- **Tri Aryl**
  - High smoke
  - Low flame
Triaryl Phosphate Esters

- Tri aryl phosphate esters tend to act in the vapor phase, therefore they tend to increase smoke evolution.
- Used where flame spread needs to be minimized.
Non-Halogenated - Phosphate Esters Flame Retardants

Alkyl Aryl Phosphate Esters

- Alkyl Aryl phosphate esters act primarily in the polymer phase by forming phosphorus based acids during combustion which aid in char formation.

- Have both good flame retardancy and excel in areas where smoke suppression is needed.
Non-Halogenated - Phosphate Esters Flame Retardants

Tri Alkyl Phosphate Esters

➢ Trialkyl phosphate esters are not primarily used for flame retardancy, and are usually used outside PVC applications.

➢ When used they offer exceptional low temperature properties and performance.
## Valtris: Non-Halogenated Phosphate Esters

<table>
<thead>
<tr>
<th>Valtris Phosphate Ester Products</th>
<th>Fire Retardant</th>
<th>Smoke Suppression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Santicizer® 154</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Santicizer® 141</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Santicizer® 148</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Santicizer® 2148</td>
<td>+</td>
<td>++++</td>
</tr>
<tr>
<td>Santicizer® 2248</td>
<td>+</td>
<td>+++++</td>
</tr>
</tbody>
</table>
Valtris: Non-Halogenated Phosphate Esters
Phosphate Esters – Alkyl Aryl - Flame Retardant/Smoke Suppressors

Santicizer® Trade Name

• Santicizer® 141 – 2 Ethylhexyl Diphenyl Phosphate
  – Fast fusing, High efficiency, Good FR
• Santicizer® 148 – Isodecyl Diphenyl Phosphate
  – Fast fusing, High efficiency, Good FR, Good smoke suppression, Low volatility
• Santicizer® 2148 – Proprietary
  – Fast fusing, Good FR, Great smoke suppression, Low temperature performance
• Santicizer® 2248 - Proprietary
  – Fast fusing, Highest smoke suppression

Structure: Phosphorus, 2 phenyl rings, Alcohol

![Phosphate Esters Structure Diagram]
Phosphate Ester – Tri Aryl - Flame Retardants

Santicizer® Trade Name
- Santicizer® 154 – t-Butylphenyl Diphenyl Phosphate
  - Very good FR
- Santicizer® TPP – Triphenyl Phosphate
  - Very good FR, Solid flake

Structure: Phosphorus, 3 phenyl rings, Alcohol
Phosphate Ester – Tri-Alkyl - Lubricants/Fluids

Santicizer® Trade Name
• Santicizer® 130 – Tributyl Phosphate
  – Hydraulic Fluids
• Santicizer® 135 – Tri-isobutyl Phosphate
  – Oil field extraction

Structure: Phosphorus, 3 butyl groups
Santicizer® 130: Tributyl Phosphate

**Properties**
- low fluid viscosity
- Low temperature applications
- Relative high boiling point
- Excellent lubricity

**Main applications**
- Aviation hydraulic fluid
- Chelating Agent mining applications
- Defoamer in concrete applications
Santicizer® 141: 2-Ethylhexyl Diphenyl Phosphate

**Properties**

- low viscosity plastisol
- Exceptional low temperature performance
- good extraction and abrasion resistance
- food contact approved

**Main applications**

- vinyl sheets
- fabric coating
- nitrocellulose coatings and inks
- PVC Nitrile Butadiene Rubber Foams
Santicizer® 148: Isodecyl Diphenyl Phosphate

Properties

• Highly stable viscosity with time
• Extremely low smoke emission
• Low volatility
• Exceptional high-temperature aging performance
• Compatible with rubbers, acrylics, nitrocellulose

Main applications

• Upholstered furniture
• Wall coverings
• Cable insulation
• Calendered films
Santicizer® 154: t-Butylphenyl Diphenyl Phosphate

Properties
- Low viscosity
- Low volatility
- Best flame retardant
- High autoignition temperature
- Highly compatible with multiple polymers

Main applications
- Upholstered furniture
- Wall coverings
- Vinyl sheets
- Fabric coating
- Vinyl nitrile foams

Tri Aryl Phosphate
**Valtris Modified Alkyl Aryl Phosphate**

<table>
<thead>
<tr>
<th>Santicizer® 2148</th>
<th>Santicizer® 2248</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Excellent Low temperature performance</td>
<td>• Similar to 2148</td>
</tr>
<tr>
<td>• Low volatility</td>
<td>• Extremely low smoke emission</td>
</tr>
<tr>
<td>• Moderate plasticizing capabilities.</td>
<td></td>
</tr>
<tr>
<td>• Low smoke emission</td>
<td><strong>Main applications</strong></td>
</tr>
</tbody>
</table>

**Main applications**

- Wire and Cable

**Main applications**

- Transportation applications
  - Aircraft
  - Public Transportation
Phosphate Esters Fire data

### 30% Phosphate Ester in each Sample

<table>
<thead>
<tr>
<th>Smoke Density</th>
<th>Smoke Density</th>
<th>ISO 11925-2 Ignitability</th>
<th>UL94 Vertical Burn</th>
<th>FMVSS 302 Interior Horizontal Burn</th>
<th>Electrical Burner</th>
<th>Oxygen Index</th>
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</thead>
<tbody>
<tr>
<td>Santicizer® 141</td>
<td>284</td>
<td>88</td>
<td>55</td>
<td>V-0</td>
<td>0</td>
<td>M2</td>
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<tr>
<td>Santicizer® 148</td>
<td>282</td>
<td>36</td>
<td>48.7</td>
<td>V-0</td>
<td>0</td>
<td>M2</td>
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<tr>
<td>Santicizer® 154</td>
<td>625</td>
<td>36</td>
<td>31.7</td>
<td>V-0</td>
<td>0</td>
<td>M2</td>
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<tr>
<td>Santicizer® 2148</td>
<td>280</td>
<td>26</td>
<td>74.1</td>
<td>V-2</td>
<td>2</td>
<td>M3</td>
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<tr>
<td>Santicizer® 2248</td>
<td>266</td>
<td>23</td>
<td>69.8</td>
<td>V-2</td>
<td>0</td>
<td>M3</td>
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<tr>
<td>DOTP</td>
<td>304</td>
<td>94</td>
<td>114.3</td>
<td>FAIL</td>
<td>24.76</td>
<td>M3</td>
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</tbody>
</table>

- **Smoke Density**: lower number better
- **ISO 11925-2 Ignitability**: burn length - lower the better
- **UL94**: V-0 best, V-2 not good
- **FMVSS302**: lower number better
- **Electrical Burn**: M1 best, M4 worst
- **Oxygen Index**: higher number better
Phosphate Esters are also plasticizers

Santicizer® 141 and 148 are better plasticizers than Santicizer® 154.

<table>
<thead>
<tr>
<th>Category</th>
<th>Product</th>
<th>Shore A = 74</th>
<th>Tensile Strength= 185 kg/cm²</th>
<th>Low-T Flex of -14 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl-aryl</td>
<td>Santicizer® 141</td>
<td>53</td>
<td>54</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Santicizer® 148</td>
<td>60</td>
<td>56</td>
<td>43</td>
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<tr>
<td>Tri-aryl</td>
<td>Santicizer® 154</td>
<td>67</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>TPP</td>
<td>73</td>
<td>80</td>
<td>70</td>
</tr>
</tbody>
</table>
Limiting Oxygen Index

LOI – indicative value for the assessment of flame retardancy. High LOI – high flame retardancy or low flammability

- Adding DOP: fast decrease of LOI
- Adding Tri aryl phosphate: slow decrease of LOI
- Adding Alkyl Aryl Phosphate: slow decrease of LOI, but faster than TAP

LOI – indicative value for the assessment of flame retardancy. High LOI – high flame retardancy or low flammability.
Example: Antimony Replacement in Calendered Films

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>Suspension PVC K70</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Chlorinated Paraffin</td>
<td>10</td>
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<td>---</td>
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<tr>
<td><strong>Santicizer® 148</strong></td>
<td>37</td>
<td>40</td>
<td>48</td>
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<tr>
<td>Antimony</td>
<td>7.5</td>
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<td>---</td>
</tr>
<tr>
<td>Aluminum Trihydrate</td>
<td>---</td>
<td>20</td>
<td>20</td>
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<tr>
<td>Zinc Borate</td>
<td>---</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>---</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>33</td>
<td>15</td>
<td>30</td>
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<tr>
<td>Stearic Acid</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Therm-Chek® Solid Stabilizer (CaZn)</td>
<td>3</td>
<td>3</td>
<td>3</td>
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<tr>
<td><strong>Shore A</strong></td>
<td>86</td>
<td>89</td>
<td>85</td>
</tr>
<tr>
<td><strong>LOI</strong></td>
<td>31.6</td>
<td>33.2</td>
<td>31.1</td>
</tr>
<tr>
<td>Tensile Strength (Mpa)</td>
<td>22.2</td>
<td>18.8</td>
<td>15.7</td>
</tr>
<tr>
<td>Max Elongation (%)</td>
<td>284</td>
<td>221</td>
<td>207</td>
</tr>
<tr>
<td>Electrical Burner (NF 92-503)</td>
<td>M2</td>
<td>M2</td>
<td>M1</td>
</tr>
<tr>
<td>ISO 11925-2/30&quot; (Burned length (cm))</td>
<td>9.3</td>
<td>6.8</td>
<td>6.3</td>
</tr>
<tr>
<td>Smoke Box 25kW: Flaming (Dmc)</td>
<td>127</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>Smoke Box 25kW: Flaming (Dmc/g)</td>
<td>64</td>
<td>31</td>
<td>30</td>
</tr>
</tbody>
</table>

- Similar Shore A
- Similar Mechanical Properties
- Similar resistance against fire propagation
- Less Smoke generation