Brominated Additives as Flame Retardants

Dr. Thomas Facklam
ADD Flame Retardants Day | Leverkusen, December 7, 2018
1. LANXESS Additives – Bromine and brominated flame retardants
2. Brominated flame retardants – trends to more sustainable alternatives
3. Reactive, oligomeric and polymeric flame retardants – today’s sustainable solutions
4. Our sustainable flame retardant solution – Emerald Innovation® 3000 for EPS/XPS
5. Conclusion
LANXESS Additives – Bromine and brominated flame retardants
Our bromine chain

Brominated performance products like
- Solutions for deep-water oil exploration, or to reduce mercury emissions from coal fired power plants
- Bromine and hydrobromic acid for brominated intermediates & finished goods

Brominated flame retardants
to make it harder for flammable materials to burn
ADD offers a variety of brominated flame retardants

<table>
<thead>
<tr>
<th>Brand names</th>
</tr>
</thead>
<tbody>
<tr>
<td>• BC-52, BC-58</td>
</tr>
<tr>
<td>• BA-59</td>
</tr>
<tr>
<td>• Emerald Innovation®</td>
</tr>
<tr>
<td>• Firemaster®</td>
</tr>
<tr>
<td>• PDBS-80</td>
</tr>
<tr>
<td>• PH-73FF</td>
</tr>
<tr>
<td>• PHT 4</td>
</tr>
<tr>
<td>• PHT 4-Diol (LV)</td>
</tr>
<tr>
<td>• Uniplex</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ADD brominated flame retardants</th>
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</thead>
<tbody>
<tr>
<td>ADD brominated flame retardants are diverse in their performance, structure, and delivery form. These are monomeric, reactive, oligomeric or polymeric additives.</td>
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<tr>
<td>Brominated flame retardants are used in a variety of applications from electronic housings to printed circuit boards and electrical connectors to flexible and rigid polyurethane foam.</td>
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<td>Brominated flame retardants provide optimal processing while maintaining outstanding physical properties in a cost effective manner.</td>
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</tbody>
</table>

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Trends and current solutions
Flame retardants
A trend to more sustainable alternatives

FR technology trends

- Increased sensitivity regarding health impact of chemicals in the public
- Growing awareness of consumer exposure to chemicals
- This is reflected in constantly updated substance lists and debates about certain chemicals
- The trend is towards additives that contribute less to consumer exposure through evaporation and migration
- Strategies to reduce emissions:
  - Reactive flame retardants that are chemically bound
  - Polymeric additives, with a high molecular weight, thus a low volatility, a high permanence and a low bioaccumulation

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Improving fire safety – our answers
Reactive and polymeric flame retardants

Sustainable solutions

- Sustainable solutions are additives that are not bioavailable and not released to the environment
- The development of reactive, oligomeric and polymeric flame retardants are our answers
- Reactive additives are incorporated into the polymer chain, have a covalent bond to the polymer and are thereby retained
- Oligomeric and polymeric additives are migration resistant and non-volatile due to their high molecular weight and resulting immobility
- Depending on its compatibility, this group of additives can be used to protect various polymers
LANXESS’ reactive and oligomeric & polymeric brominated flame retardant solutions

▪ **Sustainable solutions**
  - Reactive flame retardants, which are integrated into the polymer chain
    > Functionalized bromine containing additives
      • BA-59P – Tetrabromobisphenol A
      • PHT4 – Tetrabromophthalic anhydride
      • PHT4-Diol – Tetrabromophthalate diol
  - Oligomeric and polymeric flame retardants with the potential to be permanently incorporated
    > BC-52 & BC-58 – carbonate oligomers
    > PDBS-80 – Poly (dibromostyrene)
    > Uniplex FRP-64 – Poly (2,6-dibromophenylene oxide)
    > Emerald Innovation® 3000 – brominated styrene-butadiene polymer

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# Reactive and polymeric brominated flame retardants

## Applications

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Technology</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamides, PET</td>
<td>Polybromostyrene</td>
<td>Firemaster® PBS64-HW, Uniplex FRP-64,</td>
</tr>
<tr>
<td></td>
<td>Polybromophenyleneoxide</td>
<td>Firemaster® CP44-HF, PDBS-80</td>
</tr>
<tr>
<td>Polycarbonate, PC/ABS</td>
<td>Carbonate Oligomer</td>
<td>BC-52, BC-58</td>
</tr>
<tr>
<td>PBT</td>
<td>Carbonate Oligomer</td>
<td>BC-52, BC-58, Uniplex FRP-64, Firemaster® PBS64-HW</td>
</tr>
<tr>
<td></td>
<td>Polybromostyrene</td>
<td></td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Reactive Intermediate</td>
<td>PHT-4 Diol, PHT-4 Diol LV, Firemaster® 504 &amp; 508</td>
</tr>
<tr>
<td>Styrenics, EPS &amp; XPS foams</td>
<td>Brominated Polymer</td>
<td>Emerald Innovation® 3000</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Reactive Intermediate</td>
<td>BA-59P</td>
</tr>
<tr>
<td>Unsaturated Polyesters</td>
<td>Reactive Intermediate</td>
<td>BA-59P, PHT-4</td>
</tr>
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Reactive flame retardant solutions
Today’s examples of reactive flame retardants

**Structural design**

- Active ingredients: bromine
- Reactive OH groups
- Incorporated: into the polymer chain
- Limited functionality, typically max 2

**Principle reaction**

\[
\begin{align*}
\text{n+1 } & \quad \text{HO-R-OH} + \quad \text{n } \quad \text{O:C=N} \quad \text{N=C:O} \\
\text{HO-R-OH} = & \quad \text{mix of FR diol and other polyols} \\
\text{TDI} & \\
\text{HO-R[O} & \quad \text{N} \quad \text{N=O-R]}_n \quad \text{OH} \\
\text{flame protected PU} & \\
\text{n } \quad \text{HO-FR-OH} + \quad \text{m } \quad \text{HO-Diol-OH} + \quad \text{y } \quad \text{TDI} & \quad \rightarrow \\
\text{HO-Diol-TDI-Diol-TDI-FR-TDI-Diol-TDI-FR-TDI-Diol-TDI-FR-OH} &
\end{align*}
\]
## Reactive bromine containing flame retardants

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>Application &amp; properties</th>
</tr>
</thead>
</table>
| BA-59P     | ▪ Tetrabromobisphenol A  
▪ Bromine content: 59%  
▪ Melting point: ≈ 180°C | ▪ Epoxides  
▪ Used in printed wiring board (PWB)  
▪ High efficiency |
| PHT4-Diol  | ▪ Tetrabromophthalate diol  
▪ Bromine content: 46%  
▪ Light brown liquid  
▪ Viscosity: 90,000 mPas (25°C) | ▪ Rigid PU & PU spray foam, PUR elastomers  
▪ Thermal insulation foams  
▪ No plasticizing effect |
Oligomeric and polymeric flame retardant solutions
Sustainable solutions – polymers
Toxicological and regulatory basis

- Exemptions for polymers exist in some new substance notification regulations like REACH and TSCA*.

- Human health and ecotoxicity hazard for polymers having a large size, a lack of low molecular weight (MW) components, and un-reactive functional groups is typically predicted to be low. In general the exposure potential to compatible polymeric additives is expected to be lower than that of volatile monomeric additives because the release of it from polymers is typically lower.

- ECHA: Since polymer molecules are generally regarded as representing a low concern due to their high molecular weight, this group of substances is exempted from registration and evaluation under REACH.*

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* TSCA (40 CFR 723) details the polymer exemptions and exclusions
REACH: Guidance for monomers and polymers. April 2012, Version 2.0; Guidance for the implementation of REACH
Today’s examples of polymeric flame retardants

Structural design

- Active ingredients: bromine
- Oligomers and Polymers with a high molecular weight
- Incorporated: into the polymer matrix
- The higher molecular weight results in a lower volatility and a higher durability
## Polymeric bromine containing flame retardants

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>Application &amp; properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDBS-80</td>
<td>Polybromostyrene</td>
<td>Polyamides and polyesters</td>
</tr>
<tr>
<td>Firemaster® CP44-HF</td>
<td></td>
<td>E&amp;E: Connectors, switches. Automotive parts</td>
</tr>
<tr>
<td>Firemaster® PBS-64HW</td>
<td></td>
<td>Different molecular weights influence melt flow, glass transition, and thermal stability</td>
</tr>
<tr>
<td>BC-52</td>
<td>Phenoxy terminated carbonate oligomers of TBBA</td>
<td>Polycarbonate, PBT</td>
</tr>
<tr>
<td>BC-58</td>
<td>Bromine content: 52 – 58%</td>
<td>High thermal stability</td>
</tr>
<tr>
<td>Uniplex FRP-64</td>
<td>Poly(2,6-dibromophenylene oxide)</td>
<td>PA6 &amp; 66, PBT</td>
</tr>
<tr>
<td></td>
<td>Bromine content: 64%</td>
<td>Electrical connectors &amp; automotive parts</td>
</tr>
<tr>
<td></td>
<td>Light tan powder</td>
<td>Melt processing, light &amp; thermal stability</td>
</tr>
<tr>
<td></td>
<td>Softening range: 210-240°C</td>
<td></td>
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</tbody>
</table>
Our sustainable flame retardant solution: Emerald Innovation® 3000 for EPS/XPS

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Flame retardants for insulating materials in the building and construction industry

Our sustainable answer to growing concerns

- Insulation is an efficient and easy way to save energy
- EPS and XPS polystyrene foams are effective and useful insulating materials in building and construction
- Polystyrene foams are combustible and must be equipped with flame retardants
- The traditionally used flame retardant additive HBCD (Hexabromocyclododecane) has been identified as a substance raising very high concerns (SVHC).
- Emerald Innovation® 3000 is our answer.

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Polymeric flame retardant for polystyrene
Emerald Innovation® 3000

Description
- Brominated styrene-butadiene polymer
- High molecular weight > 100,000 g/mol
- Product based on licensed technology from Dow Chemical Company

Application
- Flame retardant for polystyrene foam
- Expanded polystyrene (EPS) foam products
- Extruded polystyrene (XPS) foam products
- Building insulation

Properties
- Effective. Provides comparable fire performance in polystyrene foam to standard flame retardants at equivalent bromine levels
- Polymeric structure overcomes concerns compared to small molecule flame retardants

Appearance: White powder
Bromine content: 65%
Softening point: 120°C (TG)
Thermal stability: > 250°C

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Improving fire safety – our answer
Polymer Emerald Innovation® 3000

- ECHA*: Polymer molecules are generally regarded as representing a low concern due to their high molecular weight
- US EPA**:
  - The butadiene styrene brominated copolymer is estimated to have low bioaccumulation potential due to its size (average MW >1,000 daltons) and lack of low MW components
  - Due to its large size, lack of low molecular weight (MW) components, and un-reactive functional groups, human health and ecotoxicity hazard for this polymer are measured or predicted to be low, although experimental data were not available for all endpoints. In general the exposure potential to the butadiene styrene brominated copolymer is expected to be lower than the other chemicals in this assessment because it is a large polymer and is unlikely to be released from the polystyrene
  - However, this alternative is inherently persistent and its long-term behavior in the environment is not currently known

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Conclusion

- The hazard profile of the butadiene styrene brominated copolymer shows that this chemical is anticipated to be safer than HBCD and the two other alternatives for multiple endpoints.

- US EPA Report about flame retardant alternatives for HBCD
  EPA Publication 740R14001
Fire testing of polystyrene blends
Emerald Innovation® 3000 and HBCD

Flame retardancy

- The LOI indicates the flammability of a material. It is the $O_2$-concentration which is required to keep a material burning.
- The LOI of XPS foam with Emerald Innovation® 3000 is equivalent to HBCD at the same bromine content.

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Fire testing – Emerald Innovation® 3000 meets flammability requirements

Emerald Innovation® 3000 offers formulators the option to achieve applicable fire safety standards for polystyrene foam insulation like EN ISO 11925-2 and German DIN 4102 B2 flammability tests.

Trials demonstrate comparable fire retardant efficiency of Emerald Innovation® 3000 versus HBCD at similar bromine levels.

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The polymeric flame retardant Emerald Innovation® 3000 is a highly efficient, sustainable fire safety solution for XPS (extruded PS) and EPS (expanded PS) insulation materials.

Due to its large size, the lack of low molecular weight (MW) components and functional groups, human health and ecotoxicity hazard for this polymer are measured or predicted to be low.

Applicable fire safety standards covering polystyrene foam insulation can be achieved with Emerald Innovation® 3000.

It is a comparable alternative to HBCD requiring reformulation to use in existing production lines; e.g. suitable stabilization necessary.

The presented results demonstrate that Emerald Innovation® 3000 can help address the increasing requirements for PS insulation materials.
Flame retardant solutions from ADD

ADD offers a broad range of flame retardants

ADD will continue to drive innovation

ADD focuses on sustainable reactive and polymeric solutions
Disclaimer

This information and our technical advice – whether verbal, in writing or by way of trials – is subject to change without notice and given in good faith but without warranty or guarantee, express or implied, and this also applies where proprietary rights of third parties are involved. Our advice does not release you from the obligation to verify the information currently provided - especially that contained in our safety data and technical information sheets - and to test our products as to their suitability for the intended processes and uses. The application, use and processing of our products and the products manufactured by you on the basis of our technical advice are beyond our control and, therefore, entirely your own responsibility. Our products are sold in accordance with the current version of our General Conditions of Sale and Delivery.

Unless specified to the contrary, the values given have been established on standardized test specimens at room temperature. The figures should be regarded as guide values only and not as binding minimum values. Kindly note that the results refer exclusively to the specimens tested. Under certain conditions, the test results established can be affected to a considerable extent by the processing conditions and manufacturing process.

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