Sustainability in the Phosphorus Value Chain

P-BASED FLAME RETARDANTS AND FIRE RETARDED PLASTICS
Clariant at a Glance
A global player in the specialty chemicals business

TOTAL SALES IN 2015
5.807 Mio CHF

Employees 2015: approx. 17.000

CARE CHEMICALS  CATALYSIS  NATURAL RESOURCES  PLASTICS & COATINGS

Strong commitment to sustainability:
Clariant in the P Value Chain

- Leading supplier of P-based flame retardants for engineering plastics and coatings
- Uses a few thousand tons of elemental phosphorus and intermediate products based on $P_4$ per year
- Flame retardant portfolio was developed to more sustainable products in several steps

Our vision on sustainable FRs:

Phosphorus based flame retardants produced from recycled P with renewable energy, as part of a future circular P-economy
FR Portfolio Development@Clariant

Step 1: Halogen-Phase-out

• Situation 1990ies: heterogeneous product mix based on Phosphorus and/or Chlorine based products

• Decision 1995 (when the business still was with Hoechst AG): phase–out of all halogenated Flame Retardants:
  • TCEP, TCPP
  • Chlorinated Phosphate-Oligomers
  • Chlorinated paraffines

\[
\begin{align*}
& \text{ClCH}_2\text{OPOPOCH}_2\text{Cl} \\
& \text{ClCH}_2\text{OPOPOCH}_2\text{Cl} \\
& \text{ClCH}_2\text{OPOPOCH}_2\text{Cl} \\
& \text{ClCH}_2\text{OPOPOCH}_2\text{Cl} \\
& \text{ClCH}_2\text{OPOPOCH}_2\text{Cl}
\end{align*}
\]\
Looking for the “Ideal Flame Retardant”

**Basic Needs**
- FR Performance
- Cost Performance
- Legal Compliance

**Stable and safe processing**
- no vapor pressure or volatility
- thermal stability
- low water solubility

**Maintain properties over polymer lifetime**
- no migration in polymer / no leaching
- low impact on mechanical properties

**Maintain properties of polymer**
- minimal interference with polymer structure
- applicable in various polymers
- colorless

**Halogen-free and safe FR**
- no bioavailability
- no physiological activity
- sustainable
FR Portfolio Development@Clariant
Step 2: Development of new sustainable P-FR-s – organic Phosphinates

- Exploration of Phosphinate Chemistry based on well available raw materials yellow phosphorus\(^1\) and sodium hypophosphite\(^2\)

\[
\begin{align*}
\text{NaO} & \quad \text{P} \quad \text{O} \\
\text{H} & \quad \text{H} \quad \text{P} \\
\text{P} & \quad \text{P} \quad \downarrow \\
\text{NaO} & \quad \text{P} \quad \text{H} \\
\end{align*}
\]

\[\text{P} + \text{RCl} + \text{NaOH} \xrightarrow{[\text{PTC}]} \text{NaO} \quad \text{P} \quad \text{R} \quad \text{H}_2 \]

- Pd-catalysed Alkylation\(^2\)
- Radical initiated Alkylation

Disubstituted Phosphinic Acids

\[\text{[2] Hill, M., Bauer, H., Krause, W., WO2009/010188}\]
FR Portfolio Development@Clariant

Step3: Commercialization of Diethylphosphinic acid derivatives

Sodium Hypophosphite

Diethyl Phosphinic Acid Sodium Salt

Diethyl Phosphinic Acid Aluminium Salt (DEPAL)

Diethyl Phosphinic Acid Zinc Salt (DEPZN)
FR Portfolio Development@Clariant
Step 4: Development of tailor made synergistic blends/recipes

- Exolit OP in combination with N-synergists and Stabilizers is an important building block for the compounding industry

- Exolit OP 1240, Exolit OP 1260 for Polyesters

- Exolit OP 1230, Exolit OP 1311, Exolit OP 1312, Exolit OP 1314, for Polyamides
How Sustainable is our Portfolio?
A new system of evaluation

THE PORTFOLIO VALUE PROGRAM SYSTEM
Main Components

SCREENING
- Product Portfolio Sustainability Screening
- CSI R&D Screening for Innovation Pipeline

CONTINUOUS IMPROVEMENT
- Product Portfolio Improvement Roadmap
- Products Meeting Clariant Sustainability Definition

PROMOTION/LABELLING
- EcoTain+ Selected Products

STAKEHOLDER AND THIRD PARTY INVOLVEMENT AND VERIFICATION

INTERNAL TRAINING AND COMMUNICATION
The Assessment Process

TWO “LENSES” ARE USED TO LOOK AT PRODUCT SUSTAINABILITY

- **Sustainability Performance against the Market**
- **Absolute Sustainability Risks & Benefits**

- **36 criteria** are applied following corporate guidelines and a criteria glossary
- **Team effort** with a maximum of product knowledge at the table and data mining
- 26 environmental criteria, 4 economical and 6 social
- The **full life cycle** of the products is addressed
The PVP System Rating Scale

<table>
<thead>
<tr>
<th>Performance of Product Grouping (relative to market standards)</th>
<th>Sustainability Benefits and Risks of Product Grouping (in relation to the absolute nature of issue)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best-in-class performer</td>
<td>Sustainability Benefit</td>
</tr>
<tr>
<td>Higher than market standard/average</td>
<td>Neutral</td>
</tr>
<tr>
<td>Average</td>
<td>Medium/potential risk</td>
</tr>
<tr>
<td>Lower than market standard/average</td>
<td>High risk</td>
</tr>
<tr>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Data insufficient for assessment</td>
<td>Data insufficient for assessment</td>
</tr>
</tbody>
</table>
FR Portfolio Development@Clariant
Step 5: PVP assessment and portfolio optimization

- **Main FR Products have achieved the EcoTain®-Label:**
  - Exolit OP 1230 (Aluminium diethyl phosphinate)
  - Exolit AP 422 (Ammonium Polyphosphate)

- **Some FR grades with needs for improvements regarding sustainability**
  - e.g. Synergistic blends containing Zinc Borate (Category 2 reproductive toxicant)

- Replacement of Zinc Borate by non-classified products as part of a sustainability roadmap
- Development of new “P-P-Synergism” Exolit OP 1400
## External Proof Points – e. g. Green Screen®

### DfE to GreenScreen Translations

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Final Benchmark Scores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony Trioxide (1309-64-4)</td>
<td>1 = Avoid - chemical of high concern</td>
</tr>
<tr>
<td>Melamine Cyanurate (CAS# 37640-57-6)</td>
<td>1 = Avoid - chemical of high concern</td>
</tr>
<tr>
<td>N-alkoxy Hindered Amine Rx Products (CAS#191680-81-6)</td>
<td>1 = Avoid - chemical of high concern</td>
</tr>
<tr>
<td>Phosphonate Oligomer (CAS#68664-06-2)</td>
<td>1 = Avoid - chemical of high concern</td>
</tr>
<tr>
<td>Zinc Borate 1332-07-6, 138265-88-0</td>
<td>1 = Avoid - chemical of high concern</td>
</tr>
<tr>
<td>Antimony Trioxide (CAS#225789-38-8)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Aluminum Hydroxide (CAS#21645-51-2)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Melamine Polyphosphate (CAS#15541-60-3)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Poly[phosphonate-co-carbonate] (CAS# 77226-90-5)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Resorcinol Bis-Diphenylphosphate (CAS#125997-21-9)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Red Phosphorus (CAS# 7723-14-0)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Substituted Amine Phosphate mixture (CAS# 66034-17-1)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Triphenyl Phosphate (CAS#115-86-6)</td>
<td>2 = Use but search for safer alternatives</td>
</tr>
<tr>
<td>Ammonium Polyphosphate (CAS # 68333-79-9)</td>
<td>3 = Use but still opportunity for improvement</td>
</tr>
<tr>
<td>Magnesium Hydroxide (CAS # 1309-42-8)</td>
<td>3 = Use but still opportunity for improvement</td>
</tr>
<tr>
<td>Polyphosphonate (CAS#68664-06-2)</td>
<td>3 = Use but still opportunity for improvement</td>
</tr>
<tr>
<td>Bisphenol A Bis-(diphenyl phosphate (CAS#181028-79-5 and 5945-33-5) (BAPP)</td>
<td>U = not enough data for assessment</td>
</tr>
<tr>
<td>Phosphoric acid, mixed esters with [1,1'-bisphenyl-4,4'-diol and phenol; BPBP (CAS#1003300-73-9)]</td>
<td>U = not enough data for assessment</td>
</tr>
</tbody>
</table>

**Recent Update:** Data gaps filled! Aluminium diethylphosphinate is now benchmark 3!
More Life Cycle Data – e.g. ENFIRO Project

**FR**

- Risk assessment
  - Hazard
    - Environment
    - Human health
  - Exposure

**Material**

- Technological assessment
  - Application
  - Fire performance
  - Leaching and air emission

**Product**

- Impact assessment studies
  - Life cycle assessment
  - Life cycle costing
  - Social life cycle assessment
End of Life Scenarios - Recyclability

PA 66  39,3  39,3
PA 6   10   10
Glass fibre HP3610  30   30
Stab. 1098/168*  0,2/0,2  0,2/0,2
Licowax E  0,3  0,3
Exolit OP 1312  20  
Exolit OP 1400  20
End of Life Scenarios - Incineration

- **Domestic waste**: 24%
- **Mech. & biol. Treatment: “High caloric fraction”**: 8%
- **Mixed plastics**: 28%

Waste incineration:

- **Off-gas**: 0.1%
- **Ashes**: 8%
- **Slag**: 52%
Conclusion

Phosphorus based flame retardants like the presented phosphinates or ammonium polyphosphate

- have a very favorable sustainability profile as shown by internal and external investigations covering the life cycle of these products and flame retarded plastics made thereof

- Remaining life cycle issues are the
  - high energy consumption and the
  - greenhouse gas emissions caused by the production of elemental P

- Both problems can be mitigated or solved, once phosphorus can be sourced from recycled phosphates and produced by using renewable energy