The Importance of Innovation in a Mature Industry: How Antioxidants make new Polymer Markets Possible

Dr. Niall Marshall
EVERSPRING MIDDLE EAST
Overview

- The polymer industry value chain
- Antioxidants and Stabilizers:
  - What are they?
  - Why are they important?
- Mature Industries and Innovation
- Innovation in the use of Antioxidants in Polyolefins
- Conclusion
Plastics Industry Value Chain

Monomer

Everspring Middle East 2018
Plastics Industry Value Chain

Monomer

Polymer Producer

Everspring Middle East 2018
Plastics Industry Value Chain

Monomer → Polymer Producer → Converter → Plastic Article

Everspring Middle East 2018
Plastics Industry Value Chain

Everspring Middle East 2018
Antioxidants and Stabilizers

- Added at low levels (~0.1%) to polymers to protect the polymer against degradation
  - most work either as radical scavengers or hydroperoxide decomposers ("vitamins")
  - some light stabilizers absorb harmful UV light ("sun-screen")
Antioxidant Chemistries

Main Stabilizer Chemistries

Aromatic amines
Hindered phenols
Phosphites & phosphonites
Thiosynergists
Hindered amines
Hydroxyl amines
Benzofuranones

Everspring Middle East 2018
**EVERSPRING**

- **Everspring Chemical Co. Ltd.**
  - established in 1988
  - based in Taichung, Taiwan, Everspring is one of the largest antioxidant producers in the world (including specialty antioxidants)

- **Supplies complete range of stabilizer chemistries**
  - Hindered phenolic antioxidants
  - Phosphite stabilizers
  - Hindered Amines
  - Hydroxyl amines

_Everspring Middle East 2018_
(Some) Phenolic Antioxidants

Everspring Middle East 2018
Plastics Industry Value Chain

Antioxidants
Processing Stabilizers
Light Stabilizers

Polymer Producer

Masterbatch Producer

Everspring Middle East 2018
Plastics Industry Value Chain

Polymer Producer

Masterbatch Producer

Converter
Antioxidant Requirements

- Reactive
  - React with the radicals, peroxides, etc. at a rate that allows it to compete with the oxidation reactions

- Chemically stable
  - The antioxidant should not itself degrade during processing and use

- Compatible with the polymer

- Safe

- Regulatory compliant (including food contact use)
Antioxidant Requirements

- These antioxidants provide very economical performance
  - e.g., typically costs < $10,00 to stabilize 1 ton of polymer
    - the basic *stabilization* of polyolefins is usually much less than this, but for demanding long term outdoor applications the cost will be somewhat higher.
Antioxidant Requirements

- These antioxidants provide very economical performance
  - e.g., typically costs < $10,00 to stabilize 1 ton of polymer

- High costs to commercialise new antioxidants
  - Chemical registration (e.g., REACH, TSCA, DSL/NDSL, IECSC, TCSI, etc.)
  - Regulatory approvals (e.g., Food Contact: FDA, EU, China, Mercosur, etc.)
  - Compliance costs depend on potential volumes (exposure)
Antioxidant Industry

- Most polyolefins produced over the last 40 years have been stabilized using one or more of the following four antioxidants:
  - EVERNOX 10-type
  - EVERNOX 76-type
  - EVERFOS 168-type
  - TNPP (polyethylene only)

- These antioxidants provide excellent stabilization performance and have broad regulatory approvals for the ~164 million tons* polyolefins consumed in 2017

*“Global Polyolefin Consumption Trends”, Nexant, SPE Polyolefins 2018
Mature Market

- A **Mature Market** is a market that has its demand and supply in equilibrium.
- A mature market has:
  - few new products being introduced
  - increased competition
  - decreased profitability
Mature Market

- Is an industry mature because there is no innovation, or is there no innovation because it is mature?
  - Or is there, in fact, innovation even in mature markets?
“Innovation – something a company can make money with...”

Dr. Hariolf Kottmann
CEO Clariant
President of CEFIC (European Chemical Industry Council)
Innovation can include

- **Strategic Innovation**
  - M&A, divestments, backward/forward integration

- **Process Innovation**
  - Production or business processes

- **Market Innovation**
  - Solve [someone’s] problems

... and they need to be willing (and able) to pay for the solution
Market Innovation Opportunities

- **Customer**
  - New markets
    - New polymers

- **Customer’s Customer**
  - New market needs
    - Processing conditions
    - Service conditions

- **Society**
  - New regulatory requirements
New Polymers

- catalyst and process advanced have resulted in polyolefins with:
  - different monomer distributions
  - different MW and MWD
  - different morphologies (heterophasic)

containing
  - different catalyst residues (initiate degradation)

and with better mechanical properties, but expected to maintain those properties for longer
New Polymers

Typical Morphology of Thermoplastic Vulcanizates

- Which phases are more susceptible to degradation? And which stabilisers are more compatible with that phase?
New Market Needs

- more severe processing conditions
  - higher shear rates
  - higher temperatures
- more demanding service conditions
  - long service lifetimes
  - outdoor exposure (sunlight / UV-light / rain)
  - used in a harsh environment
    - exposed to water / acidic / basic / alkaline / solvents (incl. fuel & chemicals)
New Market Needs

- Is the stabilizer system active enough at higher processing temperatures? Are sufficient levels of antioxidant being used?
- Is there a need for a “booster”?

Everspring Middle East 2018
New Market Needs

- Is the stabilizer system able to survive in the environment where it is expected to work? For decades?

GRI-GM13 Specification
>55% after 3 months

- 75%
- 63% after 6 months
- 52% after 6 months

Everspring Middle East 2018
New Market Needs

- Is the stabilizer system able to protect the molten polymer in air? For decades?

Everspring Middle East 2018
New Regulatory Requirements

- Regulation (EU) 10/2011 also included the term NIAS (Non-Intentionally Added Substances)
  - A non-intentionally added substance is an impurity in the substance used, or a reaction intermediate formed during the production process or a decomposition or reaction product.
    - Only “approved” products can be added
    - NIAS are not intentionally added and may not have been approved
NIAS Substances

- any substance extracted from the polymer into a food simulant which is (effectively):
  - not included in the Union List
    - includes catalyst residues, reaction products, degradation products, etc.
  - present at > 10 ppb (if not CMR)
  - has a molecular weight < 1000 Da
    - PP chain ~ 23 monomer units (partly included in extractables)

- and these substances need to undergo risk assessment.
For polymer producers:

- A “Forest of Peaks”
  - Most peaks are not from the additives, they are from the polymer!
  - Antioxidants reduce the amount of degradation (and some antioxidants have very simple reaction products – easy to identify)
  - Using the “right” antioxidants reduces the amount of NIAS from degradation.

LOI (Limit of Interest)
Conclusion

- For the polymer industry it is important that the polymer performance window (processing, service conditions and lifetime) continue to be increased, and this requires improved stabilization

- Although only a few stabilizers are widely used in polyolefins there are many other stabilizers commercialised and available – some of these (as well as new combinations of stabilizers) will provide the required improved stabilization…

- …when used with a “first principles” understanding of degradation and stabilization mechanisms
Thank you
EVERSPRING

- **EVERNOX** - primary antioxidants (phenolic antioxidants)
- **EVERFOS** - secondary antioxidants (phosphite antioxidants)
- **EVERNOX B** - primary-secondary antioxidant blends (B-blends)
- **EVERNOX MD** - Metal deactivators
- **EVERSTAB PS** – thiosynergists
- **EVERSTAB FS** – boosters (carbon-centered radical scavengers)
- **EVERSTAB ES** – enhanced stabilization systems
- **EVERSTAB LS** - hindered amine light stabilizers (HALS)
- **EVERSTAB** - UV absorbers
- **EVERCLEAR** - clarifiers
- **EVERPACK TOP** - Tailored One-Packs
**Products*: Primary Antioxidants**

- Primary antioxidants react with peroxyl (ROO•) radicals to terminate the oxidation process, providing long term stability to polymers as well as protection during processing. Most primary antioxidants are sterically hindered phenols.

<table>
<thead>
<tr>
<th>Phenolic Antioxidants</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Evernox 10</strong></td>
<td>6683-19-8</td>
</tr>
<tr>
<td>General purpose providing excellent long term thermal stability in all polyolefins</td>
<td></td>
</tr>
<tr>
<td><strong>Evernox 76</strong></td>
<td>2082-79-3</td>
</tr>
<tr>
<td>General purpose with good compatibility in PE</td>
<td></td>
</tr>
<tr>
<td><strong>Evernox MD1024</strong></td>
<td>32687-78-8</td>
</tr>
<tr>
<td>High performance with metal (Cu) deactivator</td>
<td></td>
</tr>
<tr>
<td><strong>Evernox 1330</strong></td>
<td>1709-70-2</td>
</tr>
<tr>
<td>High performance with low extractability (pipes)</td>
<td></td>
</tr>
<tr>
<td><strong>Evernox 3114</strong></td>
<td>27676-62-6</td>
</tr>
<tr>
<td>High performance with low discoloration (fibres)</td>
<td></td>
</tr>
<tr>
<td><strong>Evernox 1520</strong></td>
<td>110553-27-0</td>
</tr>
<tr>
<td>High performance suitable for use in XLDPE (wire and cable) without affecting cross-linking</td>
<td></td>
</tr>
</tbody>
</table>

* For a complete list contact Everspring Middle East
Products*: Secondary Antioxidants

- Secondary antioxidants react with hydroperoxides (ROOH), preventing the hydroperoxides from decomposing to form peroxy radicals. Secondary peroxides provide processing stability to polymers and are also called “processing stabilizers”. Most secondary antioxidants are phosphites or phosphonites although thioesters or thioethers are also used in certain applications.

<table>
<thead>
<tr>
<th>Phosphite Antioxidants</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everflos 168</td>
<td>31570-04-4</td>
</tr>
<tr>
<td>General purpose, hydrolytically stable, providing good processing stability</td>
<td></td>
</tr>
<tr>
<td>Everflos 626</td>
<td>26741-53-7</td>
</tr>
<tr>
<td>High performance processing stabilizer</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thioester Antioxidants</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everstab PS800</td>
<td>123-28-4</td>
</tr>
<tr>
<td>Improved long term thermal stability when used with phenolic antioxidants in high temperature applications</td>
<td></td>
</tr>
<tr>
<td>Everstab PS802</td>
<td>693-36-7</td>
</tr>
<tr>
<td>Improved long term thermal stability when used with phenolic antioxidants in high temperature applications</td>
<td></td>
</tr>
</tbody>
</table>

* For a complete list contact Everspring Middle East
Products*: Antioxidant Blends

- It is well known that blends of high performance hindered phenolic antioxidants used together with phosphites act synergistically to provide improved polymer stability.

<table>
<thead>
<tr>
<th>Phenol-Phosphite Antioxidant Blends</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Evernox B110</td>
<td>1:1</td>
<td>Evernox 10: Everfos 168</td>
</tr>
<tr>
<td>Evernox B210</td>
<td>1:2</td>
<td>Evernox 10: Everfos 168</td>
</tr>
<tr>
<td>Evernox B310</td>
<td>1:3</td>
<td>Evernox 10: Everfos 168</td>
</tr>
<tr>
<td>Evernox B410</td>
<td>1:4</td>
<td>Evernox 10: Everfos 168</td>
</tr>
<tr>
<td>Evernox B201</td>
<td>1:2</td>
<td>Evernox 76: Everfos 168</td>
</tr>
<tr>
<td>Evernox B401</td>
<td>1:4</td>
<td>Evernox 10: Everfos 168</td>
</tr>
</tbody>
</table>
**Products*: Light Stabilizers**

- Hindered amine light stabilizers (HALS) react with the radicals formed by high energy ultraviolet (UV) light and terminate the oxidation process. In addition to providing light stability HALS also improve the long term thermal stability of polymers.

<table>
<thead>
<tr>
<th>Hindered Amine Light Stabilizers</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everstab LS 622</td>
<td>70198-29-7</td>
</tr>
<tr>
<td>General purpose low molecular weight tertiary-amine HALS for low color applications</td>
<td></td>
</tr>
<tr>
<td>Everstab LS 944</td>
<td>71878-19-8</td>
</tr>
<tr>
<td>General purpose high molecular weight secondary-amine HALS</td>
<td></td>
</tr>
<tr>
<td>Everstab LS 770</td>
<td>52829-07-9</td>
</tr>
<tr>
<td>High performance monomeric secondary-amine HALS</td>
<td></td>
</tr>
<tr>
<td>Everstab LS 119</td>
<td>106990-43-6</td>
</tr>
<tr>
<td>High performance high molecular weight tertiary-amine HALS providing good long term stability</td>
<td></td>
</tr>
</tbody>
</table>

**Hindered Amine Light Stabilizer Blends**

<table>
<thead>
<tr>
<th>Everstab LS 783</th>
<th>1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everstab LS 622: Everstab LS 944</td>
<td></td>
</tr>
</tbody>
</table>

* For a complete list contact Everspring Middle East
# Products*: Light Stabilizers

- Ultraviolet (UV) absorbers stabilize polymers by absorbing the harmful UV light preventing the formation of radicals.

<table>
<thead>
<tr>
<th>Ultraviolet Absorbers (UVA)</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everstab 326</td>
<td>General purpose benzotriazole UVA with broad food contact approvals</td>
</tr>
<tr>
<td>Everstab 327</td>
<td>General purpose benzotriazole UVA</td>
</tr>
<tr>
<td>Everstab 328</td>
<td>General purpose benzotriazole UVA with good color</td>
</tr>
<tr>
<td><strong>Everstab 234</strong></td>
<td><strong>High performance benzotriazole UVA for high temperature applications (low volatility)</strong></td>
</tr>
<tr>
<td>Everstab 360</td>
<td>High performance benzotriazole UVA for high temperature applications</td>
</tr>
<tr>
<td>Everstab 5411</td>
<td>High performance benzotriazole UVA</td>
</tr>
<tr>
<td>Everstab P</td>
<td>High performance benzotriazole UVA</td>
</tr>
<tr>
<td>Everstab 531</td>
<td>General purpose benzophenone UVA with excellent compatibility in PE</td>
</tr>
</tbody>
</table>

* For a complete list contact Everspring Middle East