Developing Synergistic Stabilizers for Improving the Process Stability, Color, and Long-Term Performance of Polyolefins

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Outline

- Baerlocher Overview
- Creating a Synergistic Stabilizer
- Examples
- Conclusions
Your global partner for additives

Baerlocher Group of Companies serve local customer needs with innovative / customer tailored solutions.

- Global leader in PVC additives
- Leader in Ca-based solutions
- Global metal soaps specialist
- Customer focused blend solutions
- Global footprint of 1200 employees representing a trusted and reliable partner
- 190 years of experience
Specialty Additives Products

- Lubricants
  - Baerolub
  - Baeropol
- Stabilizers
- Non Polymer
  - Coatings
  - Hydrophobe
- Metal Soaps
  - Calcium Soaps
  - Hydrophobe
  - Zinc Soaps
  - Magnesium Soaps
  - Alkali Soaps
  - Aluminum Soaps
- Powdered Metal
- Rubber
- VSA

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## Manufacturing Companies: Countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Location</th>
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<tbody>
<tr>
<td>Germany</td>
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<td>Italy II</td>
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<td>Peru</td>
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<td>USA I</td>
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<td>USA II</td>
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<td>Malaysia</td>
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Creating a New Type of Stabilizer
Polymer stabilization is a well established concept

- **Antacid**
  - Destroys catalyst residuals and buffers the polymer and thus protects antioxidants

- **Secondary AO**
  - Destroys hydroperoxides in the melt that result from oxidation and therefore protects the phenol

- **Primary AO**
  - Gives long term stability and helps determine the lifetime of the resin
Other additives such as boosters, synergists, and functional additives can increase the effectiveness of standard antioxidants

- Example: Thiosynergists (i.e. DSTDP) for improved long term heat stability
- Example: Lubricant (i.e. Zinc Stearate, PPA) reduce shear during extrusion and reduce antioxidant consumption
Baerlocher investigated blends of common additives to determine their efficacy at improving performance of common antioxidants.

We found that certain blends synergistically improved the performance of commodity phenols and phosphites.

Further found that the process by which they were combined boosted efficacy.

Baerlocher named this product: RST (Resin Stabilization Technology).
Blends of various functional additives were quickly screened using mixing bowl techniques.

Determining the suppression of crosslinking in CrHDPE resin was fast and effective for small scale screening.
Early results showed that we could improve melt stability and color of both PE and PP.

Since we could make RST composition from a variety of materials it was decided that:

- RST will have the broadest food contact
- Be multifunctional
- Be cost effective
Since RST can be made from a variety of commonly used polymer additives, Baerlocher has been able to tune the properties of RST:

- **Regulatory:**
  RST is specifically composed of additives with the broadest global food contact approvals

- **Use:**
  RST is a partial or total phosphite replacement
  RST is a total antacid replacement
  RST is a partial or total lubricant replacement

- **Results:**
  Improved color of the resin
  Improved melt stability
  Excellent long term heat stability and OIT
  Reduced blooming
### RST Product Family

#### Baeropol® RST
- Pure RST additive
- For direct formulation in resins

#### Baeropol® DRS
- Alternate to pure phosphites
- Formulated for processors that do not use additive blends

#### Baeropol® T-Blends
- For formulating unstabilized resin
- For boosting stabilization of recycle or prime/virgin resin
- Use as a one-pack solution

#### RST Containing Baeropol®
- Custom blends that contain RST
- Use as one-pack or for delivery of specialty additives

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Ways to Use RST Products

- Stabilization of polyolefin resins during:
  - Resin production
  - Processing
  - Recycling

- Reduction/replacement of phosphite usage
- Replacement of antacids in formulation
Examples
- 2 MFR PP resin
- Extrusion conditions: 160, 200, 240, 240, 220 (die) °C
- Multipass 5x with strand pelletization
- All stabilized samples have 500 ppm of AO 1010 and 500 ppm of AO 168 unless noted differently
- All stabilized samples have 500 ppm of either CaSt or RST
Replacement of standard antacid with RST improves melt stability
Stabilizing Reactor Powder with RST (PP Homopolymer)

- Replacement of antacid with RST reduces yellowness

![Graph showing yellowness of materials with and without RST]
Replacement of antacid with RST improves whiteness
RST can be used by polyolefin manufacturers and compounders as a phosphite reducer.

RST can be used to replace high end phosphites with commodity PH 68 type of products.

Propose: replace high end phosphite 1:1 with PH 68 and replace antacid with RST.

Example:

<table>
<thead>
<tr>
<th>Current</th>
<th>Proposed</th>
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<tbody>
<tr>
<td>AO 10 500 ppm</td>
<td>AO 10 500 ppm</td>
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<tr>
<td>diphosphite 500 ppm</td>
<td>PH 68 500 ppm</td>
</tr>
<tr>
<td>CaSt  500 ppm</td>
<td>RST  500 ppm</td>
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</table>
RST containing samples gave comparable control of melt stability compared to most high end phosphites.

Extrusion Conditions: 240 °C

all samples contain
500 ppm AO 10
500 ppm phosphite
500 ppm antacid or RST
Use of RST as a Partial Phosphite Replacement (HDPE)

- RST gave comparable OIT compared to high-end phosphites

Extrusion Conditions: 240 °C

all samples contain
- 500 ppm AO 10
- 500 ppm phosphite
- 500 ppm antacid or RST

Oxidation Induction Time (min)

<table>
<thead>
<tr>
<th></th>
<th>PH 68</th>
<th>diPH 1</th>
<th>diPH 2</th>
<th>diPH 3</th>
<th>PH 68 92D</th>
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<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>8</td>
<td>30</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>5</td>
<td>14</td>
<td>12</td>
<td>5</td>
</tr>
</tbody>
</table>
The diphosphite samples gave better color compared to PH 68 as expected.
RST gave color comparable to most high end phosphites compared to standard PH 68.

All samples contain 500 ppm AO 10, 500 ppm phosphite, 500 ppm antacid or RST.

Extrusion Conditions: 240 °C
Use of RST as a Partial Phosphite Replacement (HDPE)

- RST gave color comparable to most high end phosphites compared to standard PH 68

![Bar chart showing whiteness index for different samples.](chart.png)

**Extrusion Conditions:** 240 °C

**all samples contain**
- 500 ppm AO 10
- 500 ppm phosphite
- 500 ppm antacid or RST

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Complex rheology showed that RST gave excellent control of rheology at 5 passes.

Use of RST as a Partial Phosphite Replacement (HDPE)

- All samples contain 500 ppm AO 10
- 500 ppm phosphite
- 500 ppm antacid or RST

Extrusion Conditions: 240 °C
Use of RST in Cast film (LLDPE)

- RST can also be used to assist with switching away from the phosphite TNPP in cast resins
- RST can allow for lower phosphite dosage
- Less additives means less blooming

Example:

<table>
<thead>
<tr>
<th></th>
<th>AO 76 500 ppm</th>
<th>AO 76 500 ppm</th>
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</thead>
<tbody>
<tr>
<td>TNPP</td>
<td>1000 ppm</td>
<td>PH 68 500 ppm</td>
</tr>
<tr>
<td>Antacid</td>
<td>1000 ppm</td>
<td>RST 500 ppm</td>
</tr>
</tbody>
</table>
Use of RST in Cast film (ZN LLDPE)

- RST gives better melt stability compared to standard formulations

Melt Index

Extrusion Conditions: 220 °C
Use of RST in Cast film (ZN LLDPE)

- RST dramatically boosts OIT while using less AO

Extrusion Conditions: 220 °C

Oxidation Inductin Time (minutes)
RST improves yellowness for the catalyst rich cast film grade.
Post addition of T-Blends to Polyolefins

- Addition of stabilizer to post consumer recycle allows for retention of the resins initial aggregated properties
- Addition to PCR allows recyclers to have stability similar to prime resin and allows for long term control over properties
  - Stable rheology
  - Improved long term stability
Pass 0 is to turn flake into pellets

PCR HDPE flake has poor stability during multipass extrusion

Addition of T-Blend stabilizer results in essentially no change to rheology during 3 passes through the extruder
Addition of T-Blends to PCR (Oxidation Induction Time)

- PCR HDPE flake has poor initial OIT and falls during multipass extrusion.
- Addition of stabilizer resulted in better initial OIT as well as retention during 3 passes through the extruder.
Conclusions
RST products have been designed for formulation simplification

RST brings value by:

- Reducing phosphite usage
- Replacing high end phosphites with commodity phosphites
- Replacing antacids in polyolefin formulation
- Improving color of the resin
- Enhancing stability of the resin
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