Outline

- Baerlocher Overview
- Stabilization
- Examples
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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

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

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we add character to plastics
Manufacturing Companies: Countries

Germany
UK

Italy I
Italy II

Turkey

Brazil
Peru

USA I
USA II

Argentina
China

India
Malaysia
Stabilization
Stabilization of Polyolefins is Complicated

"Stabilization" : Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc. 2002
**Free Radical Process in Polymers**

**Chain initiation:**

\[ \text{R} - \text{H} \rightarrow \text{R}^+ \]

\[ \text{R} - \text{R} \rightarrow \text{R}^+ \]

**Chain propagation:**

\[ \text{R}^+ + \text{O}_2 \rightarrow \text{ROO}^+ \]

\[ \text{ROO}^+ + \text{RH} \rightarrow \text{ROOH} + \text{R}^+ \]

\[ \text{RO}^+ + \text{RH} \rightarrow \text{ROH} + \text{R}^+ \]

\[ \text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^+ \]

\[ \text{R}^+ + \text{C}=\text{C} \rightarrow \text{R} - \text{C} = \text{C}^+ \]

\[ \text{R} - \text{C} - \text{R}^2 \rightarrow \text{R}^\cdot - \text{C} - \text{R}^2 + \text{R}^3^+ \]

\[ \text{R}^+ \rightarrow \text{Fragmentation} \rightarrow \text{Olefin} + \text{R}^+ \]

**Chain branching:**

\[ \text{ROOH} \rightarrow \text{RO}^+ + \cdot \text{OH} \]

\[ 2\text{ROOH} \rightarrow \text{RO}^+ + \text{ROO}^+ + \text{H}_2\text{O} \]

**Chain termination:**

\[ \text{R}^+ + \text{ROO}^+ \rightarrow \text{ROOR} \]

\[ \text{R}^+ + \text{R}^+ \rightarrow \text{R} - \text{R} \]

\[ \text{R}^+ + \text{RO}^+ \rightarrow \text{R} - \text{O} - \text{R} \]

\[ 2\text{R}^+ \rightarrow \text{Disproportionation} \rightarrow \text{RH} + \text{Olefin} \]

\[ 2\text{ROO}^+ \rightarrow \text{Disproportionation} \rightarrow \text{K} + \text{OH} + \text{O}_2 \]

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"Respect Integrity Excellence"

"we add character to plastics"

Barlocher
Thermo-Oxidation Cycle

- Heat
- Shear
- Light
- Time

Oxygen

Polymer

POO•

P•

POOH

Delta

Polymer

Catalyst Residues

PO• •OH

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Effect of Polymer Degradation

- Color
- Taste and Odor
- Loss of mechanicals
- Gels
- Reduced lifetime
- Inconsistent parts and process
- Inability to regrind/recycle
Small amounts of degradation can result in large changes in mechanical properties.

Stabilizers
Antacids are alkaline additives added to polymers with the purpose of neutralizing acidic species:

- Catalyst residues – Ziegler Natta Catalyst in polyolefins
- Protects antioxidants from degradation
- Improve color in chrome and metallocene catalyzed polyolefins
- Help to buffer the polymer to prevent side reactions with antioxidants

They assist in the overall stabilization of the polymer to prevent further degradation by being the first line of defense in stabilization.
Antacids

- Metal soaps (stearates) are the most common antacid since they also act as lubricants.
- Hydrotalcites and metal oxides/hydroxides are less common but more effective on a pound/pound basis.
Secondary Antioxidants react in the melt phase with hydroperoxides to prevent the formation of free radicals:

- Elimination of free radicals prevents the initiation of degradation
- Fewer free radicals prevents the consumption of primary antioxidants

Secondary antioxidants preserve the primary antioxidant to allow for long term stabilization at room temperature
Secondary Antioxidants

- Phosphite chemistry is the most common secondary antioxidant
- Phosphites react with hydroperoxides in the melt phase to form phosphates
- Phosphites chemically can be unstable and hydrolyze readily

![Phosphite structures](image.png)
Primary Antioxidants

- Primary Antioxidants react in the solid or melt phase with free radicals to terminate the degradation cycle:
  - Elimination of free radicals prevents stops degradation
  - Stopped degradation allows for longer shelf life, better color, better odor, retention of mechanical properties

- Primary antioxidants protect the polymer to allow for long term stabilization at room temperature
Primary Antioxidants

- Hindered phenolic chemistry is the most common primary antioxidant
- Phenolics react with oxygen centered radicals to stop radical propagation
- Phenolic AOs are stable but increase the color of the resin when degraded

![Chemical structures of Irganox 1010 and Irganox 1076]
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
Thermo-Oxidation Cycle

Heat
Shear
Light
Time

Catalyst Residues

Polymer

Oxygen

POO•
P•

Polymer

PO• •OH

Antacids

Primary AO

Secondary AO

POOH

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Other Stabilizers

- Light Stabilizer – HALS
  - Primary antioxidant that captures oxygen centered radicals
- Light Stabilizer – UV absorbers
  - Absorbs UV to prevent damage to polymer
- Thioesters
  - Secondary AO that decomposes hydroperoxides
- Hydroxylamines
  - Primary AO that captures carbon centered radicals
Functional Additives

- Slip
- Antiblock
- Lubricants
- PPA
- Visual enhancers
- Nucleator
- Clarifiers
- Antistats
- Fillers

Most functional additives have no influence on polymer stability

Certain additives may slightly improve polymer stability such as:
- Nucleators creating tortuous path
- Lubricants reducing shear during extrusion

Some additives can harm stability such as:
- Fillers and pigments that may absorb additives or increase shear
Additive Forms

- Neat Additives
  - Lowest cost, usually powdery, difficult to handle, need multiple feeders, need more analytical

- Preblends
  - Higher cost, usually dust free, easy to handle, reduces feeder needs, easier to analyze

- Masterbatch
  - Highest cost, easy to handle, takes up a lot of space, low activity, can cause gel issues
Examples
Experimental Considerations

All stabilizers should be optimized in any formulation:

- Reduce Metal Corrosion
- Optimize Stabilization
- Reduce Color
- Improve Melt Stability
- Improve Regrind Stability
- Optimize Oxidation Induction Time
- Application Testing
One of the main uses of antacids are to protect extruders and tooling from acidic residues

- Ziegler/Natta catalysts can contain high levels of acidic chloride residues

- Experimental:
  - Properly stabilized Z/N LLDPE
  - 250 ppm and 750 ppm of CaSt added as acid neutralizer

- Resin was tested against a polished brass sheet at 200 °C for 2 hours
  - Corrosion is noted by color change and pitting of the metal
Mold Corrosion

- 250 ppm of CaSt shown to be not enough acid neutralizer for LLDPE used. Apparent by corrosion to brass plate

- 750 ppm of CaSt was sufficient neutralizer for LLDPE used
Addition of CaSt improves overall melt stability of Z/N PP.
- All samples contain phenol and phosphite

- Addition of metal soap improved stability compared to no metal soap.

- 1:1 Ca:ZnSt showed a surprising synergy for stabilization compared to Ca or Zn.
All metals soaps improved color

Ziegler-Natta HDPE – Influence of metal soap type on stability

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Proper stabilization allows for maximized retention of MI.
- Use of antacid prevents color development when catalyst residue reacts phenolic AO.

**Ziegler-Natta LLDPE – Influence formulation on stability**

**LLDPE Extrusion Series YI**

- **no adds**
- **500 ppm 1076, 1000 ppm TNPP, 150 ppm ZnO**
- **500 ppm 1076**
- **500 ppm 1076, 150 ppm ZnO**
Conclusions
Conclusions

- Stabilizers are necessary for polyolefins to function properly.
- Stabilizers must be optimized to provide maximum benefit while minimizing cost.
- Most PE and PP are stabilized with a combination of: antacid, phosphite, and phenolic antioxidants.
- Higher levels of stabilizer allow resin to be more readily recyclable.