Polymer Bound Stabilizers For Polyurethanes

Milliguard™ AOX and UVX Stabilizers

6 November 2012
Milliken & Company

• Since 1865, Milliken has sought to
  ▪ Provide products that exceed customers’ expectations in quality and value
  ▪ Manufacture and conduct business with responsibility and absolute integrity

• Milliken has evolved into a diversified innovator and manufacturer

• Our focus remains on basic principles of:
  ▪ Innovation
  ▪ Excellence
  ▪ Integrity
Milliken’s Chemical Division
Core Technology Areas:

- Performance Colorants
- Polymer Additives
- Antimicrobials
- Industrial Chemicals
- Specialty Applications
Performance Colorants

Polymeric Colorants for thermoset resins

Reactint Colorants are a unique technology developed by Milliken Chemical for coloring polyurethane and other thermoset resins.
Modify the behavior and/or functionality of actives to allow use of materials that otherwise could not be used

- Improve solubility of actives in base materials
- Improve compatibility of actives in base systems
- Reduce or eliminate migration or mobility of actives
- Add slow release effects to actives
- Reduce VOC footprint of organic materials
- Improve safety profile of active ingredients
- Improved durability
- Improved performance
We’re There to Help

• With application and development centers around the world, we have the ability to provide technical assistance long after the sale:

Wherever you are in the world, we are there to help.
Sources of Yellowing/Degradation

- UV Exposure
- NOx Fumes
- Thermal Degradation

Yellow
Thermally Induced Discoloration in Slabstock Foam Manufacturing:

Yellow

Thermal Degradation
How the Degradation Process Begins

RH

Heat/Light

O₂

ROO*

2 RH

ROO*

ROO*

ROOH

*OH

RH
**Methods of Stabilization**

- **RH**
- **Heat/Light**
- **O₂**
- **ROO⁺**
- **ROOH**
- **ROO⁻**
- ***OH**
- **ROH, H₂O**
- **2 RH**
- **Hindered Phenols/Amines**

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Methods of Stabilization

Heat/Light

RH

O₂

ROO*

R*

ROOH

Phosphites

ROH, H₂O

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Methods of Stabilization

Heat/Light

Carbon Centered Radical Scavenger

RH

O₂

ROO* → R* → ROO* → RH

ROOH

2 RH

RO* *OH
Polymeric lactone-based carbon-centered radical scavenger

This chemistry is our core competence!

Benefits inherent to the polymer bound nature of Milliguard AOX:

• Reactive primary hydroxyl allowing the additive to be chemically bound into the polyurethane matrix—preventing migration and surface bloom

• Liquid form allowing ease of handling and metering

• Compatible with most all polyurethane slabstock formulations
# Toxicity of Lactone Based Antioxidants

<table>
<thead>
<tr>
<th></th>
<th>First Generation Lactone</th>
<th>Milliguard™ AOX Polymeric Lactone AO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular Weight</strong></td>
<td>350</td>
<td>810</td>
</tr>
<tr>
<td><strong>Material Form</strong></td>
<td>Solid</td>
<td>Liquid</td>
</tr>
<tr>
<td><strong>Biodegradability</strong></td>
<td>Persistent</td>
<td>Persistent</td>
</tr>
<tr>
<td><strong>Bioaccumulation Factor</strong></td>
<td>60,000 (Bioaccumulative)</td>
<td>3.2</td>
</tr>
<tr>
<td><strong>Fish Toxicity</strong></td>
<td>Chronically Toxic</td>
<td>Non-Toxic</td>
</tr>
</tbody>
</table>
Impact of Milliguard AOX-1 on Auto Oxidation Temperature of Minimally Stabilized Polyol (100 ppm Hindered Phenol)

Auto Oxidation Temperature by DSC

Milliguard AOX-1

Temp. (°C)

110 120 130 140 150 160 170 180 190 200 210 220 230 240

Control 0,2 PHP 0,6 PHP 1 2

145 189 214 224 227
Microwave Scorch Testing of Foams Containing Milliguard™ AOX-1
- Microwave Process begins

- Foam is placed in microwave chamber @ same location.
- 400 mls of room temp water is used as reference

- Process is complete when final water temp is reached

- Uninterrupted Power Supply
• Foam is made and prepped

• Water (@ room temp) stored in large container for uniformity

• Water (400 mls) is used as reference
• Microwave is prepped by heating water prior to use of foam
• Temperature probe is fixed in place
• Internal foam temperature is monitored via digital thermometer

• Foam is cut @ desired internal temperature
• Foam is read on Colorimeter for Yellowness Index and Delta E CMC
Polyol Heat Aging Test 24 Hrs @ 160° C
Bayer’s Arcol F3040

Control (No Heat)  Base Polyol  Plus 12 PHP TDCP
Foams Made With 10 PHP TDCP Flame Retardant
Tris(1,3-dichloro-2-propyl) phosphate

Control

0.5 PHP Milliguard AOX-1
Microwave Scorch Test with TDCP Flame Retardant

Impact On Yellowness Index

40° C increase in 350 grams of H₂O temperature in 5 minutes
Microwave Testing

1.0 PHP For All Stabilizers With 18 PHP TDCP

Control

Leading Competitive Product

AOX-1

AOX-150
Microwave Testing of Scorch Reduction

Voranol 3136 - Addition of Milliguard AOX products reduce discoloration
Other Sources of Yellowing

- UV Exposure
- NOx
- Fumes
Yellowing From NO\textsubscript{x} Exposure

Burnt Gas Testing
NOx (Burnt Gas) Exposure Testing

AATCC Method 23-1999

Temperature Maintained At 60° C

Samples Rotate In Chamber

Burner
Commercial Production

- 18 parts of TDCP (FR-2) with 1 part of AOX-1 resulted in less scorch than currently seen with equal loadings of a low scorch brominated flame retardant (Firemaster 550).

- In similar formulations 3 parts of TDCP would provide unacceptable discoloration.

- Additives in many flame retardant blends may help to reduce scorch but appear to adversely affect gas fade performance.
• Non-reactive stabilizers can migrate out of coatings and into thermoplastic parts leaving the coating unprotected or “bloom” to the surface on parts not coated

• AOX-1 is reactive and non-migrating

Adding functionality to eliminate migration and VOCs

**Extraction results in polyurethane foam**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Loading</th>
<th>Extraction of Additive (MeOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Generation Lactone AO</td>
<td>1 php</td>
<td>&gt; 95%</td>
</tr>
<tr>
<td>Milliguard AOX-1</td>
<td>1 php</td>
<td>0</td>
</tr>
</tbody>
</table>

* 2 grams 1.5 pcf foam in 75 ml MeOH at RT for 1 hr; GC analysis
Primary Benefits:

- **Reduces Thermally Induced Degradation:** Significantly reduces polymer damage due to oxidation caused by high temperature exposure.

- **Synergistic Effect With Standard Antioxidants:** Effective in stabilizing carbon-centered radicals at the beginning of the degradation process unlike normal hindered phenols and hindered.

- **Effective At Low Levels:** Recommended use levels of 0.05 to 2.0 php.

- **Reactive Primary Hydroxyl:** Facilitates the covalent bonding in reactive systems to eliminate migration and surface bloom.

- **Liquid:** Eliminates the need to handle powders.

- **Excellent Compatibility:** Designed to be compatible with a variety of resin systems resulting in good miscibility with most all polyurethane chemicals.

- **Reduced Toxicity:** Proper polymer selection dramatically reduces toxicity and bioaccumulation.
Sources of Yellowing/Degradation

UV Exposure

Yellow
Types of Yellowing--Light

Light fade (LF)

0 1 2 3 4 5 6 7

Testing Effect of UV Light

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Milliguard® UVX-2 Polymeric Benzotriazole Based UV Absorber

(Polymer Chain)
AOX-1/UVX-2 Vs. Controls

Gas Fade

Control – 2 Hrs

AOX-1/UVX-2 – 2 Hrs

Light Fade

Control – 13 Hrs

AOX-1/UVX-2 – 13 Hrs
Often, additives that improve lightfastness increase gas fade yellowing…

<table>
<thead>
<tr>
<th>Additive</th>
<th>Loading (php)</th>
<th>LF (13h) (delta E)</th>
<th>Gas (2h) (delta E)</th>
<th>Gas (10h) (delta E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>N/A</td>
<td>34.6</td>
<td>34.2</td>
<td>56.2</td>
</tr>
<tr>
<td>Industry Standard UV Stabilizer Package</td>
<td>3.0</td>
<td>15.8</td>
<td>34.1</td>
<td>82.3</td>
</tr>
<tr>
<td>UVX2</td>
<td>3.8</td>
<td>7.2</td>
<td>3.6</td>
<td>10.4</td>
</tr>
</tbody>
</table>

Xenon lightfastness testing for 13 hours
NOX gas chamber for 2 and 10 hours
UVX2 added at same level based on molecular weight, not activity
UVX-2

- Universally compatible with PU components
- Essentially non-migrating
- Minimal extraction
- Improved lightfastness performance over industry standard in PU foam
- Significantly improved yellowing performance in gas fade testing in PU foam

Combination of AOX-1 and UVX-2 package demonstrates powerful antioxidant/UV stability package
Reactive, polymer-bound stabilizers provide improved solubility, compatibility, safety, overall performance and ease of use of various actives while reducing VOC’s and migration
Thank You!