Polymer Bound Stabilizers For Polyurethanes

Milliguard™ AOX and UVX Stabilizers

6 November 2012

Milliken™

Our Legacy of Innovation

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

Milliken's Chemical Division Core Technology Areas:

Performance Colorants

Polymer Additives

Antimicrobials

Industrial Chemicals

Specialty Applications

Performance Colorants

MILLIKEN

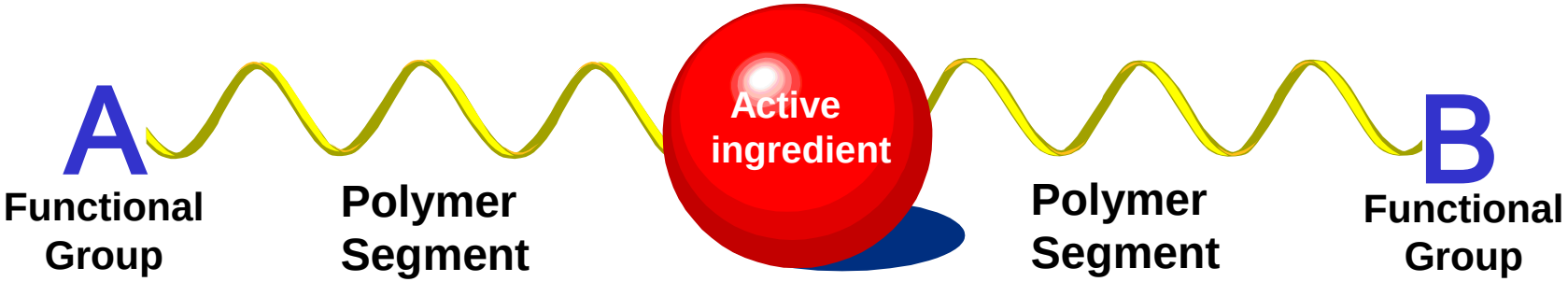
REACTINT®
COLORANTS
BY MILLIKEN

Polymeric Colorants for thermoset resins

Reactint Colorants are a unique technology developed by Milliken Chemical for coloring polyurethane and other thermoset resins.

Our core competency…

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.

Spartanburg, SC

Gent, Belgium

Pune, India

Shanghai, China

Singapore

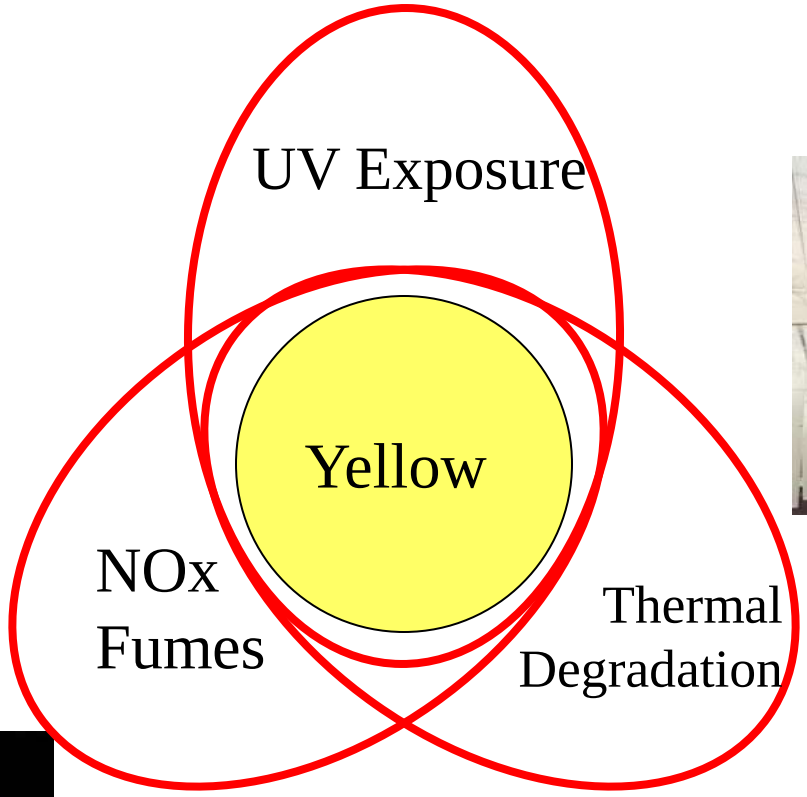
Sao Paulo, Brazil

HEADQUARTERS

APPLICATION & DEVELOPMENT CENTER

SALES OFFICE

Sources of Yellowing/Degradation

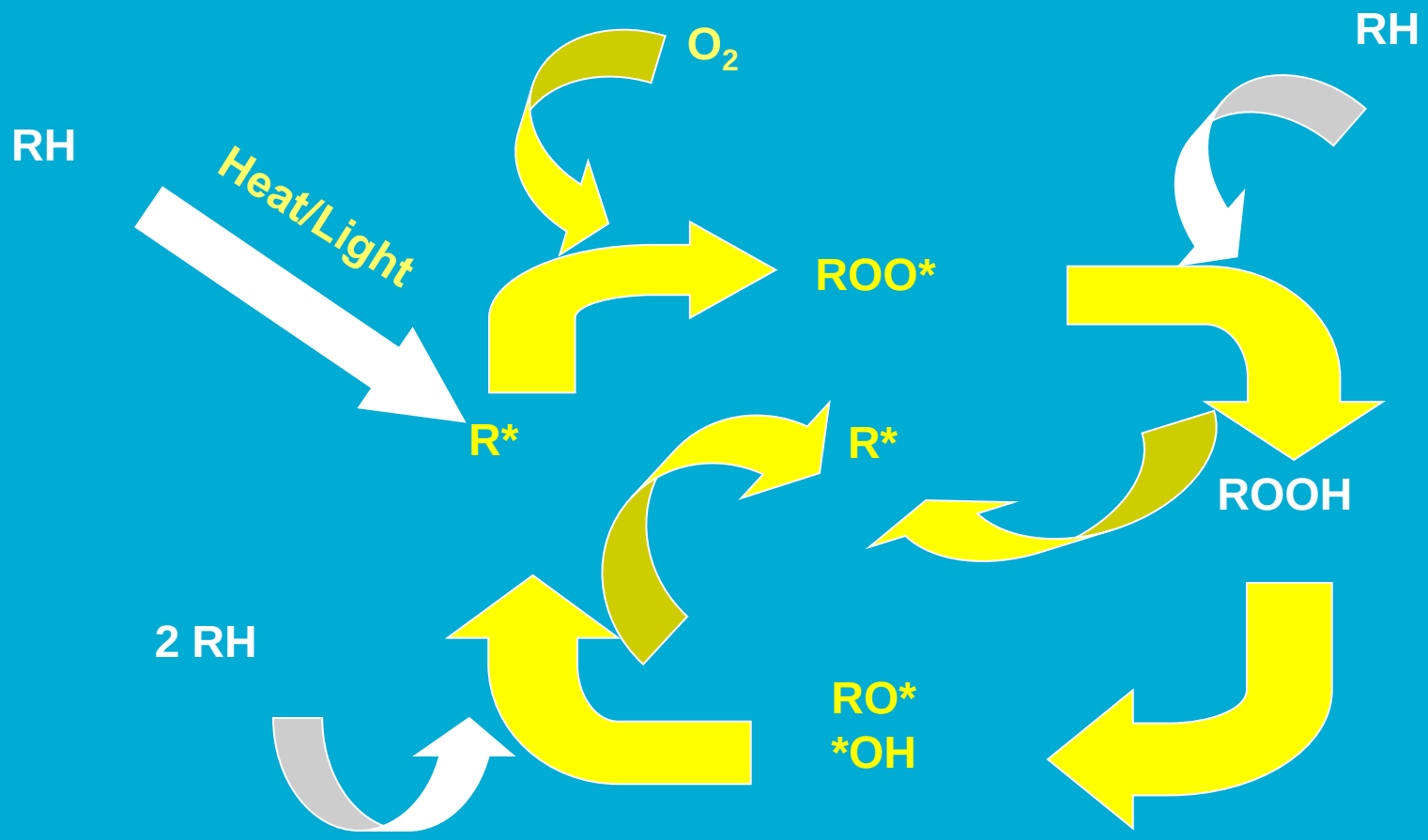


Thermally Induced Discoloration in Slabstock Foam Manufacturing:

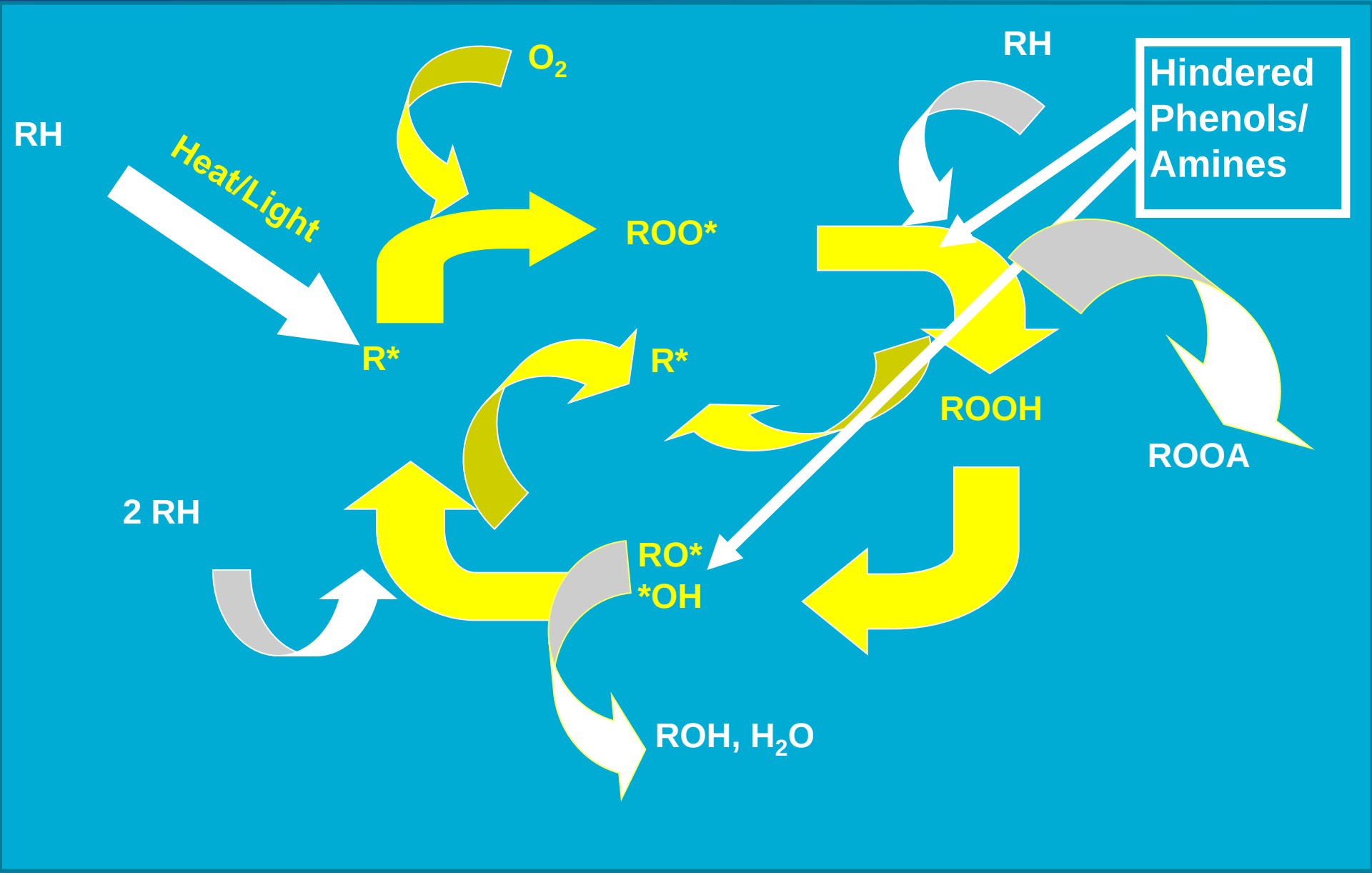
Yellow

Thermal Degradation

How the Degradation Process Begins



Methods of Stabilization



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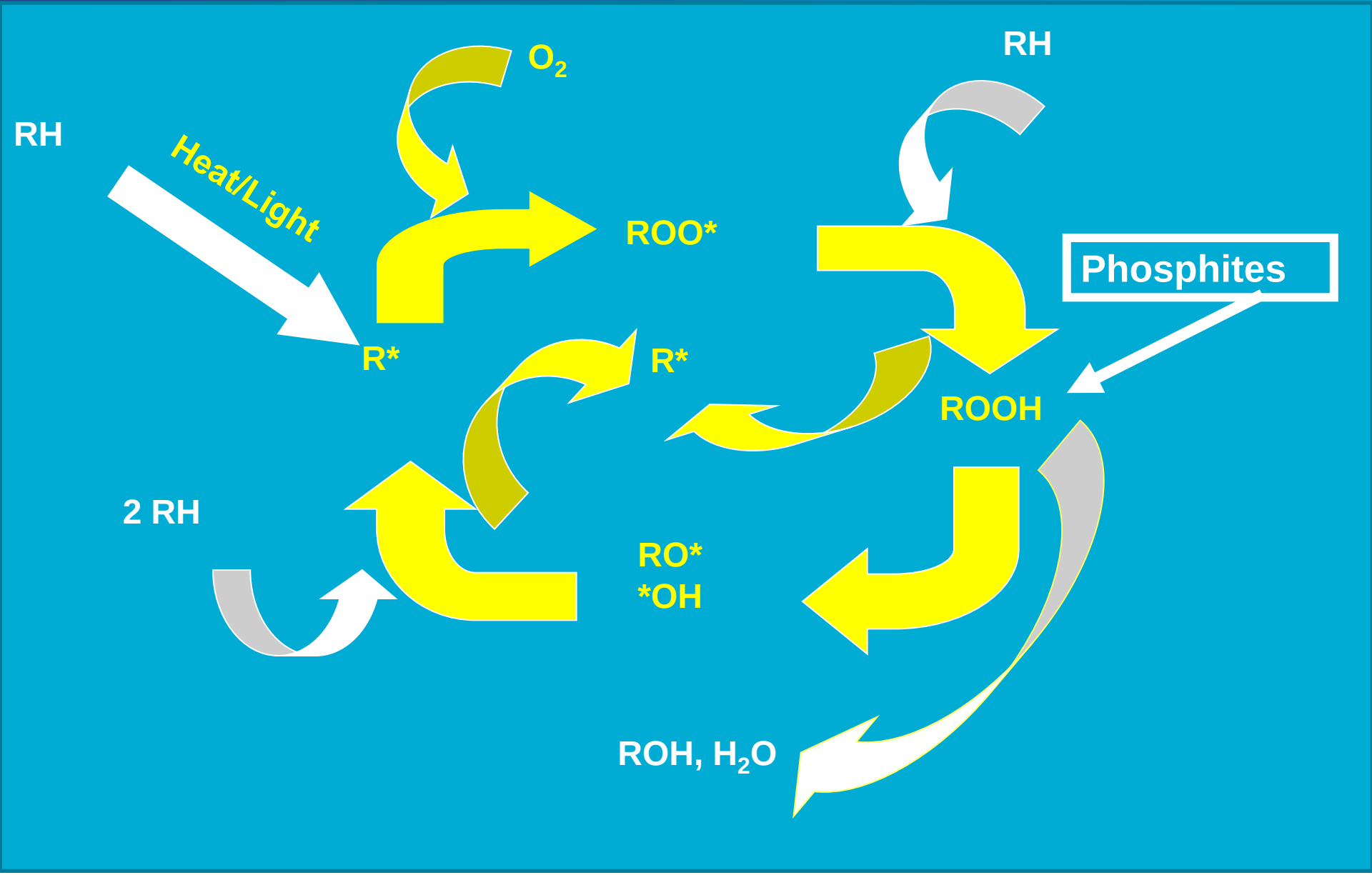

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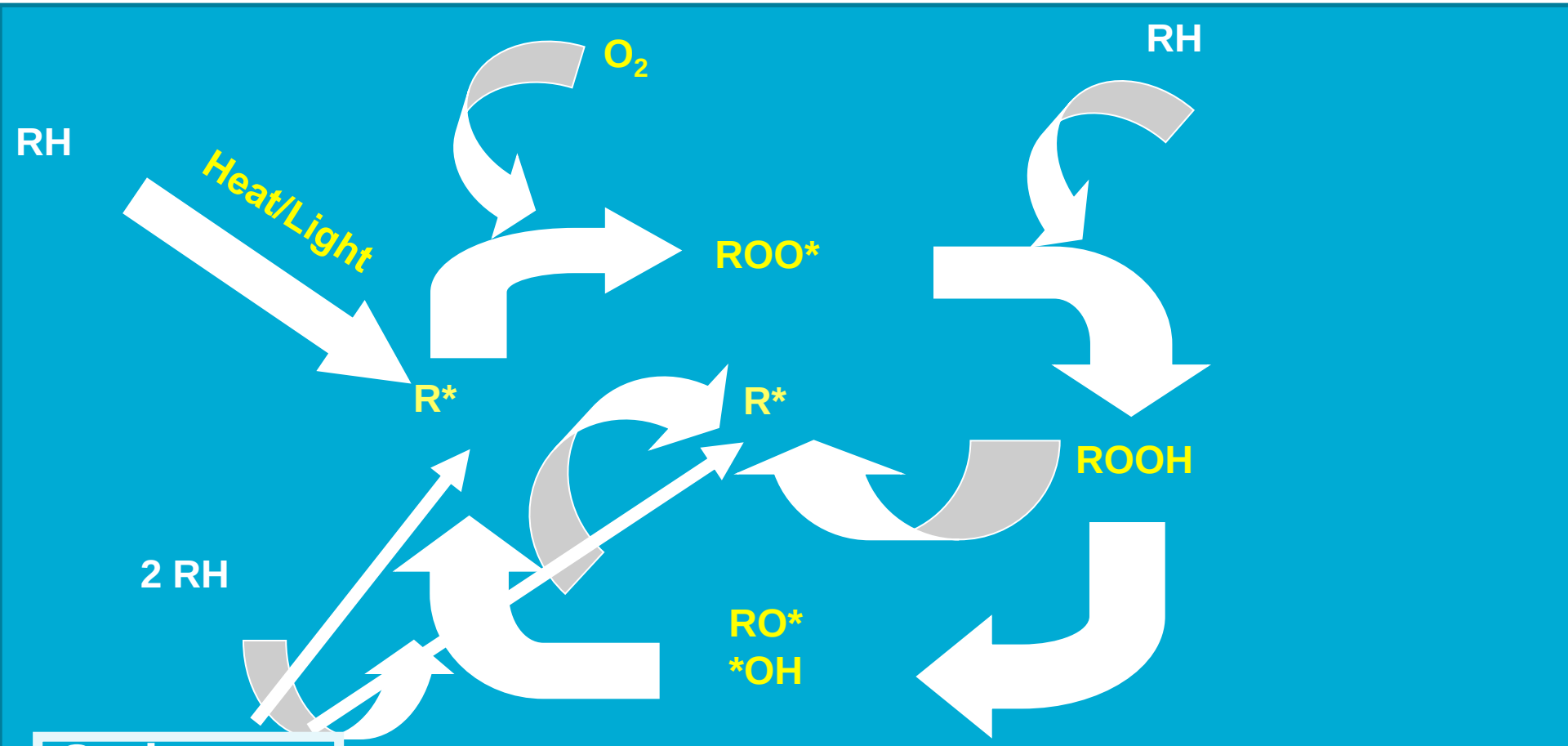
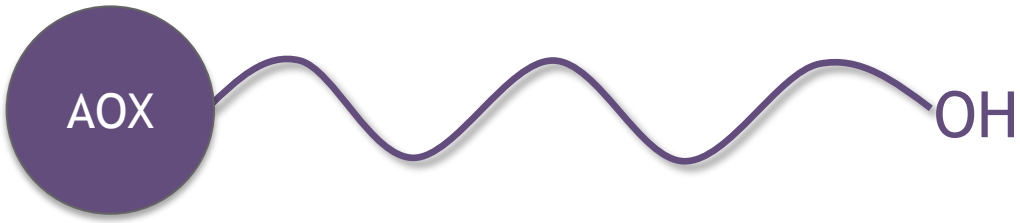


Carbon Centered Radical Scavenger

Milliguard AOX

Polymeric lactone-based carbon-centered radical scavenger

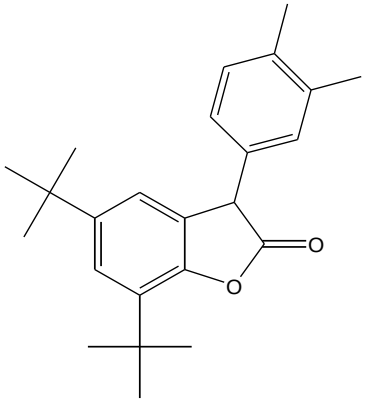


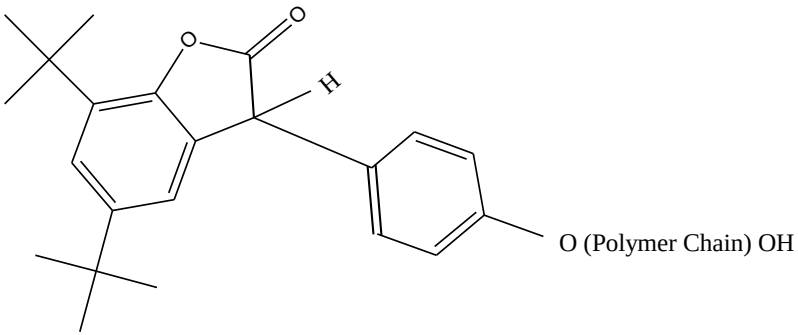
This chemistry is our core competence!

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

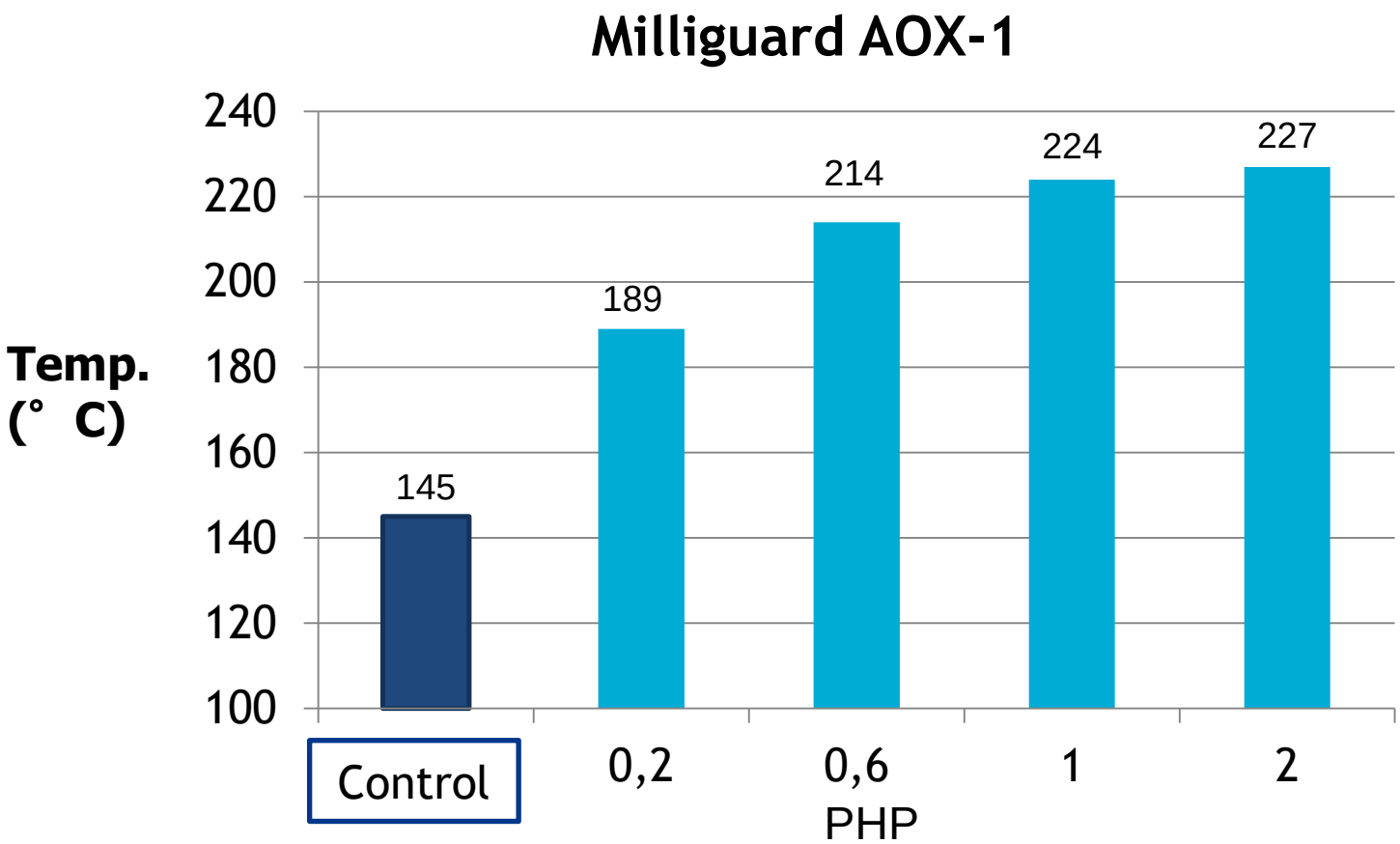




	First Generation Lactone	Milliguard™ AOX Polymeric Lactone AO
Molecular Weight	350	810
Material Form	Solid	Liquid
Biodegradability	Persistent	Persistent
Bioaccumulation Factor	60,000 (Bioaccumulative)	3.2
Fish Toxicity	Chronically Toxic	Non-Toxic

Impact of Milliguard AOX-1 on Auto Oxidation Temperature of Minimally Stabilized Polyol (100 ppm Hindered Phenol)

Auto Oxidation Temperature by DSC



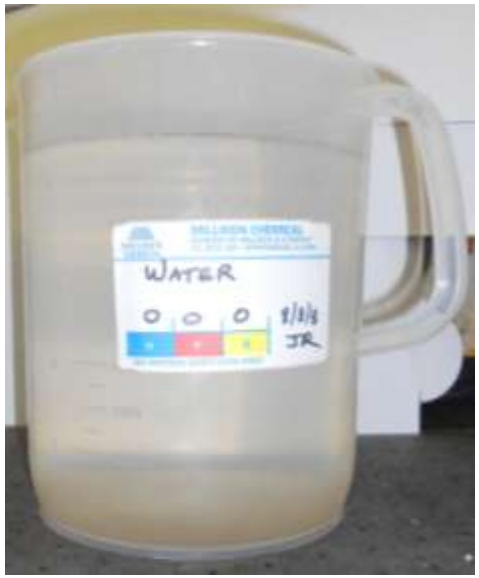
Microwave Scorch Testing of Foams Containing Milliguard™ AOX-1

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

- Uninterrupted Power Supply

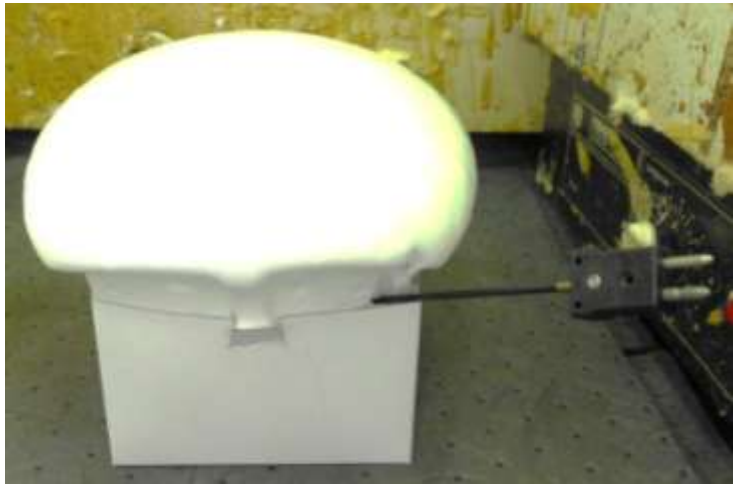
- Microwave Process begins

- Process is complete when final water temp is reached



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

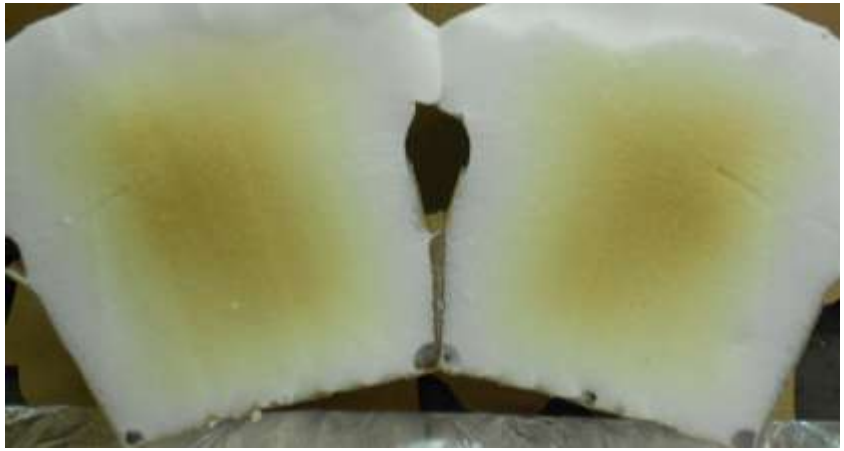
- Water (400 mls) is used as reference
- Microwave is prepped by heating water prior to use of foam
- Temperature probe is fixed in place



- Foam is made and prepped

- 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



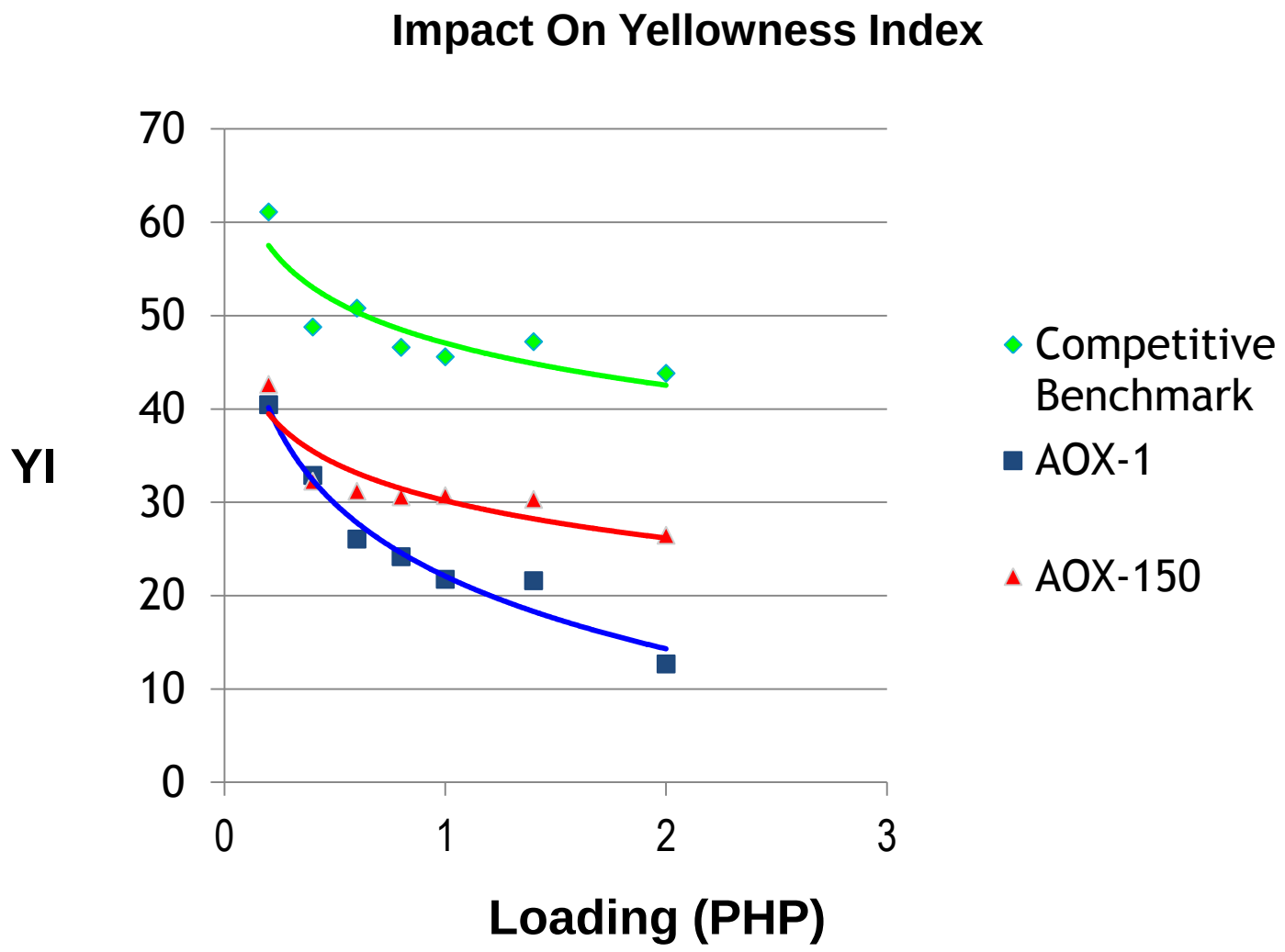
FR Affects Heat Stability of Polyol

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

Microwave Scorch Test with TDCP Flame Retardant



40º C increase in 350 grams of H_2O temperature in 5 minutes

Microwave Testing

1.0 PHP For All Stabilizers With 18 PHP TDCP

Control

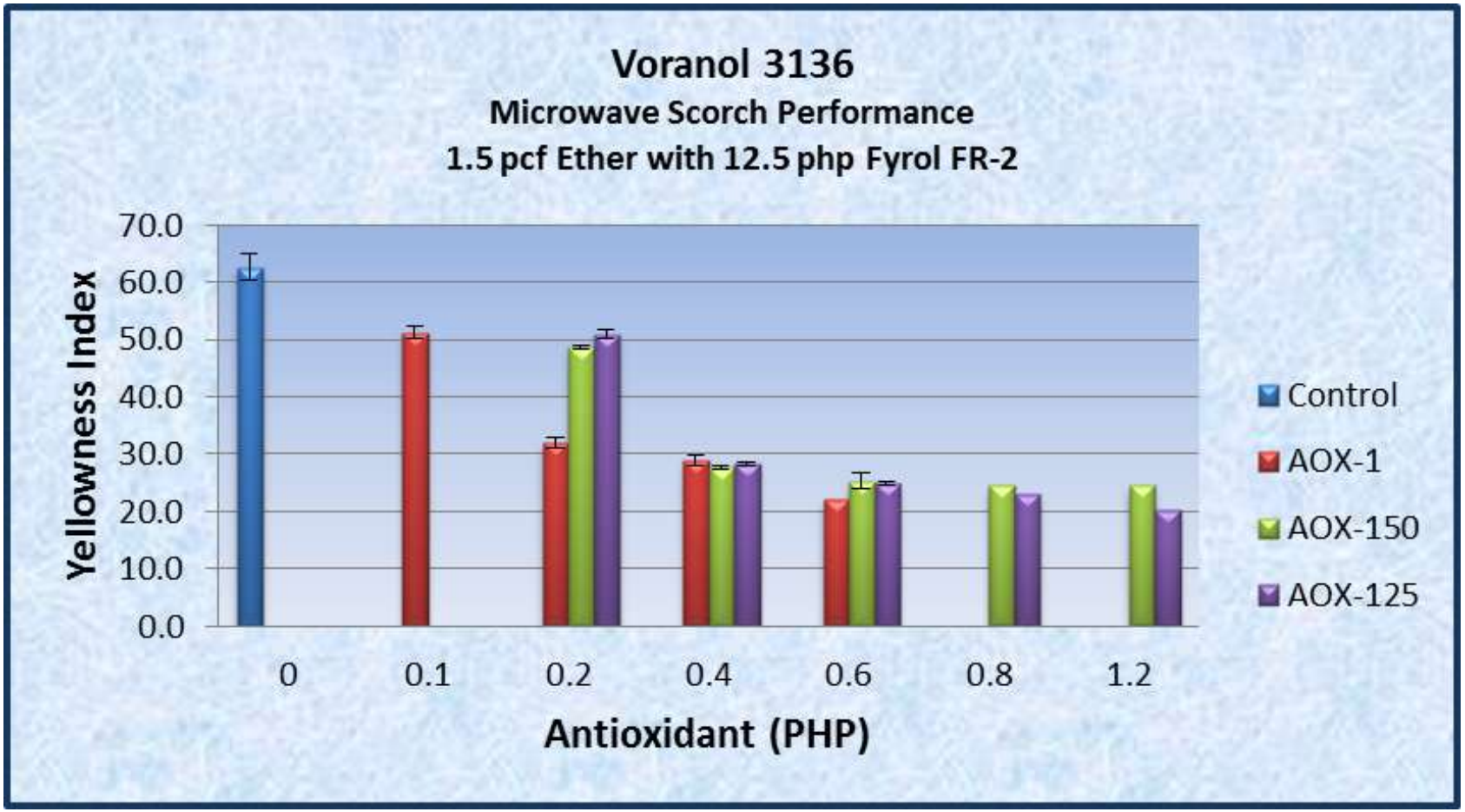
Leading Competitive Product

AOX-1

AOX-150

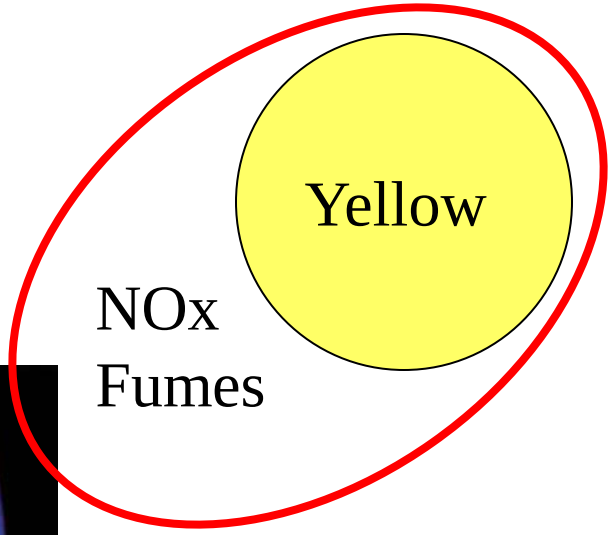
Microwave Testing of Scorch Reduction

Voranol 3136 – Addition of Milliguard AOX products reduce discoloration



Other Sources of Yellowing

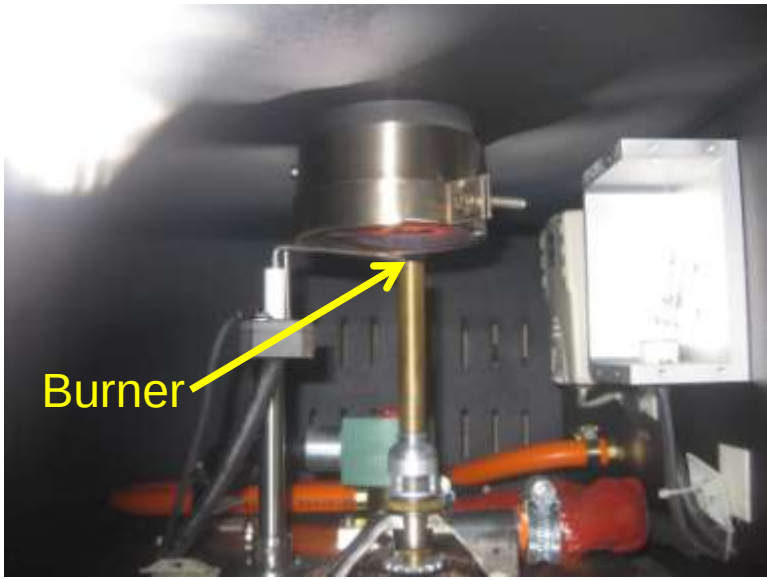
UV Exposure



Yellowing From NO_X Exposure

Burnt Gas Testing

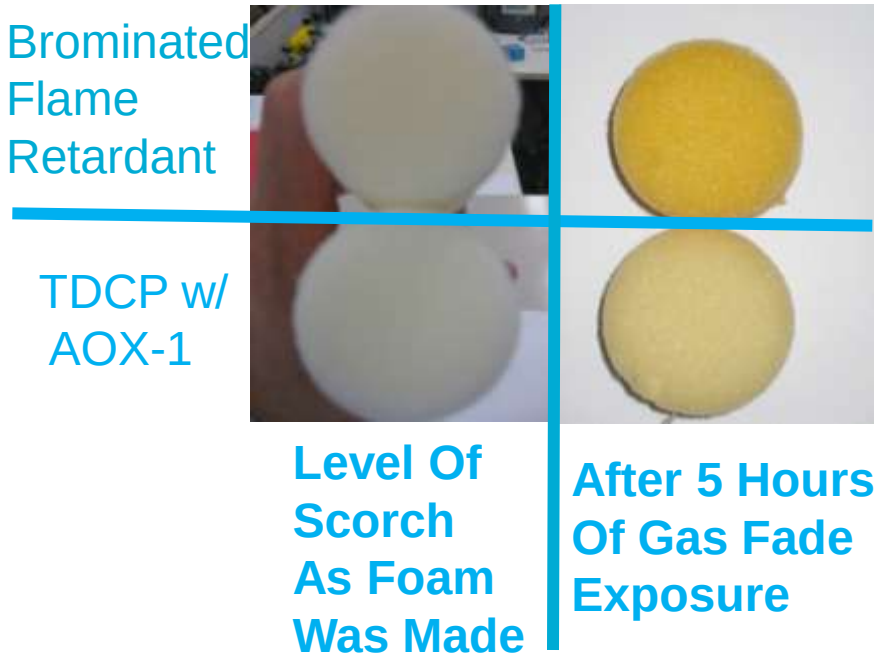
NOx (Burnt Gas) Exposure Testing



AATCC Method 23-1999

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



Polymeric/Reactive Stabilizers

- ***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***

Blooming Of Stabilizing Additives
In TPU

Joint paper presented in the <u>Journal of Coatings Technology Research</u> in July of 2004 by <u>DuPont</u> and <u>Ciba</u> entitled "Migration of Reactable UVAs and HALS in Automotive Plastic Coatings."

Extraction results in polyurethane foam

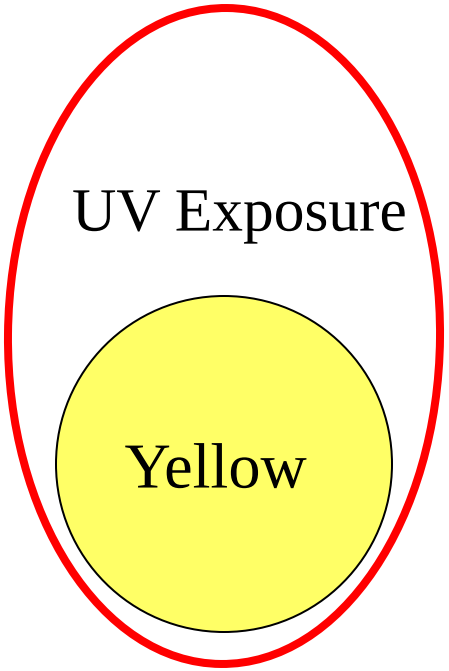
Additive	Loading	Extraction of Additive (MeOH)
First Generation Lactone AO	1 php	> 95%
Milliguard AOX-1	1 php	0

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

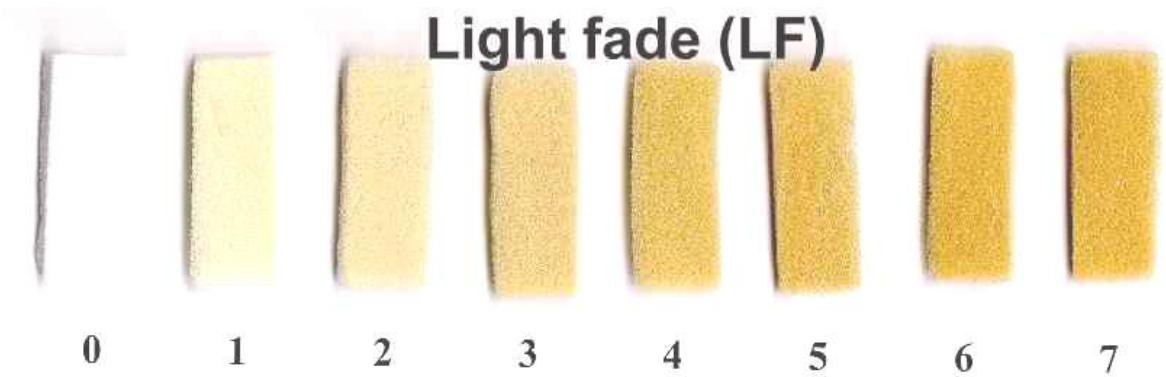
Primary Benefits:

- **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

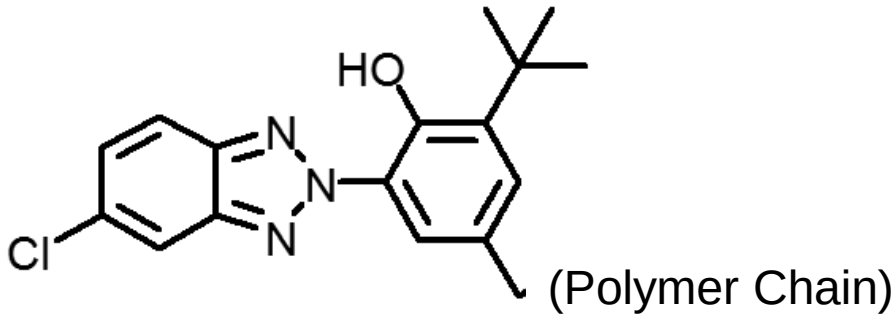


Types of Yellowing--Light



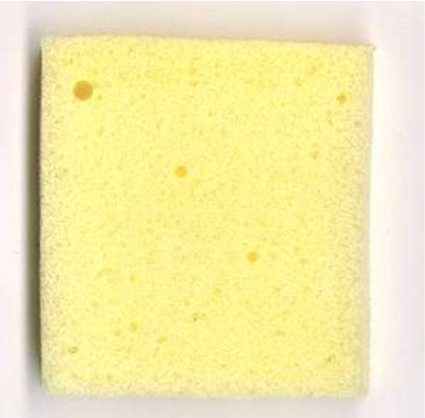
Testing Effect of UV Light

Milliguard® UVX-2 Polymeric Benzotriazole Based UV Absorber



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

Protection of PU Foam from Yellowing

Often, additives that improve lightfastness increase gas fade yellowing…

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

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

UVX2 Summary

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

In Summary…

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!

Milliken™