Stabilization Systems for Improved Discoloration Resistance for Color Critical Applications

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Presentation Outline

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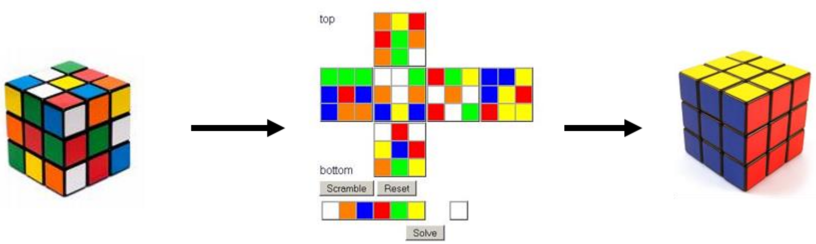
- **Introduction**
- **What is this Discoloration ?** (Educate)
  - High surface area / thin section products tend to discolor
  - This discoloration can be perceived as an inferior product
- **Technical Challenge** (Define Problem Statement)
  - Traditional Phenol/Phosphite Systems vs. New Developments
- **Comparative Data Sets** (Develop a Pragmatic Solution)
  - zn-LLDPE Solution Phase E/O Copolymer Cast Film
  - m-LLDPE Gas Phase E/H Copolymer Blown Film
  - zn-PP Slurry Phase Random Copolymer Moldings
- **Conclusions**
  - Recommendations



BASF Plastic Additives Product Portfolio
We Create Chemistry for Plastics

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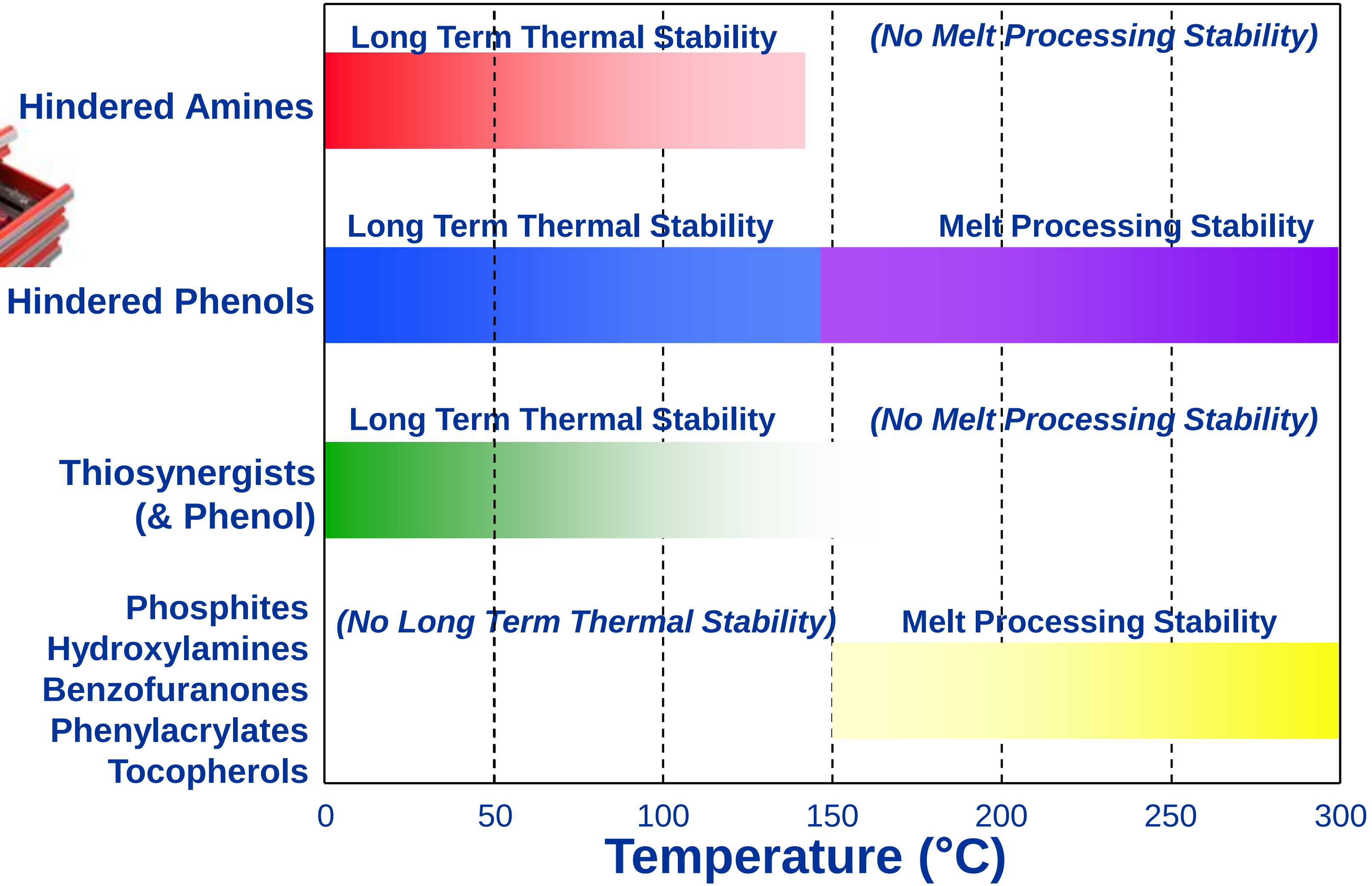
Mission: We are committed to delivering sustainable value to our customers throughout the Plastics Industry value chain and supporting them in shaping our future

- **Maintaining Strength**
  - **Ensuring resistance to heat, shear, wear & tear**
    - Antioxidants, Processing stabilizers
- **Providing Protection**
  - **Helping to shield people and products from UV radiation, fire**
    - Light stabilizers, UV Absorbers, Halogen free flame retardants
- **Enhancing Performance**
  - **Adding functionality and efficiency to products and processes**
    - Antistatic agents, Antiscratch, Clarifiers/nucleators
- **Maintaining Visual Appeal**
  - **Differentiated / Alternative Stabilization Systems**
    - e.g., Phenol free stabilization systems

Effective Temperatures for Stabilizers
How do each of the components contribute ?



What is Polymer Discoloration ?

Why is it an important topic ?

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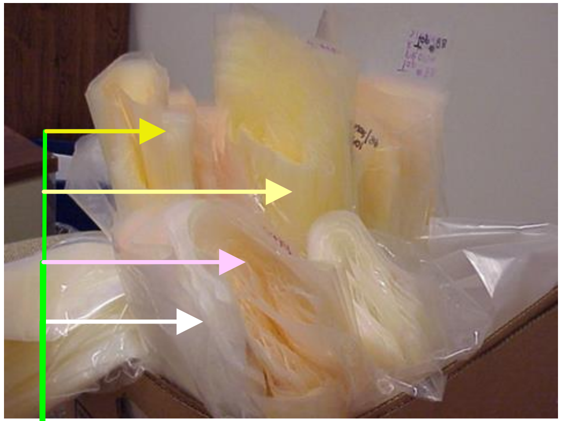
Perceptions

- Discoloration is directly related to visual appearance
- Accordingly, it is mostly related to perceptions
- For whatever reason, bright white is most appealing
- Anything other than bright white suggests problems
- Extrusion discoloration during suggests inadequate stabilization and/or formulation problems
- Post extrusion discoloration suggests poor quality
- Discoloration attributed to over-oxidation of a phenolic antioxidant and/or negative additive interactions



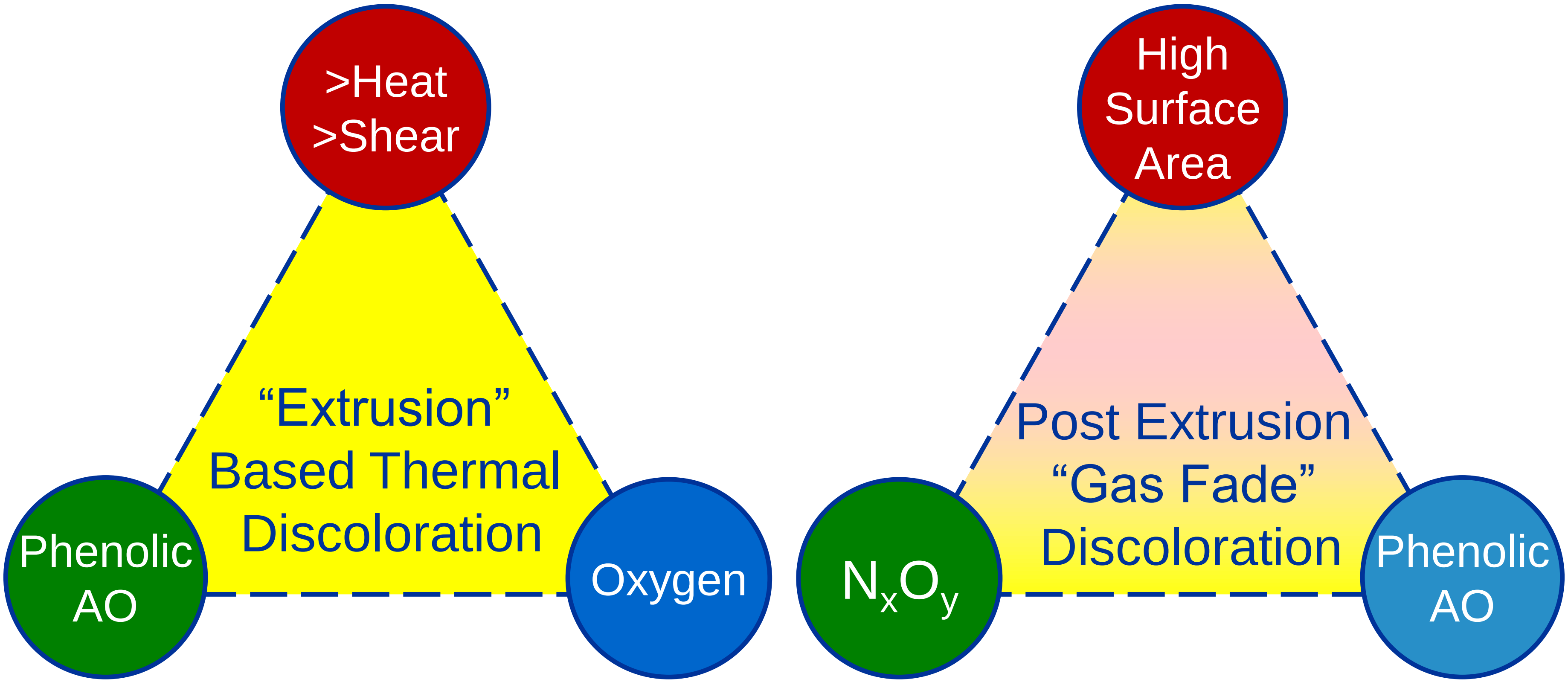
- Bright white
- Light yellow
- Bright yellow
- Xanthic
- Light pinkish
- Bright pinkish

Reality

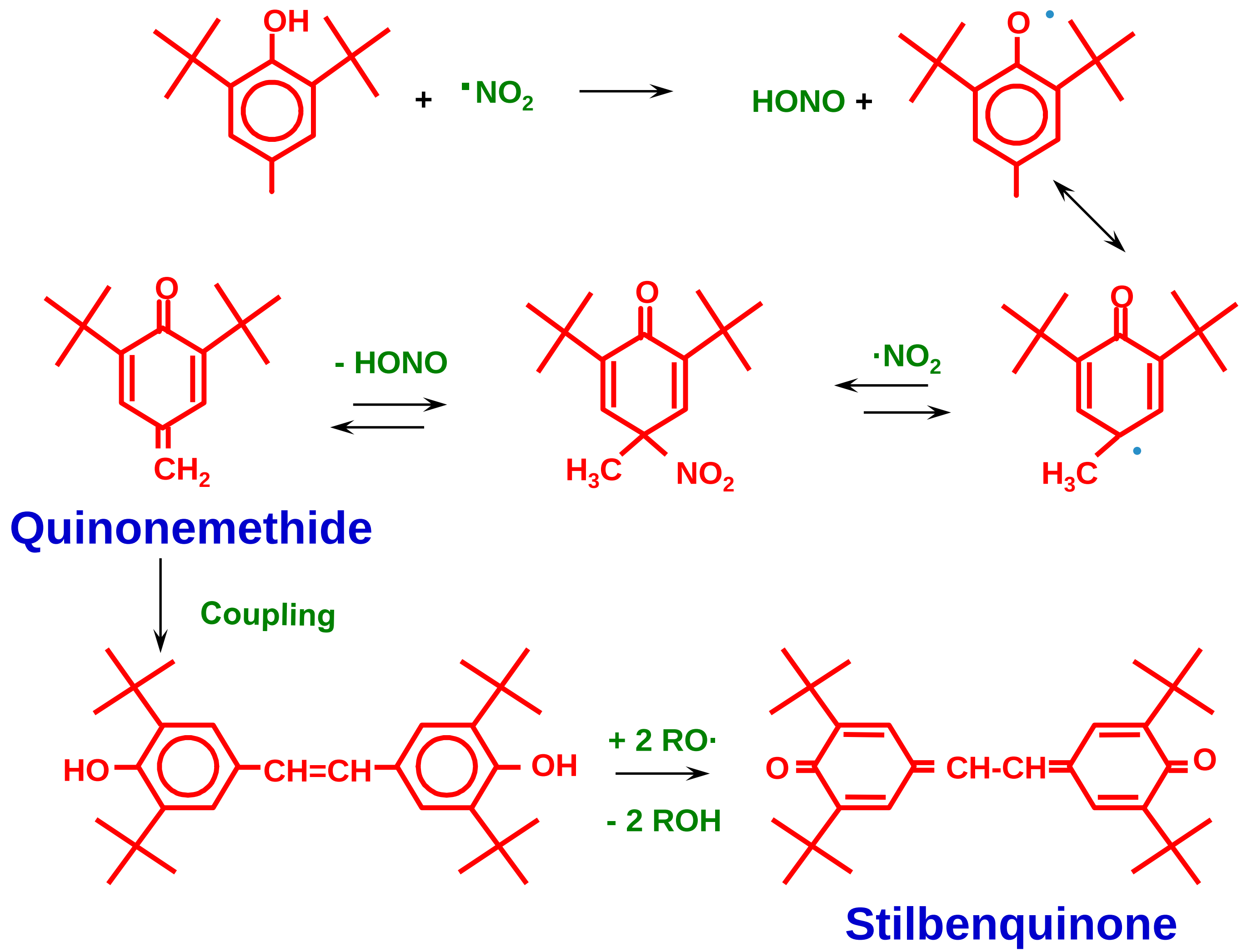
- In most cases, the polymer is fine, and is capable of fulfilling all the requirements in an end-use application; however…
- Perceptions can become reality… So issues with discoloration is a topic that must be addressed

What is Polymer Discoloration ?
Concept: "Triangle" of Discoloration

- Polymers stabilized with phenolic AO's can also be susceptible to discoloration if the stabilization system is "over-used" due to the reactivity of phenolic AO's with oxides of nitrogen (N_xO_y)

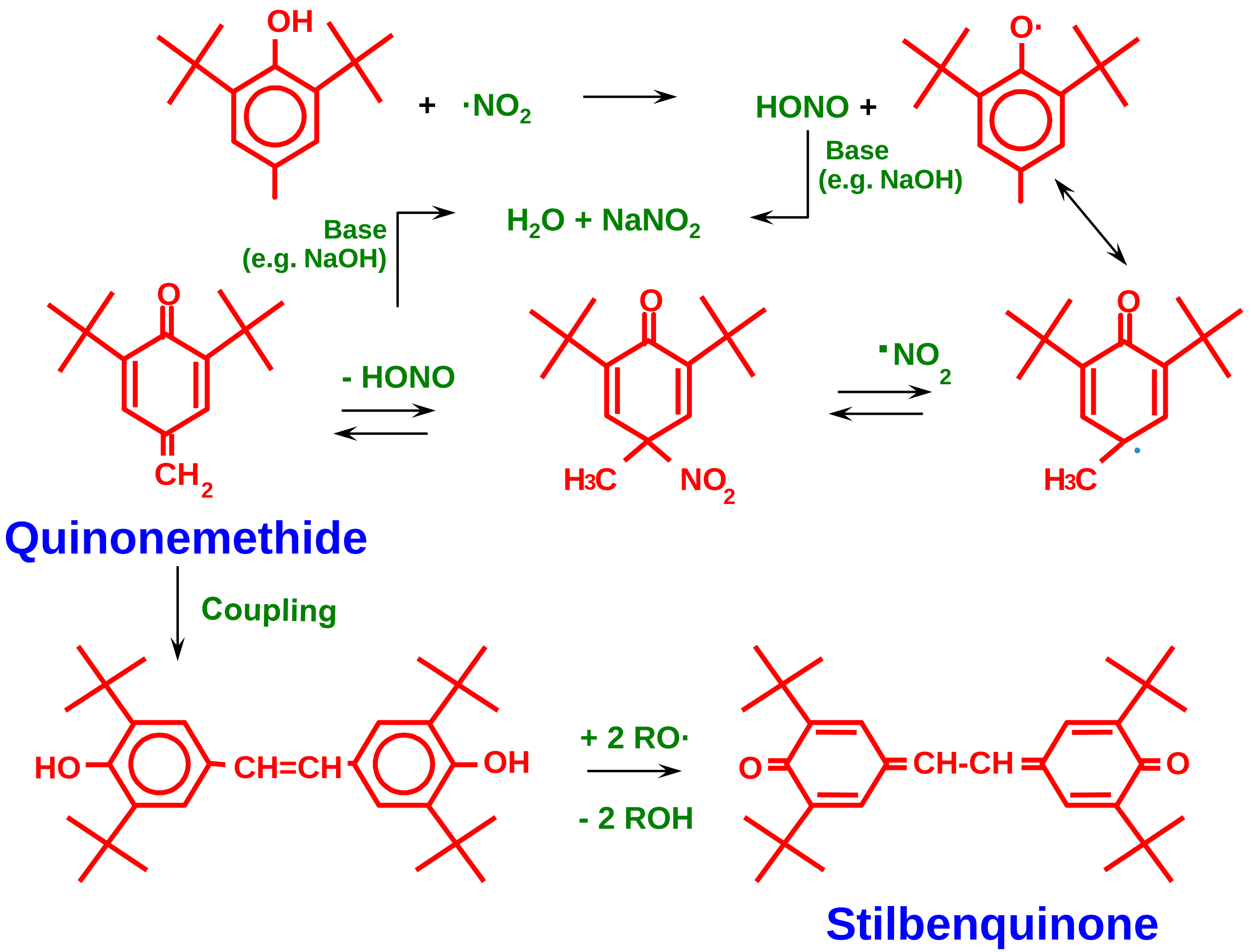


Gas Fade Discoloration Chemistry
Via Over-Oxidation of Phenolic AO

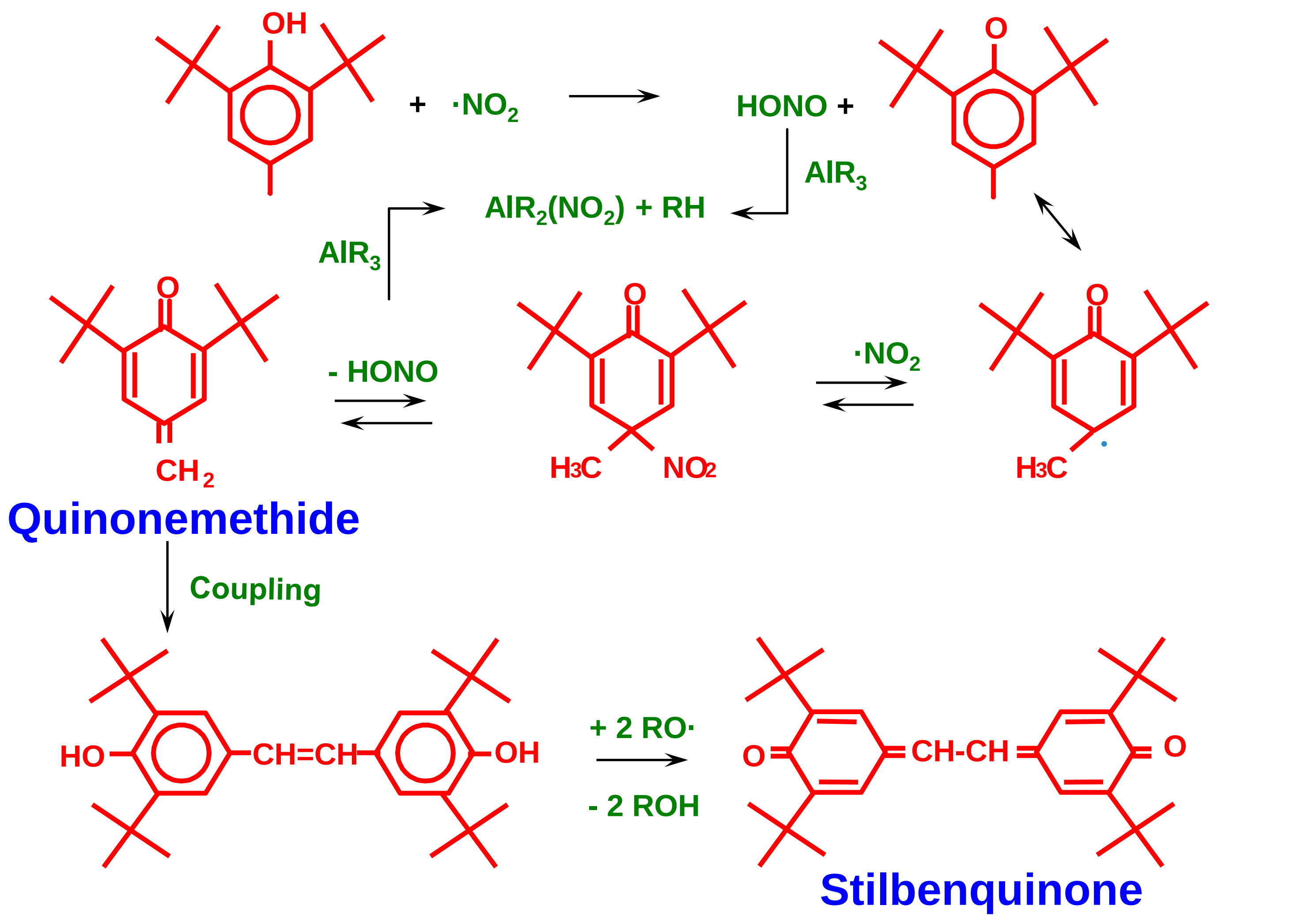


Gas Fade Discoloration Chemistry

Accelerated by Brønsted Alkalinity



Gas Fade Discoloration Chemistry
Accelerated by Lewis Acidity



Q&A Regarding of Discoloration

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- **Q. What Should I Do if the Polymer Turns Yellow, Pink, Orange… ?**
- **A. Step 1: Check the equipment for any obvious issues or breakdowns; take this out of the equation as soon as possible**
  - Look for long residence times in the extruder
  - Evaluate for hot spots, high shear / friction; dead zones
- **A. Step 2: Then start asking questions & taking notes on the situation**
  - Is this discoloration sporadic or has it been drifting upwards over time ?
  - Did you see it first ? or Did your customer ?
  - How many times has this discoloration happened before ?
  - Is it seasonal ? What time of the year is best & worst ?
  - Is the application based on a single resin, or a blend of resins ?
  - Has anything changed recently ? (new vendors, new products)
  - What do the pellet retains look like ? Do they match the QC numbers ?
  - Does the color go away when you expose it to sunlight ?

Ways to tackle Polymer Discoloration

Not a complete list, but let's get started...

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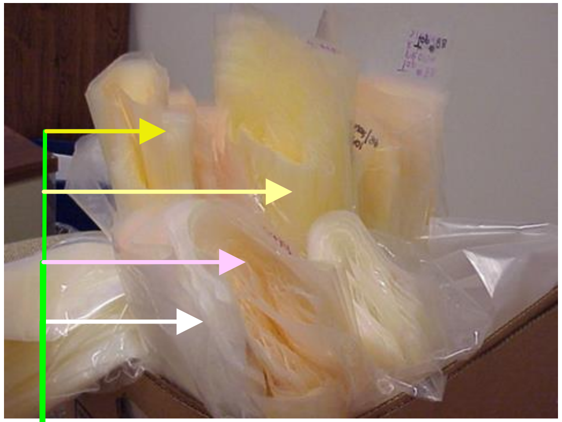
1. **Change the Phenol to Phosphite Ratio**
   - 1:1 > 1:2 > 1:4
2. **Change the Phenolic Antioxidant**
   - More color stable phenol
3. **Change the Phosphite Stabilizer**
   - Higher performance phosphites
4. **Use a Hyperactive Process Stabilizer**
   - High performance radical scavenger chemistry
5. **Change the Acid Neutralizer**
   - Somewhat surprising, but true
6. **Switch to a Phenol-free Stabilization System**



- Bright white
- Light yellow
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Note: Incremental steps lead to incremental improvements. Therefore, if a more robust improvement is necessary, then:

Q&A Overview of Discoloration

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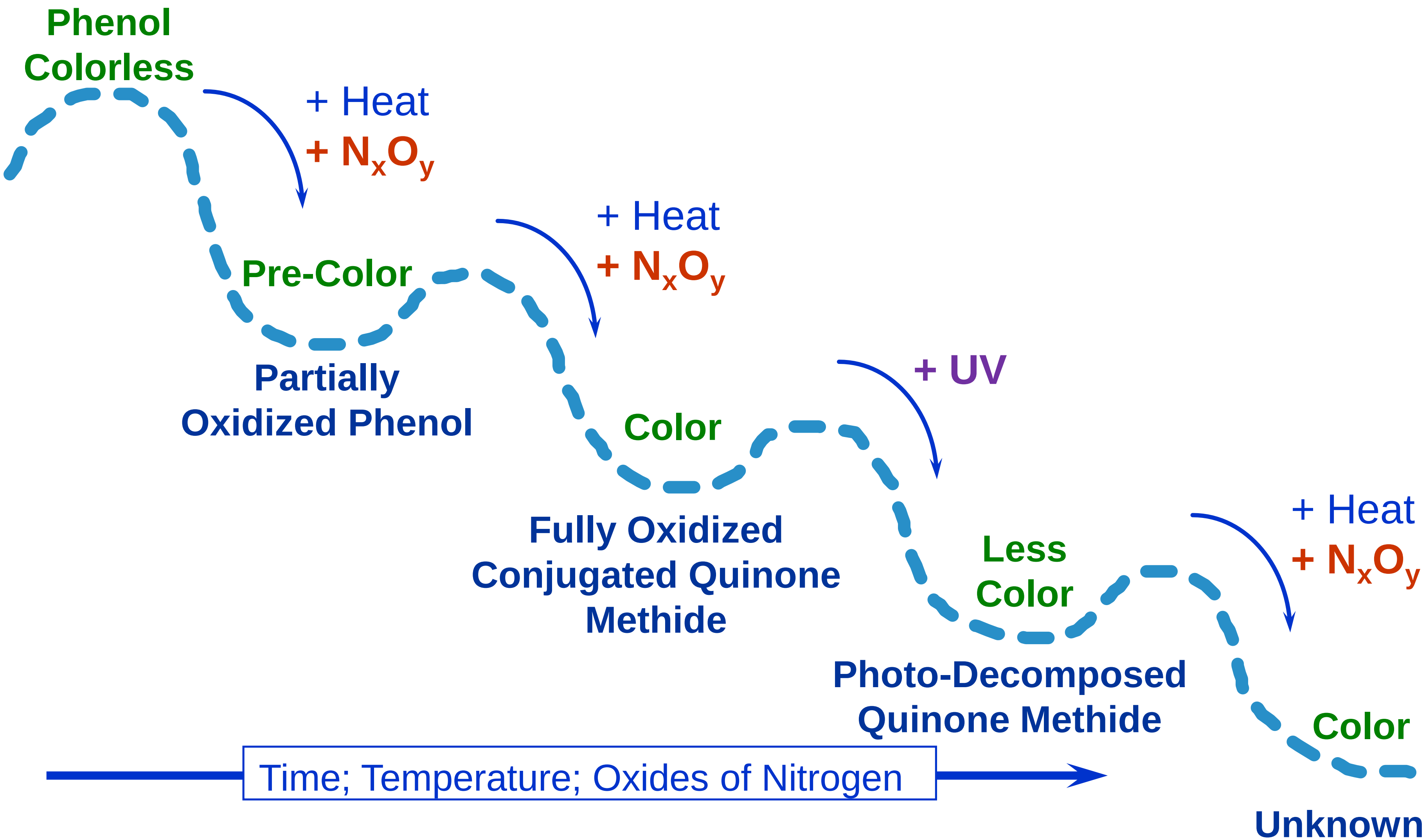
- **Q. How Should I Analyze Yellow Extract ?**

- **A. Analysis for Color Bodies is Sometimes Limited to the Number of Standards that are Available; Even BASF Does Not Have a Complete Collection.**

  - **Scan For Intact Additives and Color Bodies by TLC**
  - **Quantify Intact Additives by LC**
  - **Quantify Conversion of Phosphite to Phosphate by LC**
  - **Separate Fractions by Prep LC**
  - **Analyze Fractions by MS, GC/MS or LC/MS**

- **Keep Polymer Extract/Color Bodies Cool and in the Dark Most Color Bodies Are Not That Stable to Light or Heat**

Appearance / Disappearance of Color



Q&A Overview of Discoloration

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- **Q. What Should I do After the Analysis ?**
- **A. Determining the Structures of Color Bodies is a Challenging Endeavor, Even With Good Equipment**
  - **It May be True That the Discoloration of the Polymer is Due Primarily to the Over Oxidation of the Phenolic**
  - **However, the Fact that the Phenolic Turns Color is More of an Indication that Something is Out of Whack**
  - **In Reality, the Key Objective is to Determine the Root Cause of the Discoloration**
  - **Sometimes This is Not as Easy as it Sounds**

Purpose of this project
Challenge: Improved Discoloration Resistance

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Project Scope

- Alternative stabilization concept providing improved discoloration resistance
- Works in different types of polyolefins (both older & newer technologies)
- Focus on polyolefin grades going into high surface area thin section applications where the stabilizer system needs to be intrinsically non-discoloring post extrusion.
- 10 Projects Run: Three examples to be presented: m-LLDPE, zn-LLDPE, r-PP Copo.

Technical Objective

- Develop an effective, user friendly, stabilizer system capable of providing improved discoloration resistance for a wide variety of polyolefins, for color critical applications.

Stretch Objective

- New system to be comprised of components that are globally registered, foodlaw compliant, available as pre-packaged blends, and compatible in a various polyolefins.

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Solution Phase Cast Film Grade LLDPE

Experimental:

- **Polymer:** C_2/C_8 LLDPE Copolymer, Solution phase process, Nominal I_2 MI = 4 dg/min; Density = 0.92 g/cm^3
- **Stabilizers:** 450 ppm Phenolic (AO-2); 500-1000 ppm P-168 vs. Discoloration Resistant Stabilization System
- **Acid Scavenger:** None added.
- **Zero Pass Compounding:** Leistritz 27mm twin screw; 410^{o}F (210^{o}C); 32:1 L/D; Under Nitrogen
- **Multiple Pass Extrusion:** MPM 1" single screw; 500^{o}F (260^{o}C); 24:1 L/D; Under Air; Maddock mixing head
- **Melt Flow:** ASTM-1238; 190^{o}C; 2.16 kg; 21.6 kg; Tinius-Olsen extrusion plastometer
- **YI Color:** ASTM-1925; 125 mil Plaque; Large Area View; C Illuminant, 2^o Observer
- **Gas Fade Aging:** AATCC Test Method 23; Forced draft oven; 10 mil film; 60^{o}C; YI Color increase; Zero Pass
- **Low Temp Oven Aging:** ASTM D3045; Forced draft oven; 10 mil film; 60^{o}C; YI Color increase; Zero Pass
- **Oxidative Induction Time:** ASTM-3895; 10 mil film; Al Pans, Isothermal, 190^{o}C; $N_2 \rightarrow O_2$

Improved Processability Stabilizer Systems

Cast Film Grade LLDPE C_2/C_8 Copolymer

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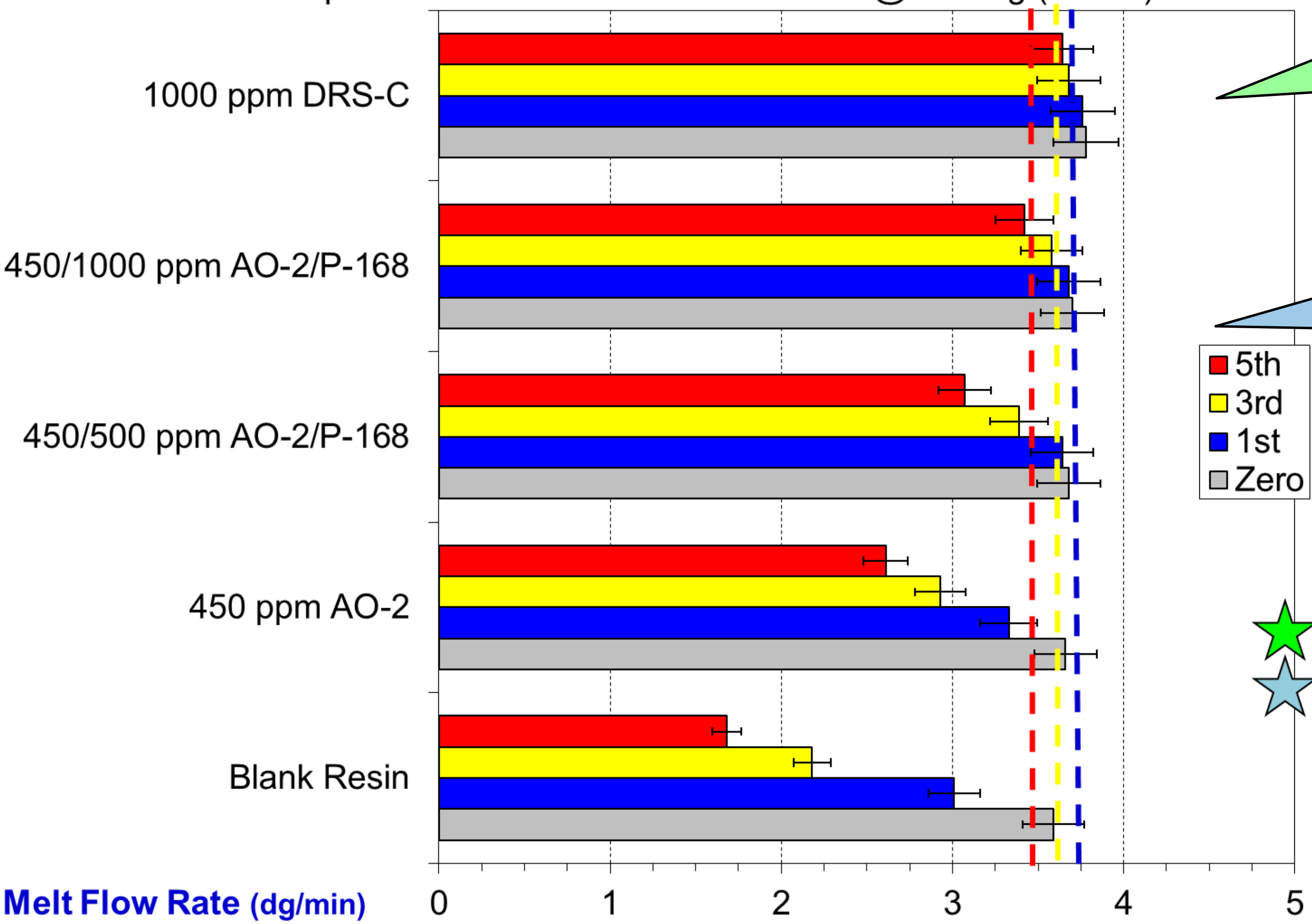
Discoloration Resistant Stabilization: Cast Film Grade m-LLDPE

Multipass Extrusion Melt Flow Rate Data @ 2.16 kg (190°C)

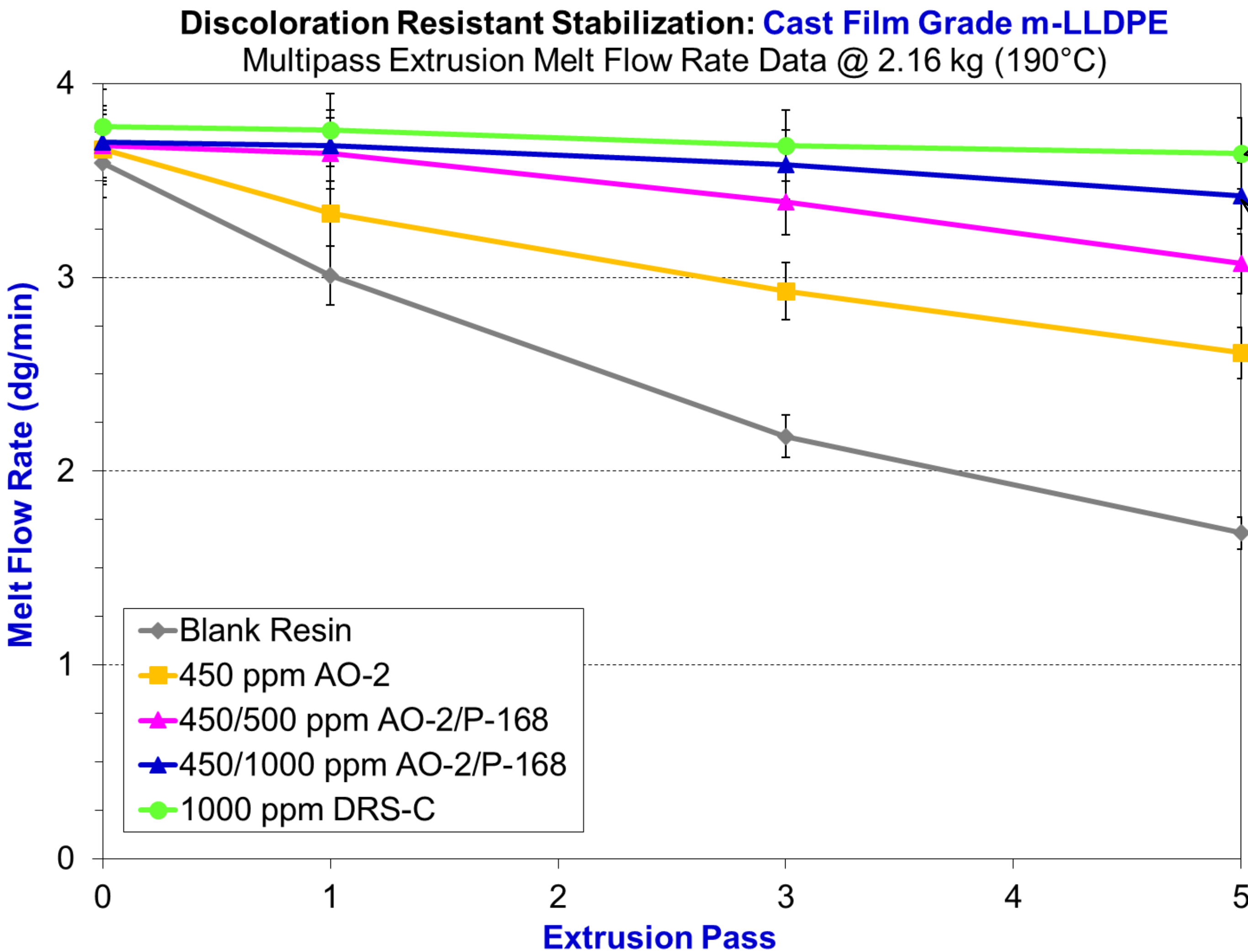


1000 ppm **"DRS"** provides equivalent performance to 1400 ppm of a traditional AO-1/P-168 Blend

1450 ppm of a traditional **AO-2/P-168** Blend is a representative industry benchmark for this grade

Improved Processability Stabilizer Systems

Cast Film Grade LLDPE C_2/C_8 Copolymer



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Cast Film Grade LLDPE C_2/C_8 Copolymer

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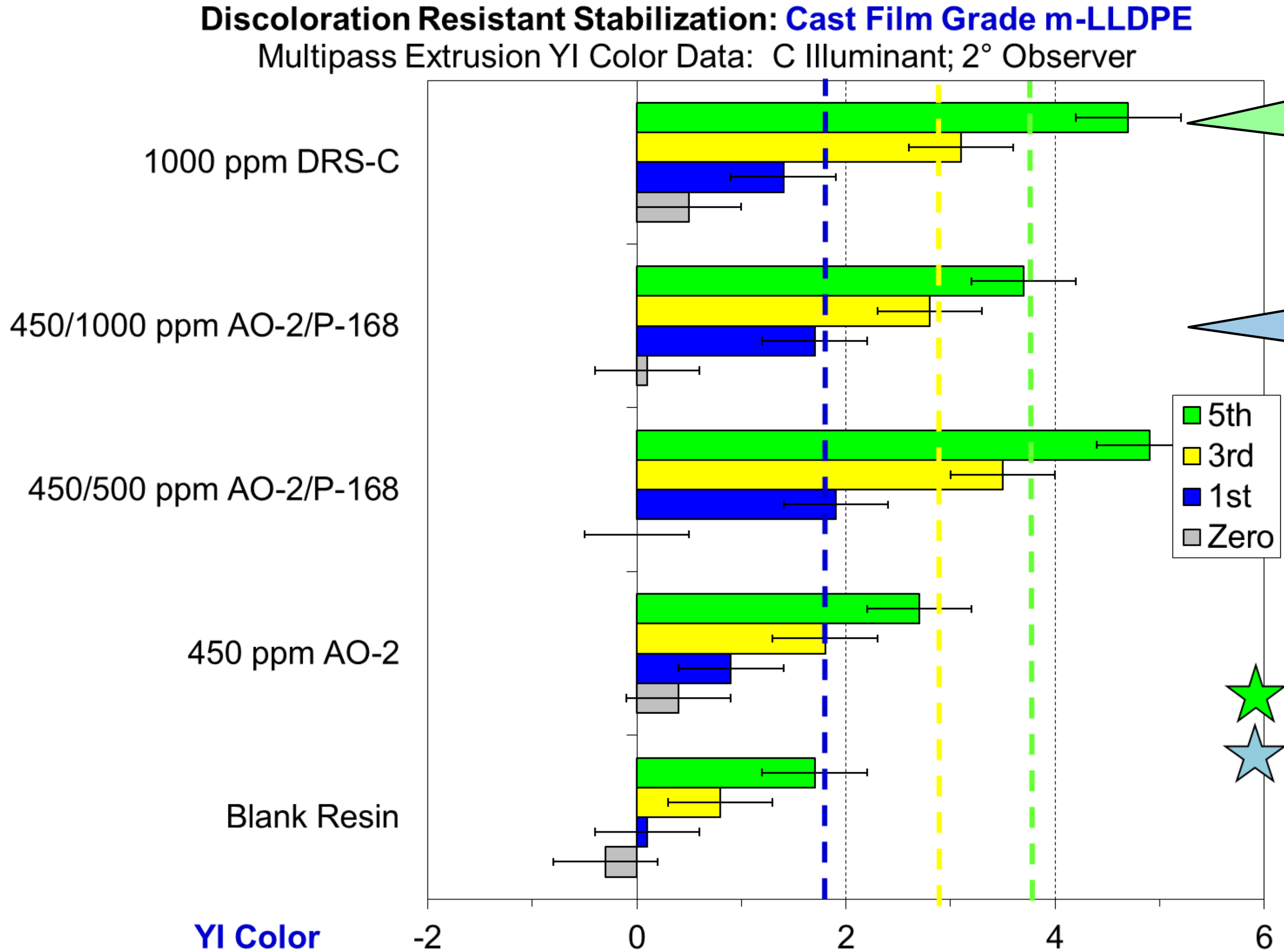

1000 ppm **"DRS"** gave a bit less color control vs. 1450 ppm of traditional AO-1010/PS-168 Blend

1500 ppm of traditional **AO-1/P-168** Blend provided good color control for this grade

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Cast Film Grade LLDPE C_2/C_8 Copolymer

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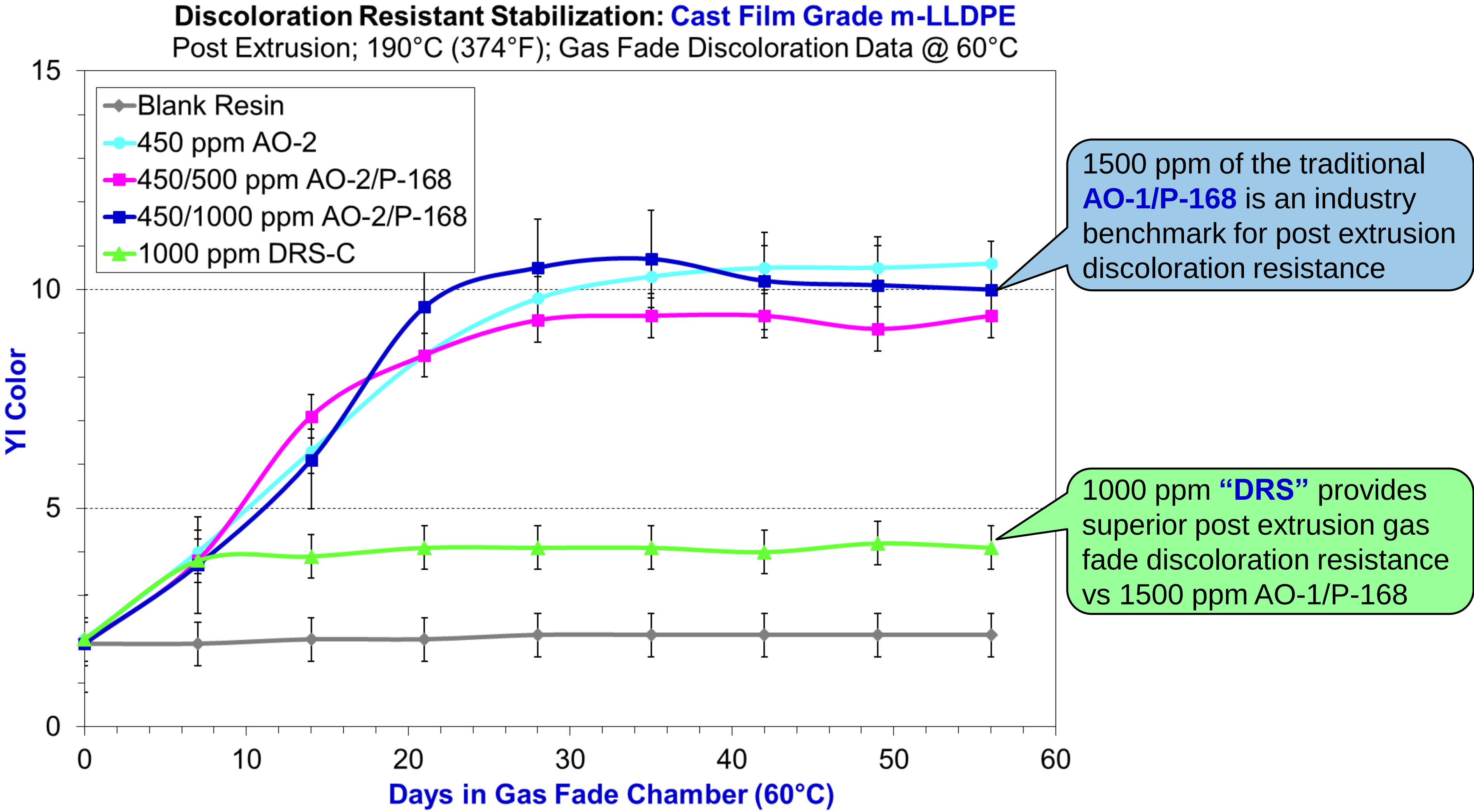


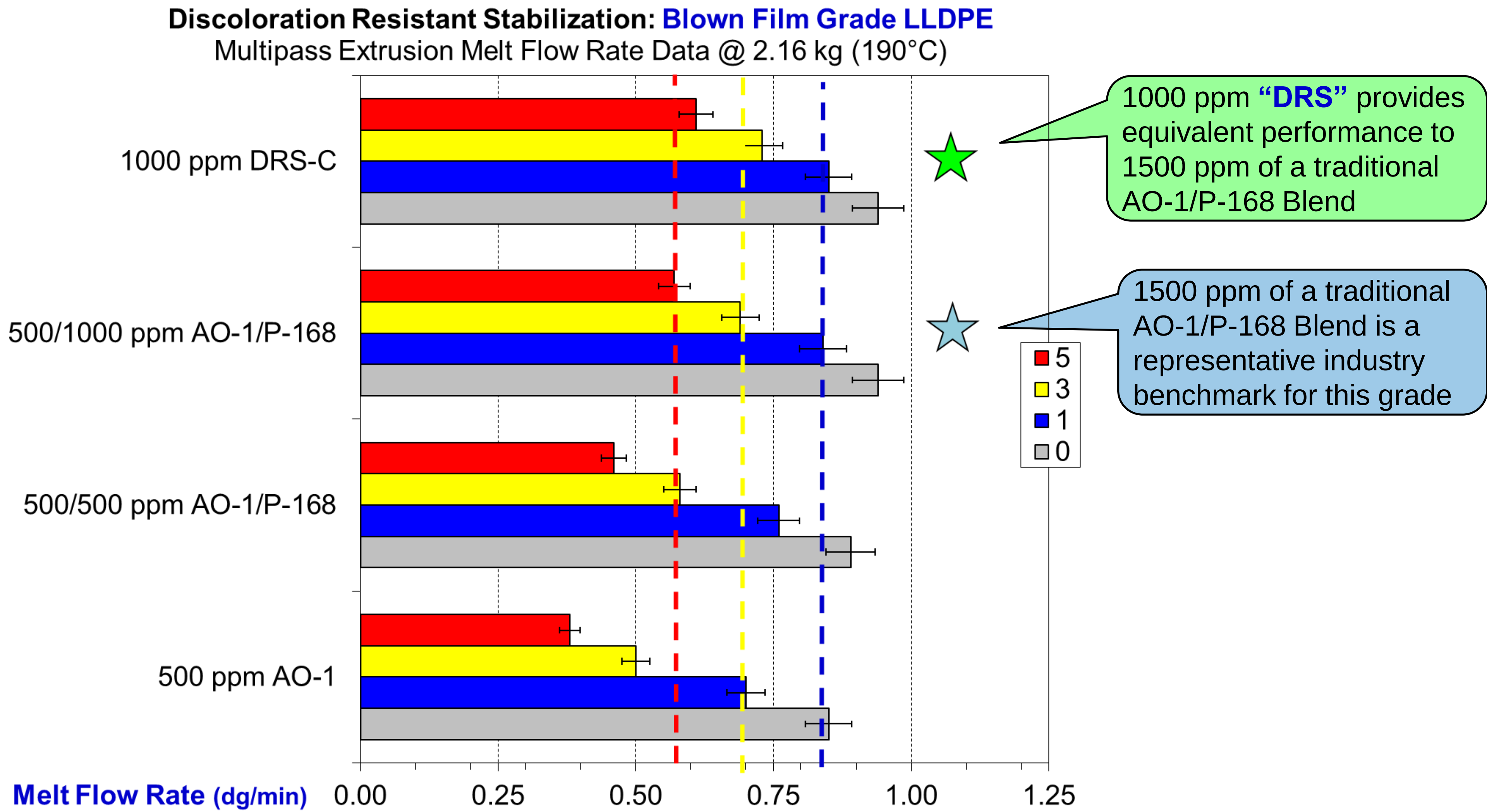
Gas Phase Blown Film Grade m-LLDPE

Experimental:

- **Polymer:** C_2/C_6 zn-LLDPE Copolymer, Gas phase process, Nominal I_2 MI = 1 dg/min; Density = 0.92 g/cm^3
- **Stabilizers:** 500 ppm Phenolic (AO-1); Various loading of P-168 vs. Discoloration Resistant Stabilizer system
- **Acid Scavenger:** Zinc Stearate was used at 500 ppm.
- **Zero Pass Compounding:** Leistritz 27mm twin screw; 410ºF (210ºC); 32:1 L/D; Under Nitrogen
- **Multiple Pass Extrusion:** MPM 1" single screw; 500ºF (260ºC); 24:1 L/D; Under Air; Maddock mixing head
- **Melt Flow:** ASTM-1238; 190ºC; 2.16 kg; 21.6 kg; Tinius-Olsen extrusion plastometer
- **YI Color:** ASTM-313; 125 mil Plaque; Large Area View; C Illuminant, 2º Observer
- **Gas Fade Aging:** AATCC Test Method 23; Forced draft oven; 10 mil film; 60ºC; YI Color increase; Zero Pass
- **Low Temp Oven Aging:** ASTM D3045; Forced draft oven; 10 mil film; 60ºC; YI Color increase; Zero Pass
- **Oxidative Induction Time:** ASTM-3895; 10 mil film; Al Pans, Isothermal, 190ºC; $N_2 \rightarrow O_2$

Improved Processability Stabilizer Systems

Blown Film Grade m-LLDPE C_2/C_6 Copolymer



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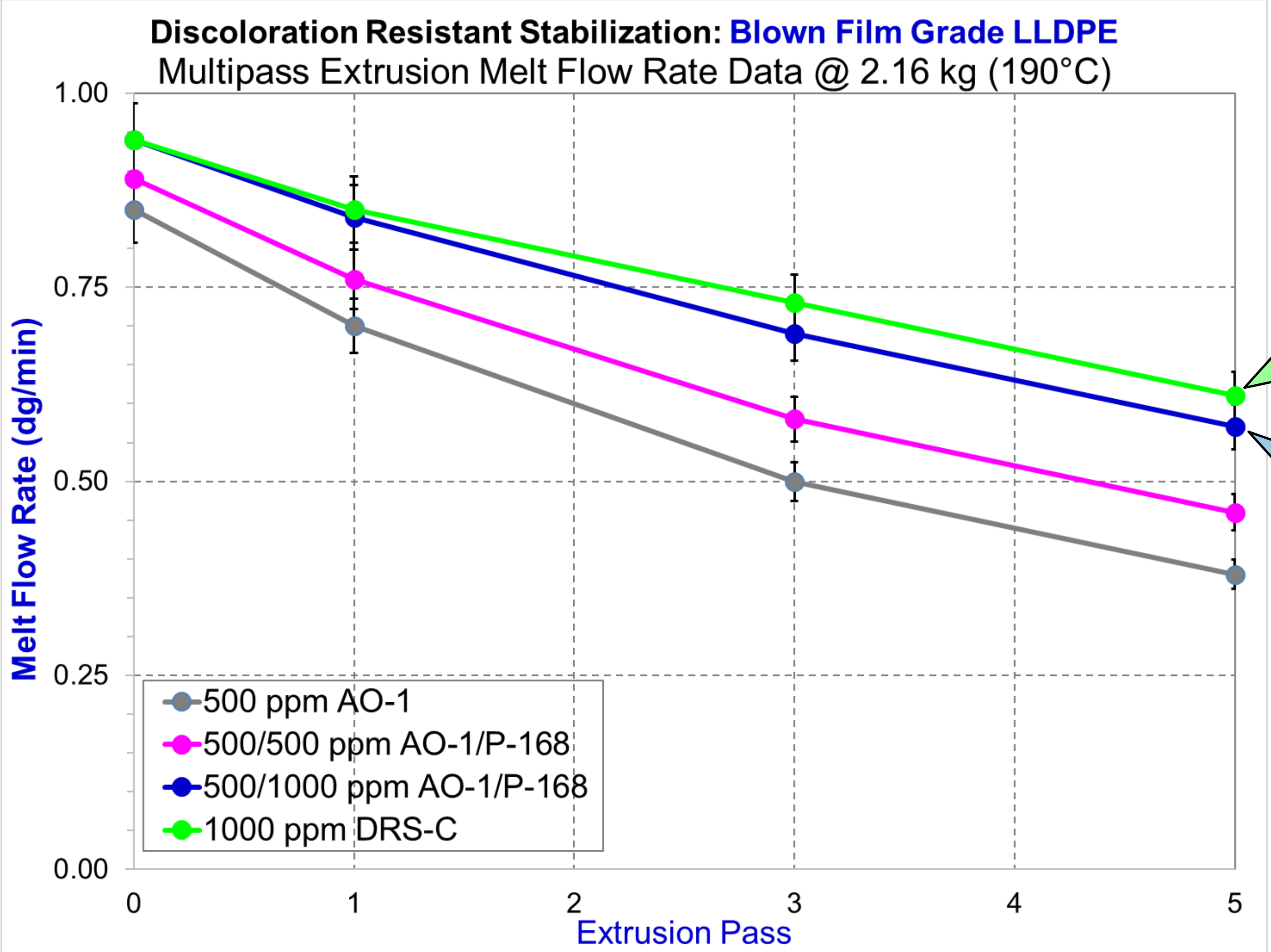
Blown Film Grade m-LLDPE C_2/C_6 Copolymer



1000 ppm **"DRS"** provides equivalent performance to 1500 ppm of a traditional AO-1/P-168 Blend

1500 ppm of a traditional AO-1/P-168 Blend is a representative industry benchmark for this grade

Improved Processability Stabilizer Systems

Blown Film Grade m-LLDPE C_2/C_6 Copolymer

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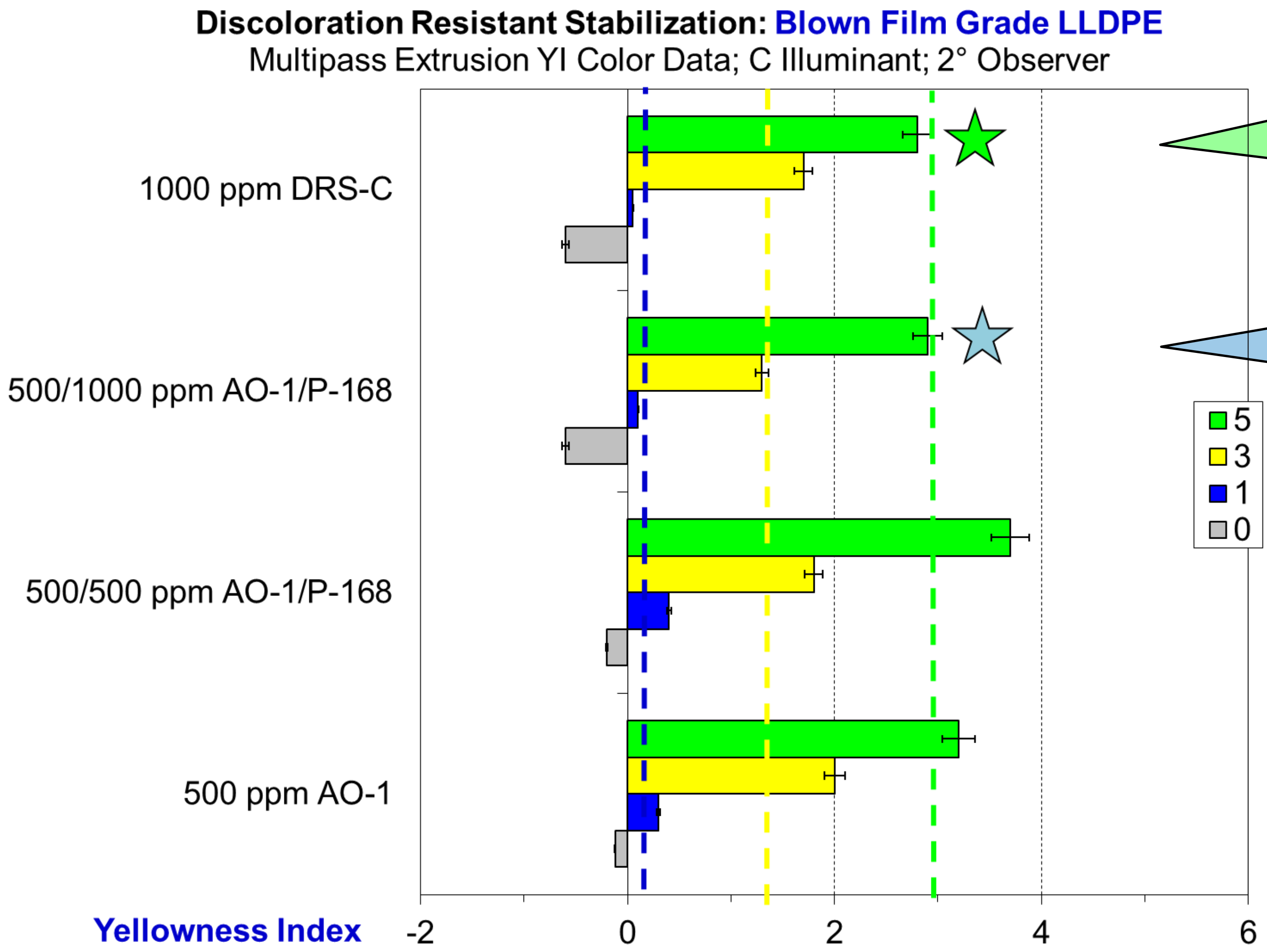

1000 ppm **"DRS"** gave similar color control vs 1500 ppm of traditional AO-1010/PS-168 Blend

1500 ppm of traditional **AO-1/P-168** Blend provided good color control for this grade

Improved Processability Stabilizer Systems

Blown Film Grade m-LLDPE C_2/C_6 Copolymer

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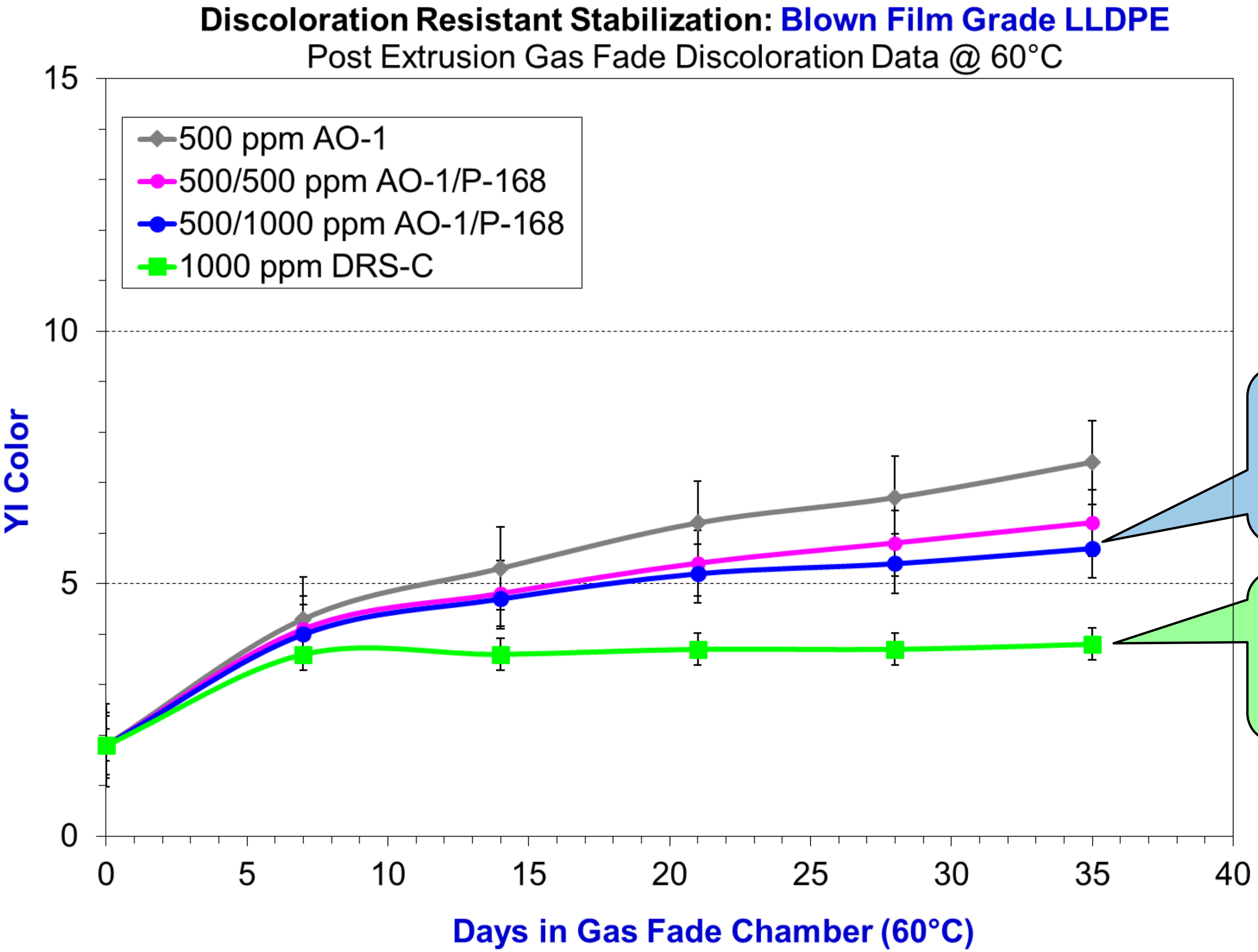

1500 ppm of the traditional **AO-1/P-168** is an industry benchmark for post extrusion discoloration resistance

1000 ppm **"DRS"** provides superior post extrusion gas fade discoloration resistance vs 1500 ppm AO-1/P-168

Molding Grade PP Random Copolymer

Experimental:

- **Polymer:** PP Random Copolymer, Slurry phase process, Nominal I_2 MI = 2.5 dg/min
- **Stabilizers:** 500 ppm Phenolic (AO-1010); Various loading of PS-168 or IPS systems
- **Acid Scavenger:** Calcium stearate was used at 600 ppm.
- **Zero Pass Compounding:** Leistritz 27mm twin screw; 410°F (210°C); 32:1 L/D; Under Nitrogen
- **Multiple Pass Extrusion:** MPM 1" single screw; 500°F (260°C); 24:1 L/D; Under Air; Maddock mixing head
- **Melt Flow:** ASTM-1238; 230°C; 2.16 kg; Tinius-Olsen extrusion plastometer
- **YI Color:** ASTM-1925; 125 mil Plaque; Large Area View; C Illuminant, 2° Observer
- **Gas Fade Aging:** AATCC Test Method 23; Forced draft oven; 10 mil film; 60°C; YI Color increase; Zero Pass
- **Low Temp Oven Aging:** ASTM D3045; Forced draft oven; 10 mil film; 60°C; YI Color increase; Zero Pass
- **Long Term Heat Aging:** ASTM D3045; Forced draft oven; 10 mil film; 135°C; Embrittlement; Zero Pass
- **Oxidative Induction Time:** ASTM-3895; 10 mil film; Al Pans, Isothermal, 190°C; $N_2 \rightarrow O_2$

Improved Processability Stabilizer Systems
Molding Grade zn-PP Random Copolymer

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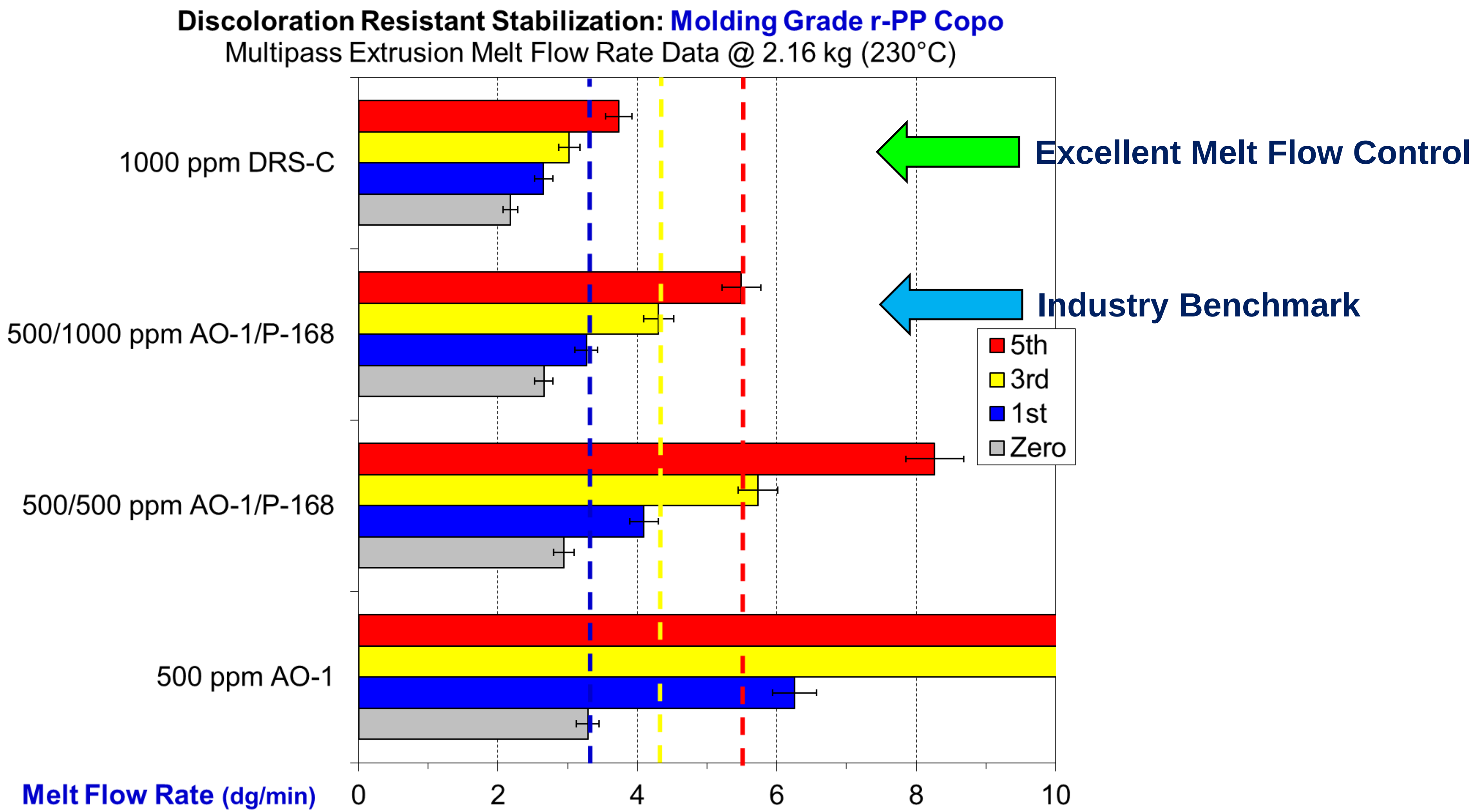

Improved Processability Stabilizer Systems
Molding Grade zn-PP Random Copolymer

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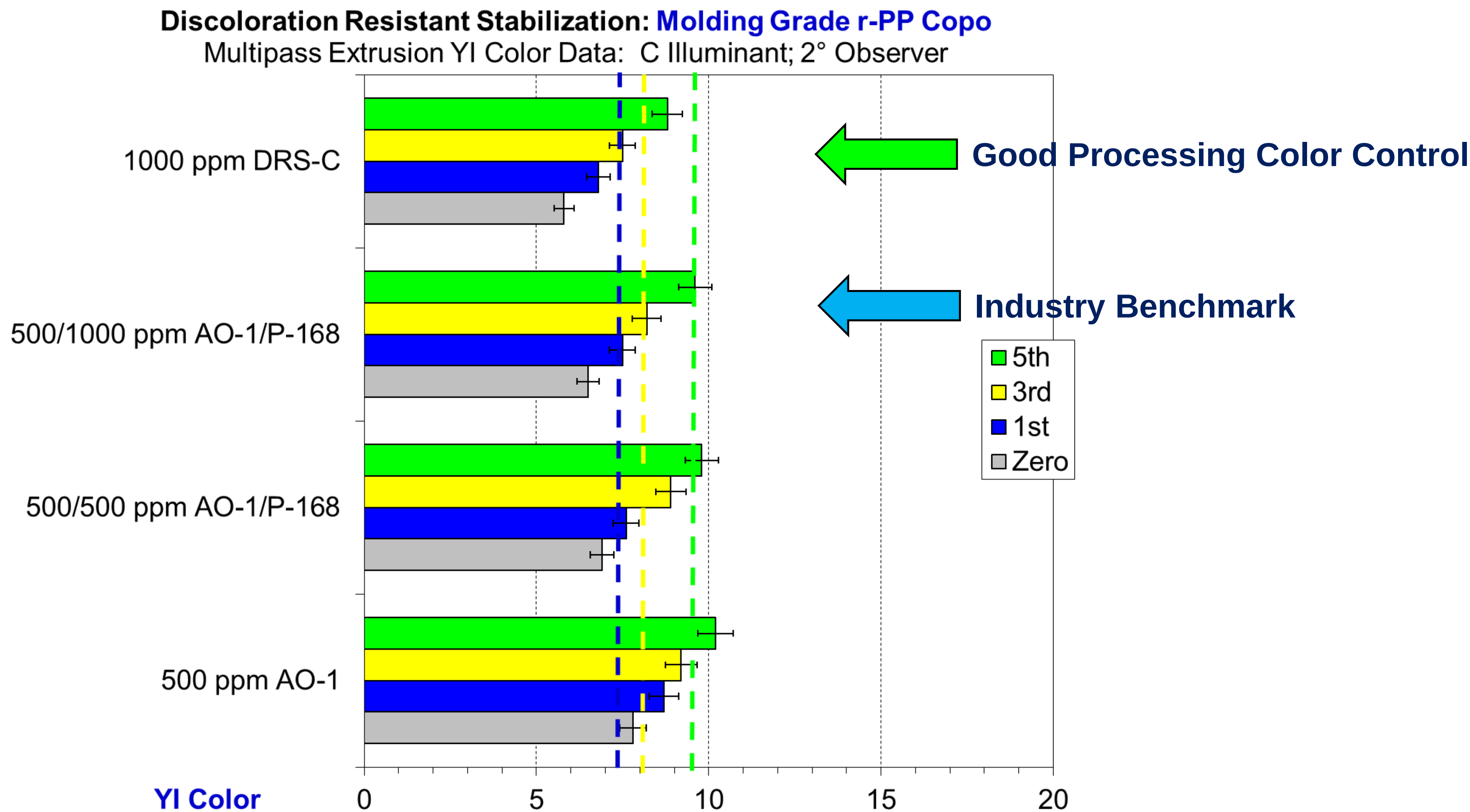

Improved Processability Stabilizer Systems
Molding Grade zn-PP Random Copolymer

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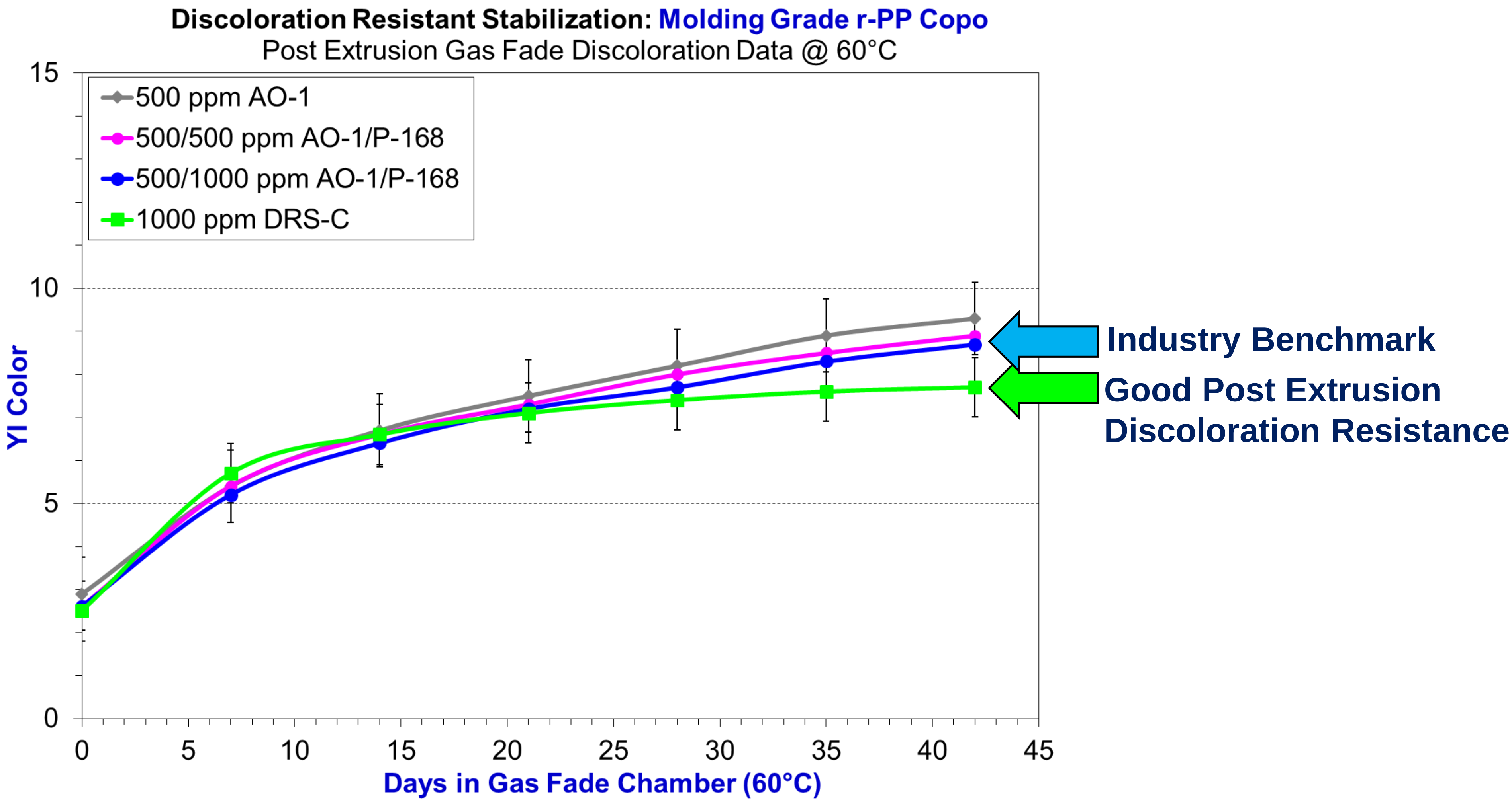

Improved Processability Stabilizer Systems
Molding Grade zn-PP Random Copolymer

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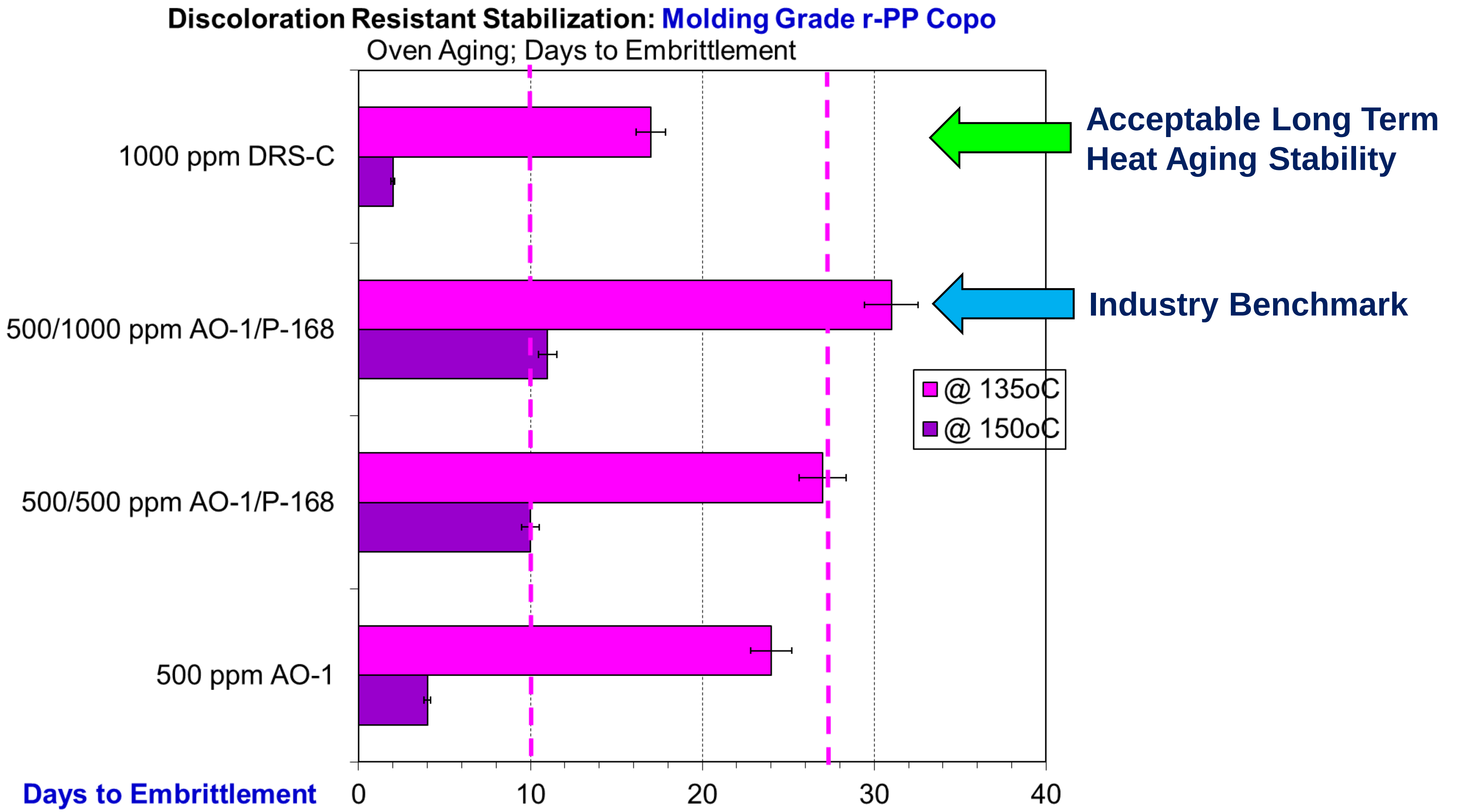

Improved Processability Stabilizer Systems
What did we learn from this project ?

- Traditional stabilizer blends based on a phenolic AO and a phosphite based melt processing stabilizer can take care of most polymers and downstream applications via optimization of loadings & ratios of the components (plus knowledge & experience; co-additives; etc.)
- However, for polymers that have been designed unique performance features for demanding applications, an alternative stabilization system may be required (e.g., simply loading more AO may not work out…)
- To address this unmet need, we developed highly effective stabilization systems that consistently deliver "good processability and **improved discoloration resistance**" in various polymer technologies.
- **Conclusion:** These "**Discoloration Resistant Stabilization**" Systems can be used to fulfill an unmet need in the industry, where polyolefins needed for color critical applications can be used in order to capture their full value in targeted markets & applications.

➔ Target + Stretch Objectives achieved with "DRS" Systems

Acknowledgments

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- International Polyolefins Conference Organizing Committee
- BASF Corporation (for permission to contribute & present)
- Gracious donations of additive free polymers to work with
- All the folks contributing to the advancement of stabilization
- You, and your attention regarding today’s presentation

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Plastic Additives ←→ Performance Chemicals

Inside of BASF’s Performance Products Segment

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BASF: world’s leading chemical company

- 111K employees
- 370 production sites
- Six “Verbund” sites

- Customers worldwide
- We strive to balance economic success with social responsibility, and environmental protection
- Using science we enable our customers and industries to meet their current & future needs

We create chemistry for a sustainable future

Chemicals	Performance Products	Functional Materials & Solutions	Agricultural Solutions	Oil & Gas
Intermediates	Dispersions & Pigments	Catalysts	Crop Protection	Oil & Gas
Monomers	Care Chemicals	Construction Chemicals		
Petrochemicals	Nutrition & Health	Coatings		
	Performance Chemicals	Performance Materials		

Target: Continue to be A Powerful Partner

Being part of the Plastics Industry via Innovation

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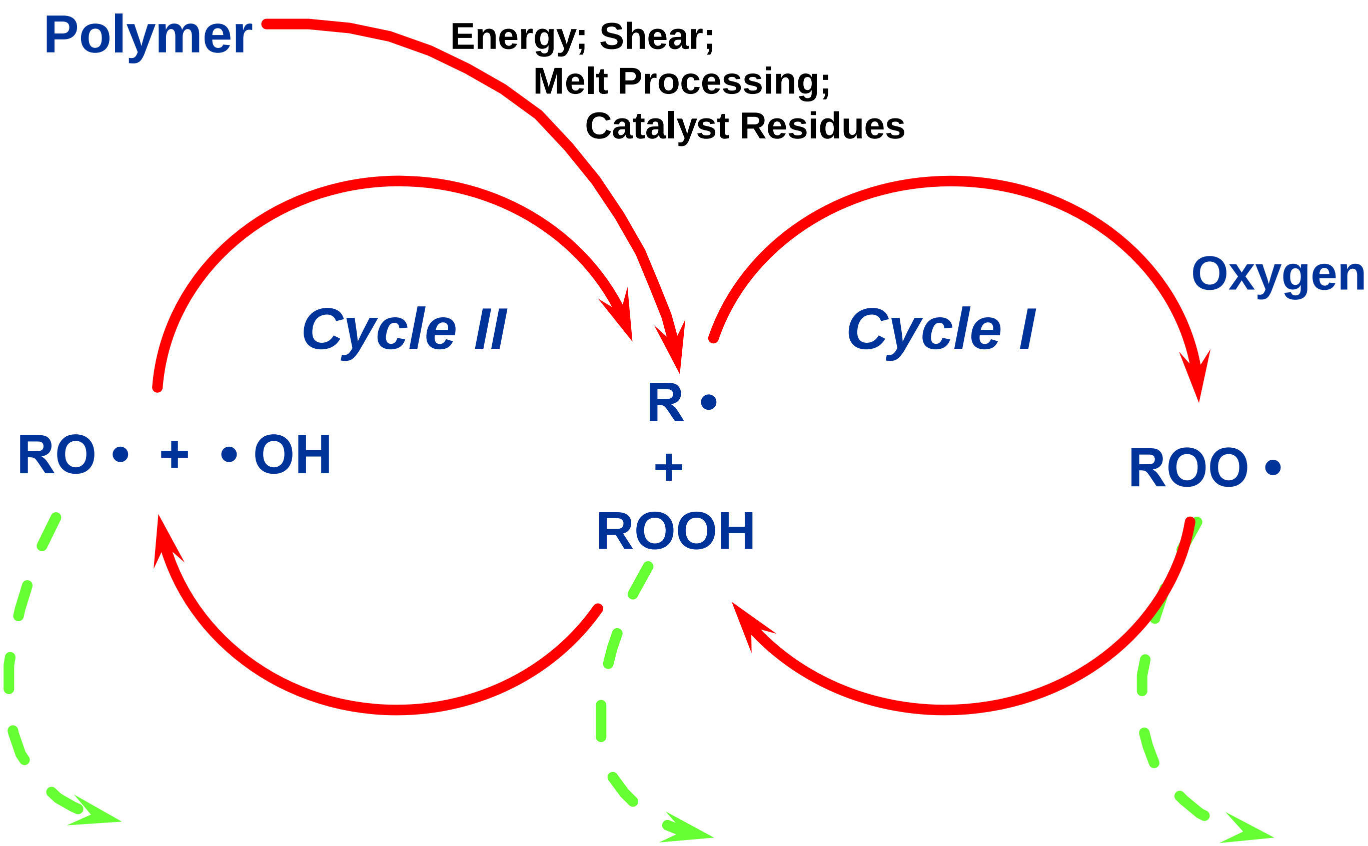
- **Products**
  - Antioxidants/process stabilizers
  - Light Stabilizers
  - Organic & Inorganic Colorants
  - Functional Pigments
  - Halogen Free Flame Retardants
  - Polymer Modifiers
- **Markets & Industries**
  - Automotive
  - Agriculture
  - Building & Construction
  - Electrical & Electronics
  - Textiles & Fibers
  - Packaging & Consumer Goods
- **Substrates**
  - Polyolefins
  - Elastomers
  - Engineering Plastics
  - Polyurethanes
  - Styrenics
  - PVC
- **Applications**
  - Woven & Nonwoven Fibers
  - Thin & Thick Films
  - Sheets & Membranes
  - Pipes & Profile Extrusion
  - Injection/Blow Molding
  - Rotomolding

➔ **Snapshot of required competencies to deliver Innovation**

Antioxidants in Action

Inhibited Auto-oxidation Cycle



Phenolic AOs react with oxygen centered radicals to yield less active products (ROH and H_20)

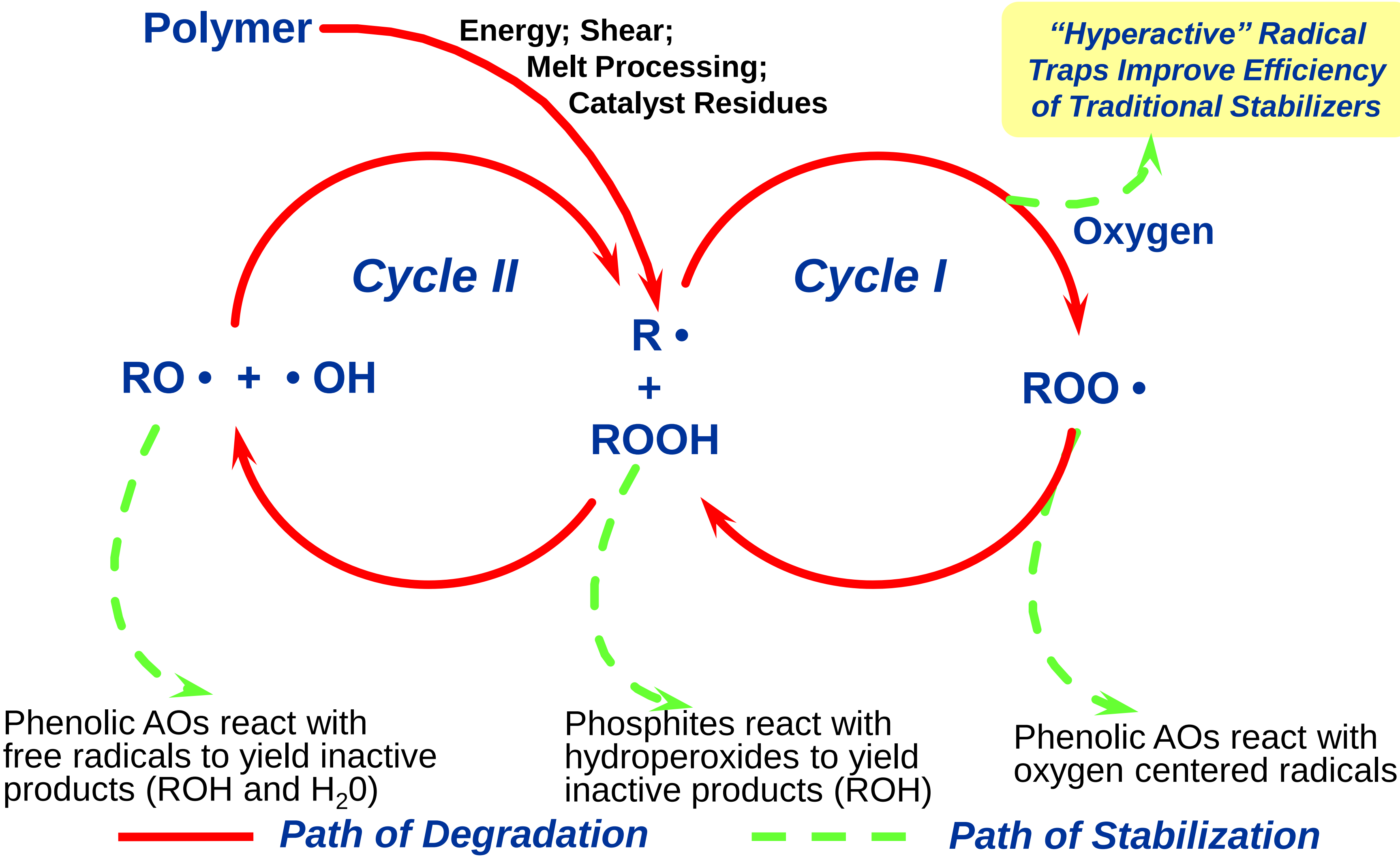
Phosphites react with hydroperoxides to yield inactive products (ROH)

Phenolic AOs react with oxygen centered radicals to yield less active products (ROH and H_20)

Path of Degradation ***Path of Stabilization***

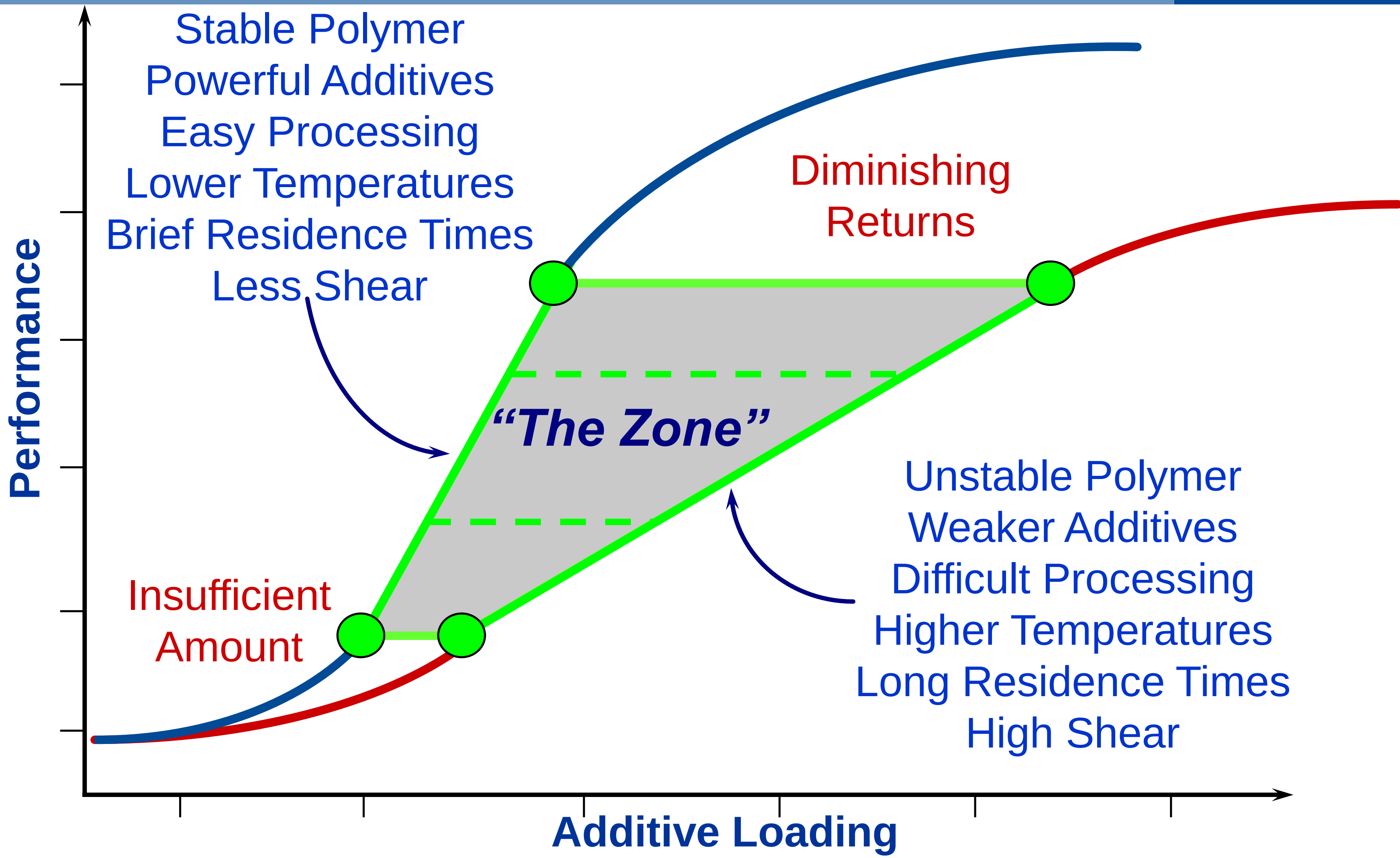
New Directions for Antioxidants

More Efficient Inhibition of Auto-oxidation Cycle



Concentration vs. Performance

Finding the right balance of cost & performance



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