Optimizing Stabilization Systems for Polyolefins
Using Traditional and Specialty Antioxidants

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Optimizing Stabilization Systems for Polyolefins
Using Traditional & Specialty Antioxidants

Introduction: What is this topic about ?

Opportunities & Challenges

Product Profile (Definition of Success)

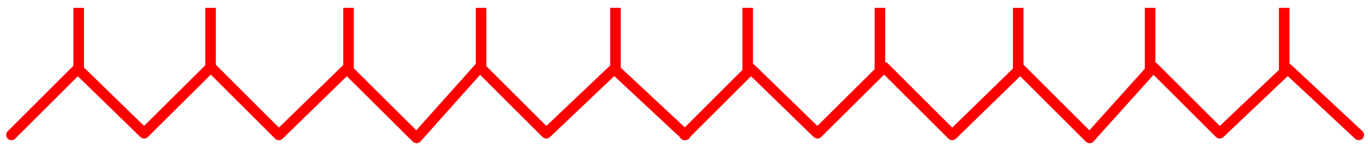
Representative Data Set (zn-PP Homo)

Conclusions & Recommendations

Opening Remark: Even after all these years
Polyolefins are still quite interesting…

Elevator Speech: Even though "polyolefins" have been around for >70 years, and have a relatively simply structure, the properties of this diverse material still provides a very nice opportunity for the cost effective replacement of other materials, such as wood, metal, glass as well as other types of thermoplastic polymers…

Polypropylene



gas phase; slurry phase; bulk phase; zn-PP; m-PP; homopolymer; random copolymer; impact copolymer;

Polyethylene

gas phase; liquid phase; slurry phase; zn-LLDPE; Zr; CGCT m-LLDPE; m-HDPE, Cr-HDPE; Ti-HDPE HMW-HDPE; UHMW-HDPE; plastomers; elastomers; tubular; autoclave; short chains; long chains;

Variables that provide design flexibility…..

- *Catalyst / Co-Catalyst*
- *Monomer / Co-Monomer*
- *Polymerization Process*
- ***Additive / Co-Additive Selection***
- ***Targets for End-Use Application***

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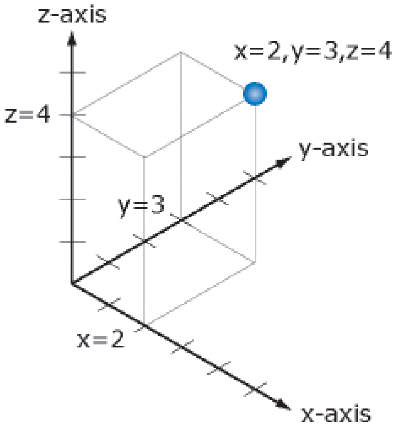
What are some end use requirements for Polyolefins ?

- **Stabilize the Physical Properties**
  - Physical properties designed for specific end use application
  - Must maintain those polymer properties
    - MW; MWD; Polymer Architecture (branching)

- **Stabilize the Processing Properties**
  - Processabilty at the converter
  - Regrind can often play a key role (economics)

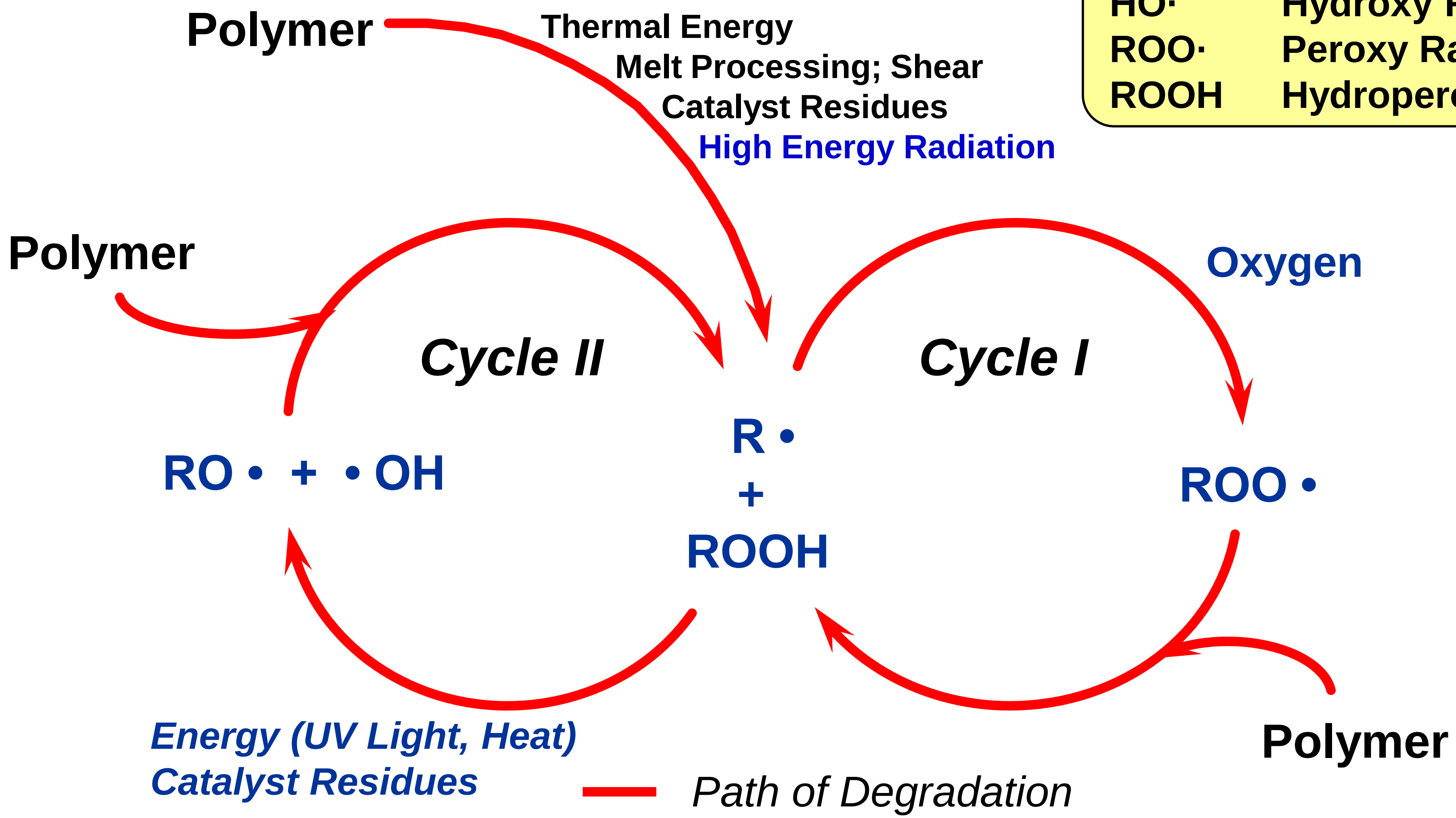


- **Stabilize the Aesthetic Properties**
  - Maintain low color of initial pellets going to converter
  - Maintain low color of the shaped parts at the converter
  - Maintain low color after Gamma Irradiation
    - **Short Term:** Just after irradiation
    - **Mid Term:** During transportation & warehouse inventory
    - **Long Term:** Storage on sight before use

Why is Polyolefin Stabilization Important ?

Polymer Auto-oxidation Cycle

R·	Alkyl Radical
RO·	Alkoxy Radical
HO·	Hydroxy Radical
ROO·	Peroxy Radical
ROOH	Hydroperoxide



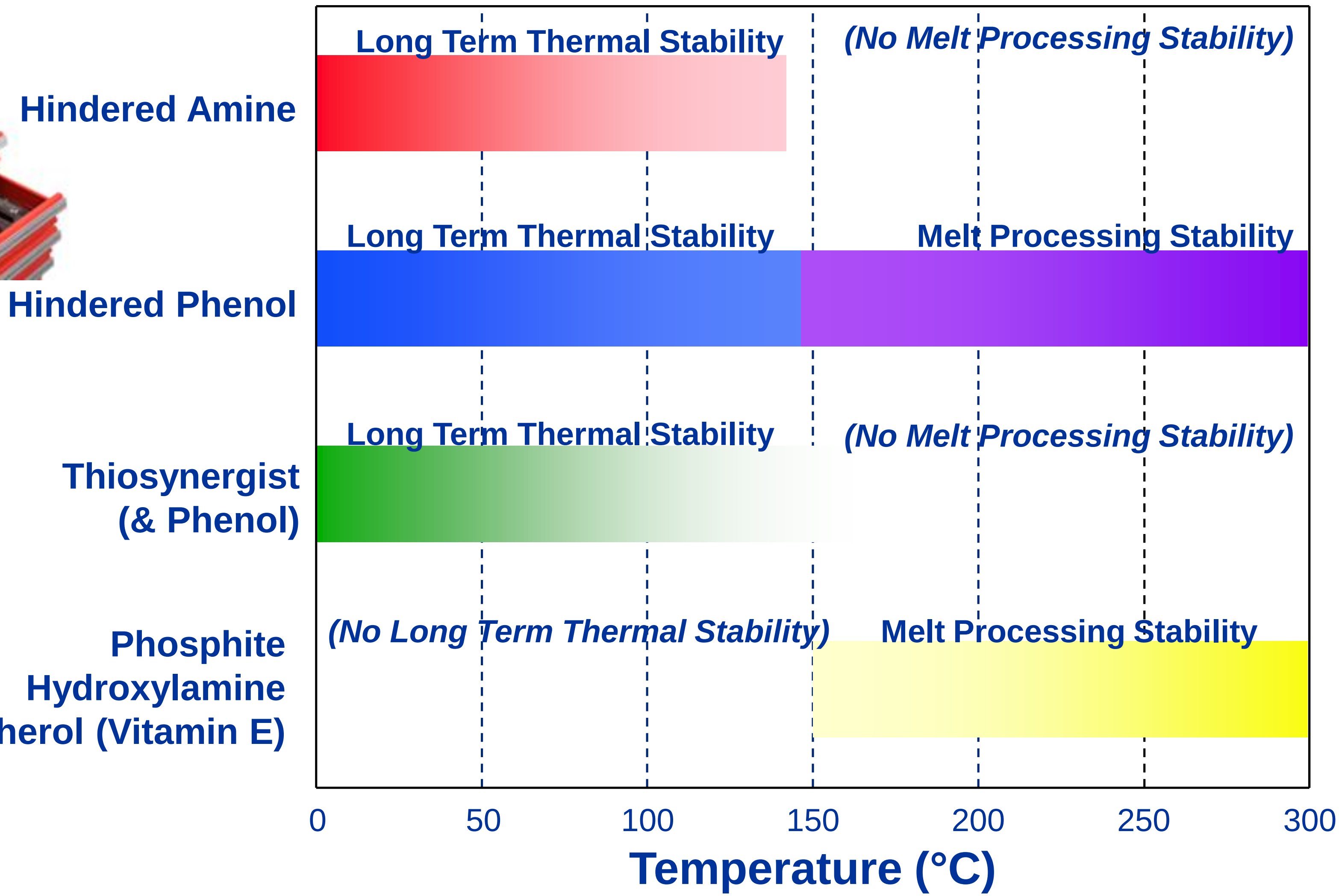
Polyolefins are carefully, designed, developed and produced, then encounter the “Reality” of being transformed based on end use application requirements

Products of Melt Processing
Formation of Radicals Leads to By-Products

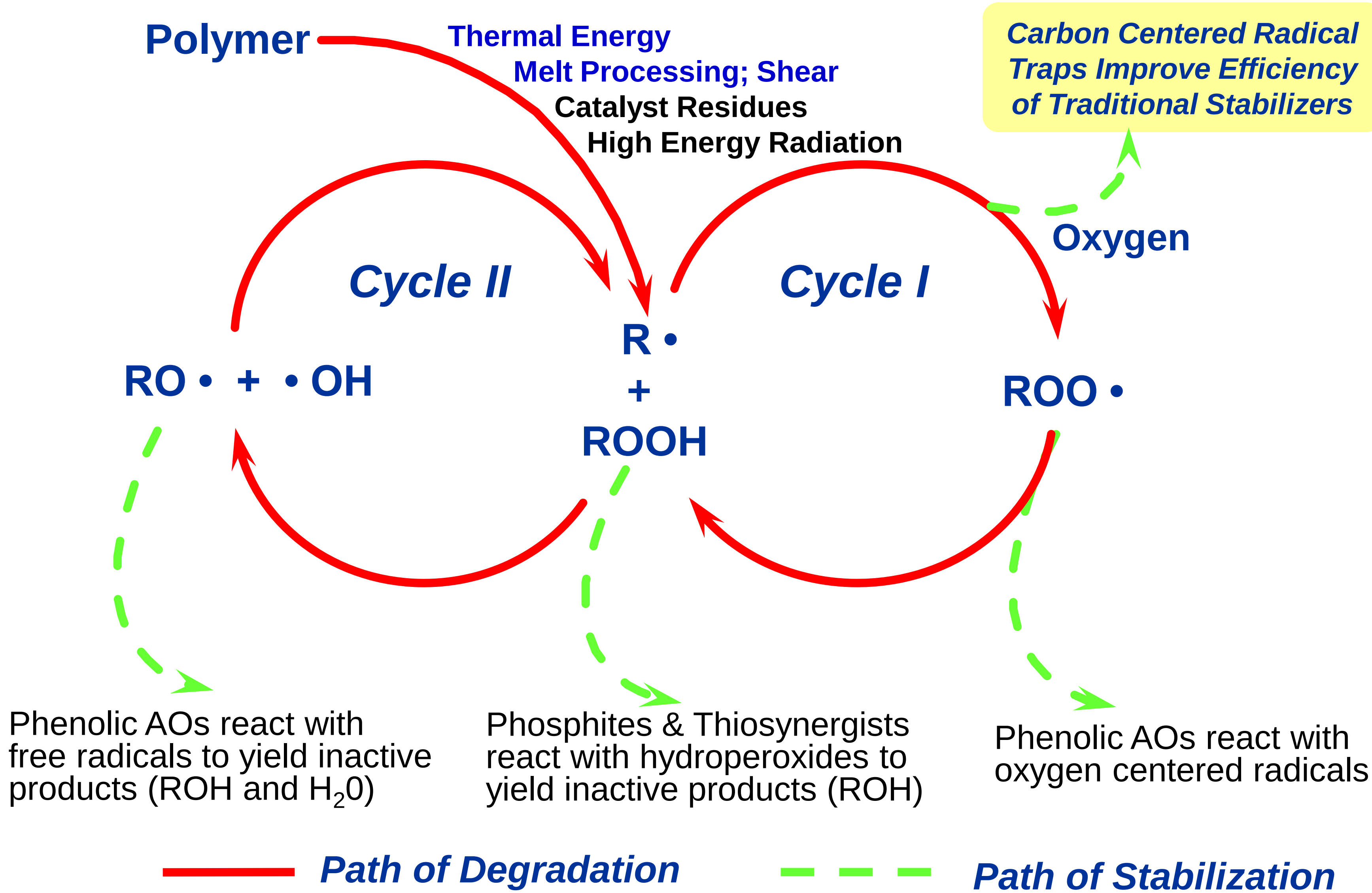
■ **Alkyl Radicals**		
■ **Peroxy Radicals**	→	***Affect Melt Processing and***
■ **Alkoxy Radicals**		***Long Term Thermal Stability***
■ **Hydroxy Radicals**		
■ **Hydroperoxides**	→	***Affect Melt Processing, Long Term Thermal & UV Stability***
■ **Alcohols**		
■ **Aldehydes**	→	***Affect Taste & Odor***
■ **Ketones**		
■ **"Polymer"**	→	***"It's Just Not the Same"***

Effective Temperatures for Stabilizers

How do each of the components contribute ?



Traditional Approach & New Directions
More efficient Inhibition of Auto-oxidation Cycle



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Product Profile: What does Success Look Like ?

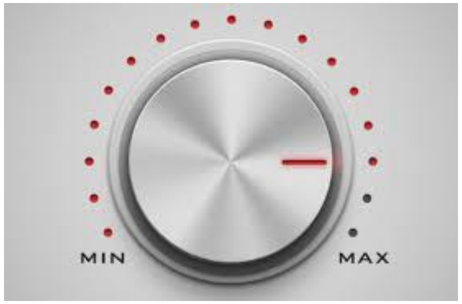
Representative Variables & Options

•**Substrates** ➢PP: Homopolymer ➢PP: Copolymer (Random; Impact; Block) ➢PE: HDPE; LLDPE; HMW-HDPE ➢Polystyrene; ABS; PC; PET; PA ➢Elastomers & Adhesives ➢PUR; Polyols	•**Polymer Performance** ➢MW Retention (2.16 kg) ➢YI Retention ➢Long Term Thermal Stability ➢Oxidative Induction Time ➢Gas Fade Discoloration ➢Oven Aging Discoloration
•**Fundamental/Ancillary Properties** ➢Traditional Systems (AO/P; AO/DSTDP) ➢Advanced Systems (PFS; HA/UVA) ➢Concentration dependence ➢Temperature dependence ➢Antagonism/Synergism w/ Co-Additives ➢Compatibility; Solubility; Miscibility	•**Applications** ➢Extrusion: Wire & Cable; Pipe ➢Moldings; Injection; Blow; Roto ➢Fiber: Wovens & Nonwovens ➢Films: Blown; Cast; Tape ➢Adhesives & Elastomers ➢Foams: Rigid; Flexible
•**Analytical** ➢Neat; Purity / Impurities (GC/MS; HPLC) ➢In-polymer (validation of concentration) ➢TGA; DSC; (Decomposition; Volatiles) ➢Residues (e.g., Chlorides for corrosivity) ➢Hydrolytic Stability (neat; in-polymer) ➢Organoleptics; Head-space analysis	•**Product Safety & Registration** ➢Persistence ➢Bioaccumulation; Biodegradation ➢Toxicity; Neurotoxicity ➢Migration I (95%; EtOH; Triglyceride Oil) ➢Migration II (10% EtOH; 3% Acetic Acid) ➢Endocrine Modulation (only screen)

How to Optimize a Stabilization System

A Six Step Program for Polyolefins

1. **Change the Phenolic Antioxidant**
   - e.g., chose a more color stable phenol
2. **Change the Processing Stabilizer**
   - e.g., use a higher performance phosphite
3. **Change the Phenol : Phosphite Ratio**
   - e.g., 1:1 ⇨ 1:2 ⇨ 1:3 ⇨ 1:4
4. **Use a Hyperactive Process Stabilizer**
   - e.g., Tocopherol; Hydroxylamine;
5. **Change the Acid Neutralizer**
   - Somewhat surprising, but true



Note: Incremental steps usually lead to incremental improvements. If a more robust improvement in discoloration resistance is necessary, then:

6. **Switch to Phenol-free Stabilization System**

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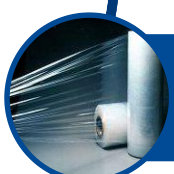

Representative Data Set (zn-PP Homo)


Conclusions & Recommendations

Molding Grade zn-PP Homopolymer

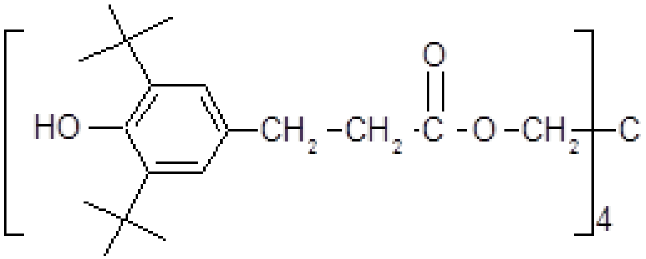
Experimental:

- Polymer: PP Homopolymer, Slurry phase process, Nominal I_2 MI = 4.5 dg/min
- Stabilizers: Various Loadings & Ratios of Stabilizers; (AO-1010; PS-168; PS-126; DSTDP)
- Acid Scavenger: Calcium Stearate (500 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-313; 125 mil Plaques; Large Area View; C Illuminant, 2° Observer
- Long Term Heat Aging: ASTM D3045; Forced draft oven; 10 mil film; 135°C; Days to Embrittlement
- Oxidative Induction Time: ASTM-3895; 10 mil film; Al Pans, Isothermal, 190°C; $N_2 \rightarrow O_2$; Time to Onset

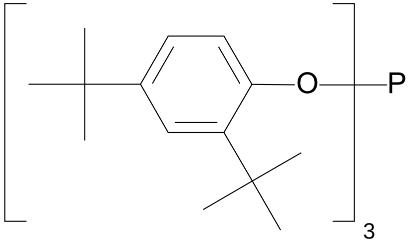
Optimizing Stabilization Systems for Polyolefins

Designation Codes for Traditional & Specialty Antioxidants

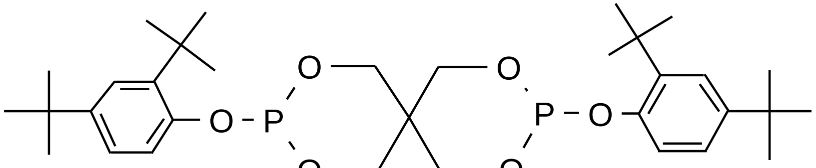
AO-1010
Traditional Phenolic AO
Irganox® 1010



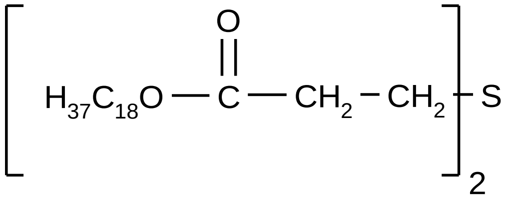
PS-168
Traditional; Phosphite (4.8% P)
Irgafos® 168



PS-126
Specialty; Phosphite (10.2% P)
Irgafos® 126



DSTDP
Specialty; Thiosynergist (4.7% S)
Irganox® PS 802

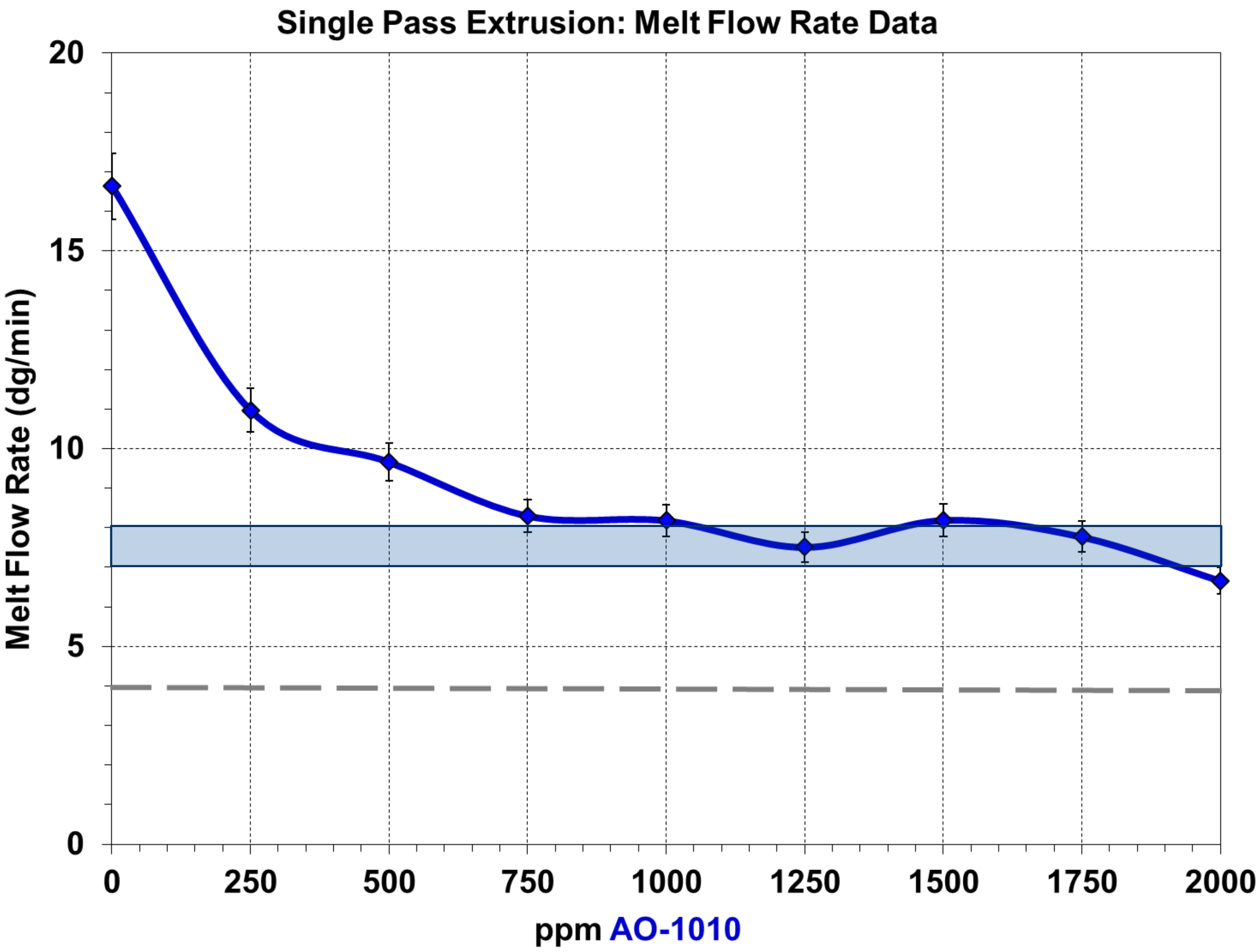


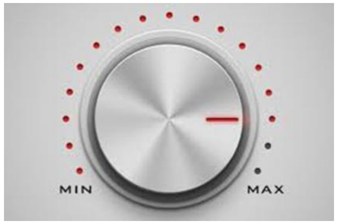
Optimization of Stabilization Systems
Molding Grade zn-PP Homopolymer

Melt Flow Rate Control → Physical Properties

Optimization of Stabilization Systems for Polyolefins

Measure 1: Melt Flow Rate Control (Physical Properties)





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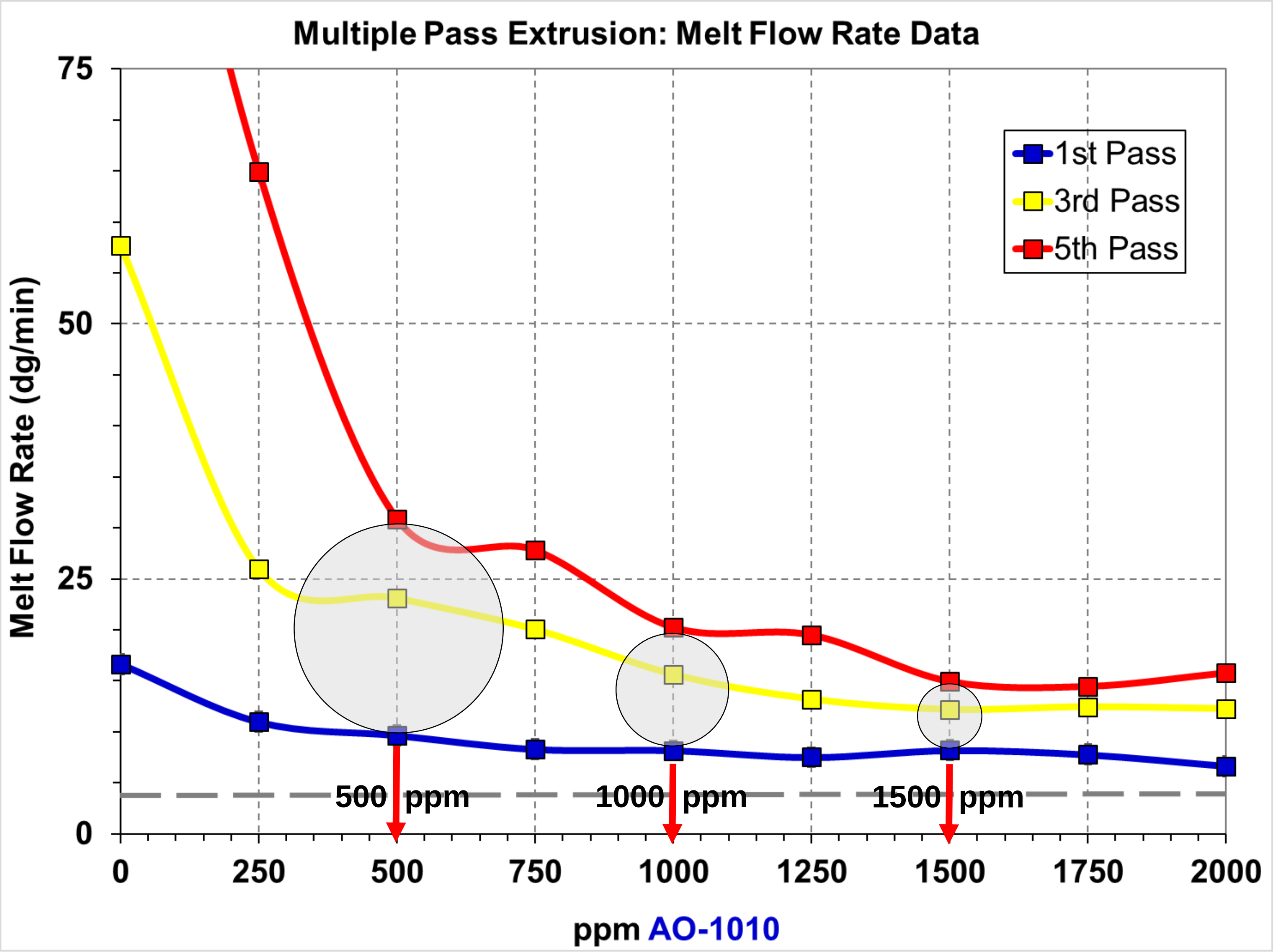

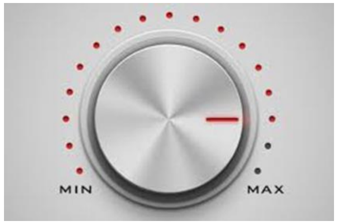

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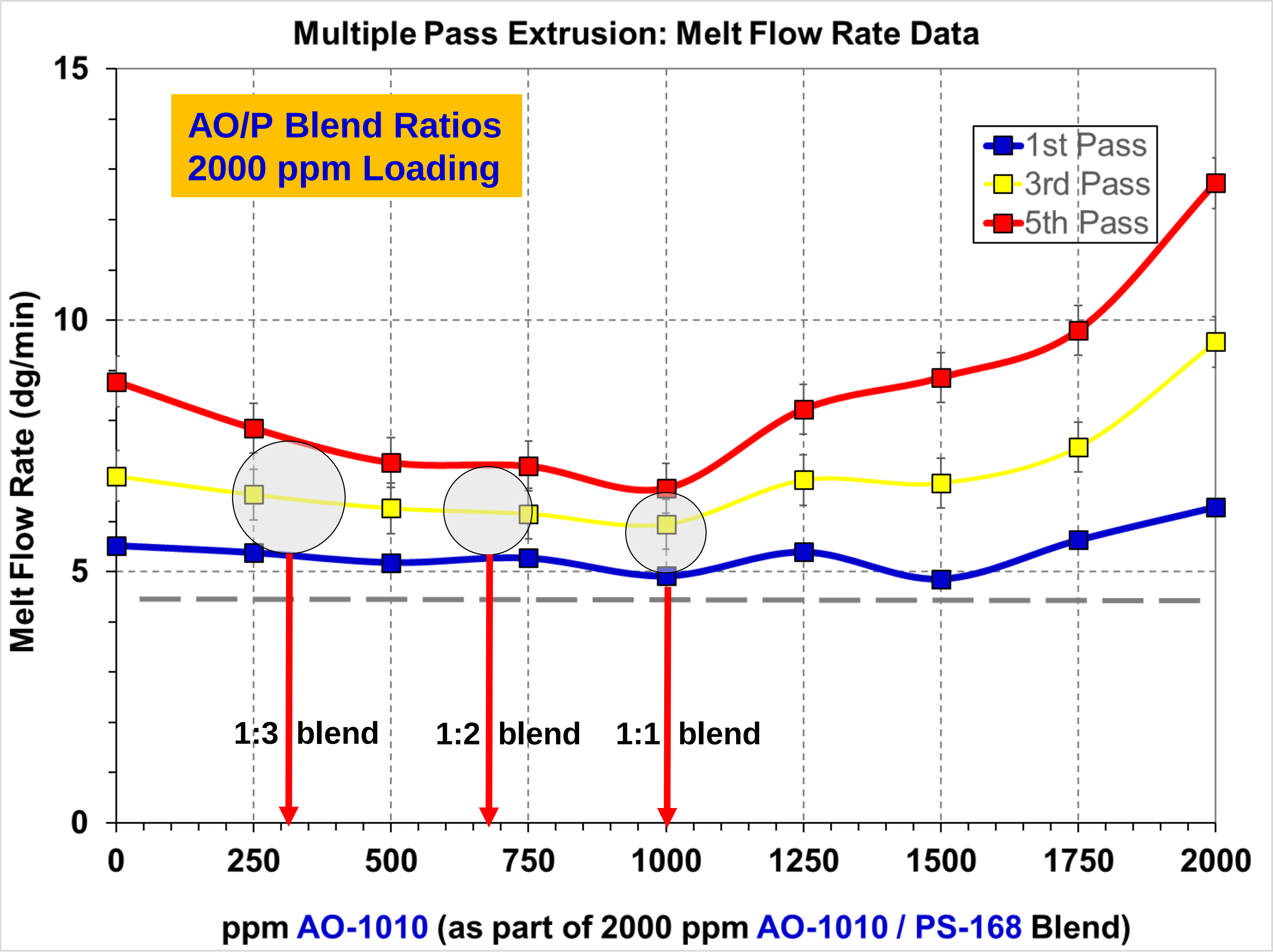

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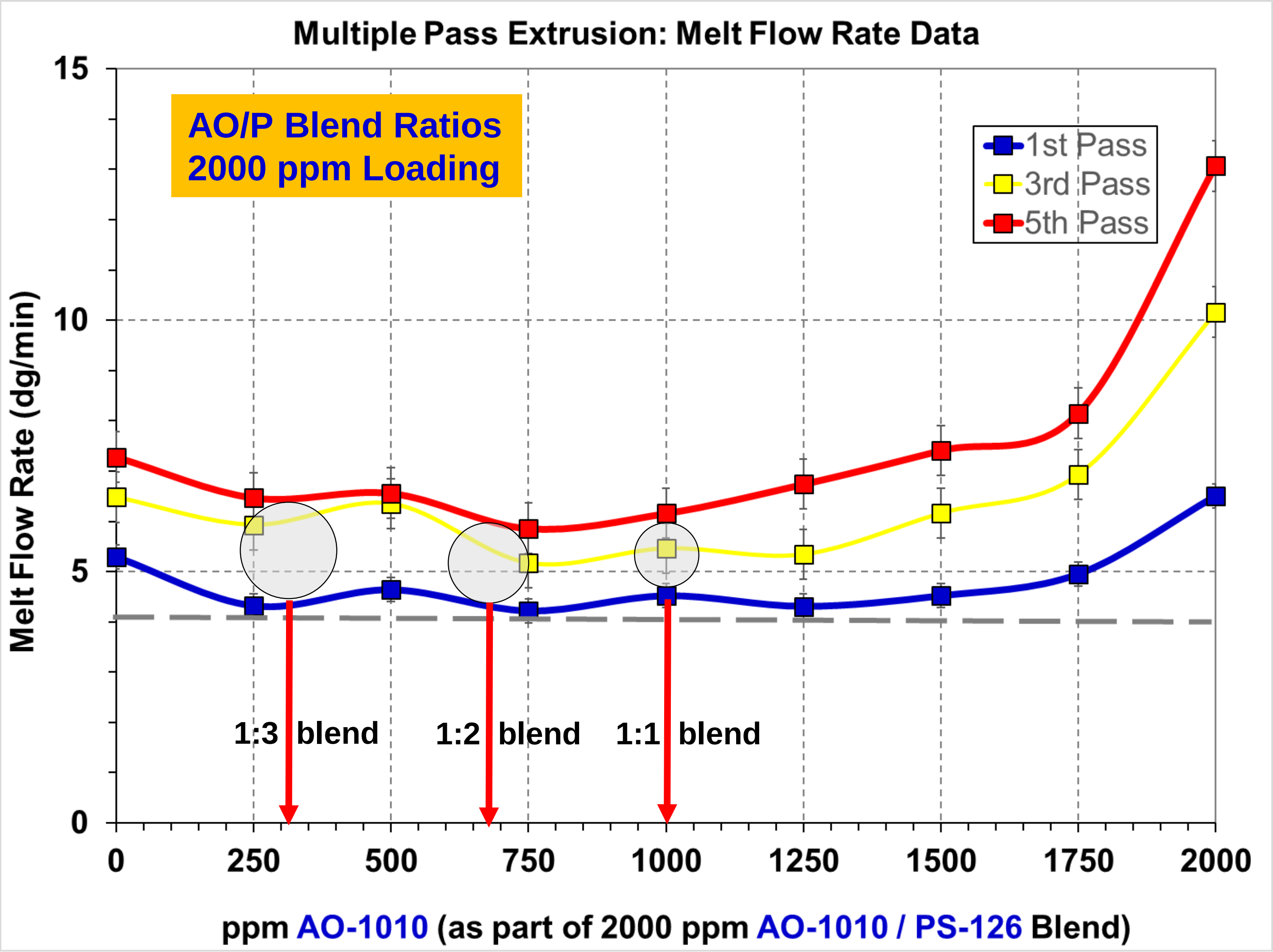

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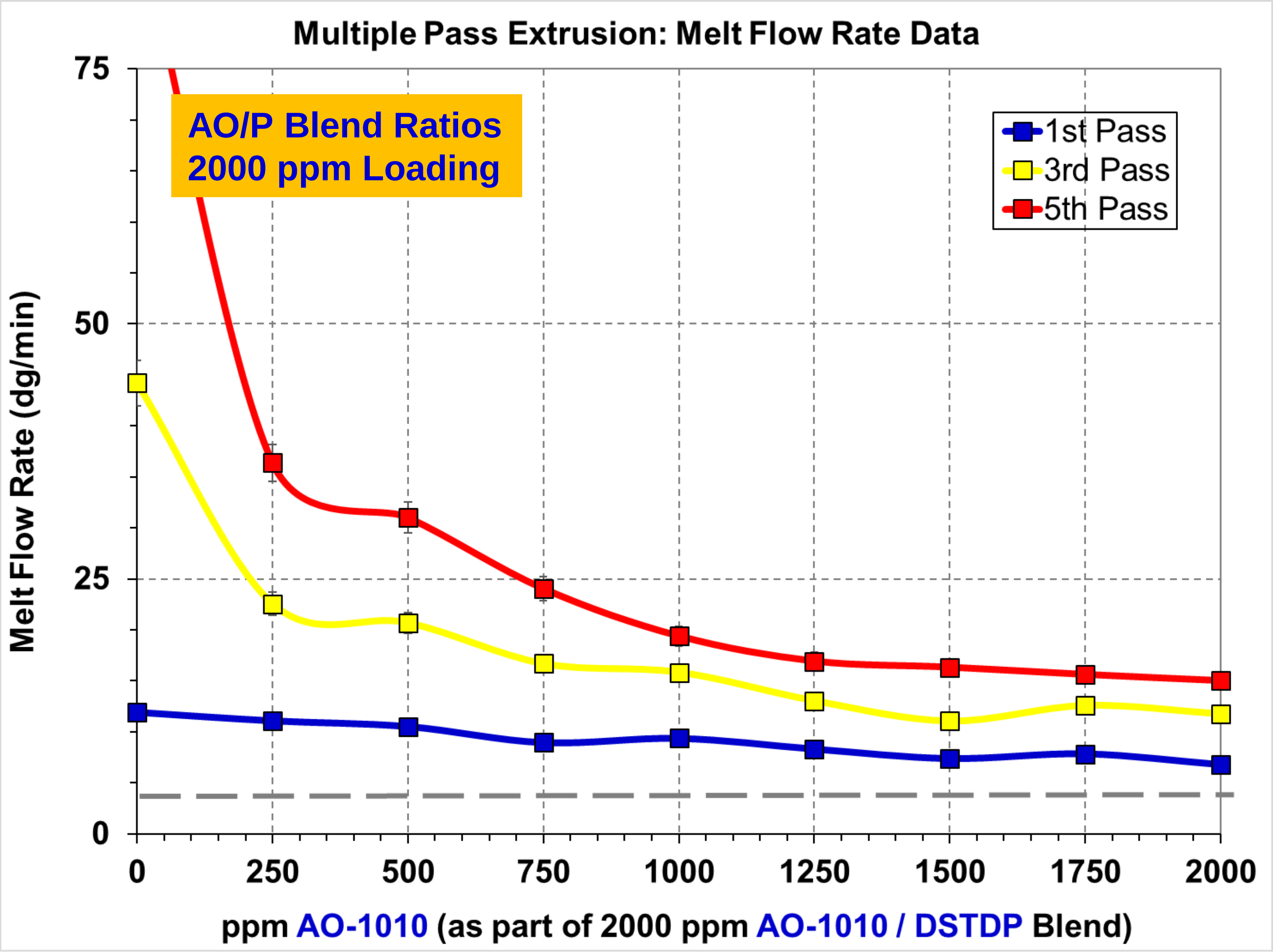
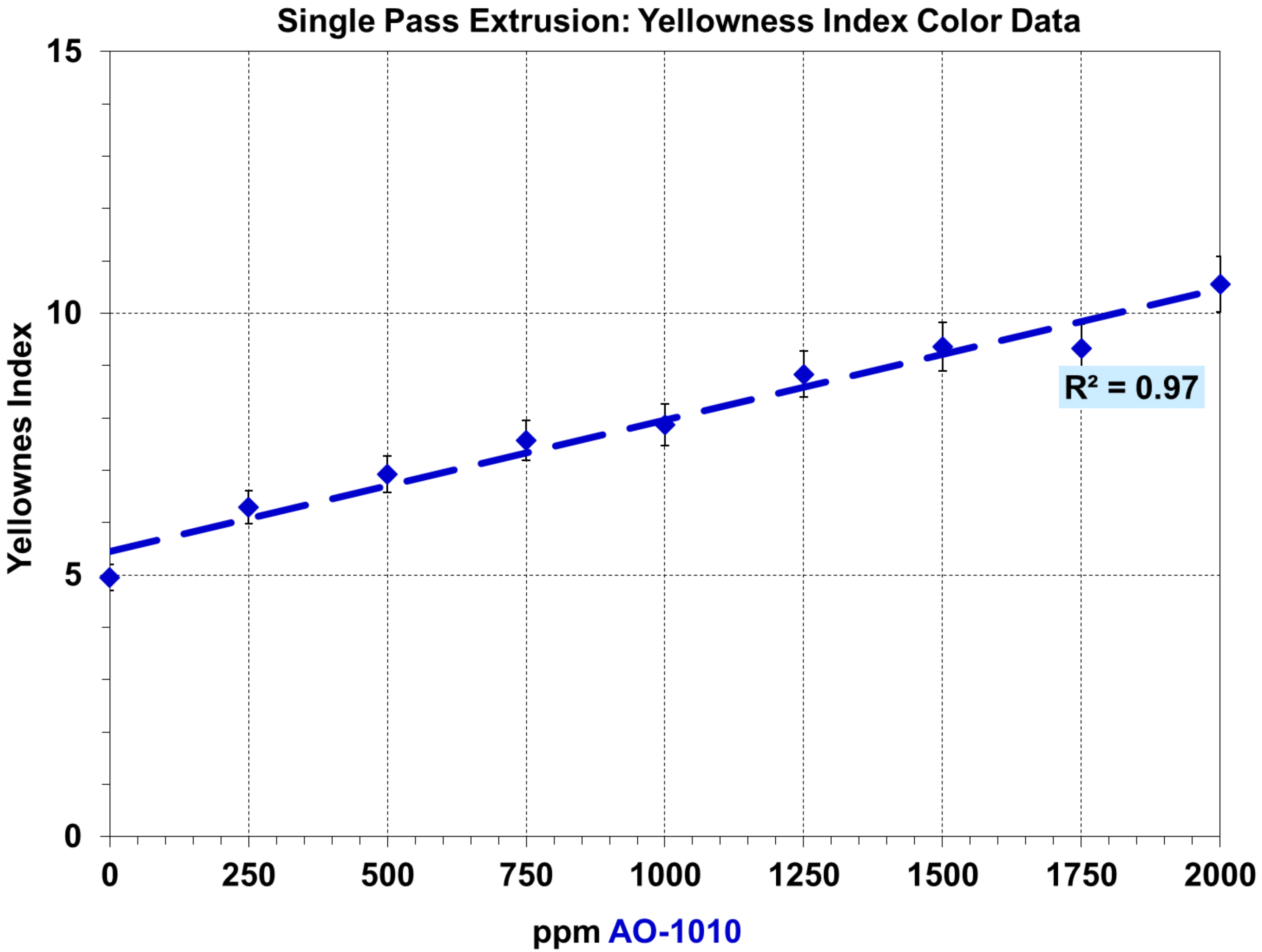


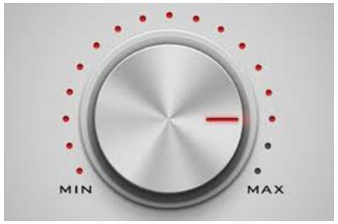
Optimization of Stabilization Systems
Molding Grade zn-PP Homopolymer

Discoloration Resistance → Aesthetic Appeal

Optimization of Stabilization Systems for Polyolefins

Measure 2: Discoloration Resistance (Aesthetic Appeal)





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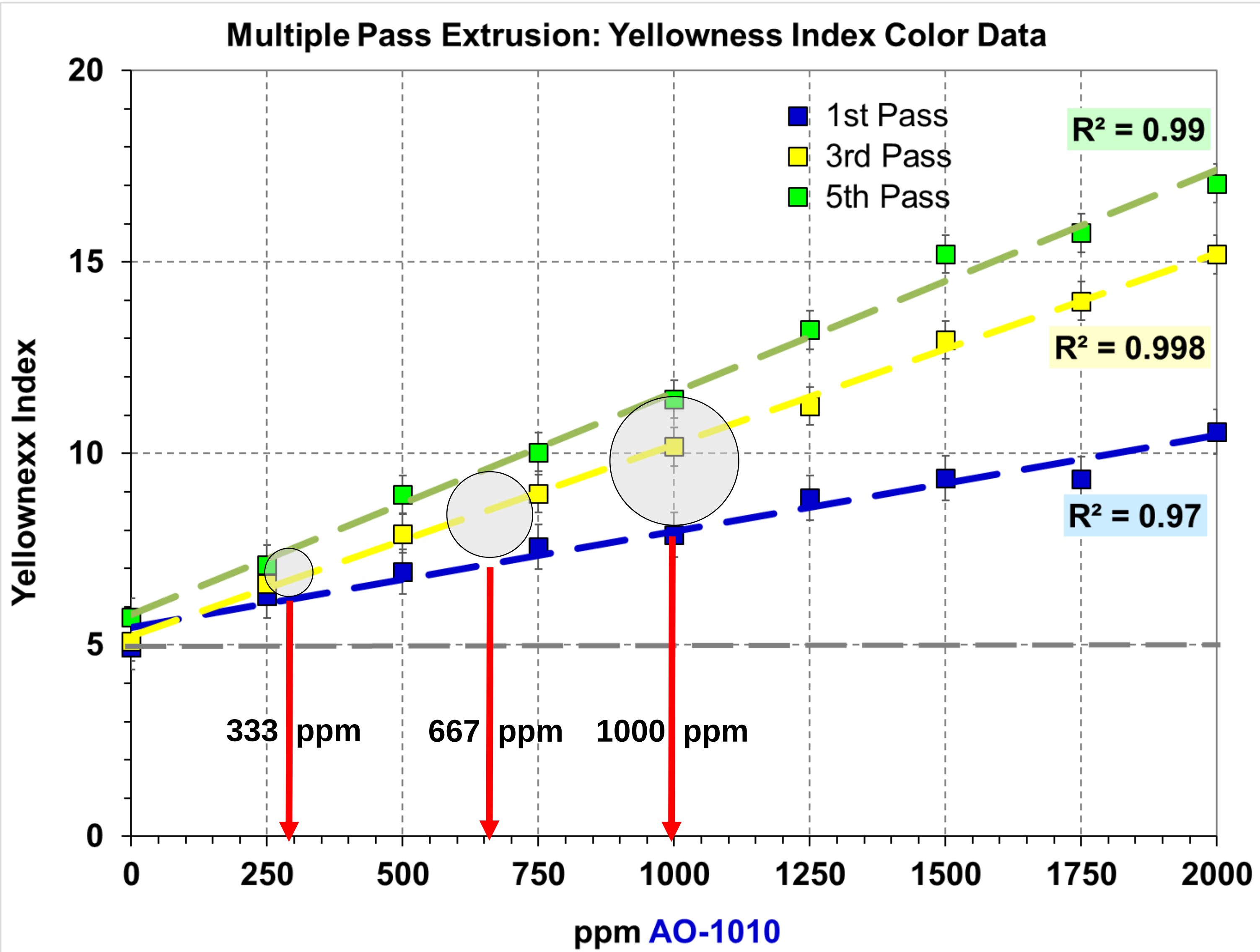
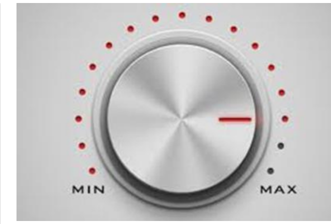
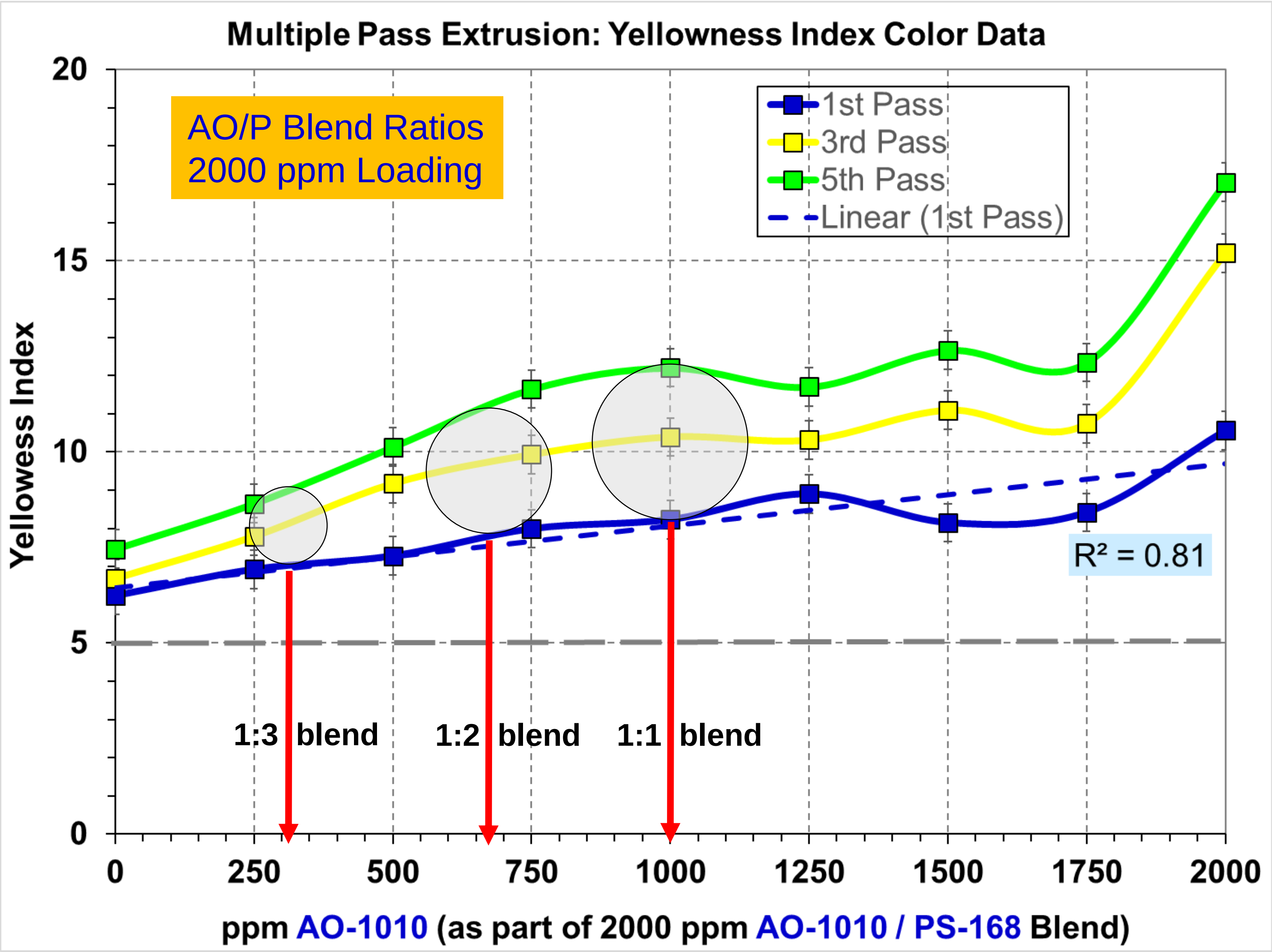




3.2 mm Plaques

Optimization of Stabilization Systems for Polyolefins

Measure 2: Discoloration Resistance (Aesthetic Appeal)



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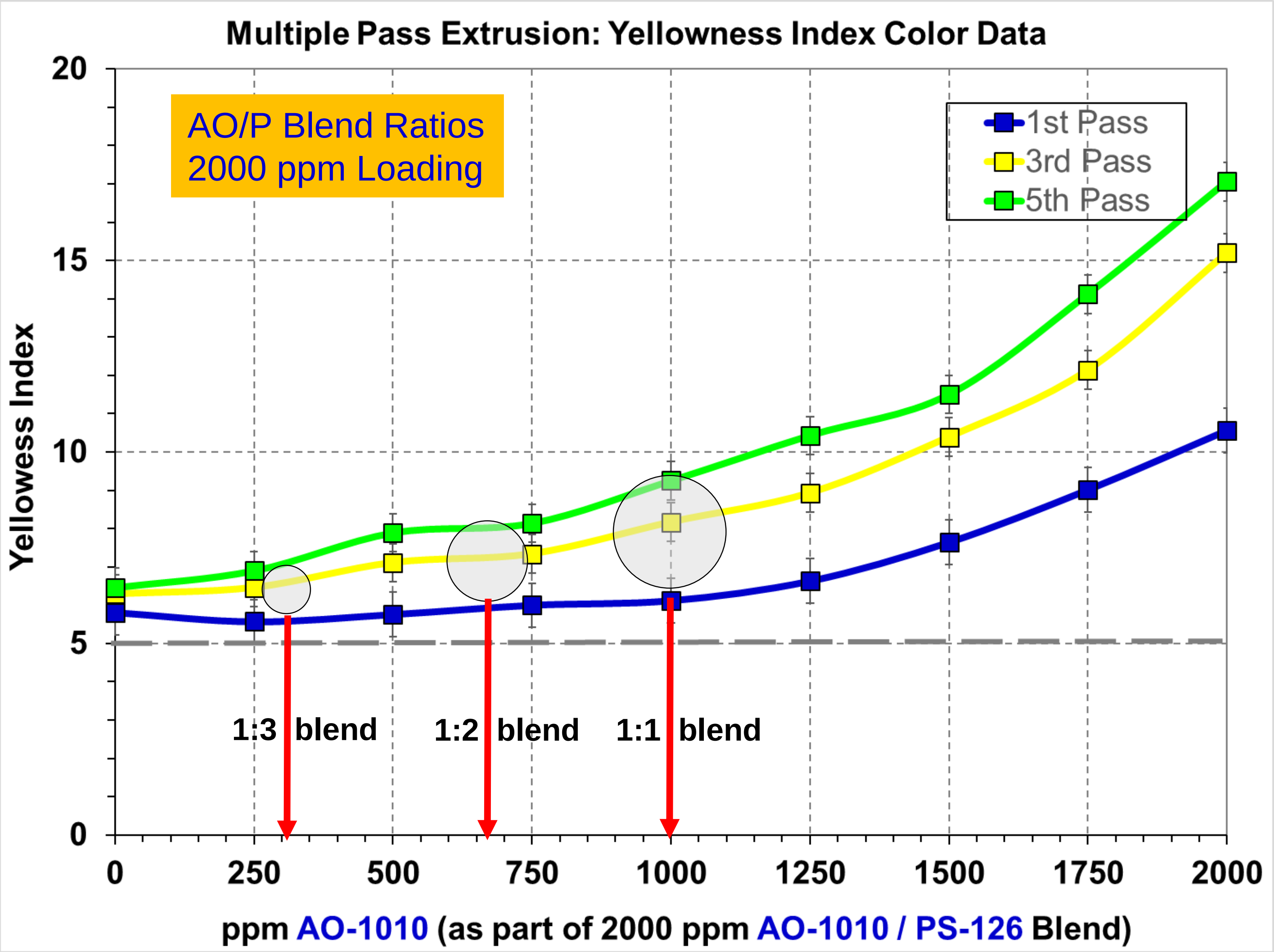

3.2 mm Plaques

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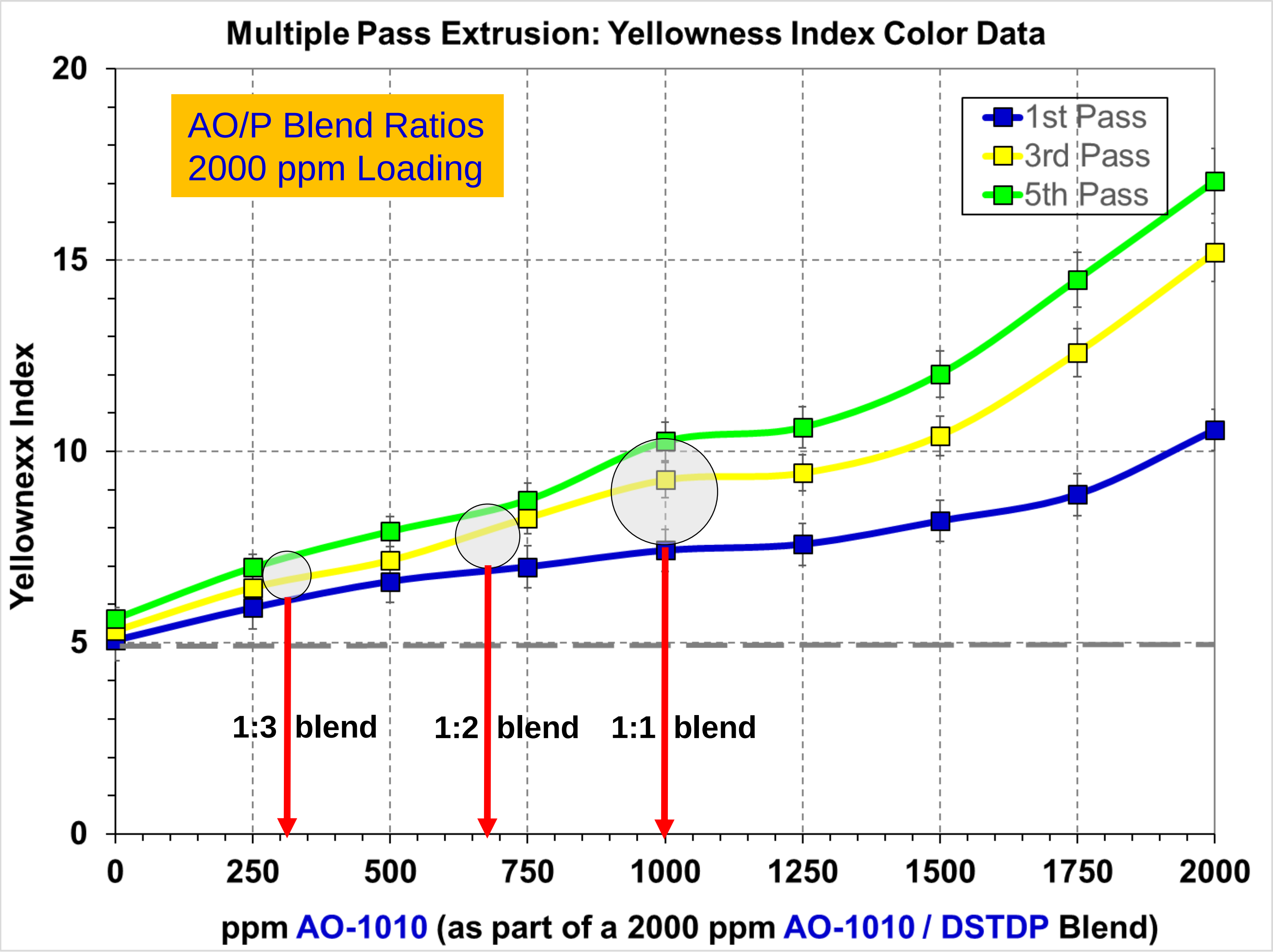


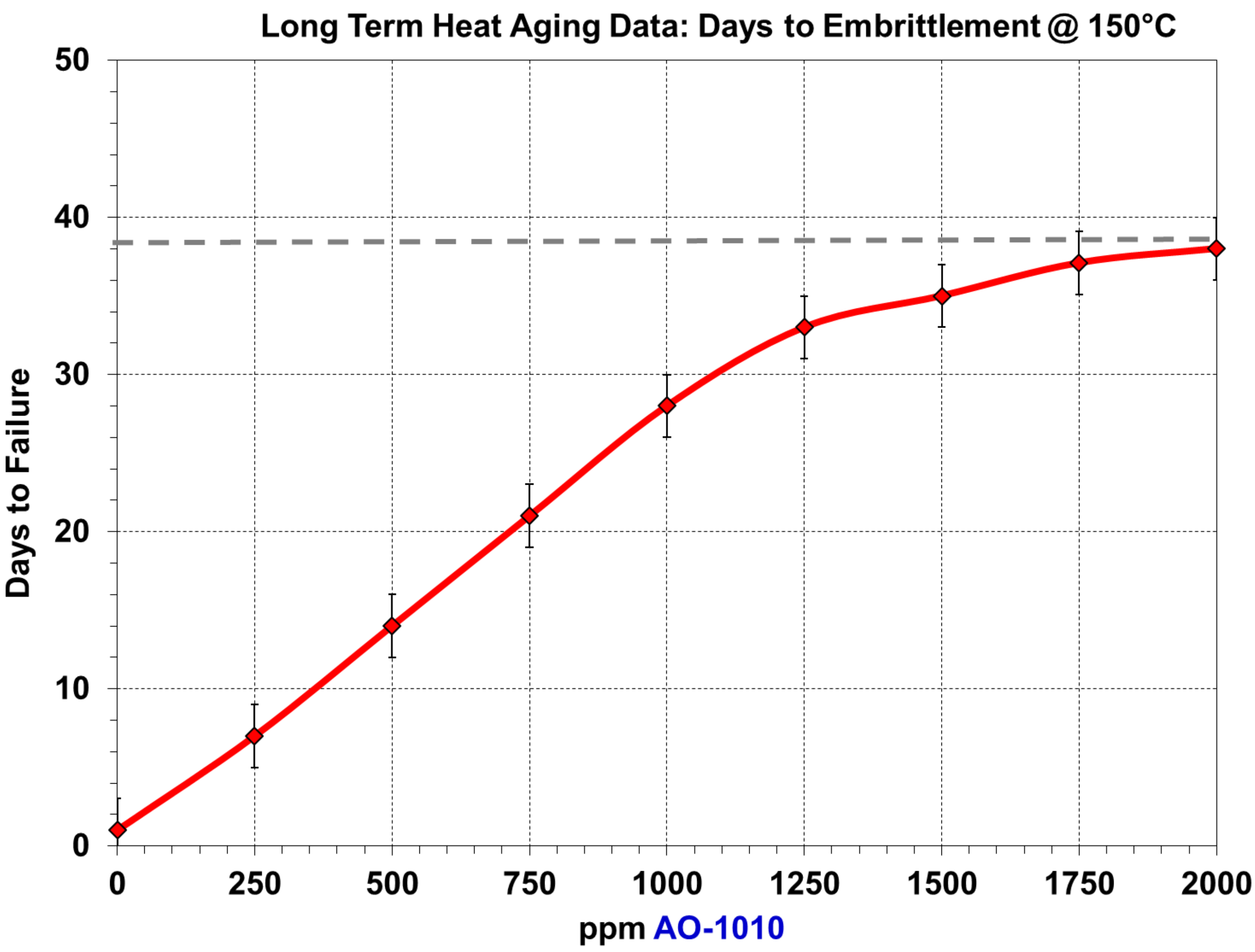
3.2 mm Plaques

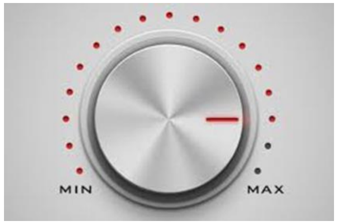
Optimization of Stabilization Systems
Molding Grade zn-PP Homopolymer

Long Term Oven Aging: Thermal Stability <u><</u>150°C

Optimization of Stabilization Systems for Polyolefins

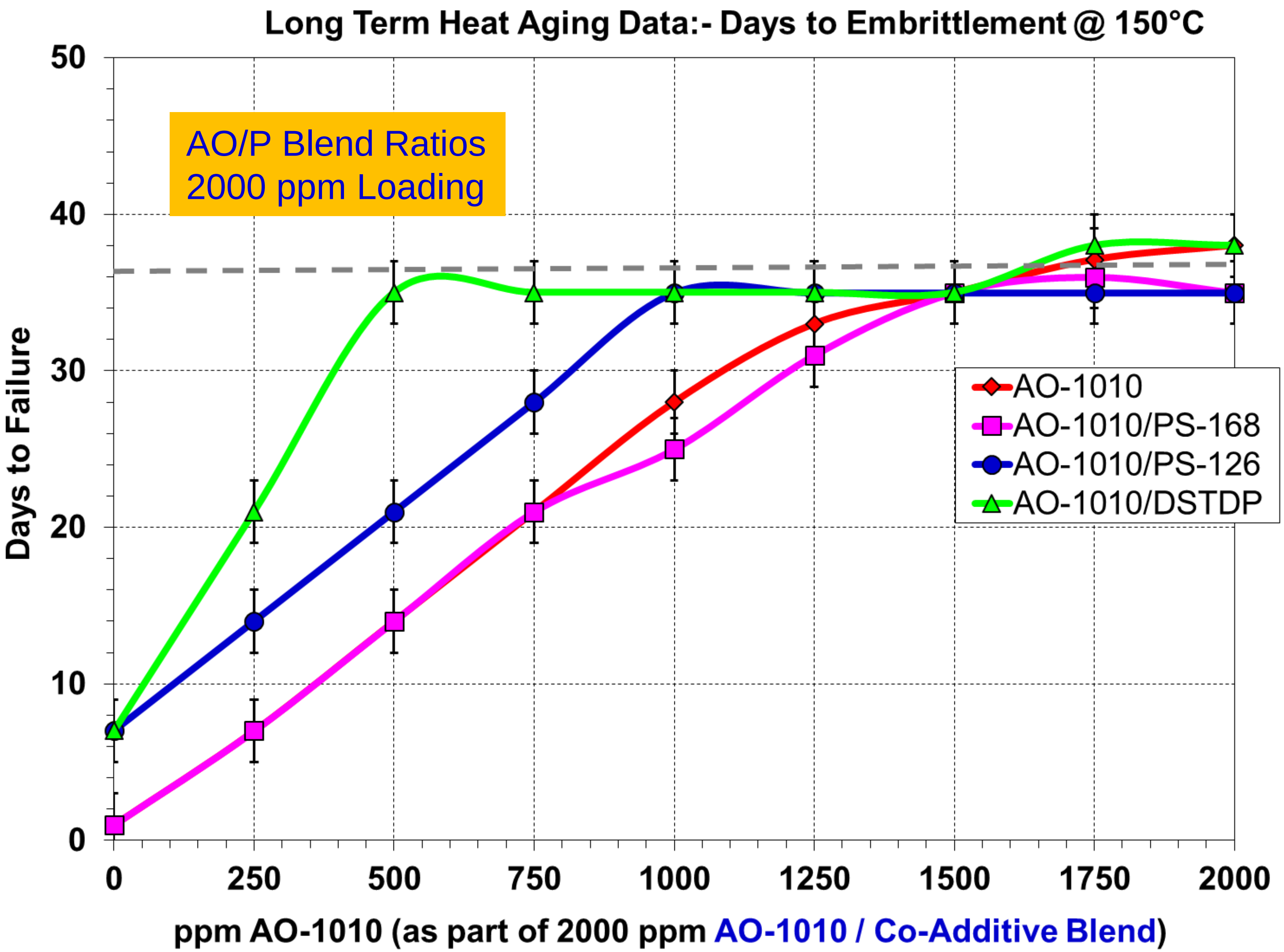
Measure 3: Long Term Heat Aging (Thermal Stability ≤150ºC)





Optimization of Stabilization Systems for Polyolefins

Measure 3: Long Term Heat Aging (Thermal Stability ≤150ºC)

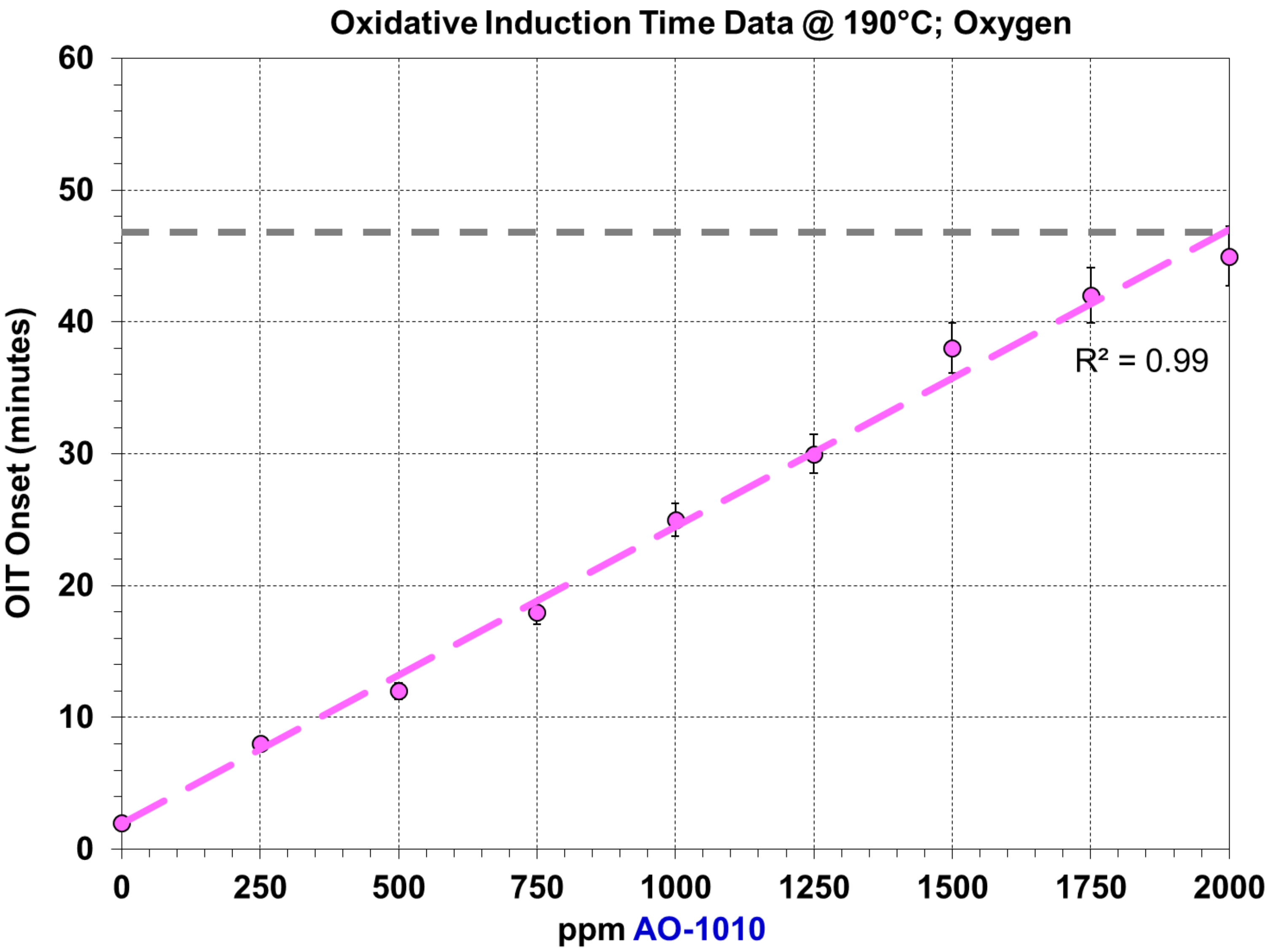


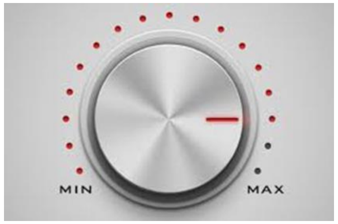
Optimization of Stabilization Systems
Molding Grade zn-PP Homopolymer

Oxidative Induction Time: Thermal Stability $\geq$190°C

Optimization of Stabilization Systems for Polyolefins

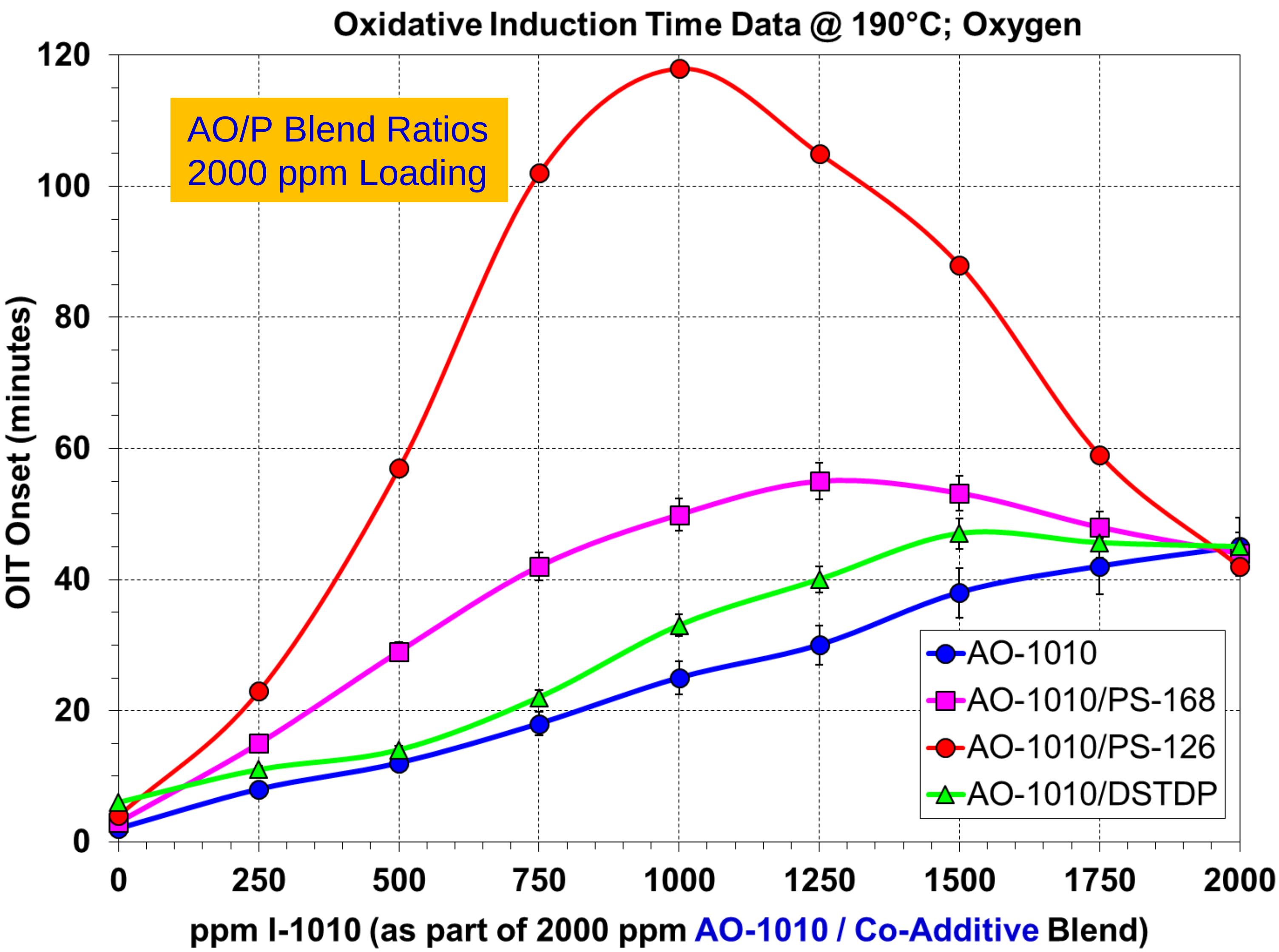
Measure 4: Oxidative Induction Time (Thermal Stability 190°C)





Optimization of Stabilization Systems for Polyolefins

Measure 4: Oxidative Induction Time (Thermal Stability 190°C)



Optimization of Stabilization Systems for Polyolefins
What did we learn ?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Multiple Pass Extrusion / Processing

- **Polymer Molecular Weight (MW) → Retention of Physical Properties**
  - Exposed to different forms of heat histories, polypropylene will undergo MW reduction (chain scission) in the absence of stabilizers, which will dramatically impair the processability, as well as the retention of physical properties
  - As shown in this work, there is a good dose response to stabilizing components (phenolic, phosphite) and more importantly phenolic/phosphite blends regarding:
    - Retention of MW during melt processing (above melt point of the polymer)
    - Retention of MW during oven aging (below melt point of the polymer)
- **Extrusion Color Maintenance → Retention of Aesthetic Appeal**
  - Polypropylene, in the absence of stabilizers, is relatively colorless, but it useless
  - Addition of stabilizing additives can increase color, but can be managed by finding the optimized ratio of phenolic AO & phosphite melt processing stabilizer.
- **Stabilization System Optimization → Delivering Value to Customers**
  - Phenolic AO / Phosphite loadings and blend ratios can be optimized to give the best balance of melt flow control, processability, retention of physical properties, color maintenance and long term thermal stability

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- **Your Attendance and Attention**

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