NOVA Chemicals
Polyethylene

Gas Fading Discoloration of Polyethylene Resins

Understanding the Influence of Additives

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Outline

Discoloration of Polyethylene Resins

- Sources of Discoloration
- Overview of Gas Fading

Gas Fading Case Studies

- Traditional Stabilization Systems
- Alternative Stabilization Systems – “Phenol-Free”

Discoloration of Polyethylene Resins

Sources and Mechanisms

Overview

It is widely accepted that the over-oxidation of phenolic antioxidants contributes most significantly to the discoloration of polyethylene

Oxidation during extrusion/processing

- Color formation observed immediately after extrusion

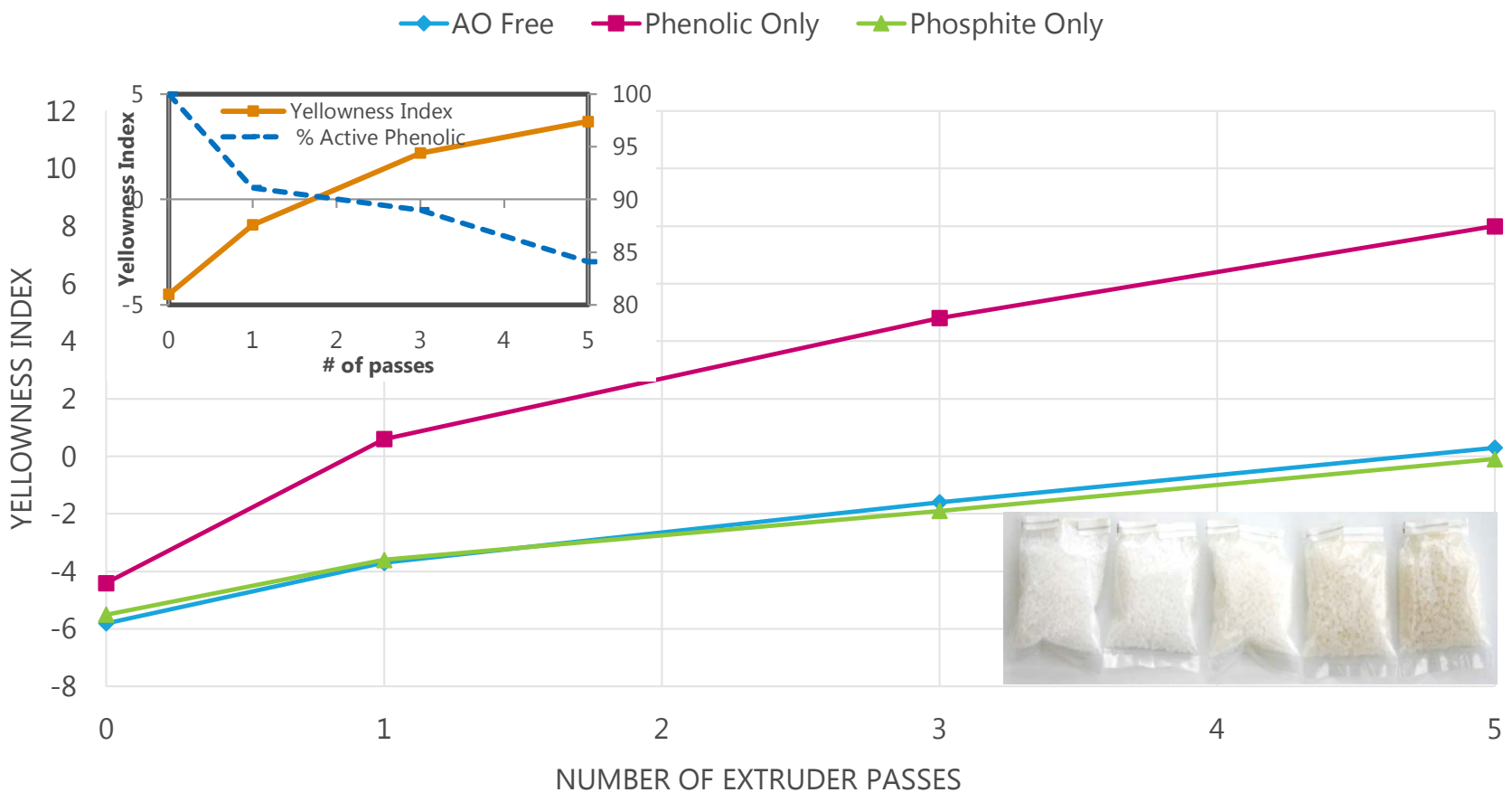
-1.4 YI → 73 YI

Oxidation via gas fading

- Color formation during storage (occurs over days or weeks)
- Reaction of phenolic antioxidant with NOx gases

Phenolic Oxidation

Phenolic antioxidants are oxidized in the process of stabilizing the polymer during extrusion and process



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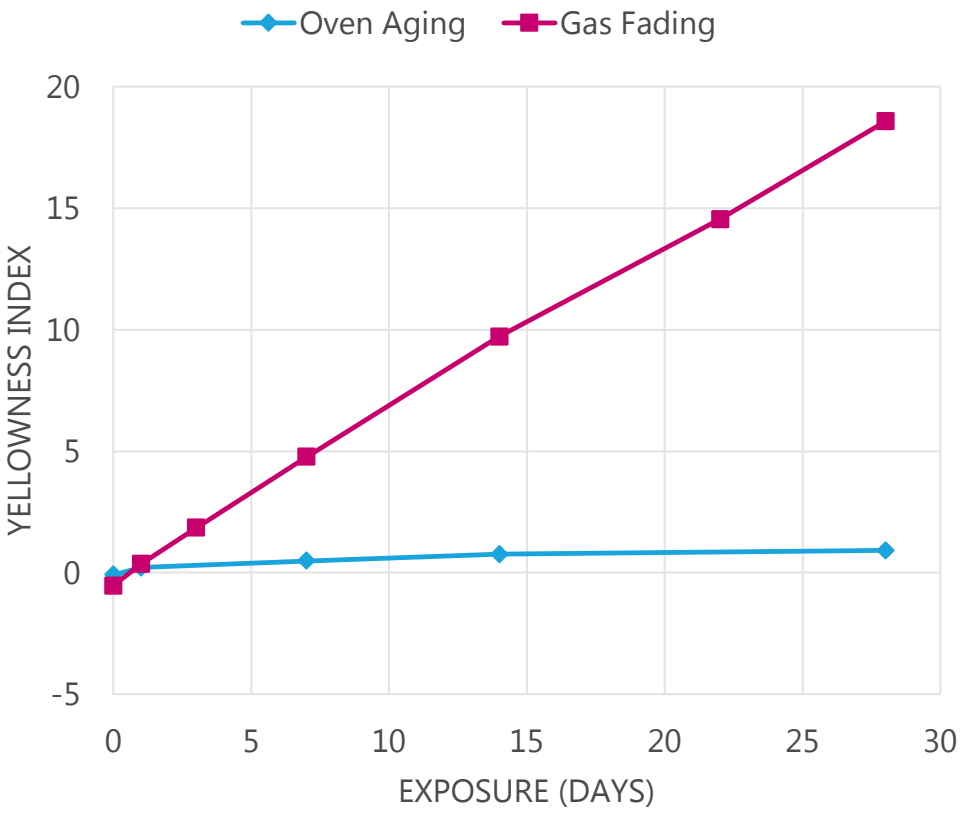
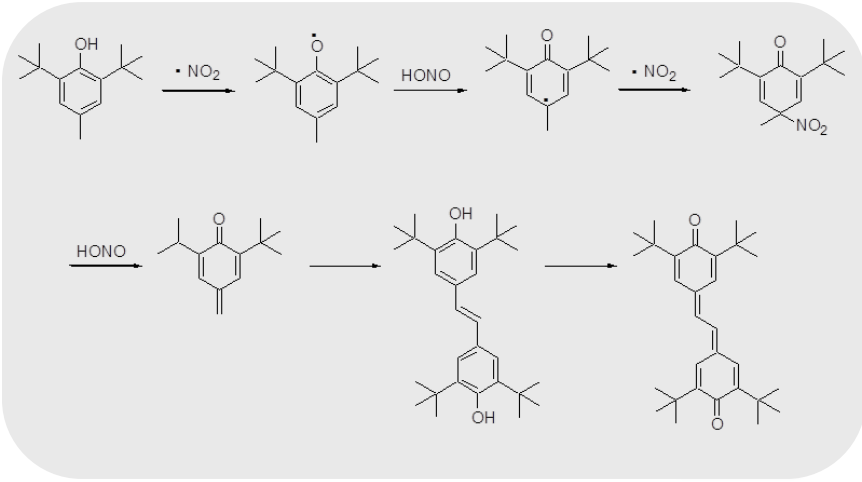
Gas Fading

Phenolic antioxidants are oxidized via the interaction with atmospheric pollutants (NOx gases) to form colored species





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Nitrogen Oxides

Nitrogen oxides (NOx) consist mainly of nitric oxide (NO) and nitrogen dioxide (NO_2)

Nitrogen oxide is readily converted to nitrogen dioxide in air;

$$2\ NO\ (\text{colorless}) + O_2 \rightarrow 2\ \mathbf{NO_2}\ (\text{reddish-brown})$$

NO_2 is a strong oxidant which can promote the oxidation of phenolic antioxidants and generate colored species even at very low concentrations

Sources:

- ***Gas/propane powered appliances/equipment (i.e. forklifts)***
- ***Automobile exhaust***
- *Cigarette smoke*
- *Space heaters*

Concentrations in winter often exceed summer levels by 1.5 - 2 times

- *Increased use of heating, lower ventilation rates, and higher outdoor concentrations*
- *Typical indoor concentrations range from **0.01 - 0.03** ppm*
- *When propane fueled equipment is in use concentrations can increase to **0.2 - 0.3** ppm*

Jarvis DJ, Adamkiewicz G, Heroux ME, et al. Nitrogen dioxide. In WHO Guidelines for Indoor Air Quality: Selected Pollutants. Geneva: World Health Organization; 2010. 5.

Factors That Affect Gas Fading

Resin Properties
- Density
- Film/part thickness

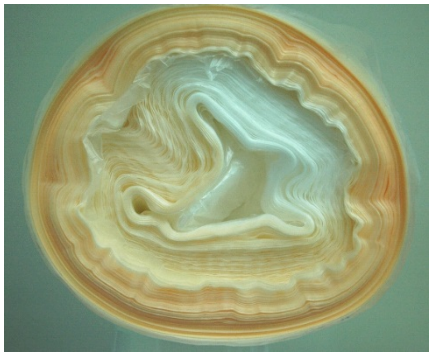
Storage Conditions
- Use of Overwrap
- Contact with Lignin/Cardboard

Additives
- Antioxidant selection
- Ratios
- Antagonistic Interactions

Gas Fading

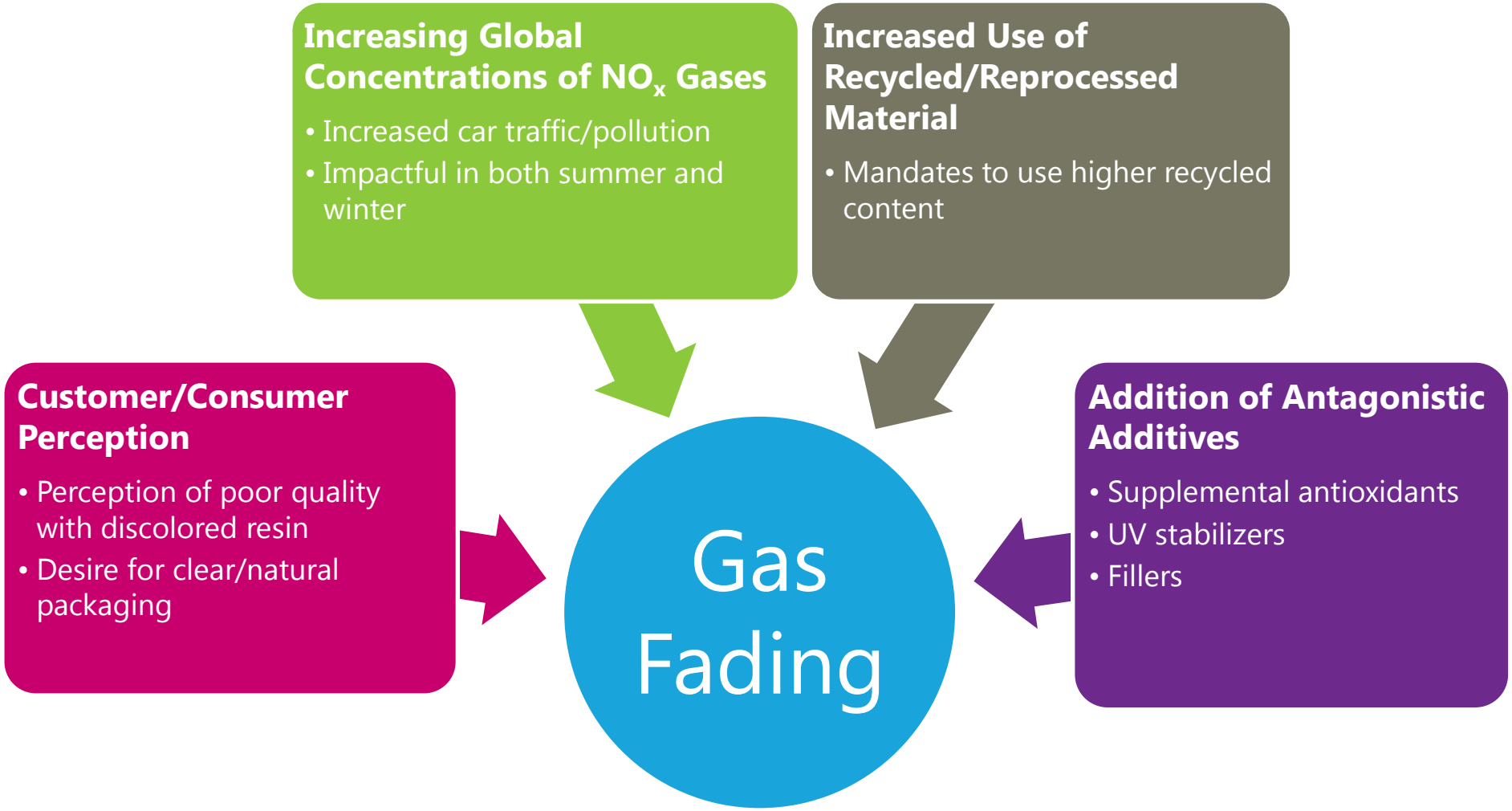
Atmospheric Pollutants (NOx)
- Forklift exhaust
- Automotive exhausts
- Ventilation
- Heating units

Processing Conditions
- Temperature
- Pressure
- Use of Regrind



Gas Fading of Polyethylene Resins

Why is this important to you?



Traditional Stabilization Systems

Combinations of Phenolic and Phosphite Antioxidants

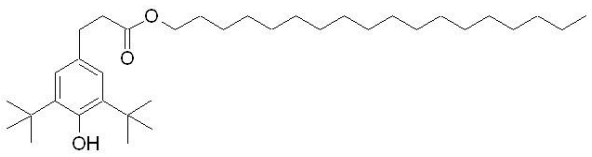
Traditional Antioxidants

Primary and secondary antioxidants protect the polymer in different ways and often work together synergistically

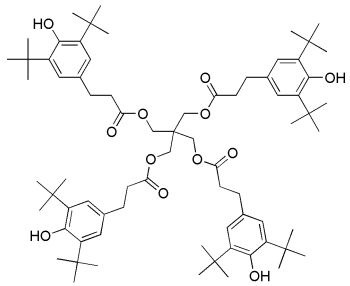
Primary antioxidants (phenolics): quench radicals by donating H·

$ROO\cdot + PhOH \rightarrow ROOH + PhO\cdot$ or

$RO\cdot + PhOH \rightarrow ROH + PhO\cdot$



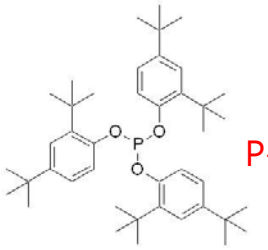
AO-1



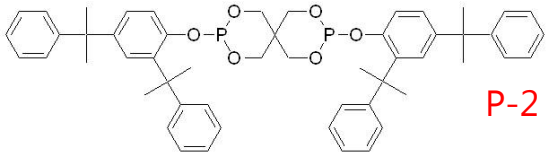
AO-2

Secondary antioxidants (phosphites): decompose hydroperoxides before they dissociate into free radicals, prevents the unnecessary consumption of the phenolic antioxidant

$ROOH + P(OR)_3 \rightarrow O{=}P(OR)_3 + ROH$



P-1



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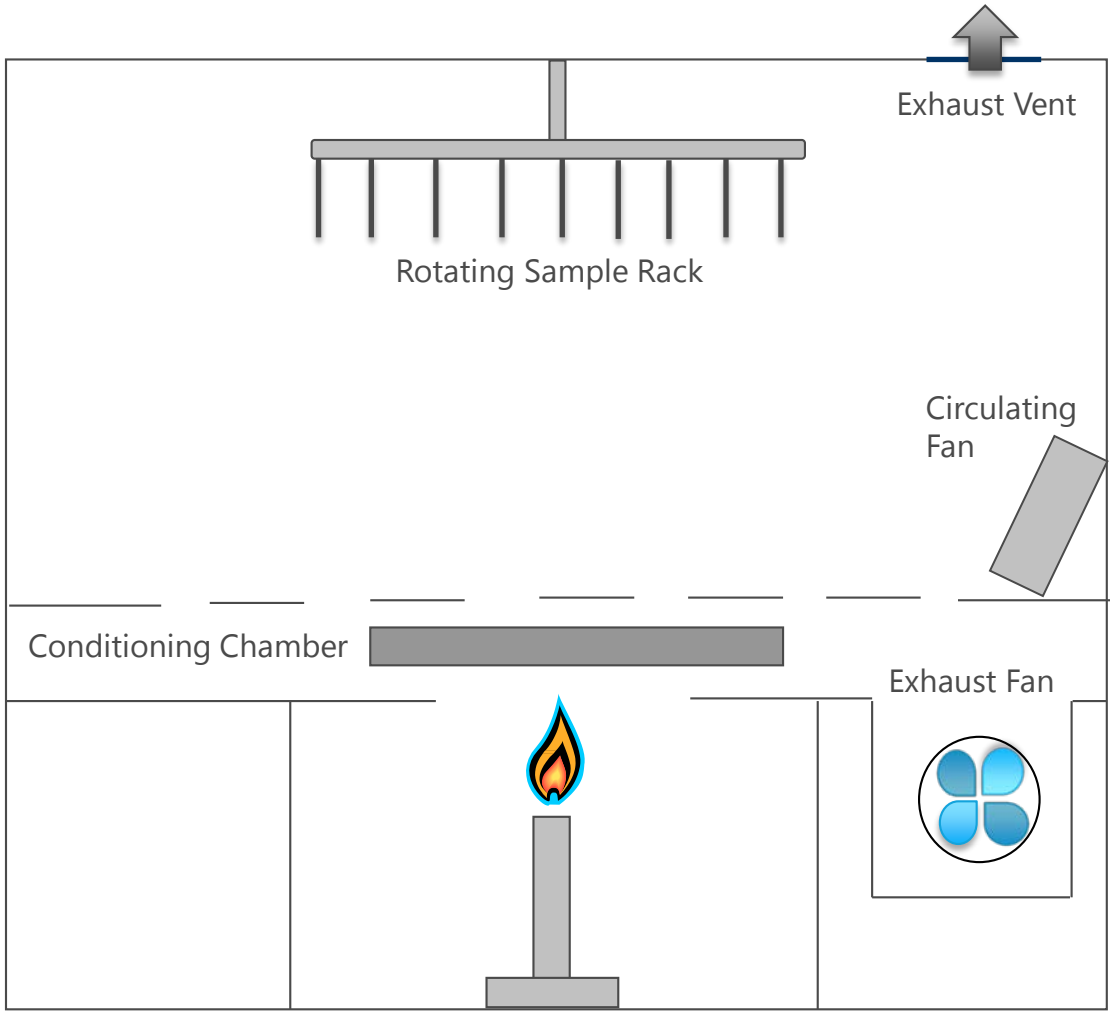
Gas Fading Exposure Studies

Atmospheric Fume Chamber

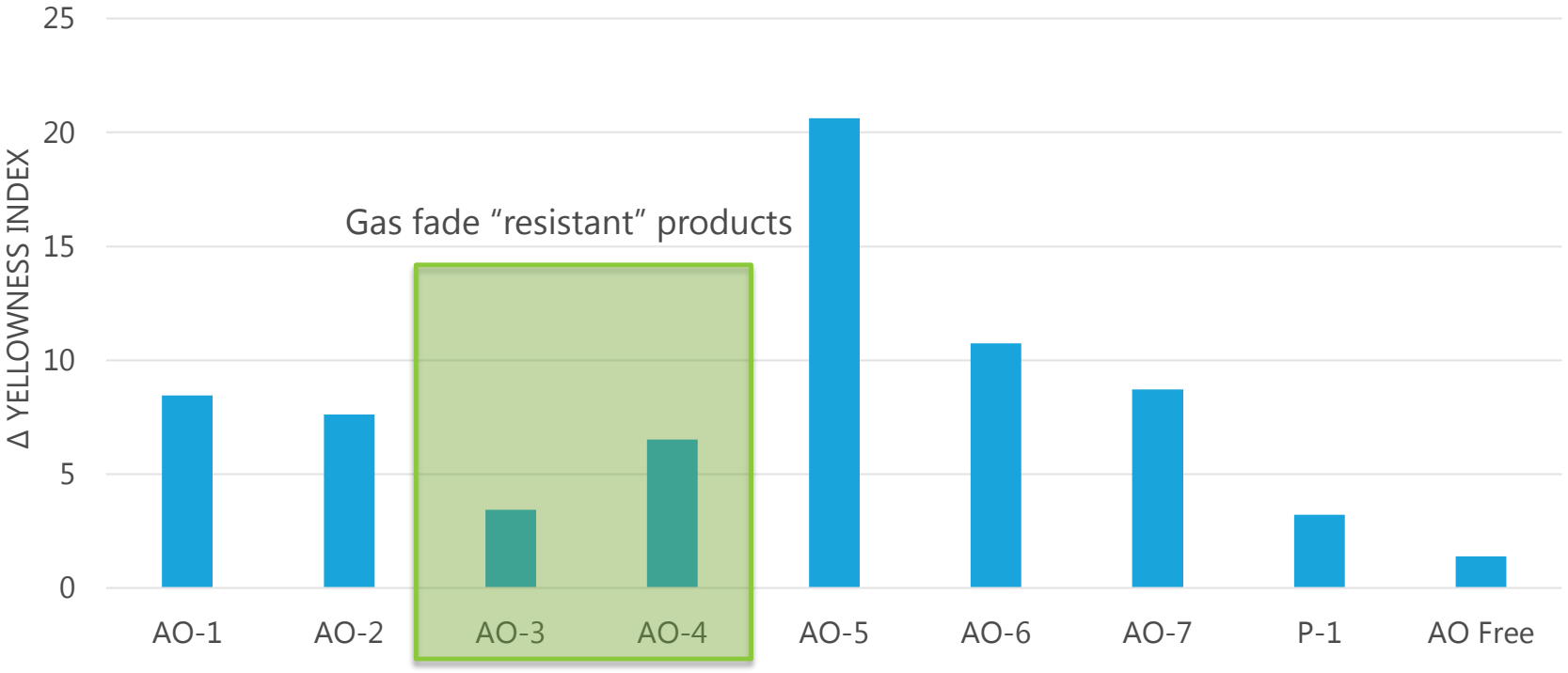
Specifications	
Manufacturer	Instrument Mktg. Svcs.
Model	8727ES
Gas Type	Natural Gas
Temp Control	Yes (140° F); Exhaust vent
Rack	8 tine; 5 RPM
Max Capacity	48 color plaques
NO_x gases w/i fume chamber	~2-3 ppm



Gas Fading Performance of Primary Antioxidants

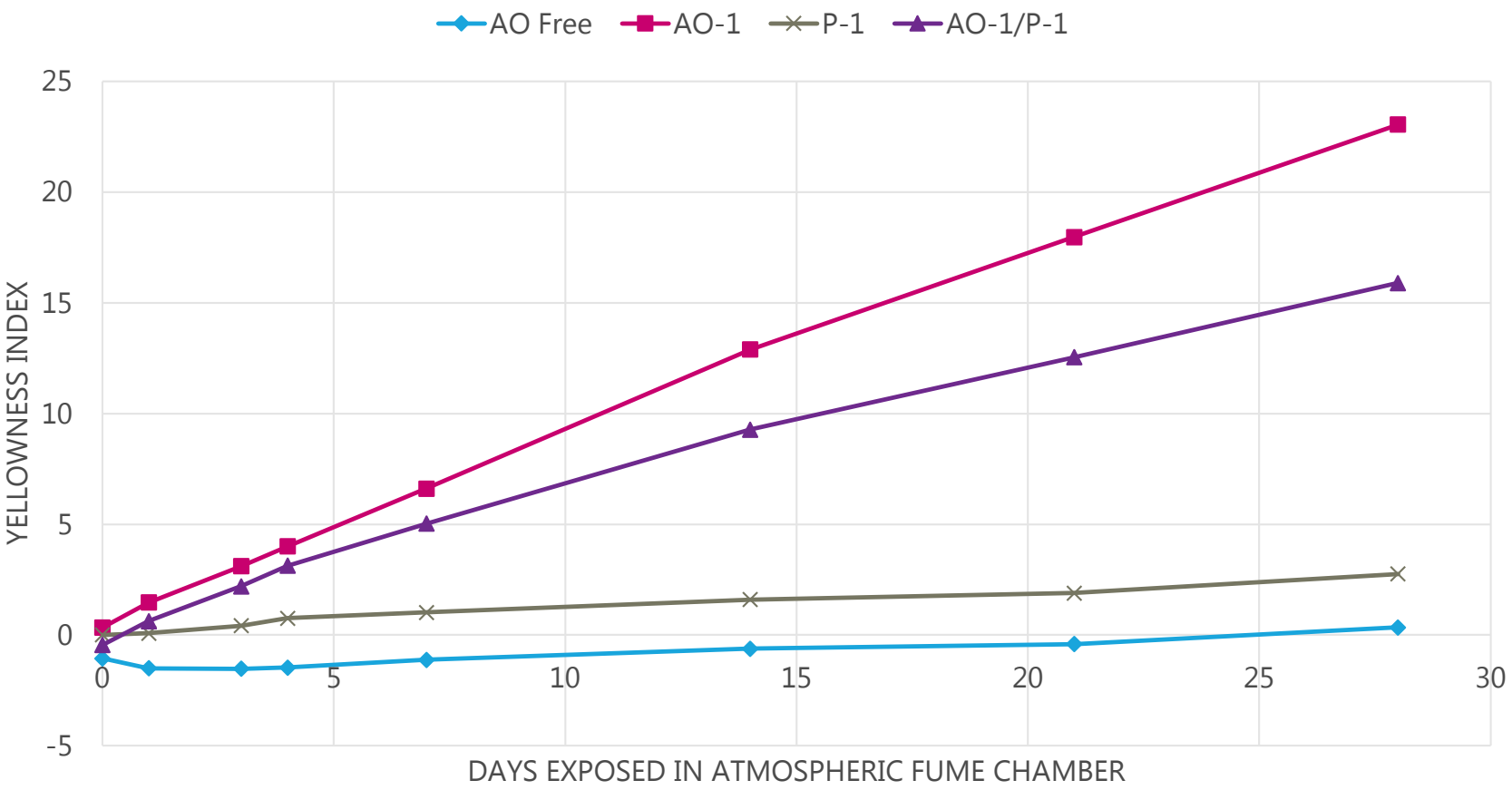
All phenolic antioxidants are susceptible to gas fading

Change in yellowness index after 28 days exposure to atmospheric fume chamber



Synergistic Interactions
Phosphite Antioxidants

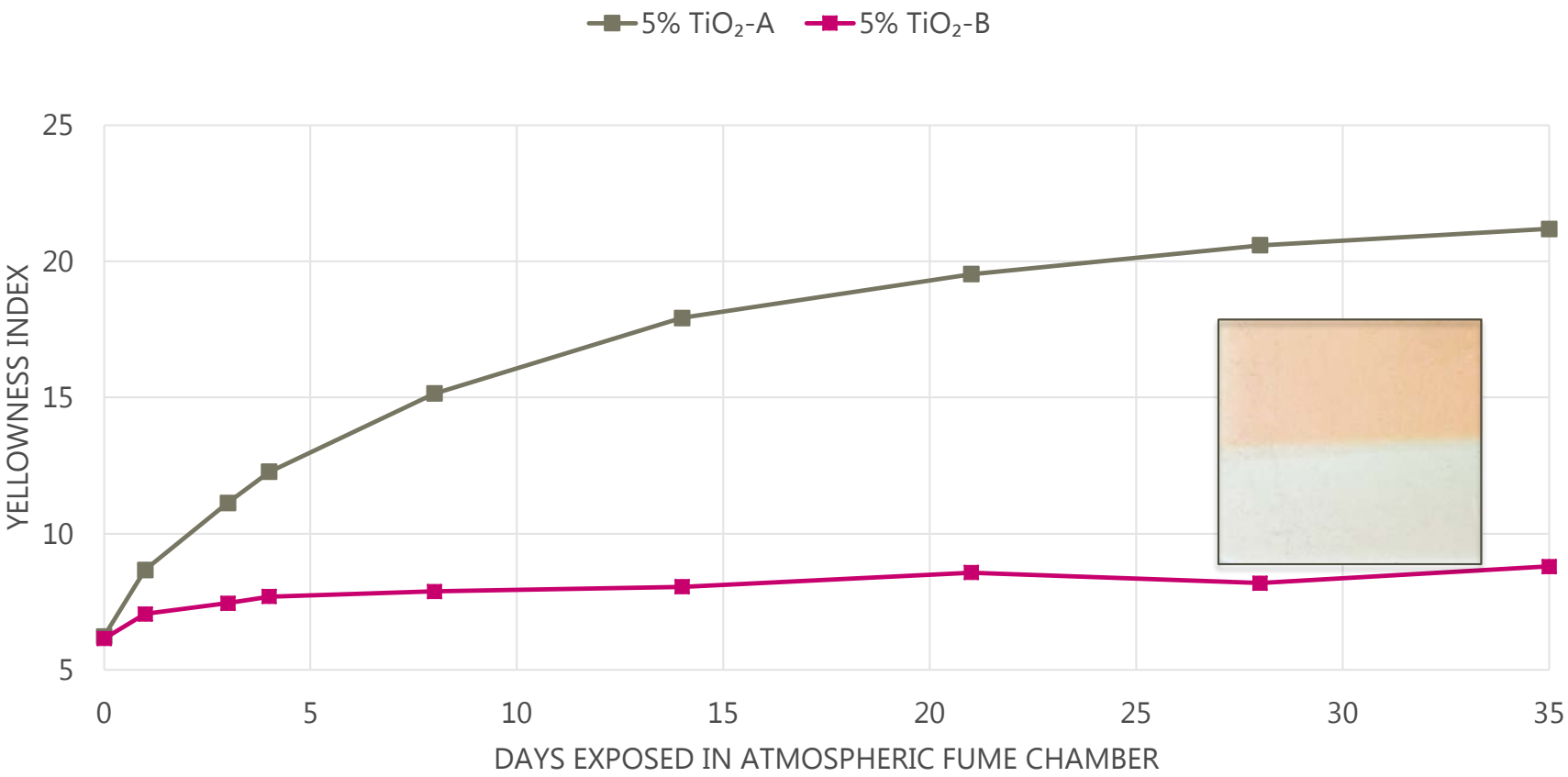
Phosphite antioxidants help to protect the phenolic antioxidant and can reduce the severity of gas fading discoloration



Antagonistic Interactions
TiO_2

The surface chemistry of TiO_2 is known to promote oxidation of phenolic antioxidants and can accelerate color formation via gas fading

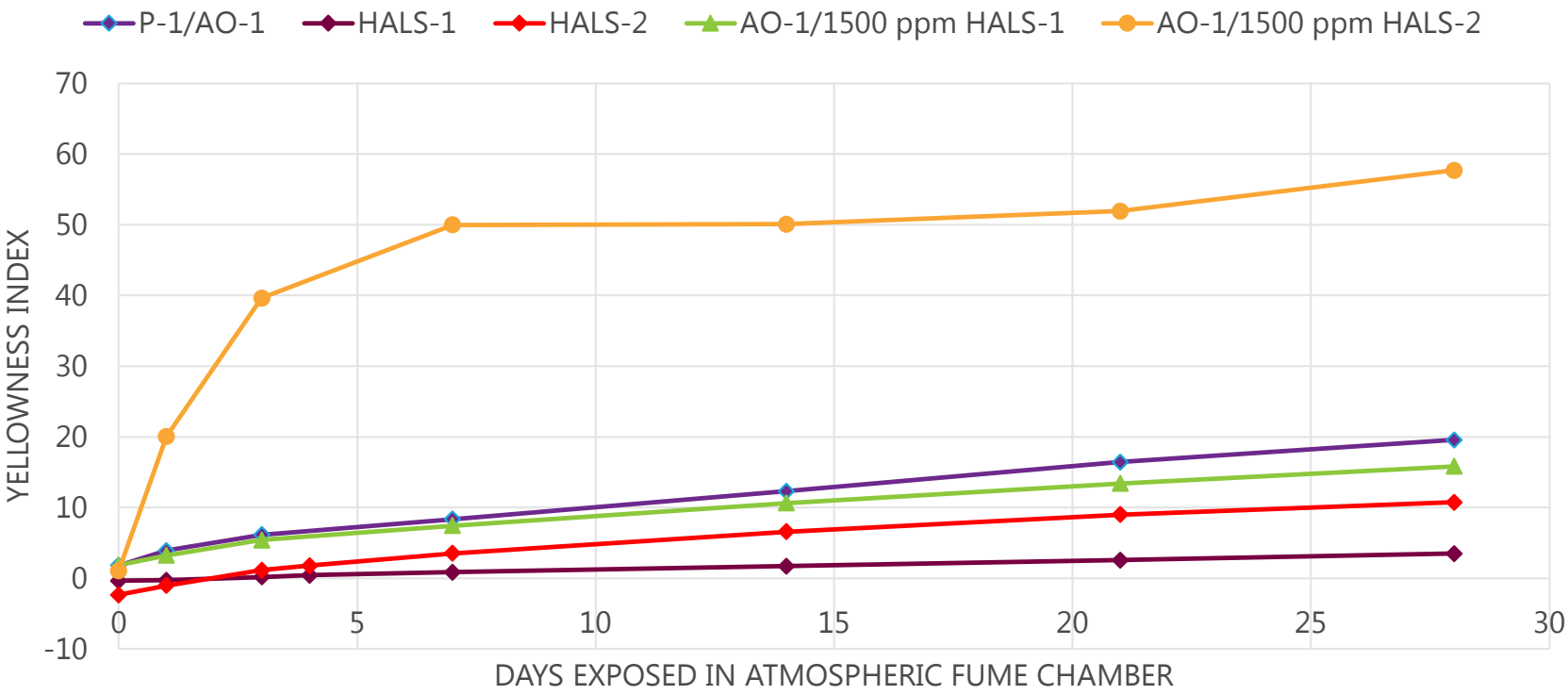
TiO_2-A and TiO_2-B are commercial varieties of TiO_2 with different surface coatings



Antagonistic Interactions
Hindered Amine Light Stabilizers (HALS)

The alkalinity and reactivity of select HALS can exacerbate the gas fading phenomenon in the presence of phenolics

HALS-1 is an N-H variety and is highly alkaline (pKa = 9.5)
HALS-2 is an N-R variety and has a lower alkalinity (pKa = 6.5)



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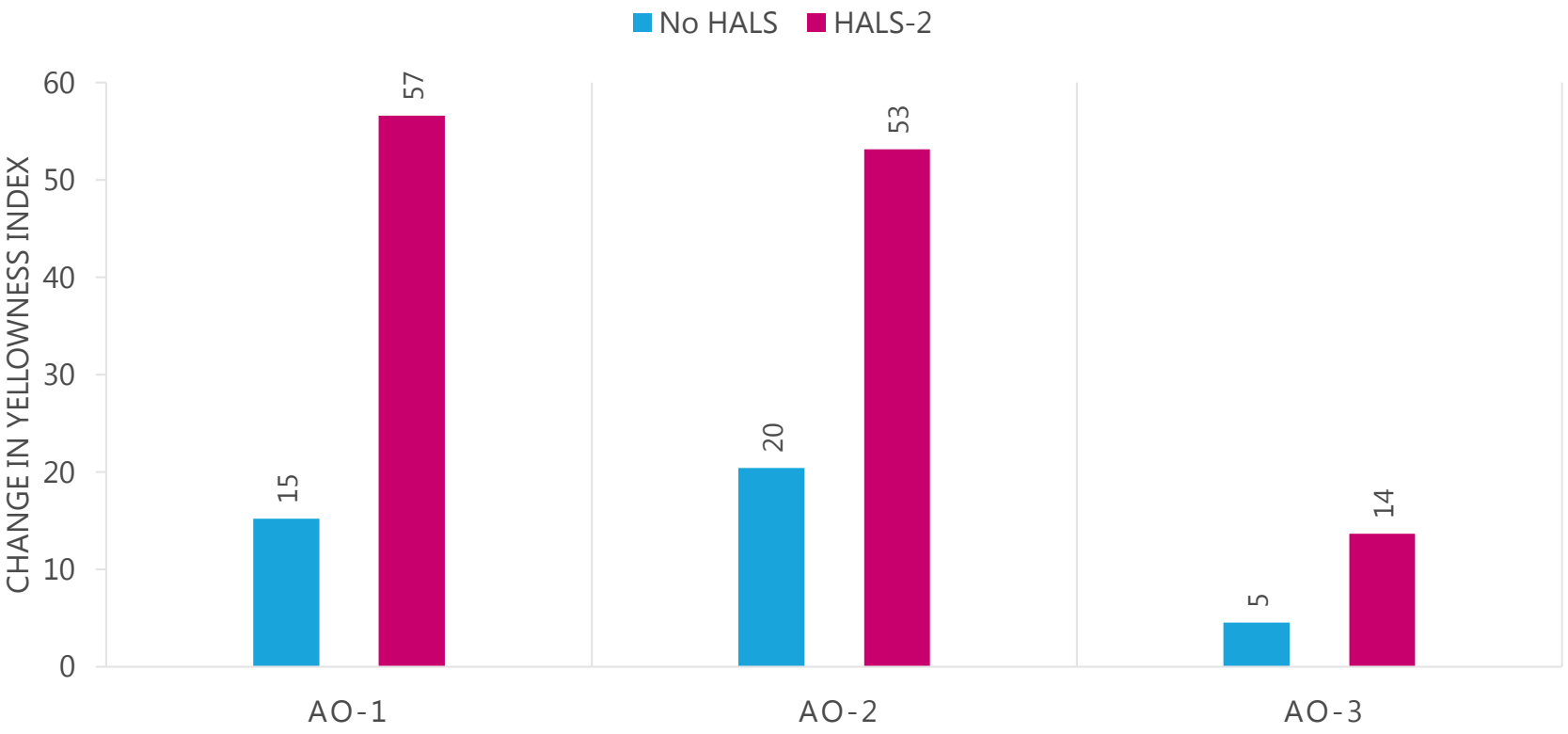
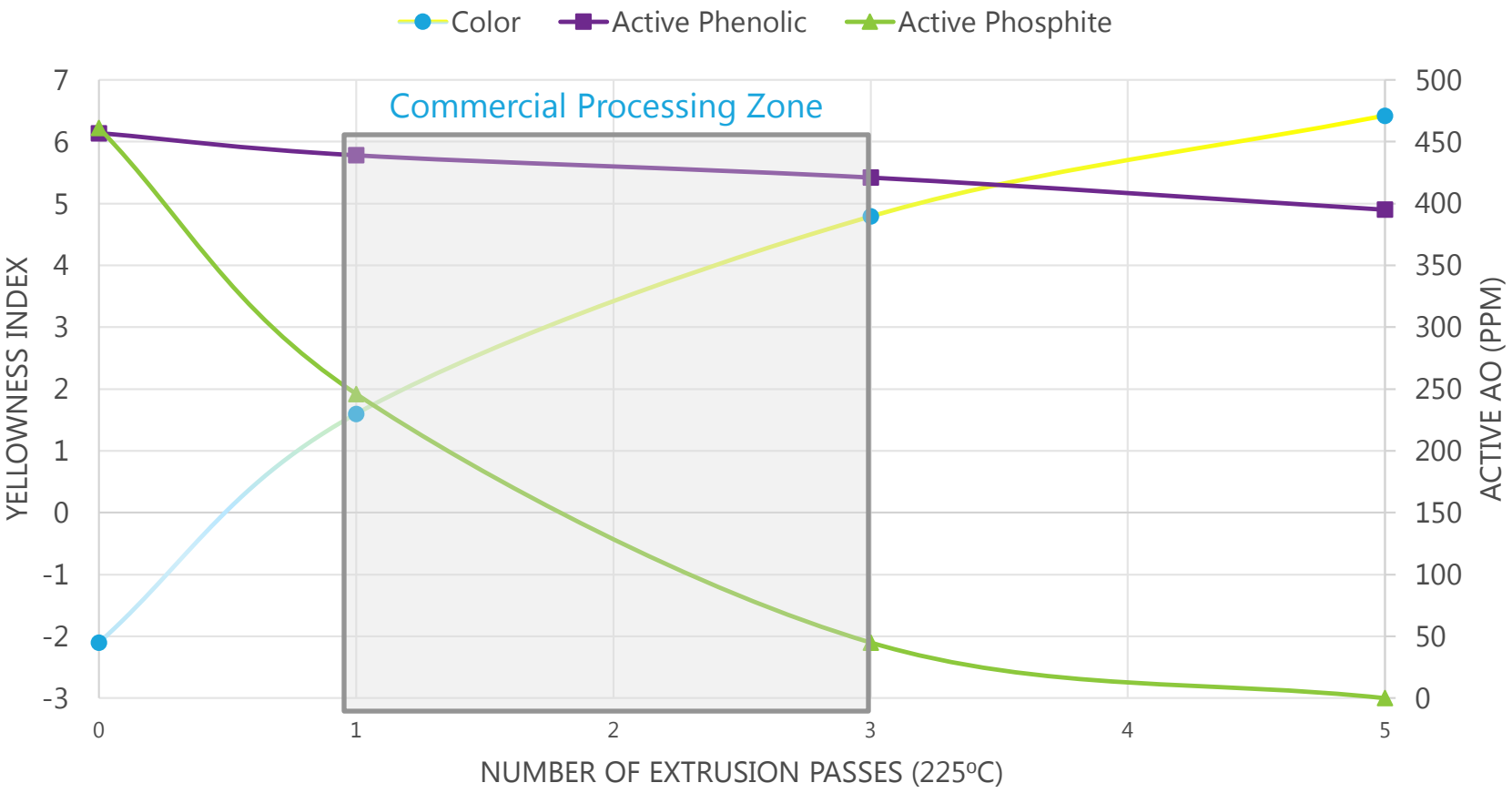
Comparison of Phenolics

Some phenolic antioxidants are less impacted by these antagonistic interactions



Multiple Pass Extrusion

During the extrusion process, antioxidants are sacrificially consumed in the process of protecting the properties of the resin



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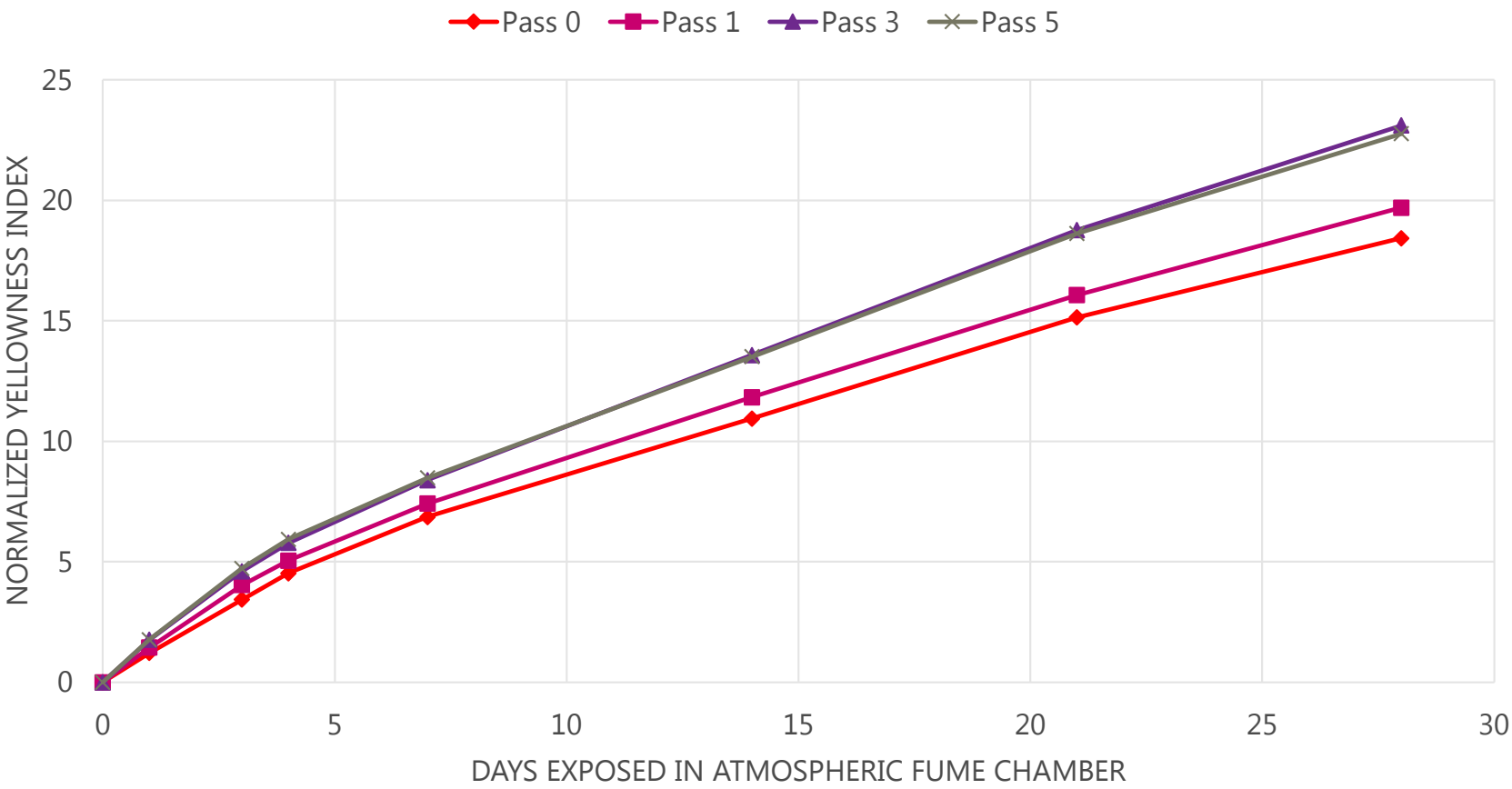
Effect of Extrusion on Gas Fading Severity

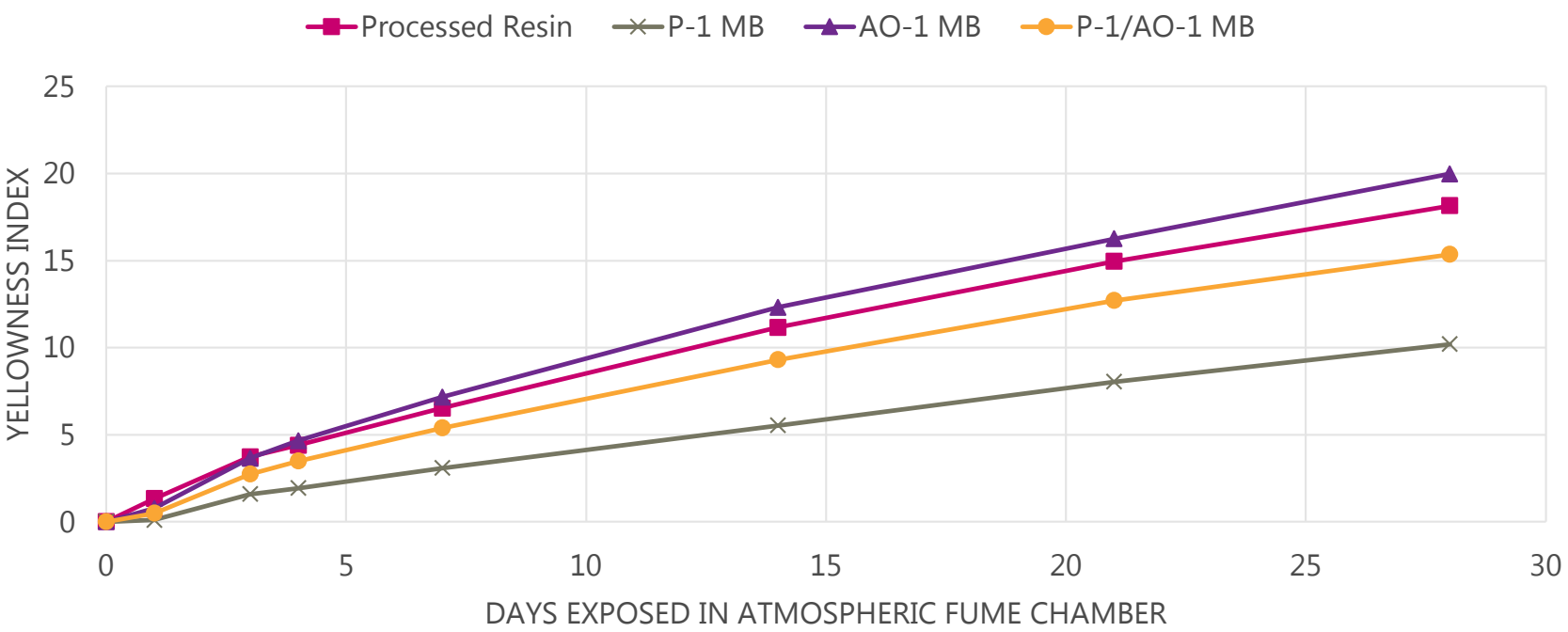
Successive extrusion of resin (and the consequent consumption of phenolic antioxidant) has minimal impact on the rate and severity of gas fading discoloration



Addition of Stabilizer Masterbatch

The addition of a stabilizer masterbatch can have a significant effect on the severity of gas fading

Processed resin	– 1:1 ratio of phenolic/phosphite (~20% active phosphite remaining)
P-1 MB	– 1:3 ratio of phenolic/phosphite (~75% active phosphite remaining)
AO-1 MB	– 3:1 ratio of phenolic/phosphite (~60% active phosphite remaining)
P-1/AO-1 MB	– 1:1 ratio of phenolic/phosphite (~75% active phosphite remaining)



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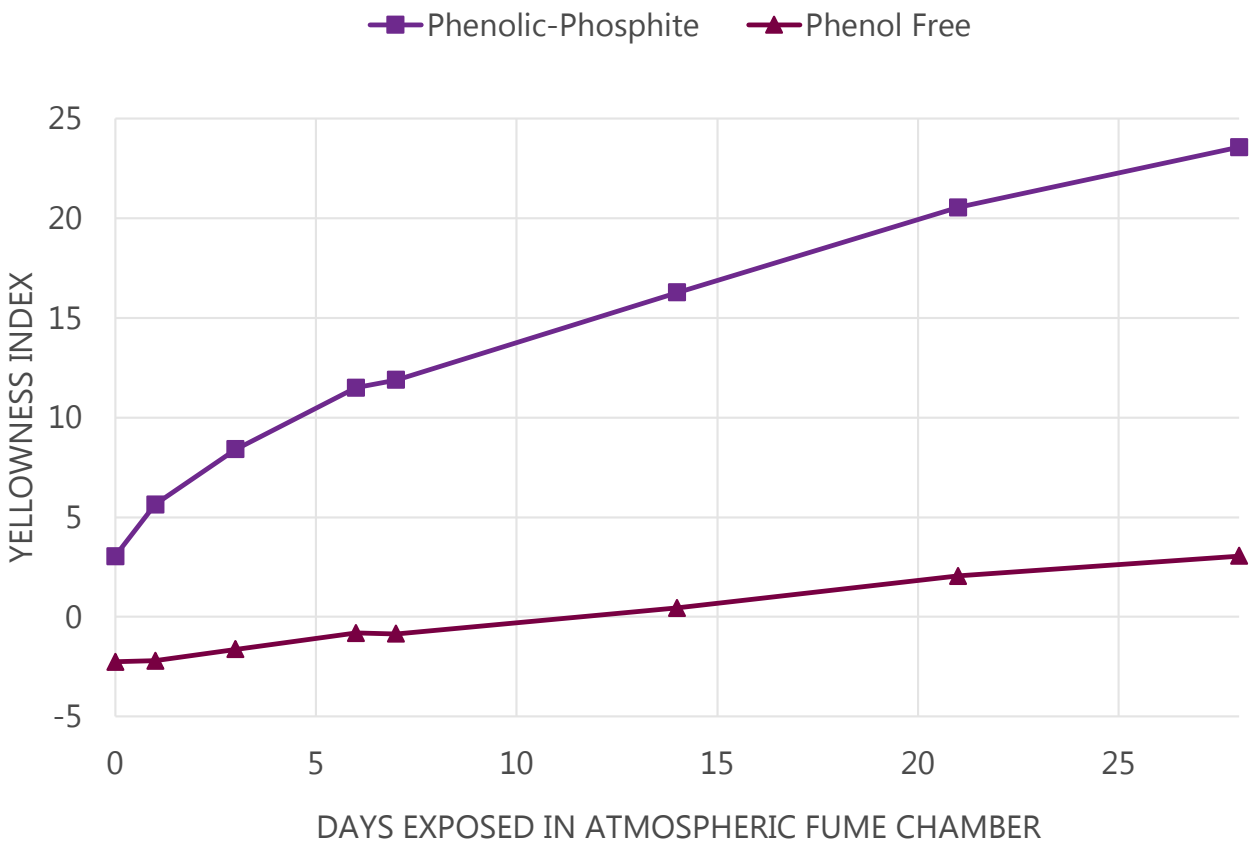
“Phenol-Free” Stabilization Systems

Phenol-free additive packages provide best in class color performance

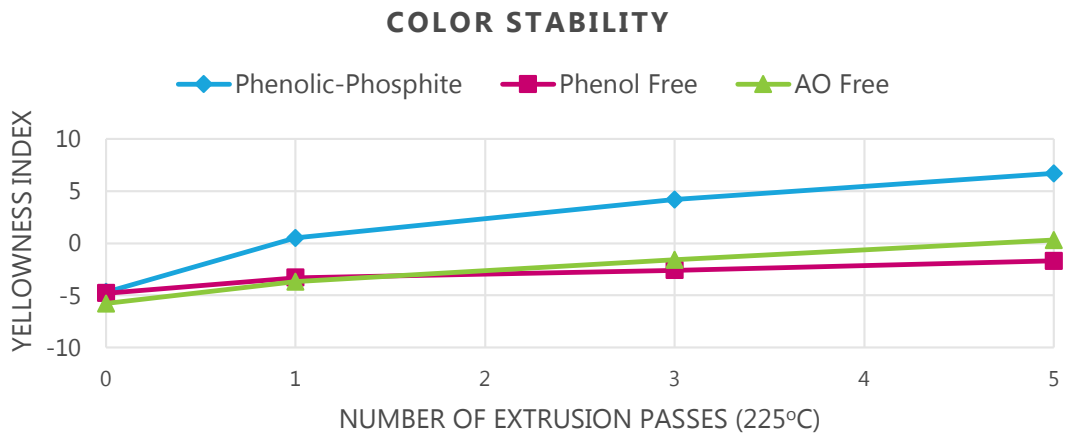


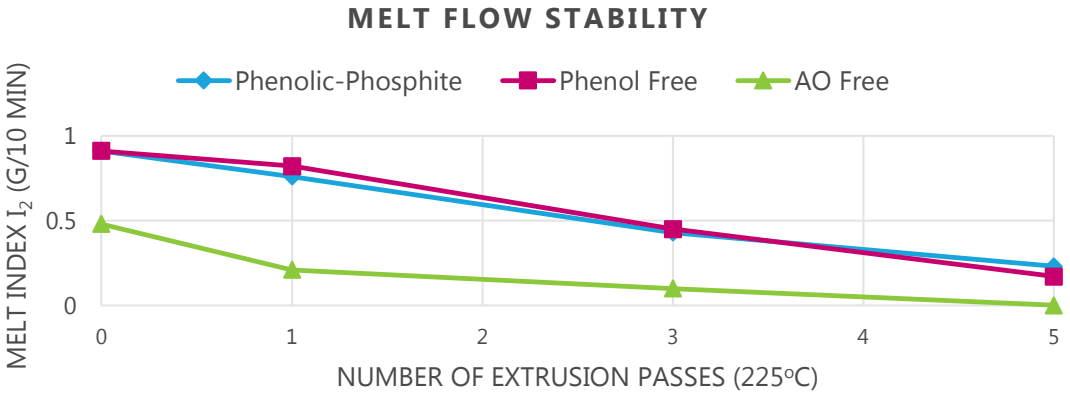
“Phenol-Free” Stabilization Systems

The most effective strategy to prevent discoloration associated with gas fading is to remove the phenolic antioxidant from the stabilization system

In addition to providing excellent gas fading resistance;

- Excellent color stability during extrusion
- Equivalent melt flow stability to conventional phenolic/ phosphite formulations





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Conclusions and Recommendations

Considerations for controlling gas fading in polyethylene

1. Antagonistic interactions with other additives can accelerate the rate and severity of gas fading
   - Important to select appropriate co-additives to mitigate these interactions
2. Phosphites work synergistically with phenolics to reduce the effect of gas fading
   - The ratio of phosphite/phenolic should be considered if gas fading is a persistent issue
3. Excessive degradation of the antioxidants (or use of reprocessed material) has minimal impact on the rate and severity of gas fading
   - The addition of an AO masterbatch can have an impact on the severity of gas fading
4. All phenolic antioxidants are susceptible to color formation and gas fading
   - Different chemistries can control the rate and severity of this reaction
5. The use of “non-traditional” stabilization packages without a phenolic antioxidant can substantially reduce (or even eliminate) discoloration associated with gas fading

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