STRATEGIES TO REDUCE BLOOM, EXUDATION, AND MIGRATION OF ADDITIVES FROM POLYOLEFINS

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Stabilizers Effect Many Properties

- Stabilizers are widely used in PE film applications to maintain properties for a variety of applications

- Melt process stability, maintenance of MW
- Initial color and maintenance of color
- Reduction of gels during film processing
- Maintenance of mechanical and physical properties during long term heat aging

- Gas fade – NOx aging
- **Plate-out during processing or post processing bloom/exudation/migration**
- Organoleptics and consumer exposure
- Safety and environmental issues
- FDA Food Contact Clearances
- Cost

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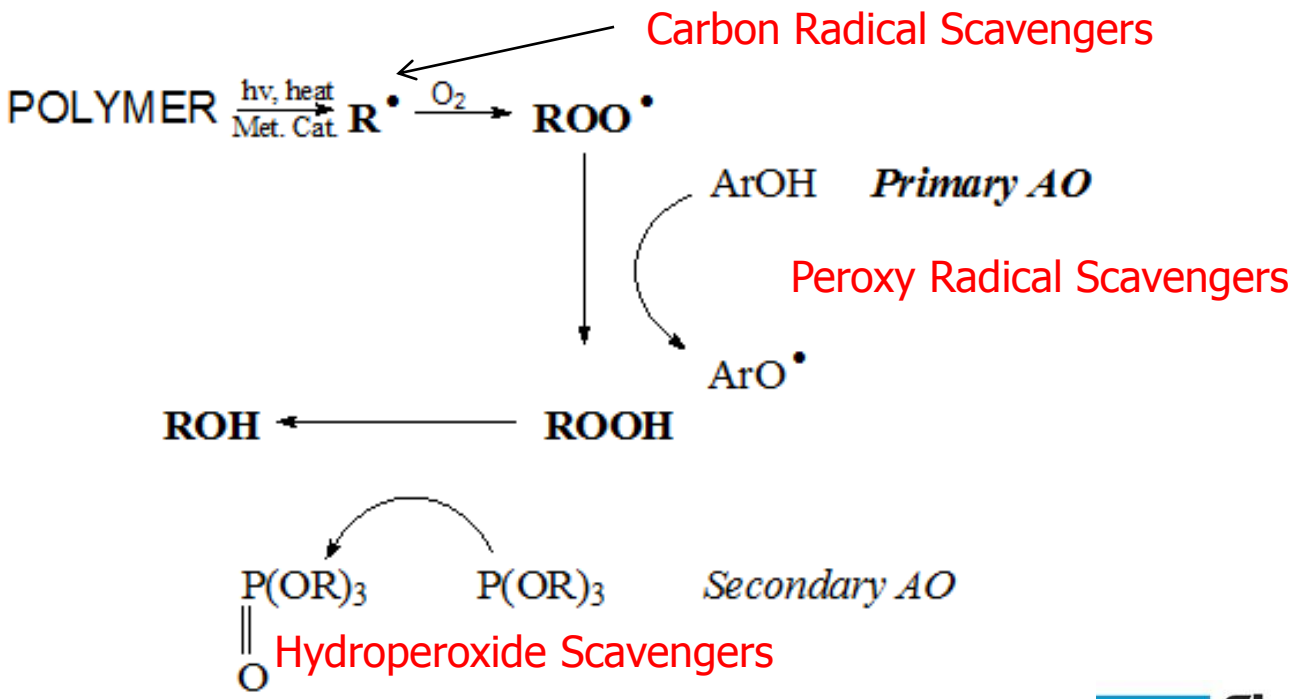
Polyolefin Stabilizers

- Most polyolefin stabilizer packages include a primary antioxidant (such as a hindered phenolic) and a secondary antioxidant (usually an organophosphite)



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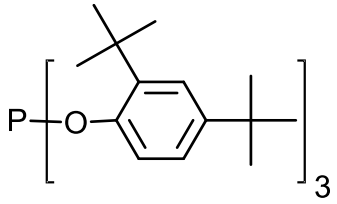
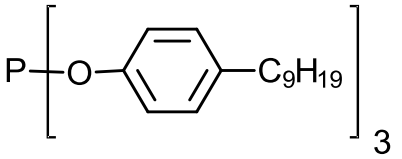
Polyolefin Stabilizers

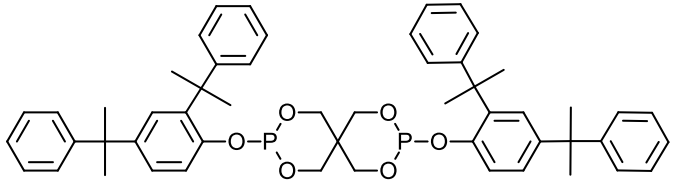
Common Phosphites



SP-1



TNPP



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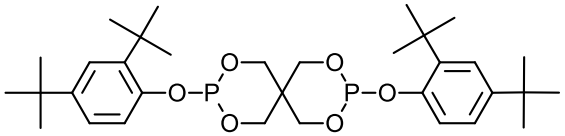
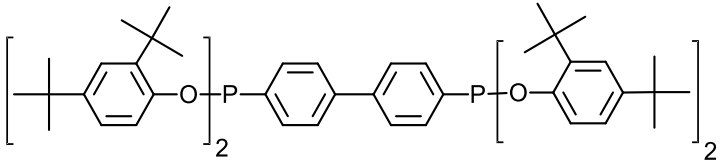
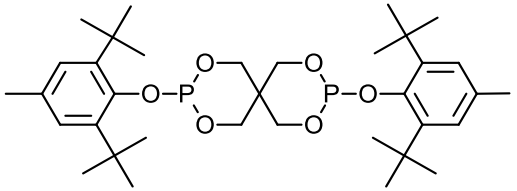


SP-3

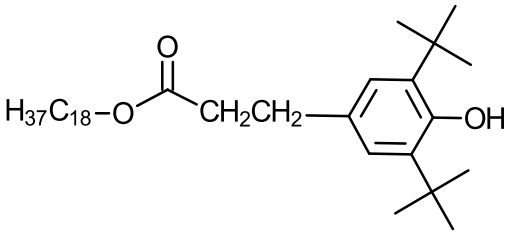


SP-4

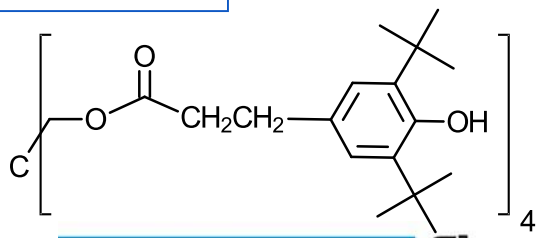


SP-5

Common Primary Antioxidants



DN76



DN10

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LGP11 Liquid Polymeric Phosphite

- Does not contain alkylphenols
- Equivalent MI performance to TNPP
- High molecular weight, yet low viscosity
- Reduced migration, plate-out, and bloom
- Significant improvements in color during:
  - Melt processing
  - Long term heat aging
  - Gamma irradiation
- FDA clearance for use in LLDPE, HDPE, PP, and HIPS
- 2000ppm, Conditions of Use A through H, all food types

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Additive Plate-Out/Bloom/Migration

- **Plate-out** refers to exudation of phosphite during processing often leaving deposits on equipment.
- **Bloom** is exudation after processing causing a haze, film, or powder on surface of polymer.
- **Migration** refers to transfer of additive into other substances in contact with polymer such as food substances.

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Plate-Out/Bloom

- Additives can plate-out onto equipment during production
- Plate-out during production can cause delays to clean equipment and reduce output.
- Bloom can occur in finished good or film after production producing a haze or film on the surface of the polymer.
- Post production bloom can cause quality issues.
- Solid phosphites can contribute to plate-out and bloom due to compatibility.

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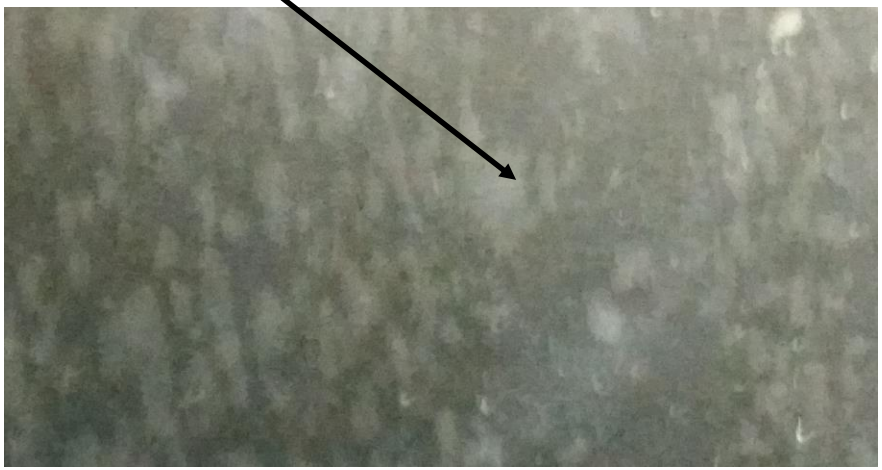
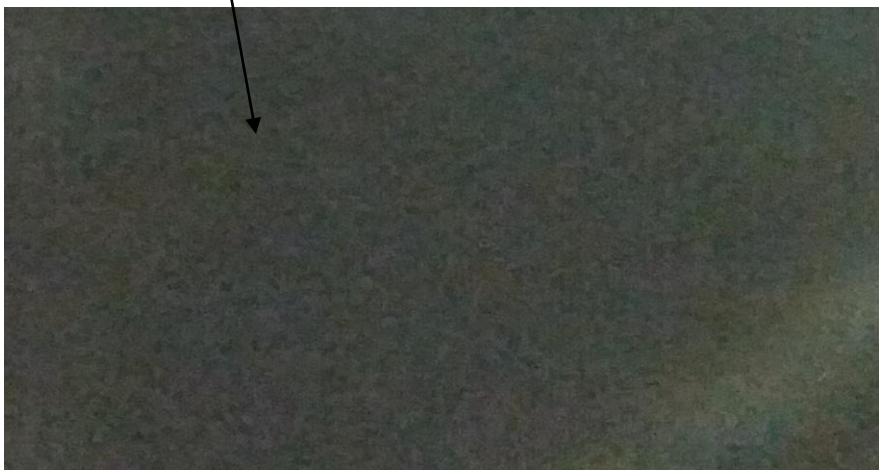
Plate-Out/Bloom

- Cast film is very sensitive to bloom and plate-out

White film on surface indicates additive is blooming



Film is clear



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Options to Reduce Plate-Out/Bloom

- 3 options to reduce or eliminate plate-out and bloom
  - **Lower additive level until it is compatible.**
  - Switch to compatible additive.
  - Use of anti-bloom technology.

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Lower use level of Incompatible Additive

- Lowering use level of solid phosphite below a certain threshold may prevent plate-out and bloom issues.
- Generally, if SP-1 is used below 1000ppm in cast film compatibility issues will be minimal for most applications.
- However performance may suffer when lower levels of phosphite are used
- A compatible liquid additive can be used to replace SP-1 or used in combination with SP-1 to keep phosphorus level at needed levels.

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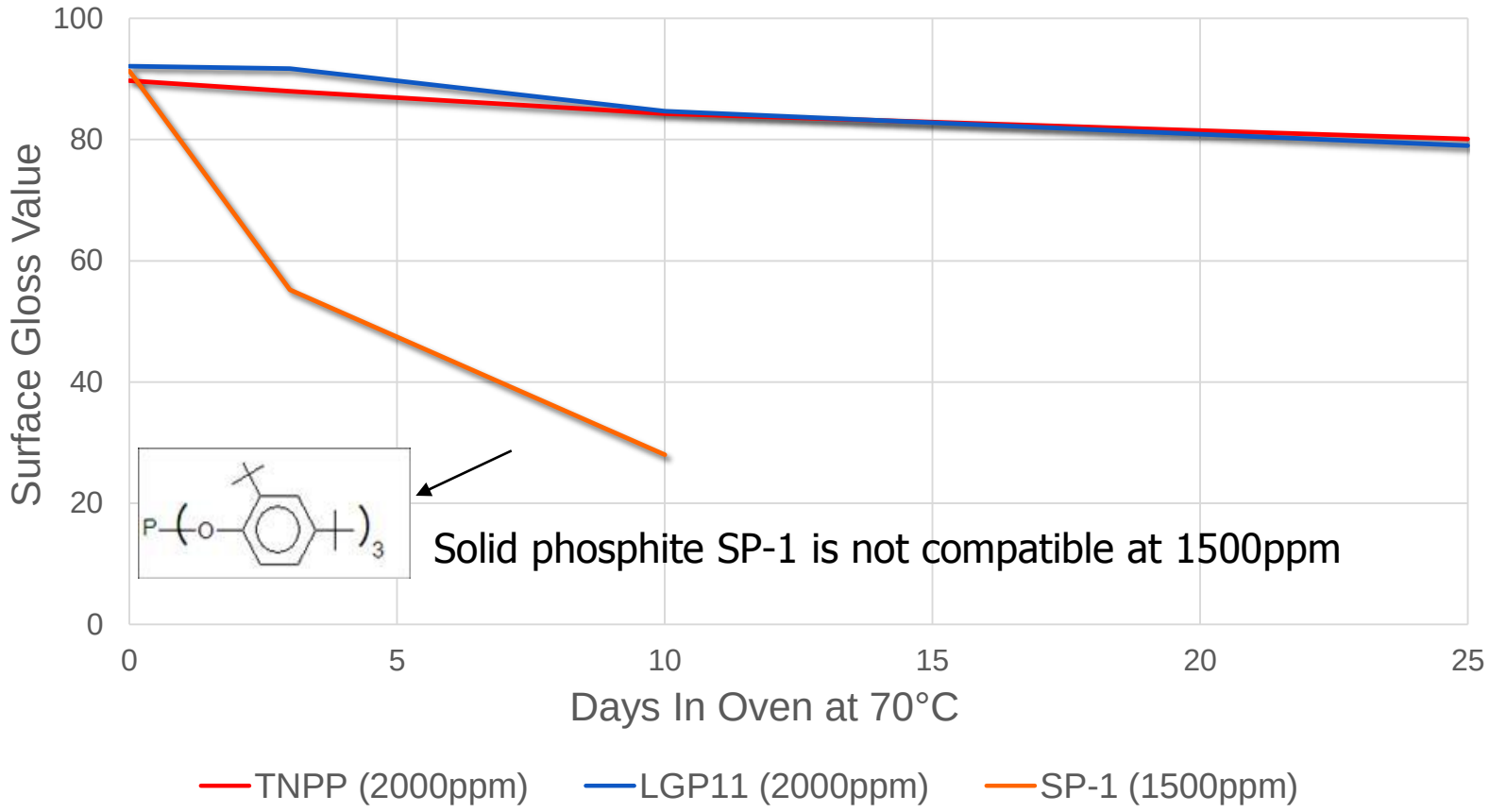
Bloom/Exudation Measurement

- Compound LLDPE formulation in Brabender-Bowl (torque rheometer) followed by compression molding and quench cooling. This results in highly amorphous LLDPE.
- Aging the compression molded plaques at 60°C accentuates any potential of the additives to bloom.
- Bloom can be monitored by measuring the surface gloss. Surface gloss is reduced if an additive blooms. The composition of the bloom can also be identified by surface ATR-FTIR.

Compatibility @ 2000ppm in LLDPE



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Formulating for Improved Compatibility

- To reduce plate out of solid phosphite you can use:
  - Liquid phosphite, such as LGP11 or TNPP
  - Use high performance phosphite at lower levels
  - Add a high performance primary antioxidant (carbon radical scavenger) to allow reduced level of SP-1
  - Blend of liquid phosphite with SP-1

- LGP11 can also be used to improve the compatibility of formulations containing SP-1
- Reducing SP-1 to less than 1000ppm (by adding LGP11) greatly reduces or eliminates the blooming effect.
- In addition, there is synergy between using a “fast” phosphite and a “slow” phosphite

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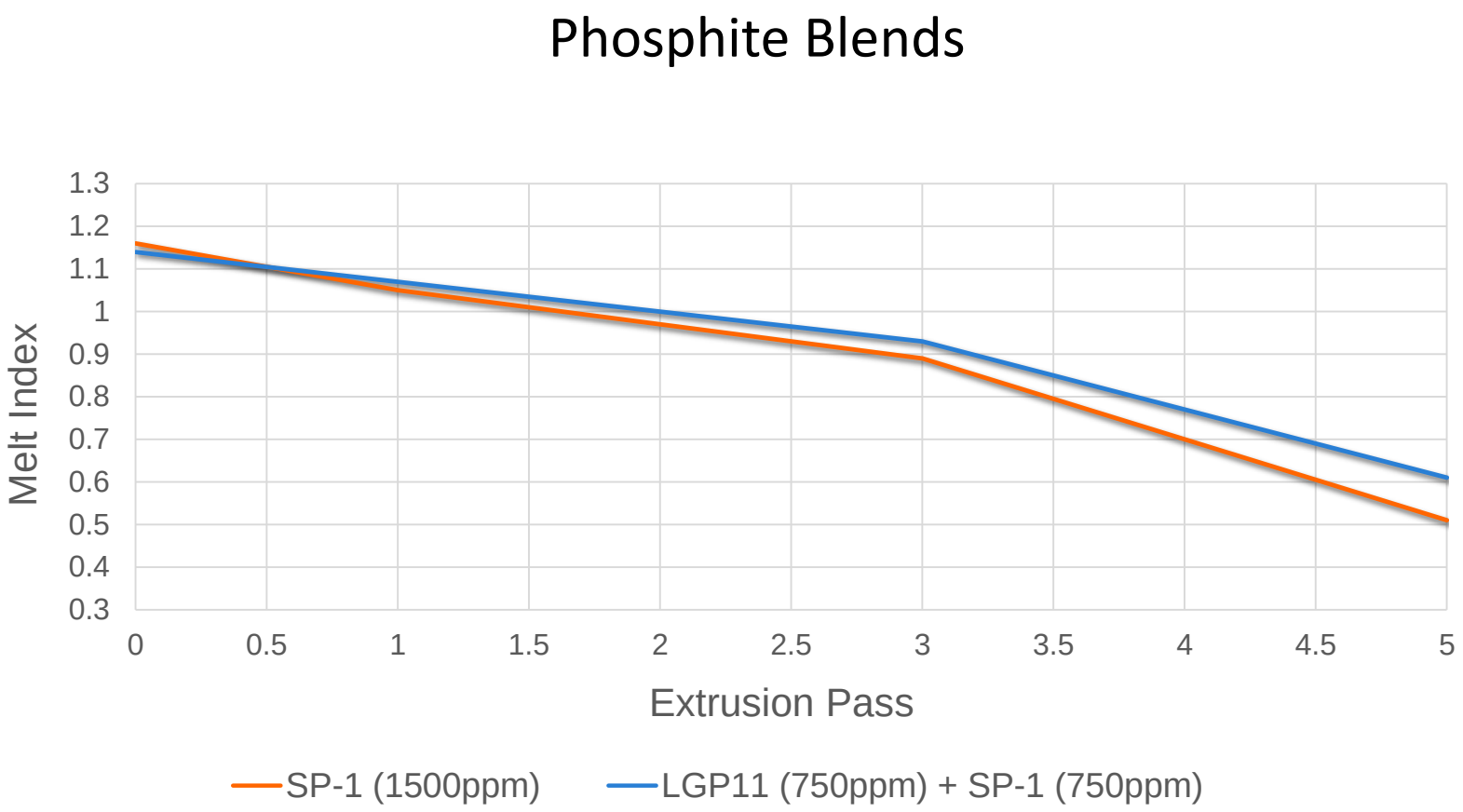
Melt Flow Index – LLDPE (2.16kg/190°C)



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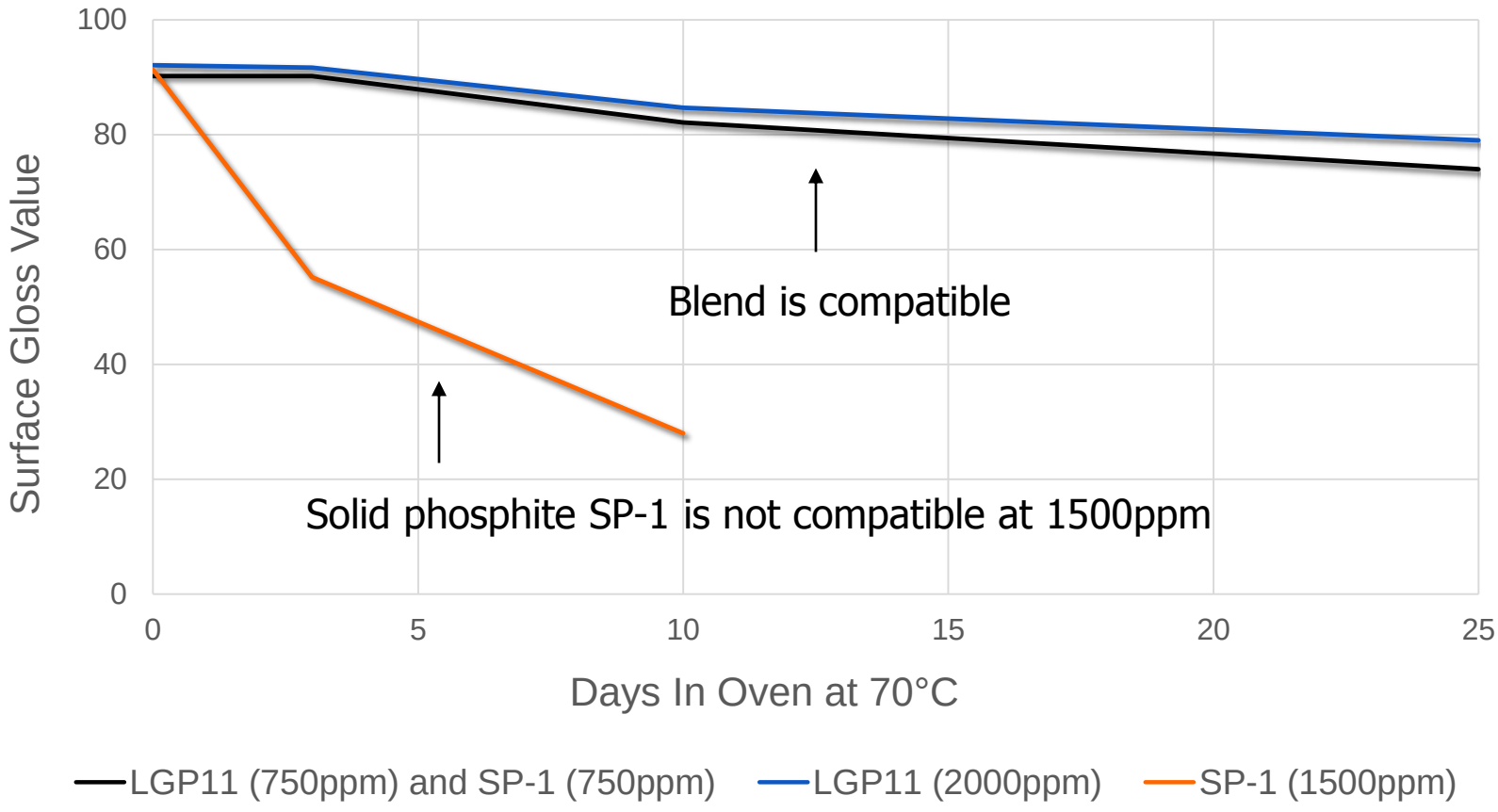
Compatibility in LLDPE



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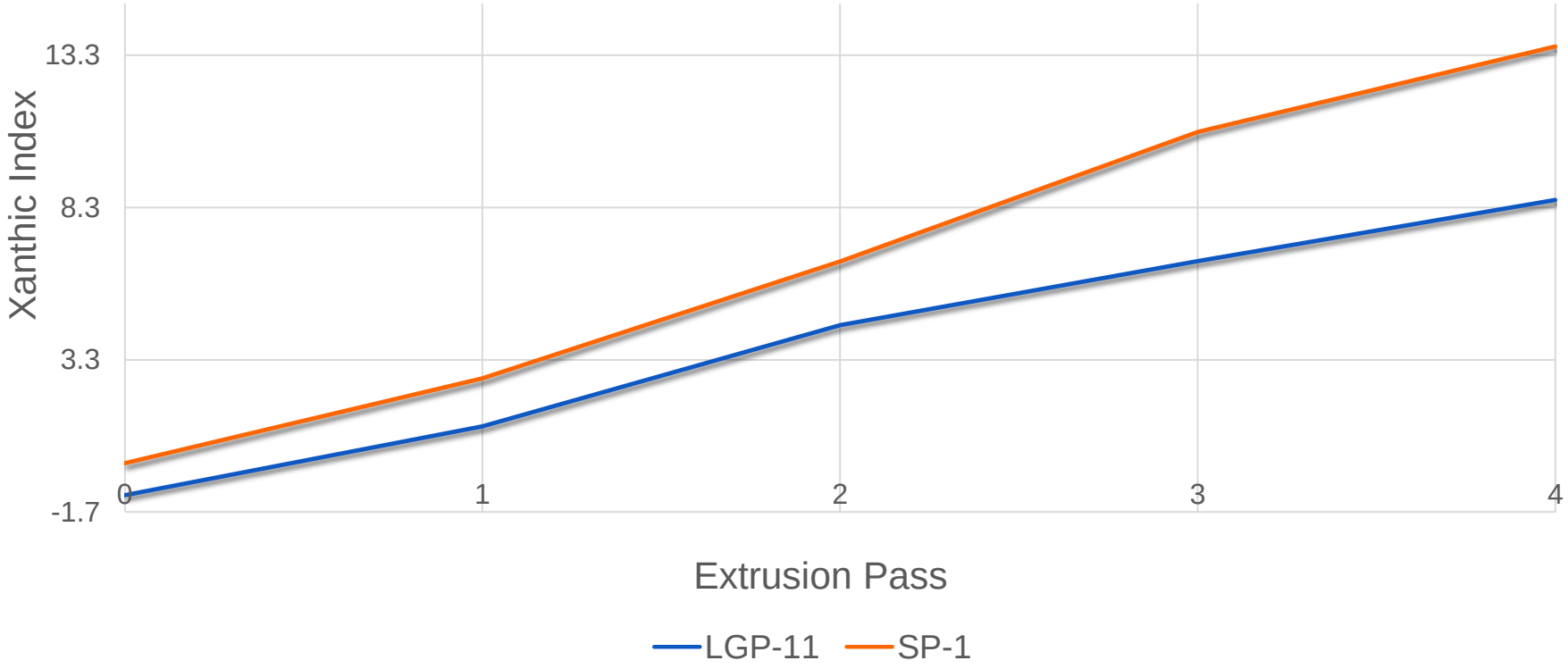
Color (XI)



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Options to Reduce Plate-Out/Bloom

- 3 options to reduce or eliminate plate-out and bloom
  - Lower additive level until it is compatible.
  - **Switch to compatible additive.**
  - Use of anti-bloom technology.

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Switch To a More Compatible Additive

- Switching to a high molecular weight liquid phosphite like LGP-11 eliminates bloom and plate-out issues.
- LGP-11 is a unique polymeric phosphite that is very compatible with polymer at high levels.
- LGP-11 can be used to replace SP-1 or TNPP at a part for part level.

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Compatibility – Plate Out

- The compatibility of a phosphite during cast film production can be mimicked through the use of a laboratory two-roll mill.
- A red pigment is included into formulations. Migration of the additives will cause an increase in levels of pigment sticking to the roles.
- The pigmented formulation is melt processed for a specific period of time and then removed.

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Compatibility – Plate Out

- Blank/straight LLDPE resin is then processed on the roll mill. Any material that was deposited on the mill will be compounded into the blank resin. Thus the color increase is proportional to the amount of plate-out (that also contains the red pigment).

- A filled purge compound is then used as a clean out formulation to remove lasts traces of plate-out on the mill.

- Samples at each point are collected for color measurement.

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Formulations

Material (ppm)	A	A2	A3	B	B2	B3	C	C2	C3
LGP-11	2000	Blank LLDPE	Purge Compound		Blank LLDPE	Purge Compound		Blank LLDPE	Purge Compound
TNPP				2000					
SP-1							2000		
AO-1	500			500			500		
Process Aid	800			800			800		
Pigment	1000			1000			1000		

Blank LLDPE = No phosphite or AO

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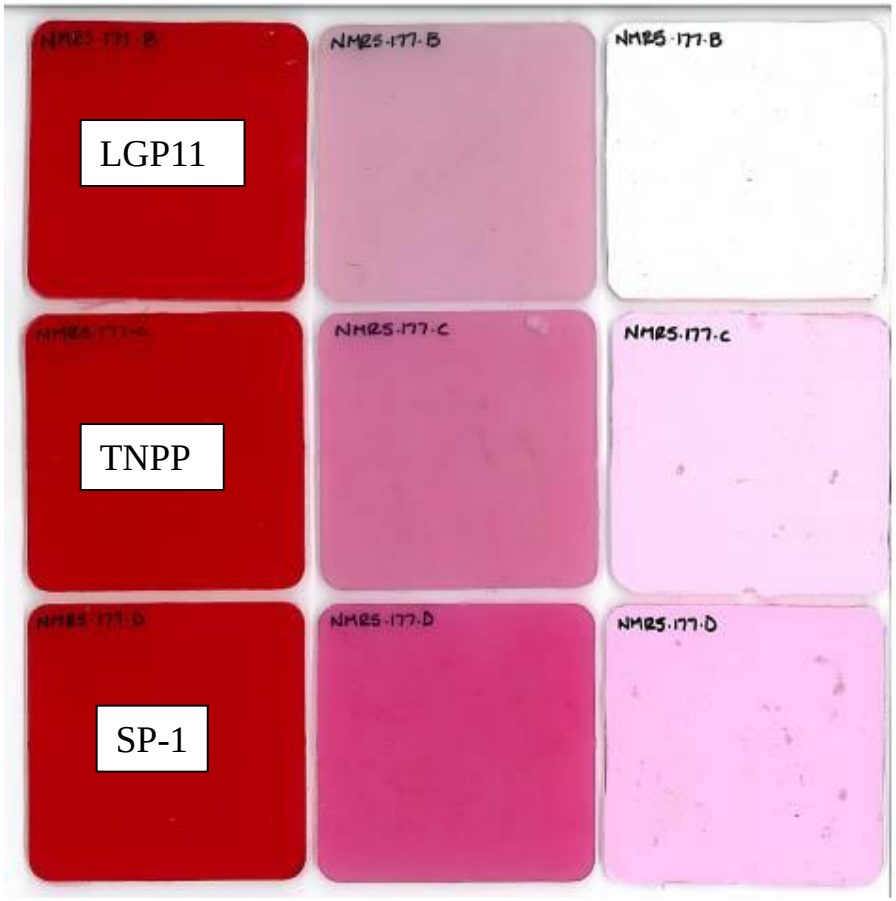
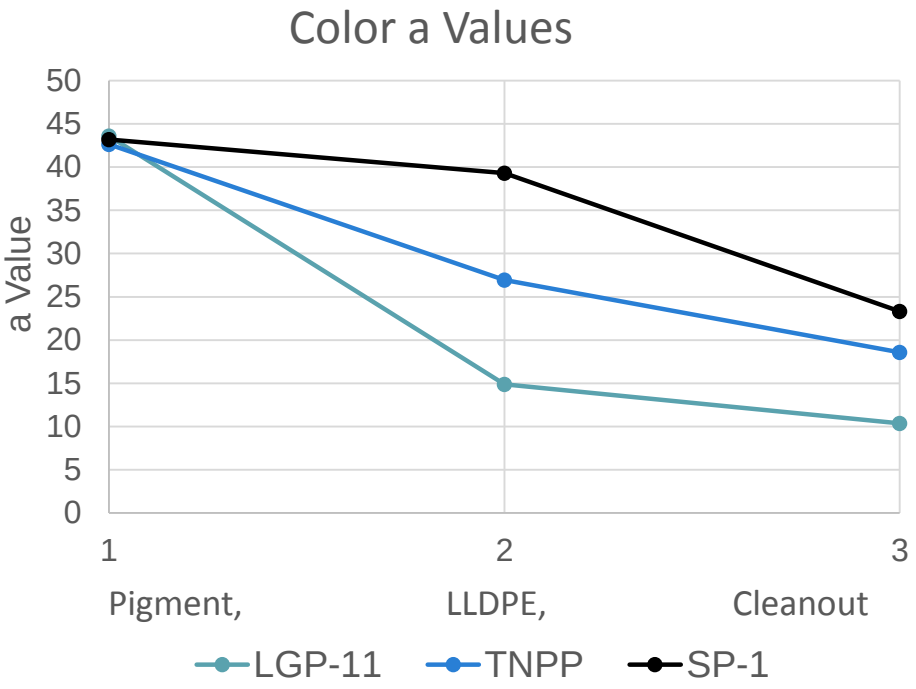
Plate-Out Results

Pigmented Formulation → Blank LLDPE → Purge/Cleanout

Less Color = Less Plate-Out
(less material left on mill)





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Color Measurements

	L	a	b	XI
LGP11 – Pigment	37.21	43.60	12.02	152.79
LGP11 – LLDPE	68.27	14.88	-4.93	4.79
LGP11 – Purge	94.55	**10.37**	-2.32	4.48
TNPP – Pigment	36.48	42.63	12.20	154.69
TNPP – LLDPE	59.49	26.96	-6.92	16.15
TNPP – Purge	88.47	**18.59**	-5.86	5.20
SP1 – Pigment	36.57	43.20	11.75	153.37
SP1 – LLDPE	51.41	39.32	-6.09	41.54
SP1 – Purge	84.19	**23.31**	-6.74	8.26

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Solid Feeding LGP-11

- Many polyolefin plants can only handle solid *or* liquid phosphites.
- Low MW phosphite like TNPP can generally only produce masterbatches containing 1-2% making it difficult to use in solid feeders.
- LGP-11 masterbatches can be produced containing up to 10% levels of phosphite.
- Higher levels of LGP-11 can be incorporated when inorganic acid scavengers are ZnO and DHT4V are used.

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Options to Reduce Plate-Out/Bloom

- 3 options to reduce or eliminate plate-out and bloom
  - Lower additive level until it is compatible.
  - Switch to compatible additive.
  - **Use of anti-bloom technology.**

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Anti-bloom Additives

- Dover has patented anti-bloom additives that when used in combination with SP-2 can prevent plate-out and bloom.
- Anti-bloom additive must be “intimately mixed” with solid phosphite to achieve desired effect.
- Anti-bloom additives have FDA approvals for use in polyolefins.
- Dover can produce blends of SP-2 with anti-bloom additives.

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Anti-Bloom Additive – ZN-LLDPE

- Formulations were compounded in a Brabender bowl mixer at 160C.
- Plaques were compression molded and aged at 70°C in an oven for 8 days.

Material, ppm	A	B	C
Phosphite, SP-2		550	550
Anti-Bloom Additive			650

*Formulations contain 500ppm of DN76

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Surface Gloss Measurement

Material, ppm	A	B	C
Phosphite,SP-2		550	550
Anti-Bloom Additive			650

Gloss Value	A	B	C
Before oven aging	91.9	92.7	96.1
After oven aging	55.9	43.5	66.3

Gloss values show reduction in bloom

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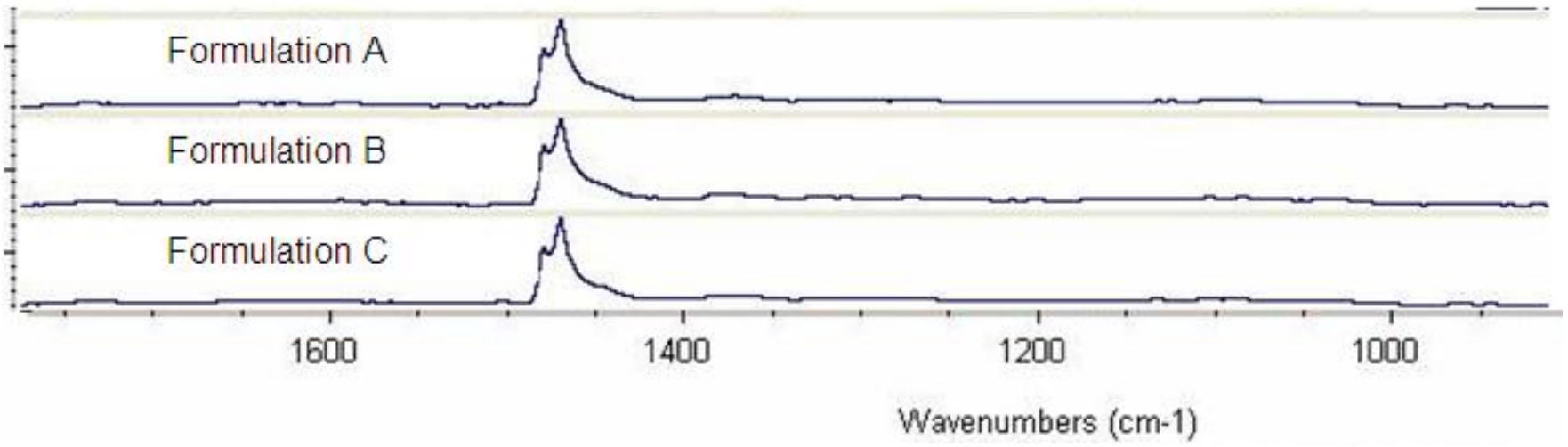
ATR-FTIR Surface Analysis

Samples Before Oven Aging at 70°C

Material, ppm	A	B	C
Phosphite,SP-2	-	550	550
Anti-Bloom Additive	-	-	650

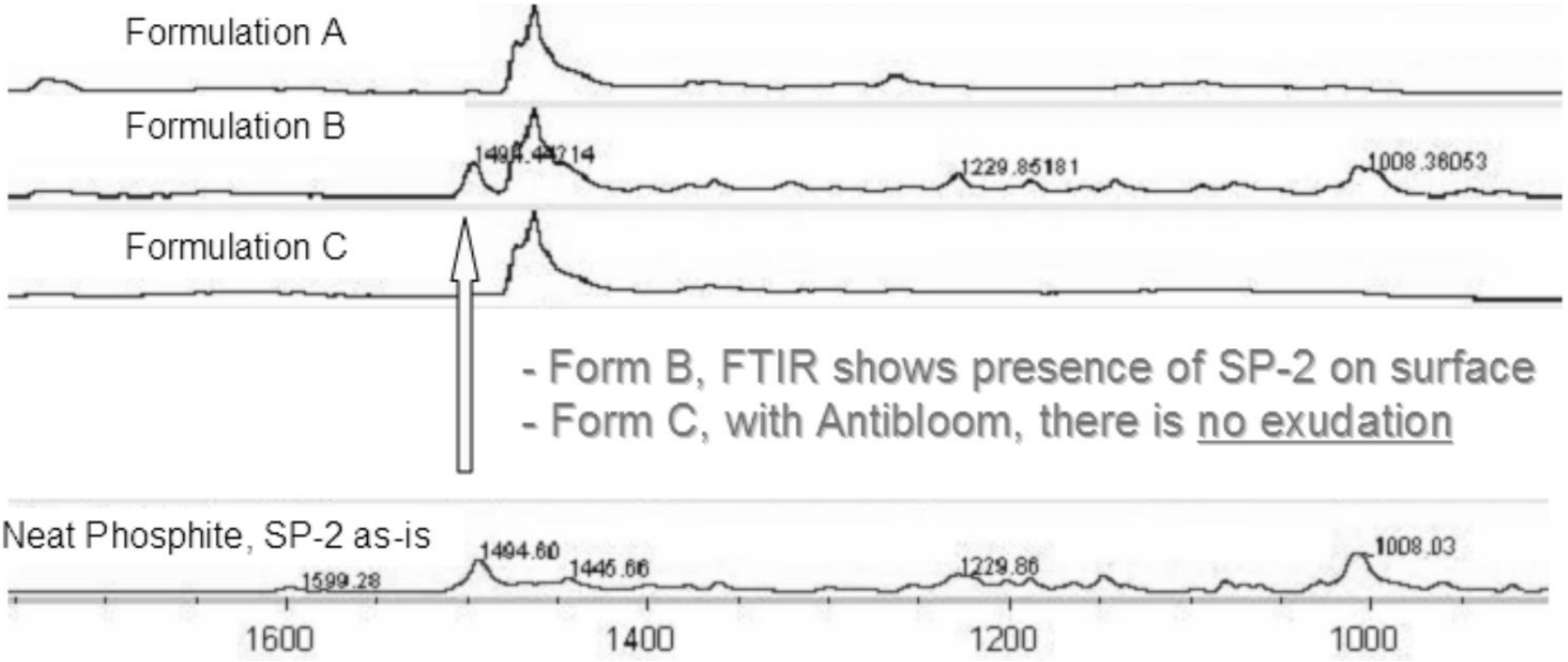
ATR-FTIR of LLDPE surface: no difference in FTIR, no bloom



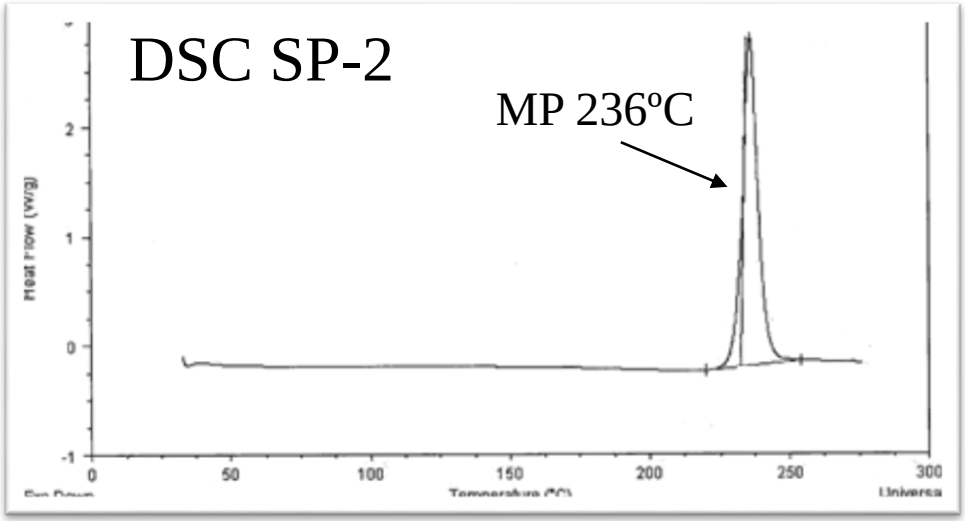
ATR-FTIR Surface Analysis

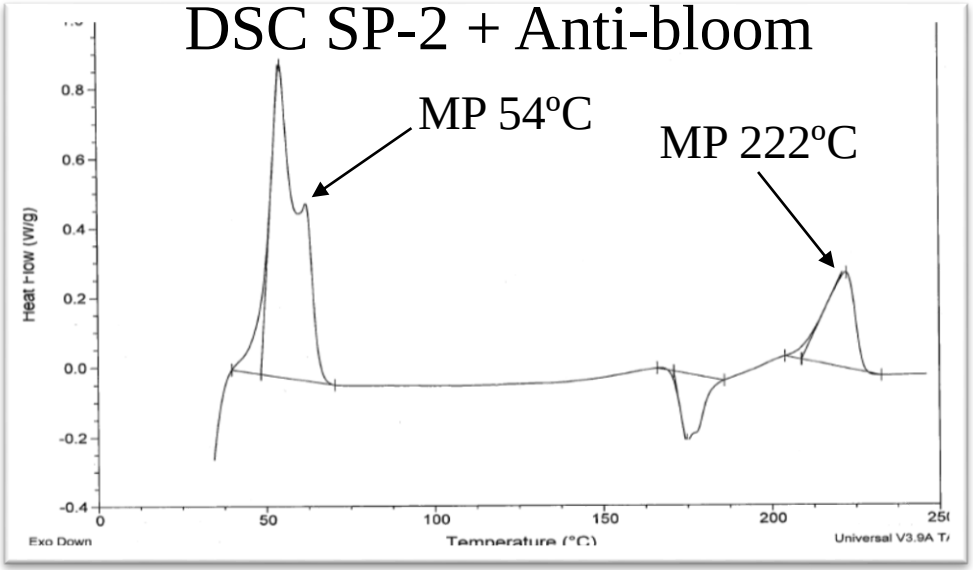
Samples AFTER Aging at 70°C, 8 Days

Material, ppm	A	B	C
Phosphite,SP-2	-	550	550
Anti-Bloom Additive	-	-	650



How Does Anti-bloom Work?





- SP-2 is a high melt point highly crystalline phosphite
- Highly crystalline substances are often incompatible in amorphous polyolefins.
- Addition of Anti-bloom lowers melt point and potentially reduces crystallinity of SP-2

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Plate-Out/Blooming Conclusions

- There are a number of options to reduce or eliminate plate-out and bloom while maintaining performance.
  - Lower additive level until it is compatible.
  - Switch to compatible additive.
  - Use of anti-bloom technology.

- Eliminating these issues gives numerous benefits.
  - Less down time due to cleaning equipment.
  - Safer since equipment needs to be cleaned less frequently.
  - Keeping phosphite levels high allows process to be run hotter and faster to increase line speeds/production.

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Migration- Food Packaging

- Additives can migrate when polymer comes into contact with substance which additive is soluble in.
- Especially important for food packaging.
- Many additives are soluble in “fatty foods”.

- NIAS- Non Intentionally Added Substance
- NIAS becoming an important issue in Europe.
- Additives may contribute. Oxidation and hydrolysis products of phosphites may be considered NIAS.

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Migration - Fickian Diffusion

At a given time/temperature/concentration, migration is related to the diffusion coefficient, which is dependent upon Molecular Weight

$$M_t = 2C_{po}(D_p t/\pi)^{1/2} \quad *$$

M_t = Migration at time t
C_{po} = Concentration in the polymer
D_p = Polymer diffusion coefficient

$$D_p = 10^4 \exp(A_p - aM_w - bT^{-1}) \quad **$$

Molecular Weight

Diffusion coefficient of additive/migrant
M_w is the molecular weight of the additive, T is temperature (K)
a and b are constants (0.01 and 10450 respectively)
A_p depends on the polymer and temperature

* Crank, J., "The Mathematics of Diffusion", 2nd ed., Oxford University Press, London, 175
** A.Baner, J.Brandisch, R.Franz, O.G. Piringer, *Food Additives and Contaminants*, 1996, **13(5)**, 587-601

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FDA-Type Migration Study of Additives Into Food

Selected additives were compounded into LLDPE using a Brabender torque rheometer at a concentration of 1000ppm. Formulations were then compression molded into plaques.

Plaques were exposed to 95% ethanol at 70°C for 2 hours. 95% ethanol is considered a fatty food simulant. Solutions were then analyzed for additive content.

Additive migration was measured as µg of additive that migrated per inch squared surface.

$$\frac{\mu g\ (additive)}{in^2\ surface} \xrightarrow{\text{Assume } 10g\ food/in^2} \frac{(\mu g\ (additive)/10)}{grams\ food} \Rightarrow \textbf{ppm in Food}$$

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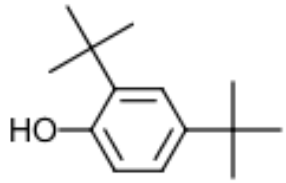
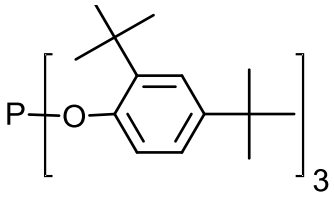
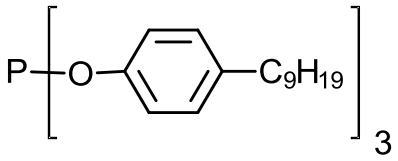
Additive Migration (Molecular Weight)



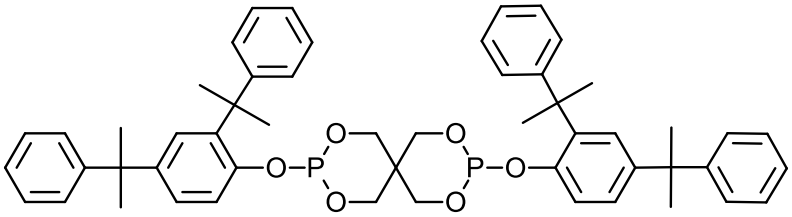
DTBP (MW = 206)



SP-1 (MW = 646)



TNPP (MW = 688)



SP-2 (MW = 852)

LGP-11 (MW > 1500)

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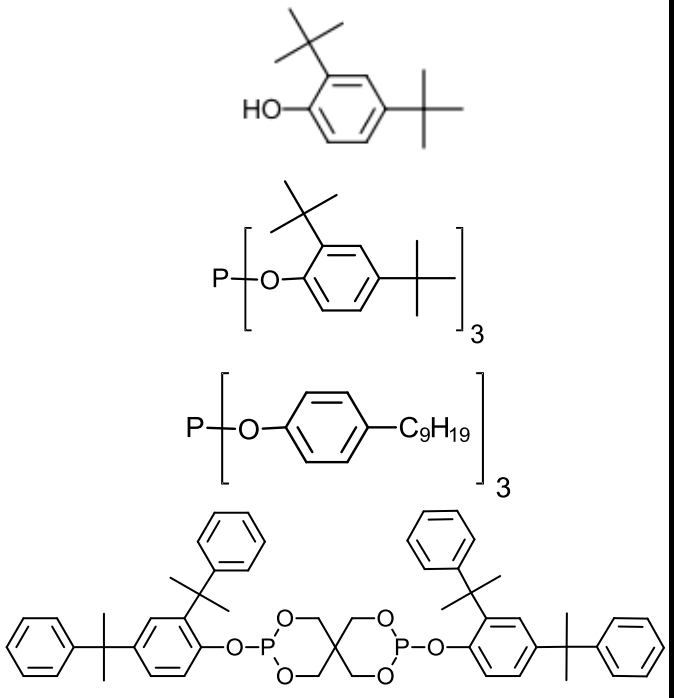
Migration of Additives - Fatty Food Simulant



Additive	MW (g/mole)	Ppm in Food
DTBP	206	**15.2**
SP-1	646	**5.2**
TNPP	688	**5.9**
SP-2	852	**2.2**
LGP-11	>1500	**<0.5**

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NIAS(Non-Intentionally Added Substances)

- Phosphites oxidize in polymer as part of stabilization process.
- These oxidation products may be considered as NIAS
- Hydrolysis products of phosphites can also potentially be considered NIAS
- SP-2 is unique since oxidation products and hydrolysis products were included in toxicology testing and are included as part of SML.
- Therefore these products are *not* considered NIAS.
- Species with MW greater than 1000Da are not considered part of NIAS. >90% of LGP-11 is above 1000Da limiting NIAS species.

Geueke, Birgit., "Dossier-Non-intentionally added substances (NIAS)", April 2013, Food packaging Forum

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Conclusions

- Additive migration, bloom, and plate-out can cause significant quality, production, and safety issues.
- There are multiple strategies that can be employed to reduce these issues while maintaining performance and production output.
- High molecular weight additives are ideal for food packaging applications to reduce migration into food and exposure to public.

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Thank You!

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