Polymer Stabilizers: Current Challenges and Future Trends

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Outline

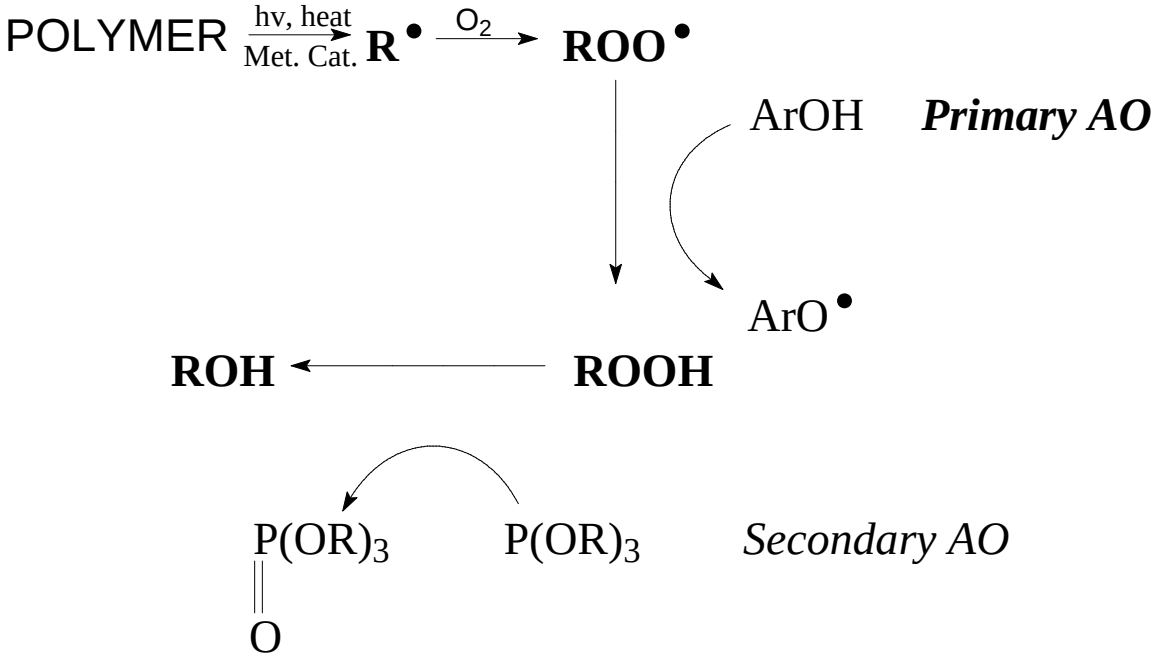
- Stabilizer overview
- Primary focus on organophosphite stabilizers
  - Structure activity correlations with activity, thermal and hydrolytic stability, compatibility and other ancillary properties.
- Polyolefin Stabilizers
- PVC Stabilizers

Key Properties of Polymer Stabilizers

- Process Stability
  - Protect polymer during melt processing
- Long Term Aging
  - Protect polymer after article has been formed
- Cost Performance
- Ancillary Properties
  - Compatibility, hydrolytic stability, volatility, etc.
* Environmental Profile
  - Environmental issues, whether real or perceived, are driving formulation changes and offering opportunities for new technology

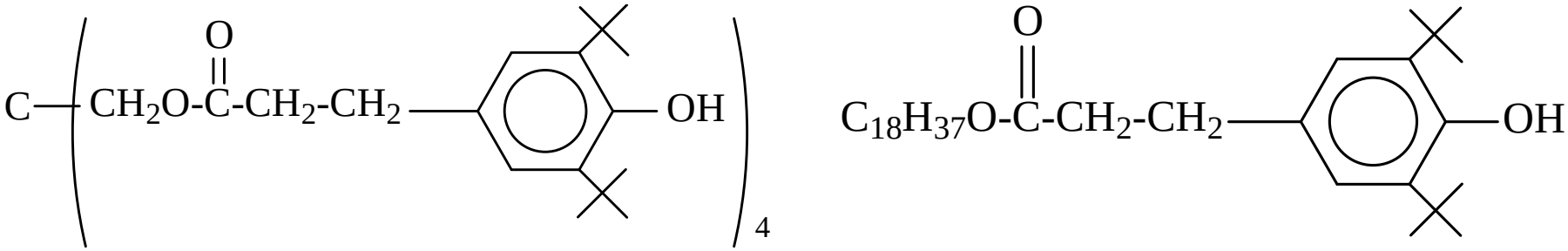
Polyolefin Stabilization

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



Primary Stabilizers

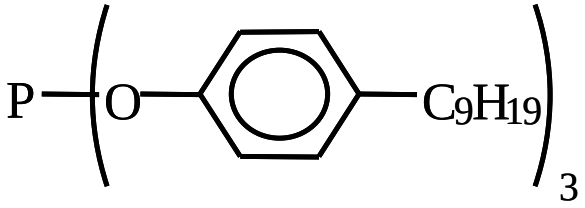
- A few commodity hindered phenolic stabilizers dominate the global market. However, there have been advances in the performance of new hindered phenolics, in addition hydroxyl amines and even Vitamin E have emerged as alternative high performance primary stabilizers.



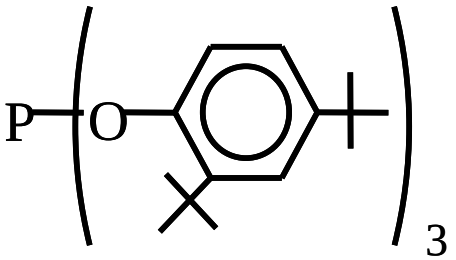
Commodity Hindered Phenolic Primary Stabilizers

Phosphite Stabilizers

- The global market is dominated by two commercial commodity phosphites. Choice is dependent upon physical form. There are several solid high performance phosphites that are also available.
  - Tris(nonylphenyl) Phosphite, Liquid



  - Tris(Di-t-butylphenyl) Phosphite, Solid



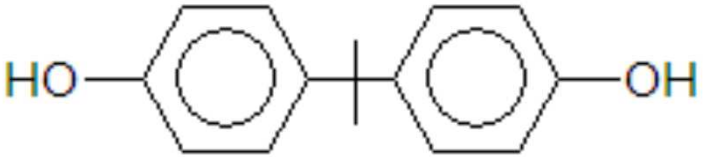
Key Phosphite Properties

- Good performance (and cost)
  - Preserve Melt Flow (MI) and Color (YI) during processing
- Good hydrolytic stability
  - Phosphite does not hydrolyze during shipping and handling or during extrusion and aging
  - Hydrolyzed phosphites potential cause of "black specs"
- Good compatibility
  - No plate out issues on equipment during processing
  - No bloom issues on the article upon aging
- Broad FDA and Global Food Approvals

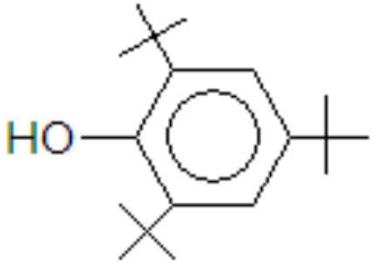
New Phosphite Development

- Much of the new development is aimed at improving environmental issues surrounding current commercial stabilizers (real or perceived)
- Certain alkylphenols in particular have received increased media attention
- The phosphite ligand structure will define its properties and performance. The alkylphenol ligands can be removed, but the alternative ligands must balance performance, hydrolytic stability, compatibility, etc.

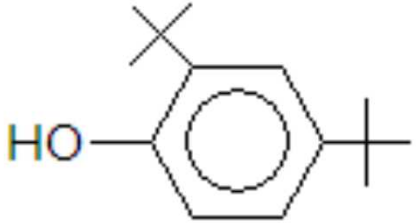
Alkylphenols in the "Spotlight"



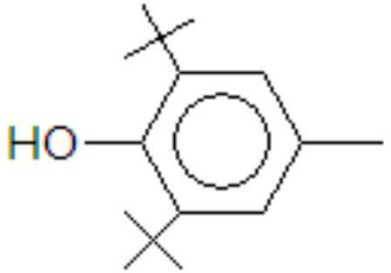
Bisphenol A



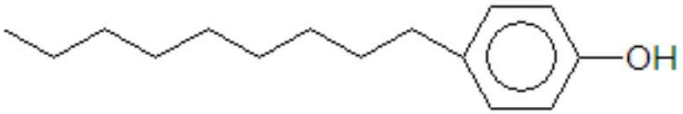
TTBP



DTBP

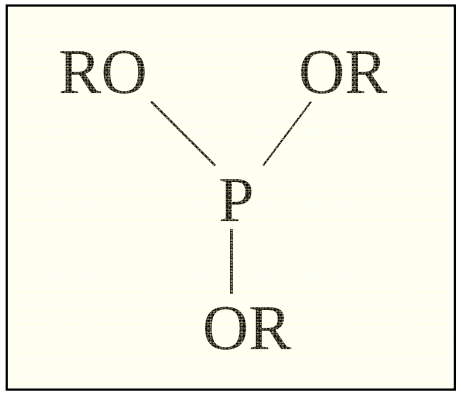


BHT



Nonylphenol

Monophosphites



R1=R2=R3=alkyl — Alkyl Phosphites

R1=R2=R3=aryl — Aryl Phosphites

R1≠R2≠R3=alkyl/aryl — Alkyl/Aryl

Examples R = phenyl, 2-ethylhexyl, isodecyl, nonylphenyl

Di- and Complex High MW phosphites

Examples R = Pentaerythritol, BPA, Dipropylene Glycol

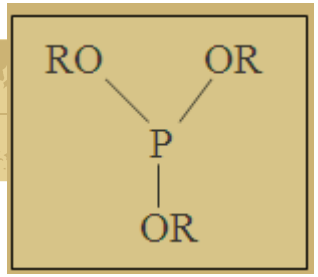
Balancing Activity, Hydrolytic Stability and Compatibility

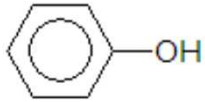
- All phosphites are sensitive to hydrolysis/degradation. Using a hindered phenol as a ligand increases hydrolytic stability.
  - Hindered aryl > aryl > alkyl

- Polyolefins are hydrophobic by nature. Adding a ligand that is too polar will cause the phosphite to plate-out (on equipment during processing) or bloom (exude to surface upon aging).

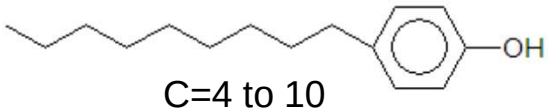
- Adding a higher MW ligand will slow down migration and reduce volatility. However, a ligand that is too high in MW will result in reduced % P and performance.

“TOOL BOX”



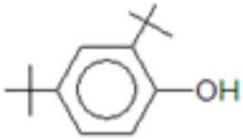


Poor compatibility, poor hydrolytic stability and VOC

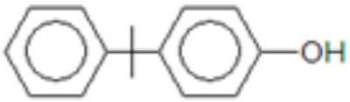


C=4 to 10

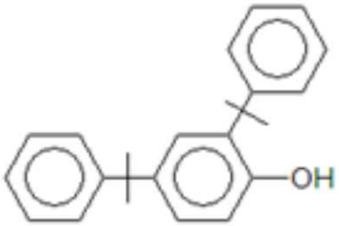
Good compatibility, good hydrolytic stability, but linear mono-alkylphenols in “Spotlight” and <C5 are “volatile”



Fair compatibility, excellent hydrolytic stability, but Increasing focus on ppb levels in water/pipe in EU



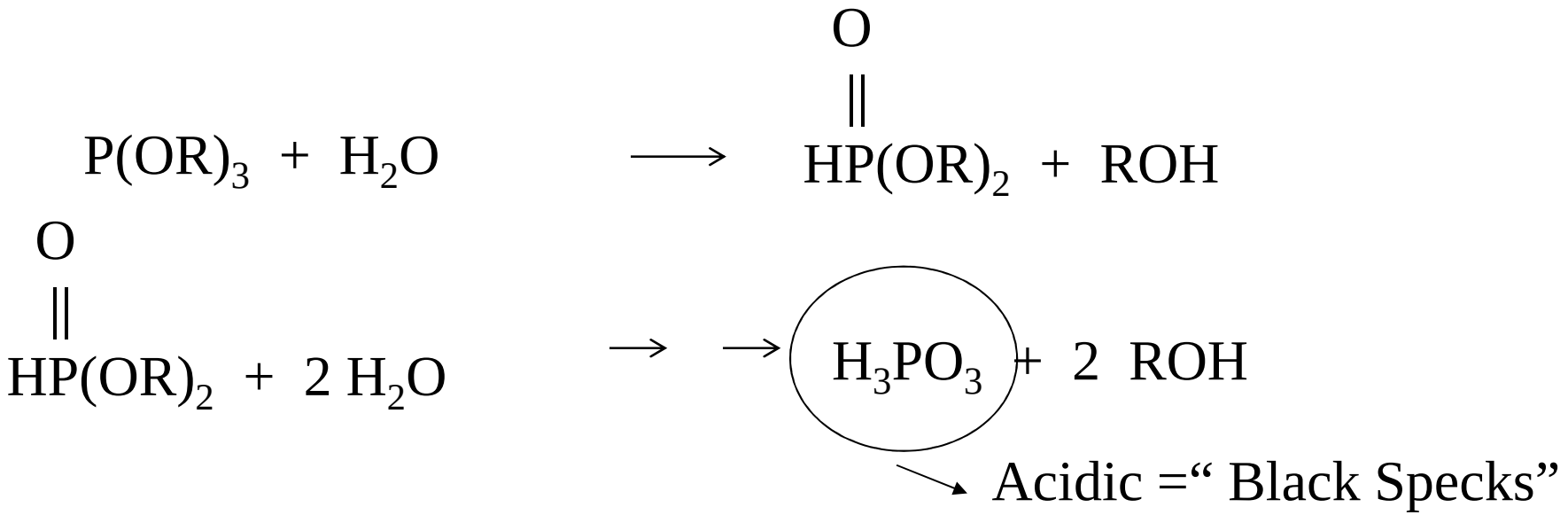
Fair compatibility, good hydrolytic stability



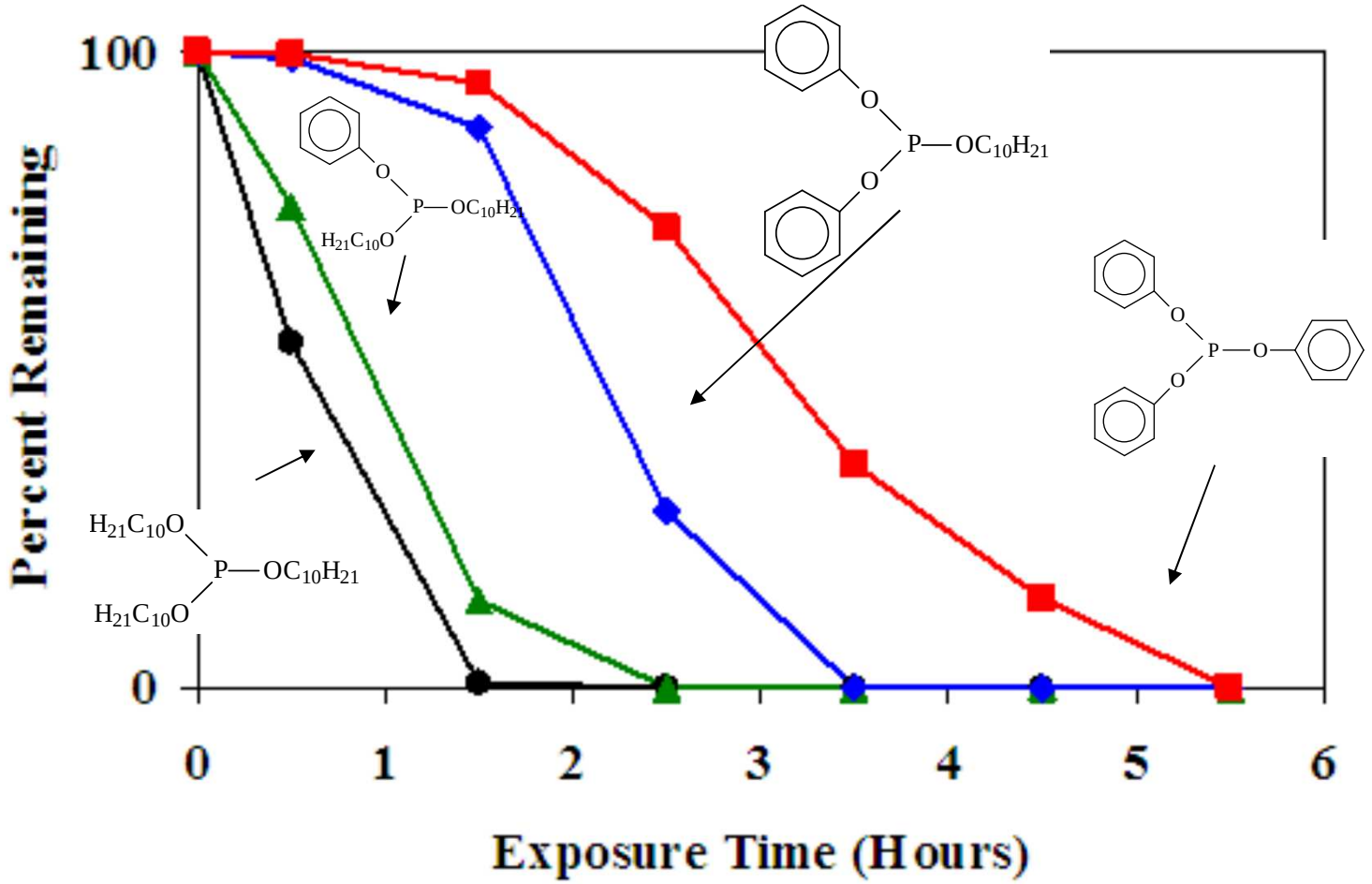
Fair compatibility, excellent hydrolytic stability
Low migration and excellent toxicity

Hydrolytic Stability

- Phosphites can be hydrolyzed/degraded when exposed to water, especially under acidic environments.
- Hydrolytic stability follows:
  - Hindered Aryl > Aryl > Alkyl

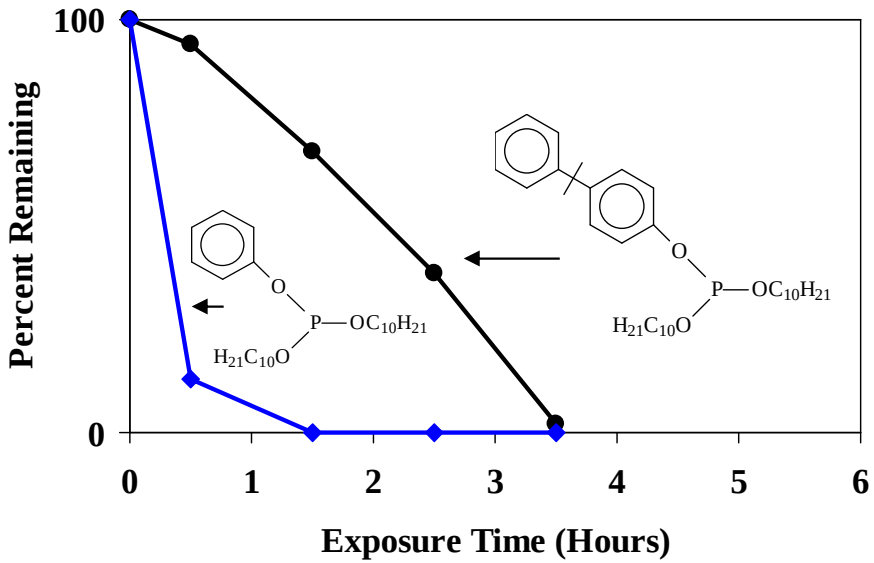


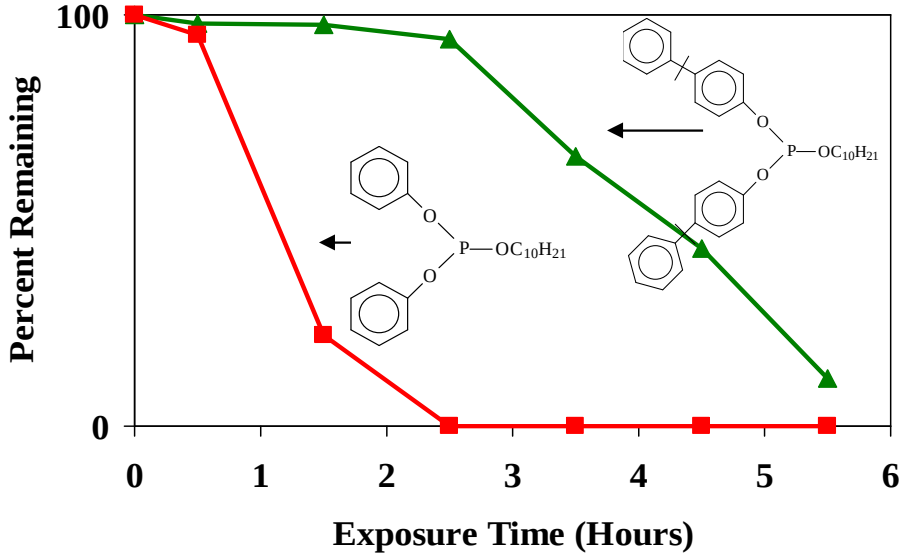
Hydrolytic Stability (Aryl>Alkyl)



(Phosphites exposed to 60°C, 85% Humidity)

Structure of Ligands Effect Hydrolytic Stability

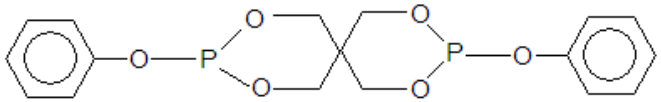




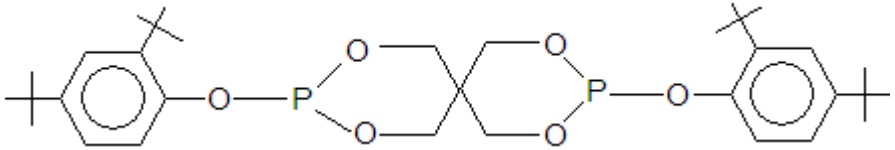
Phosphites exposed to 60°C, 85% Humidity

Hydrolytic Stability (Effect of Steric Hindrance)

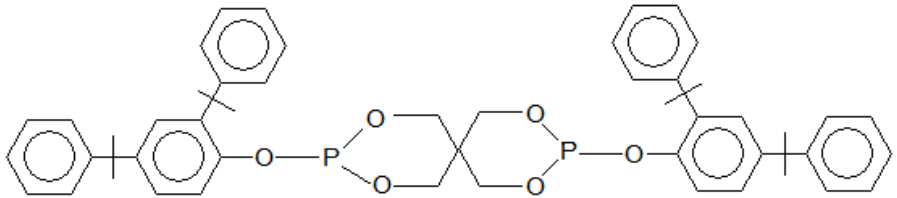
Phosphite A



Phosphite B



Phosphite C

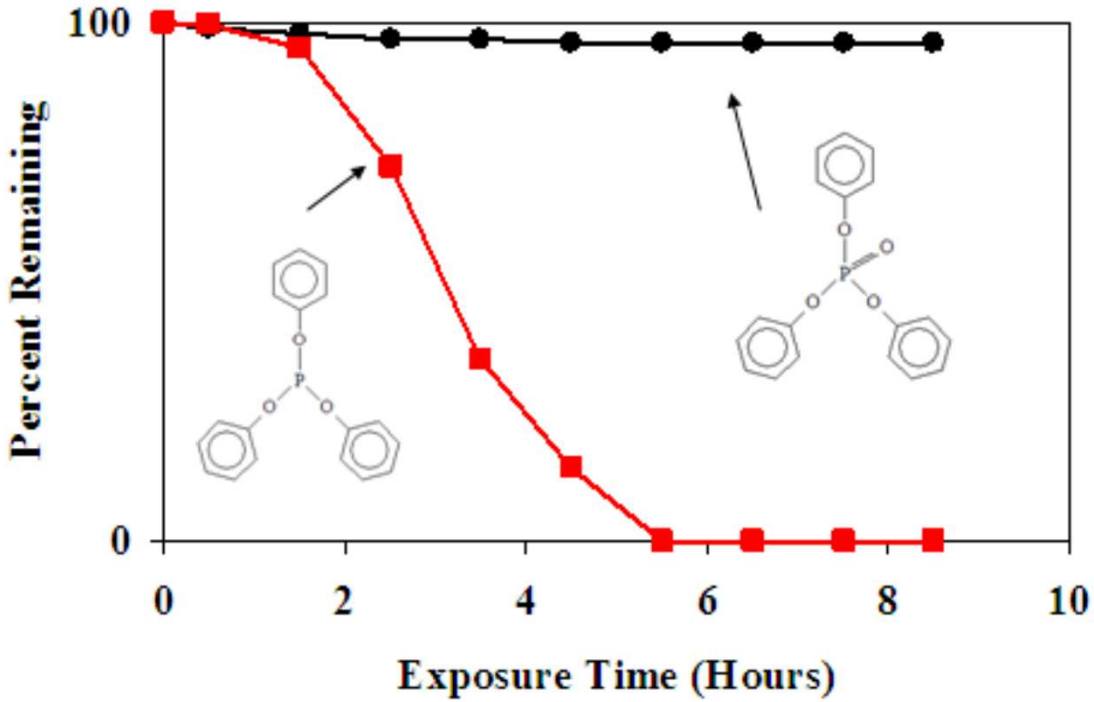


	Hours to Failure	% Hydrolyzed
Phosphite A	<10	>50%
Phosphite B	~48	25%
Phosphite C	>2000	<5%

Neat Phosphites Exposed to 40°C & 85% Humidity

Hydrolytic Stability - Phosphates

- Phosphites are used to scavenge hydroperoxides. They are converted to phosphates during melt processing. Although they are not active stabilizers, phosphates are very hydrolytically stable. That is why they can be used in PVC as plasticizers.



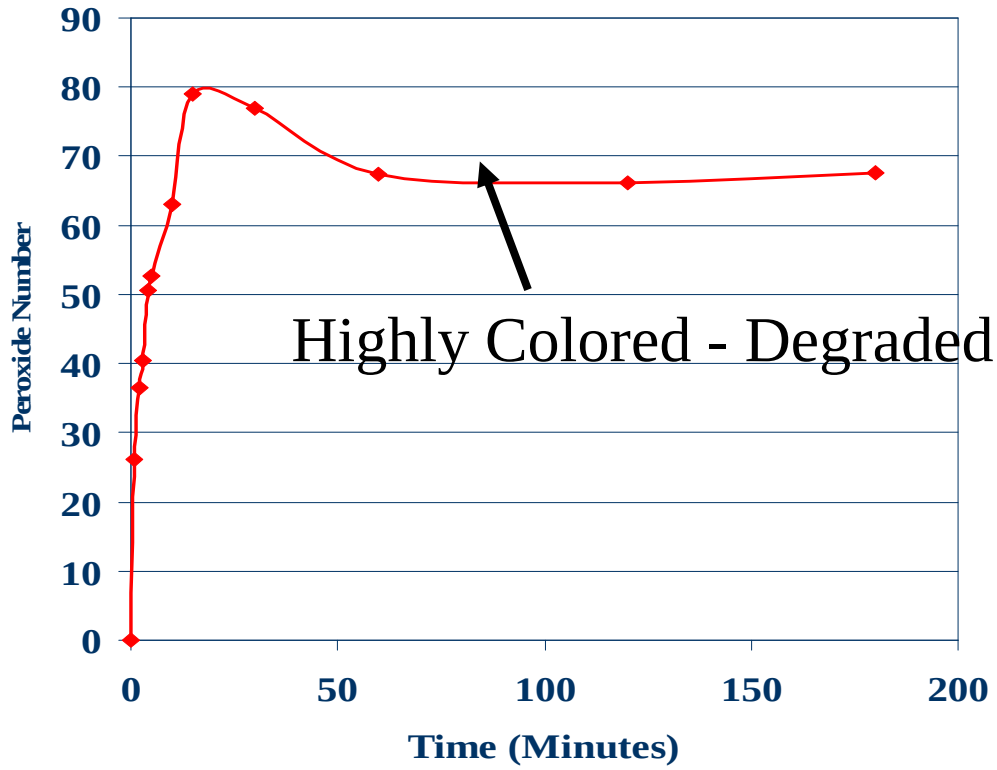
Hydrolytic Stability vs. Reactivity

- Increasing the steric hindrance of the ligand improves hydrolytic stability, but often at the cost of reactivity.
  - Hydroperoxide scavenging
  - Alkyl > aryl > hindered aryl

Model System For Polyethylene

Air Oxidation of C 14-17 Paraffin at 200 °C

Hydroperoxide Level



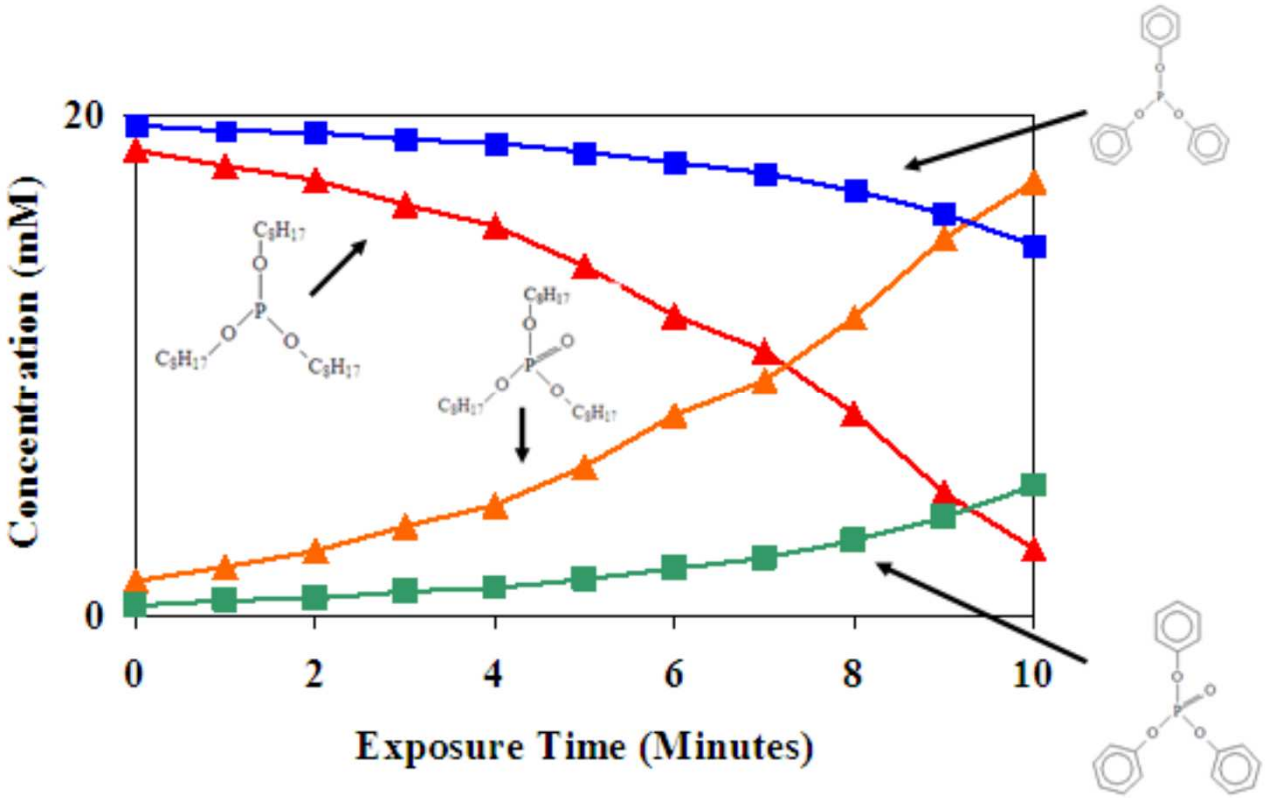
Peroxide Number vs. Time … No Stabilizers

Phosphite Activity

- Phosphites are sacrificial antioxidants.
- In general, the rate at which a phosphite scavenges hydroperoxides (and forms phosphate) is proportional to its activity, all else being equal.
- The activity of phosphites can be compared by measuring this conversion rate in a model system, paraffin solvent at 200°C.

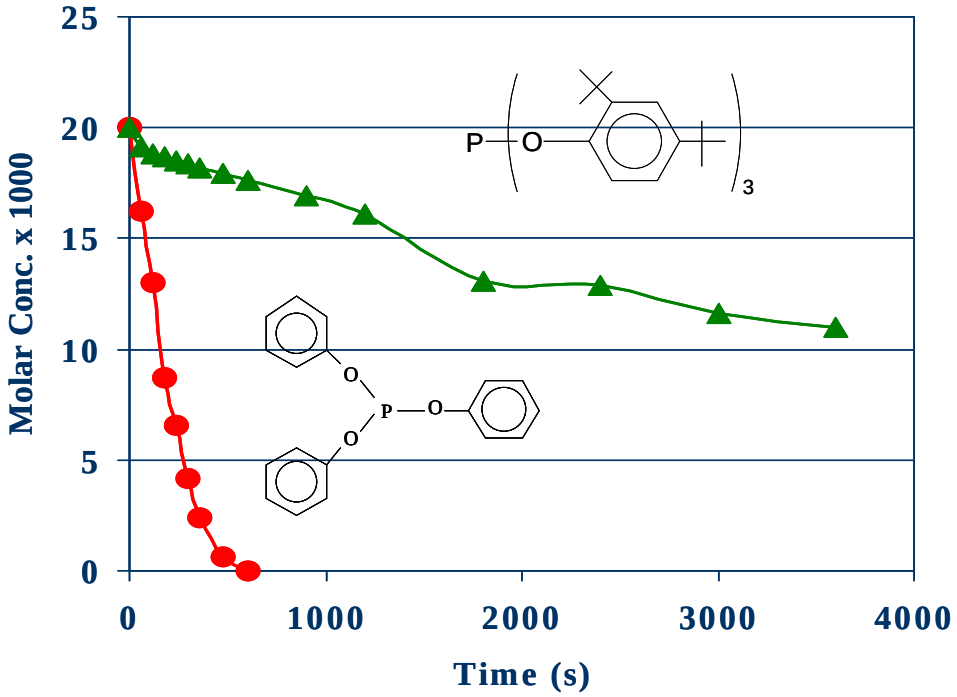
Competitive Oxidation : Alkyl vs. Aryl

In general, Alkyl Phosphites are more active at scavenging hydroperoxides than Aryl Phosphites



Concentration versus time in paraffin solvent at 200°C

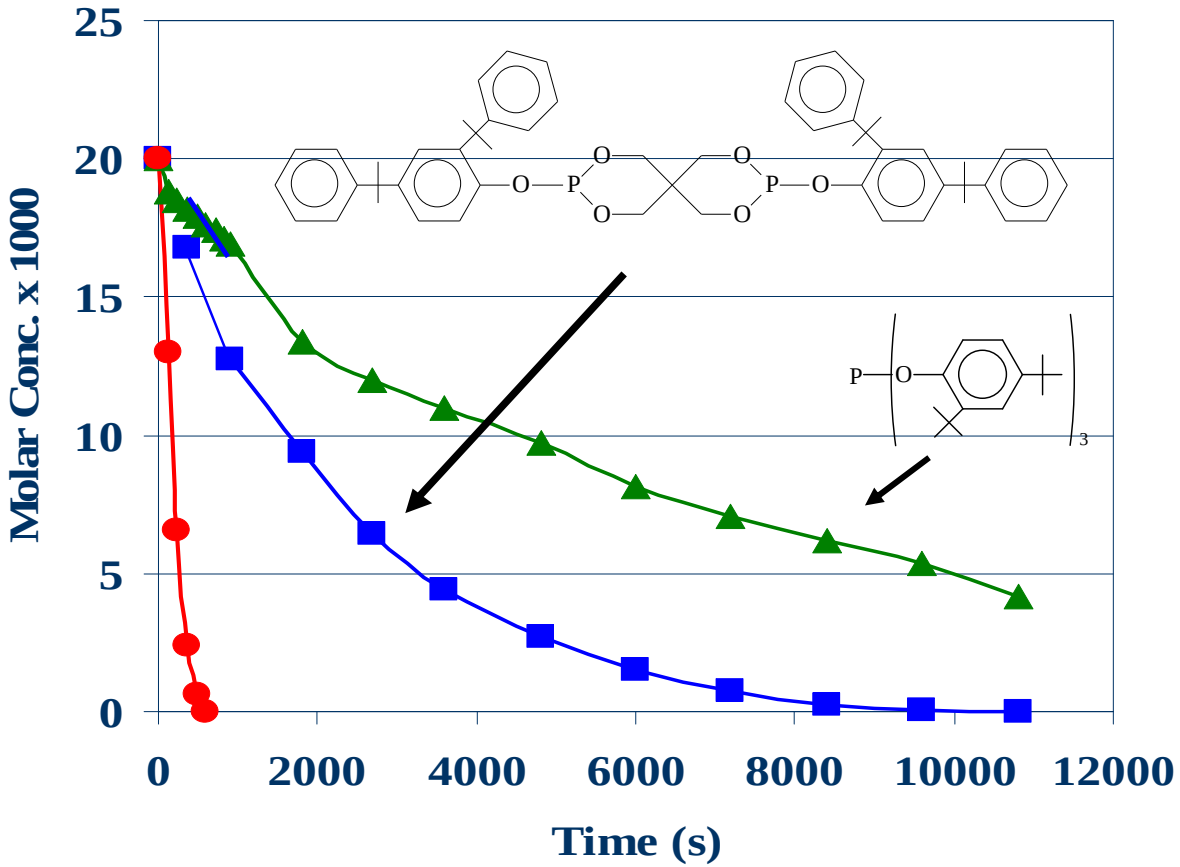
Steric Hindrance vs. Activity



Peroxide Scavenging Activity Alkyl>Aryl>Hindered Aryl

Temperature 200 C

You can still design a hindered/hydrolytically stable phosphite with excellent activity…

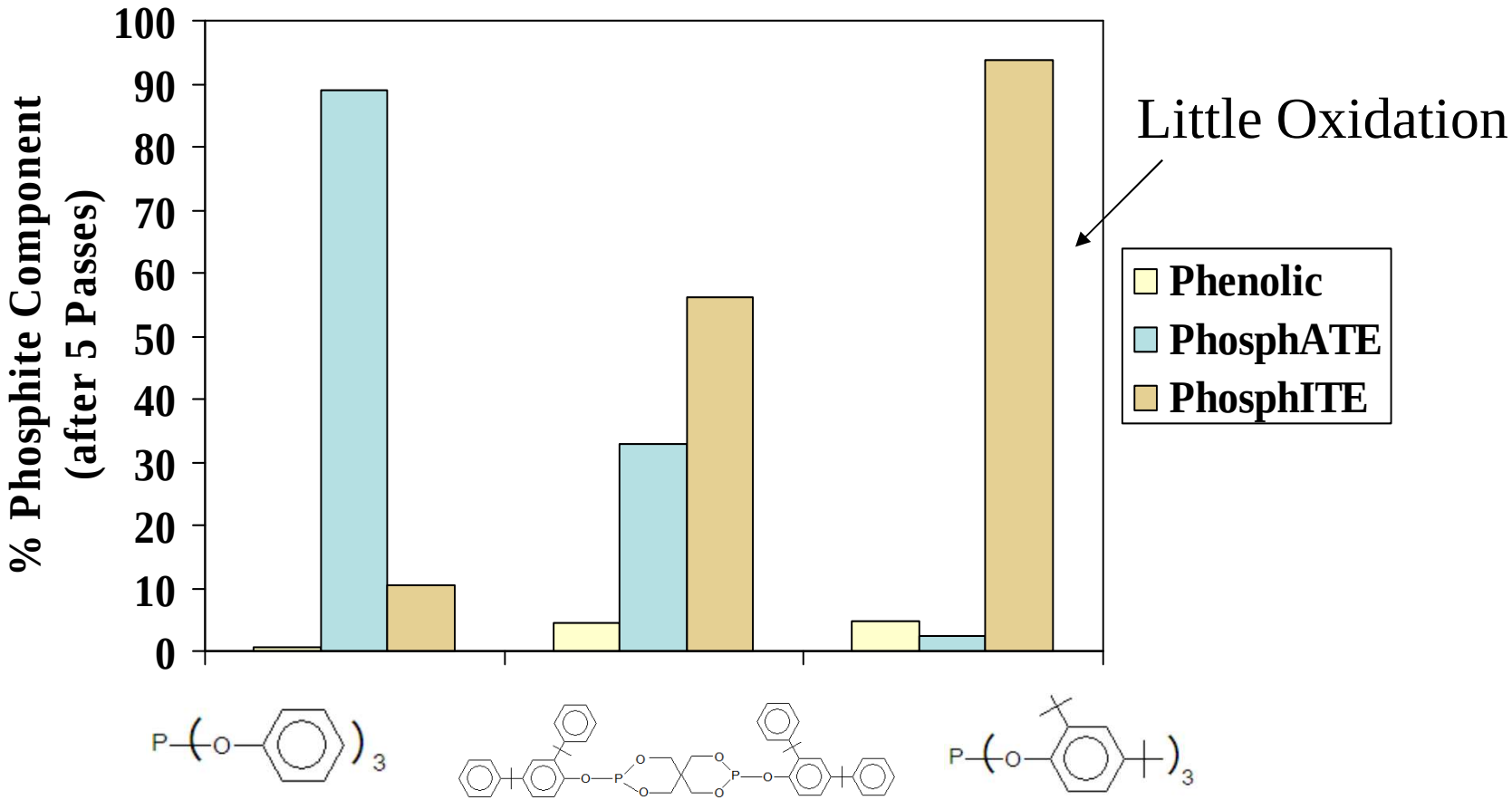


Temperature 200 C

Oxidation of Phosphites in HDPE

Multiple Pass Extrusions @200°C

% Phosphite Components After 5th Pass

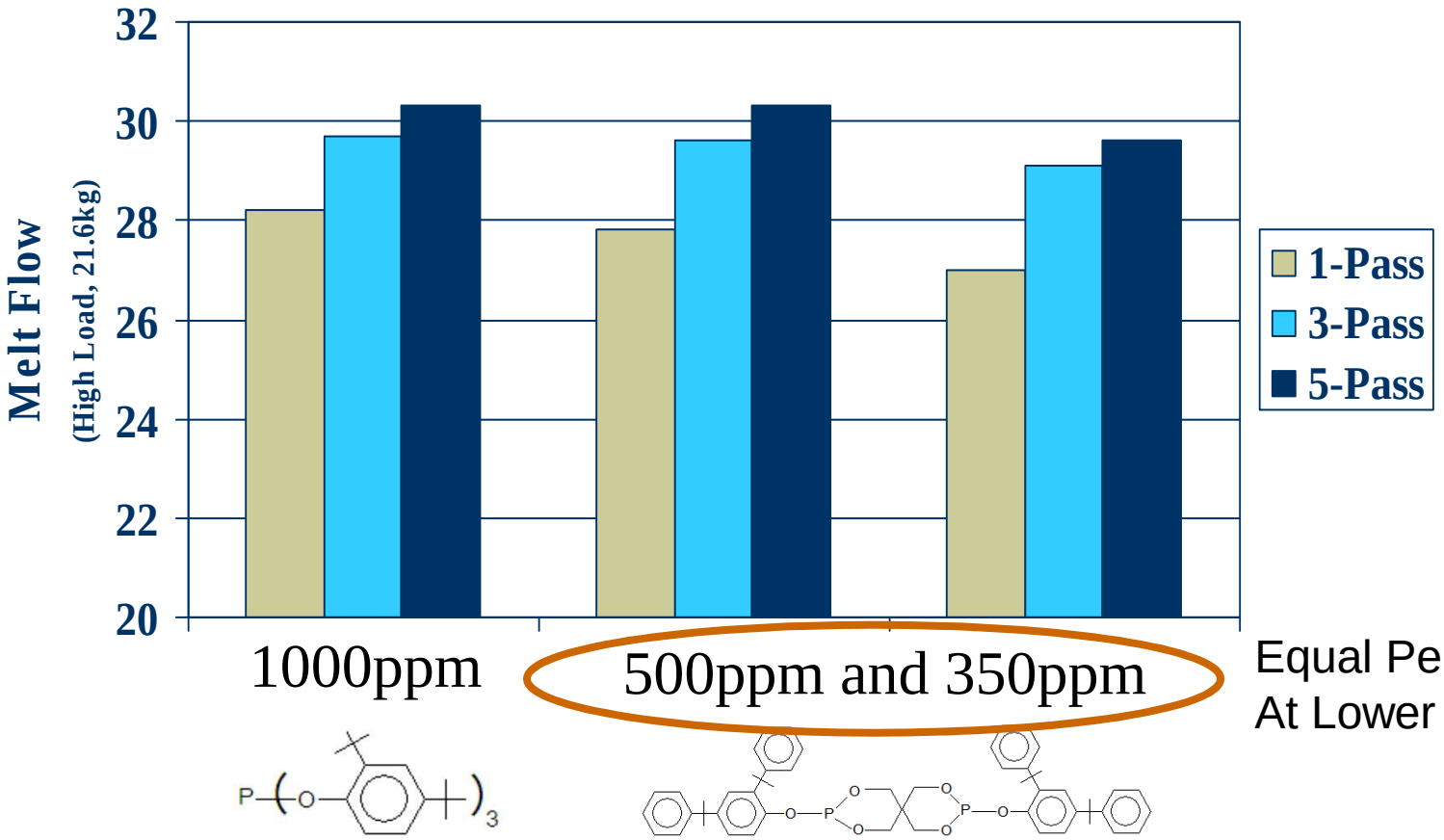


Stabilizer Performance in HDPE

- Multiple pass extrusion (laboratory single screw extruder) in HDPE at 250°C
- Retention of Melt Index (MI) and Color (YI) with respect to extrusion pass
- Loading level as indicated
- Hindered phenol present at 500ppm along with 200ppm of ZnSt

HDPE

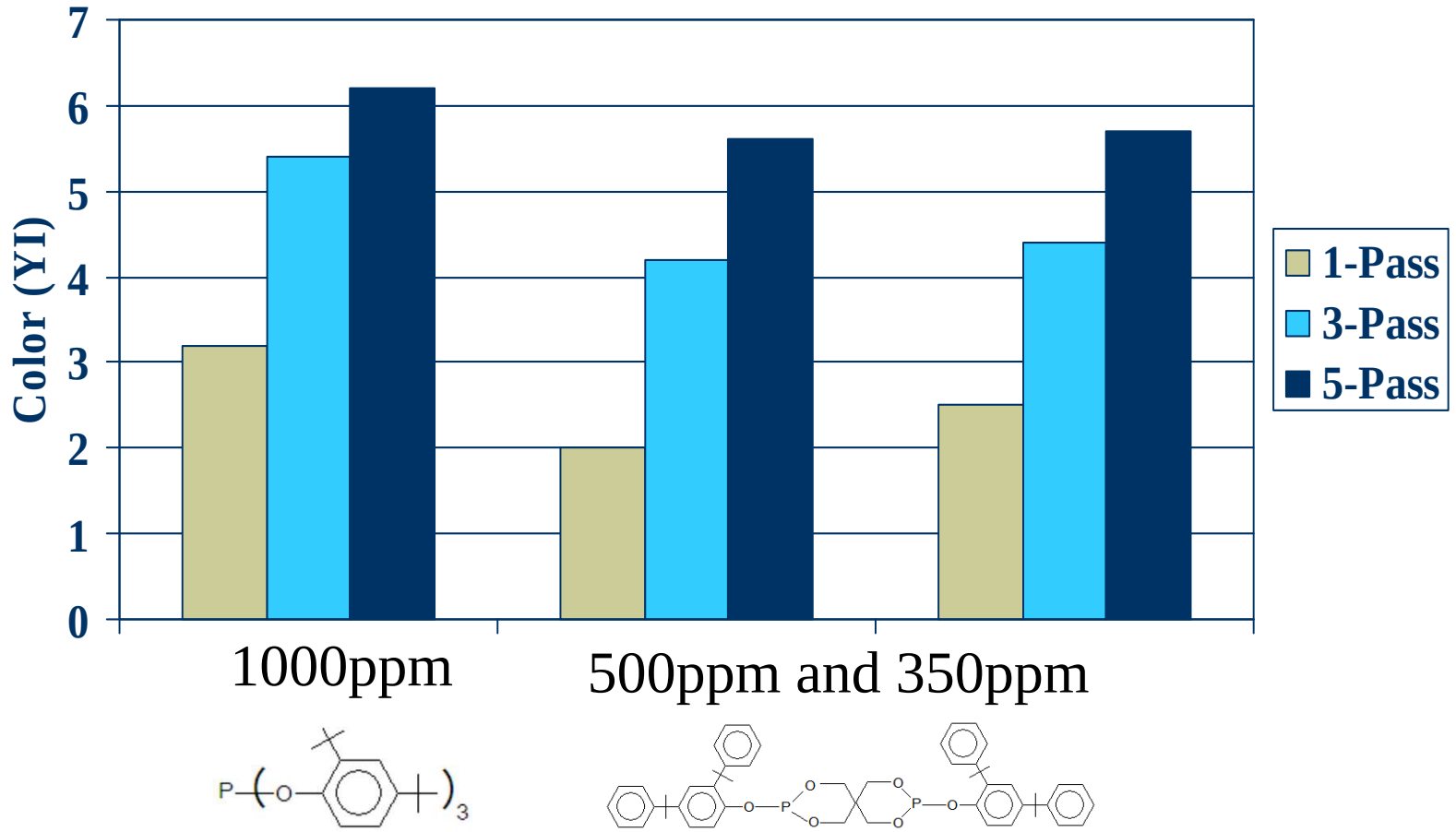
Melt Flow Stability @ 250°C



Equal Performance
At Lower Levels

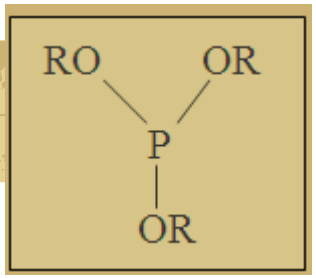
HDPE

Color Stability @ 250°C



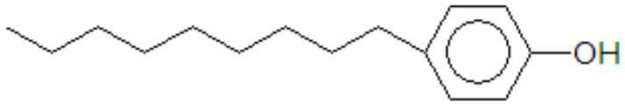
Compatibility

- Polyolefins are hydrophobic
- Increasing the polarity or crystallinity of the ligands may cause incompatibility
  - Plate-out on equipment
  - Post processing bloom
- In general, LLDPE is much more sensitive to these issues than HDPE. This is especially true in applications that result in low crystallinity/high amorphous content (such as cast film). Exudation issues may not occur in every case depending upon process parameters.

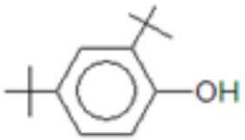


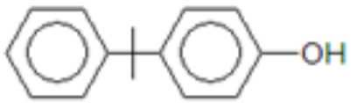
Compatibility Trends in LLDPE

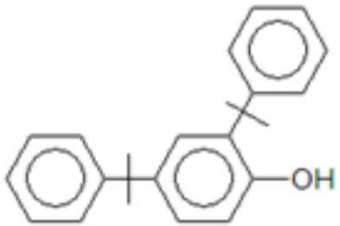
$C_nH_{2n+1}OH$ Long Chain Alcohols

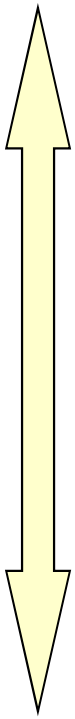


C=8 to10







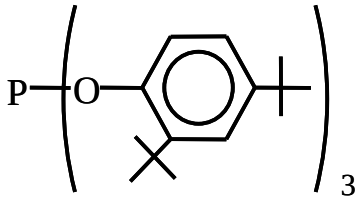


Increased Compatibility
In LLDPE

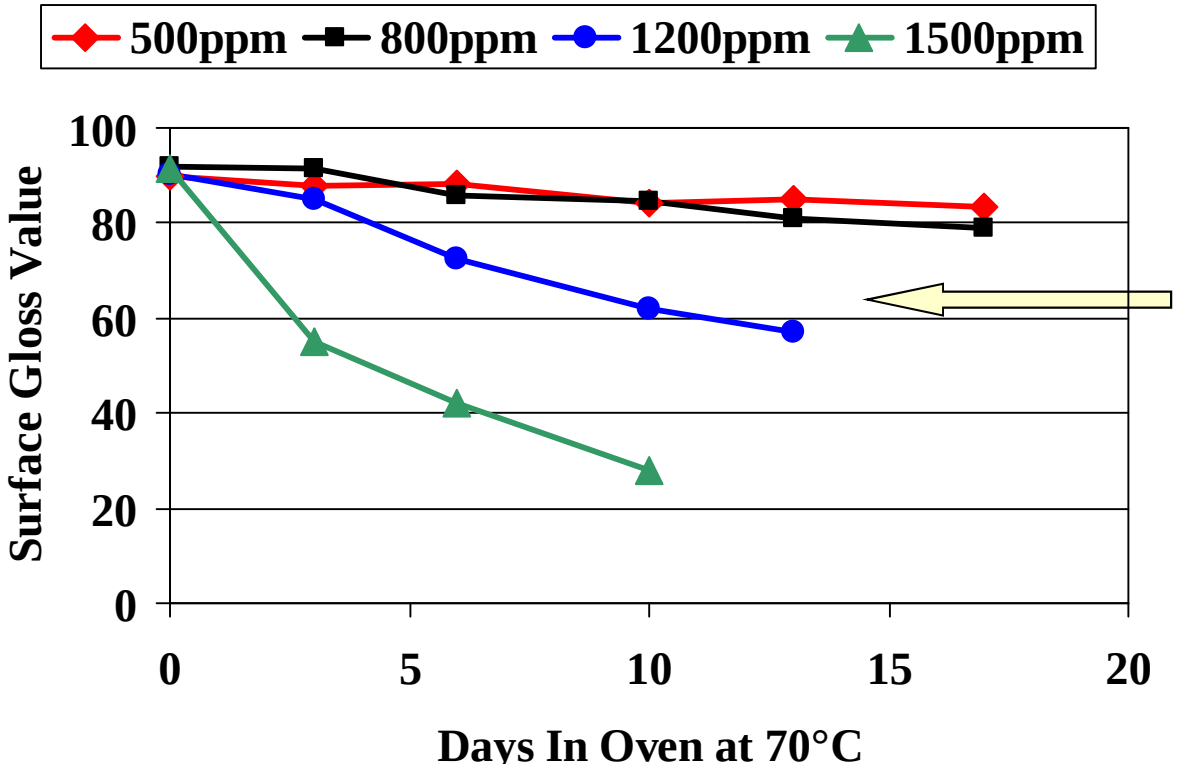
Decreased Compatibility
In LLDPE

Compatibility Measurements

- Compatibility can be studied by gloss measurements (micro-gloss at 60°) along with ATR-FTIR (surface only analysis)
- Additives are accurately measured and compounded into the specific polymer formulation through the use of a Brabender bowl/torque rheometer
- The compounded material is compression molded into plaques and quench cooled to reduce crystallinity/increase amorphous content
- The plaques are oven aged to accelerate the bloom
  - Bloom will result in loss of gloss
  - Bloom can be confirmed and identified by ATR-FTIR

Compatibility of  *in LLDPE*

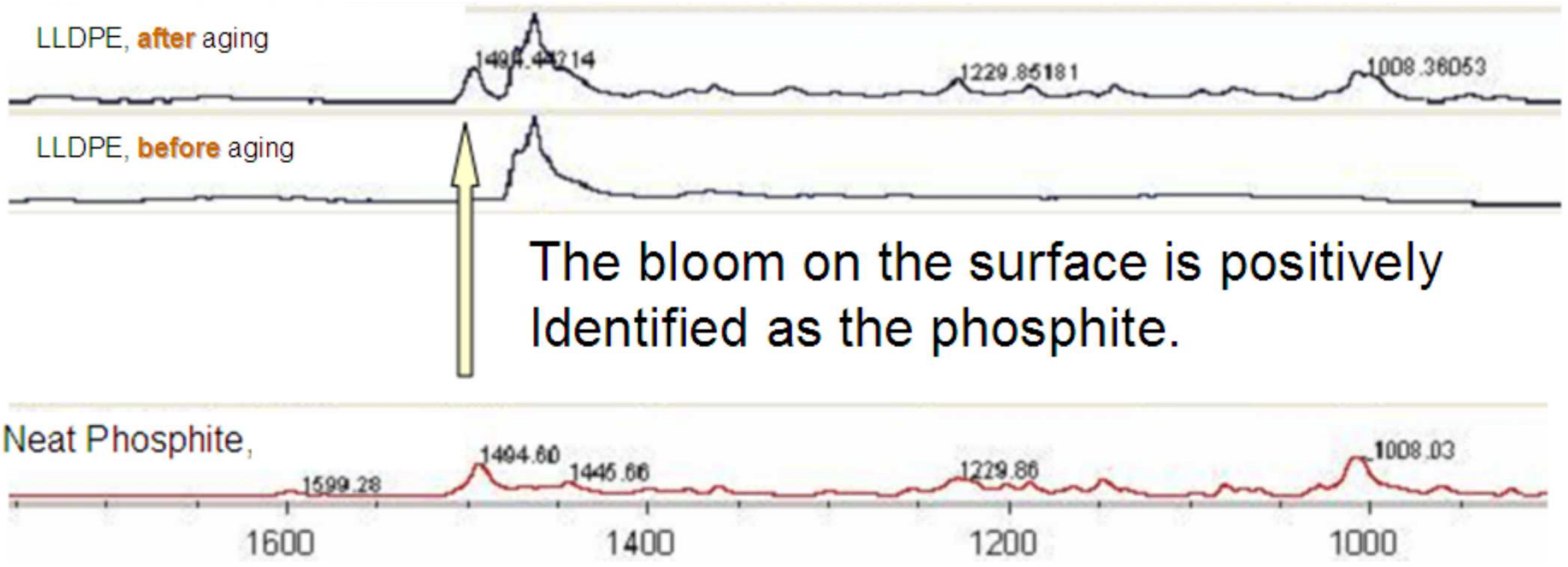
- It is known that this phosphite can bloom in LLDPE applications at levels above 1000ppm. The bloom can be accurately detected.



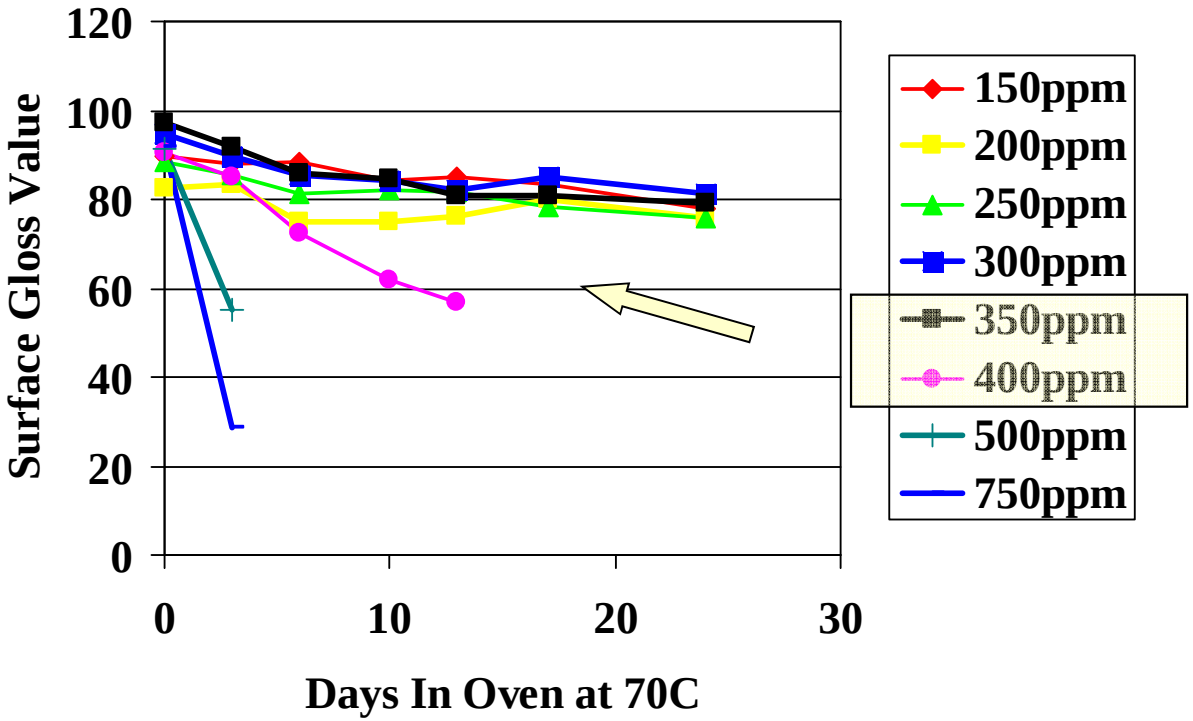
Compatibility Limit in this resin is <1,200ppm

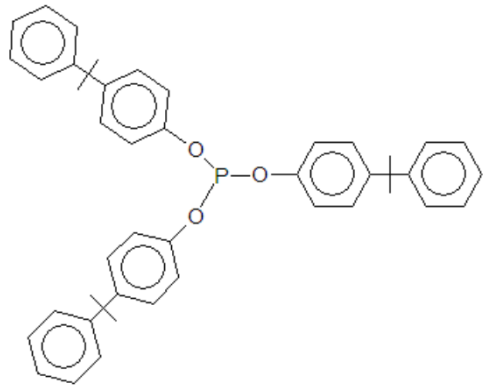
ATR-FTIR Surface Analysis

- If the phosphite is not compatible, it will bloom to the surface, decrease gloss, and can be positively identified by surface techniques such as ATR-FTIR.



Compatibility by Surface Gloss

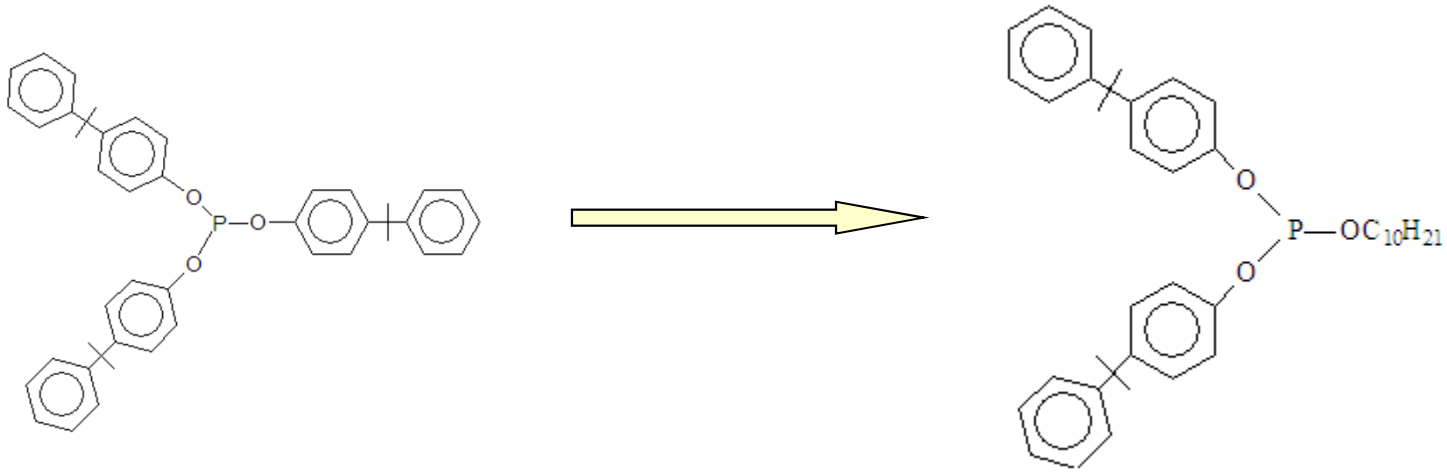




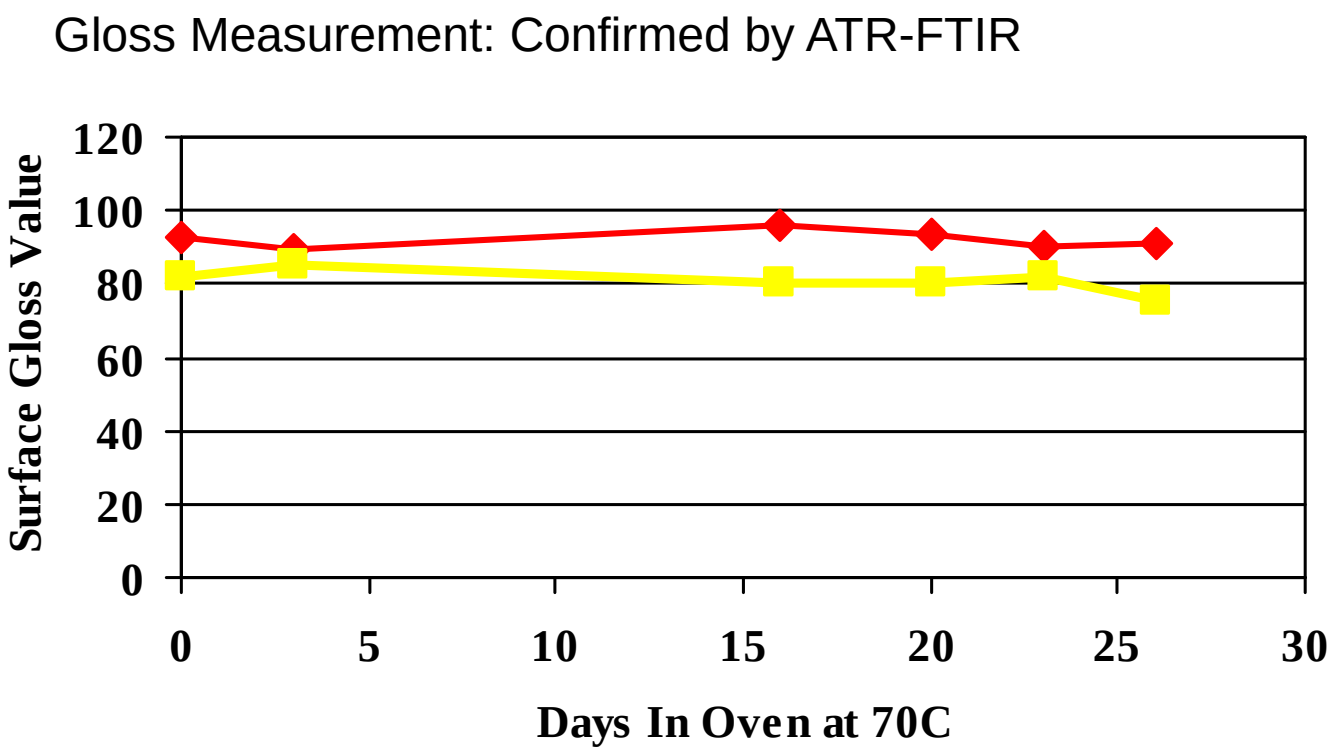
Limit of compatibility
Is ~ 350ppm

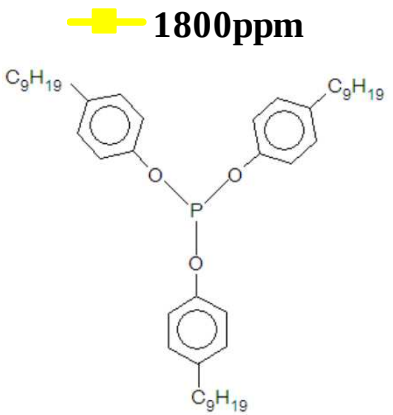
Improving Compatibility

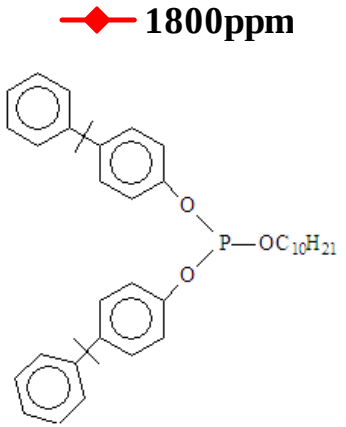
- The compatibility in LLDPE can be improved by replacing one of the ligands with a long chain alcohol



New Phosphite is as Compatible as the Industry Standard, TNPP

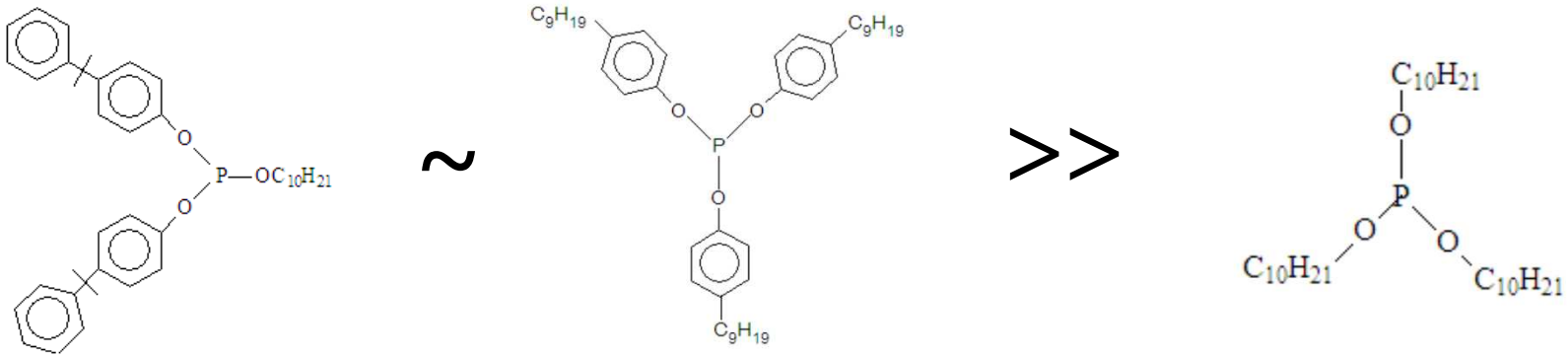






Hydrolytic Stability

- Hydrolytic stability must ultimately be measured in the polymer.
- With one alkyl ligand, the hydrolytic stability is ~ same as TNPP.
- With three alkyl ligands, phosphite is too prone to hydrolysis.

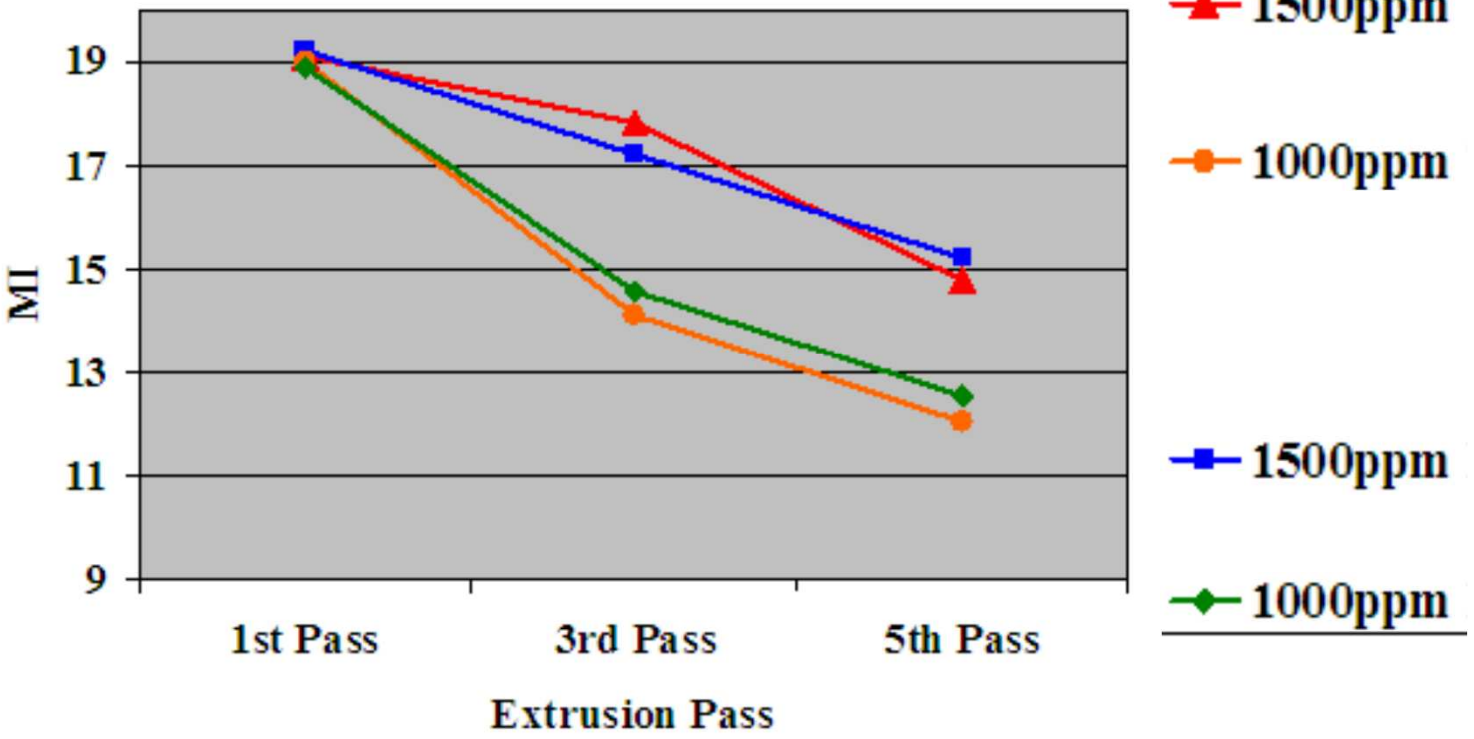


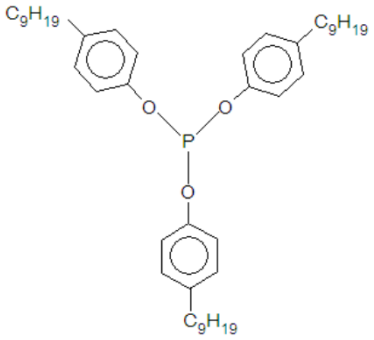
Performance Evaluation

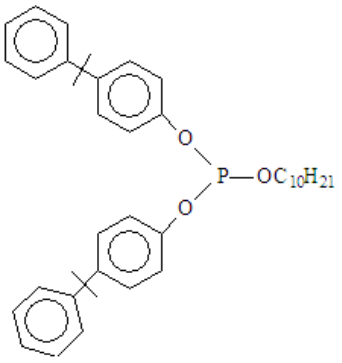
- Performance measured with multiple pass extrusion in LLDPE, MI and YI retention
- Co-rotating twin screw extruder
  - Compounding: 170-175-180-190°C
  - Multi-pass: 180-205-225-245°C
- Phosphites levels indicated, formulations also contained 500ppm primary AO

Melt Flow Index

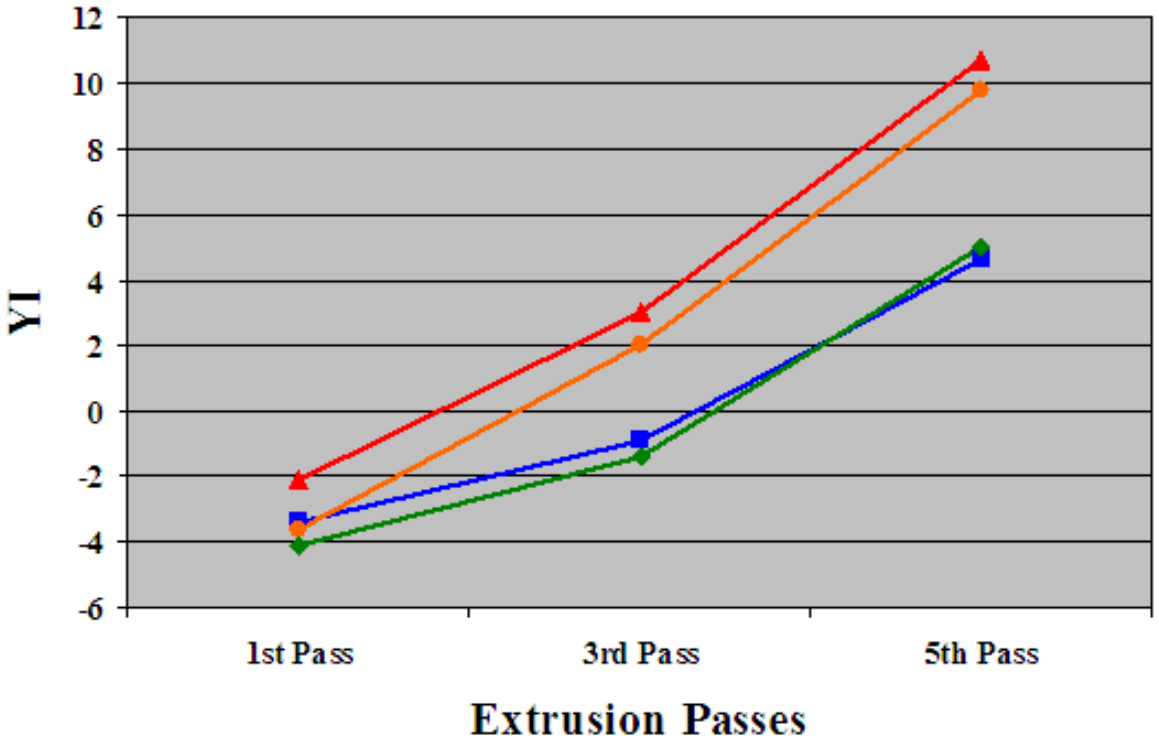
21.6kg/190°C





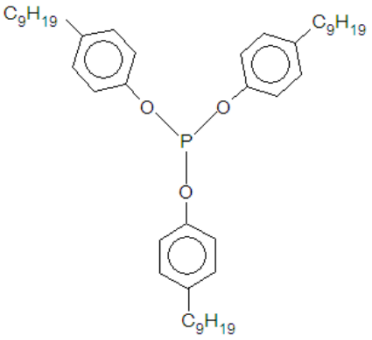


Yellowness Index



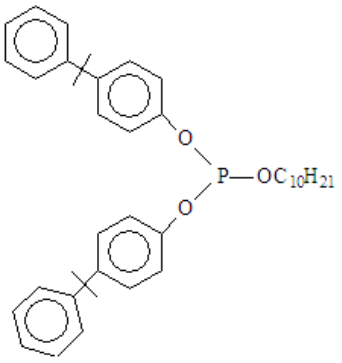
1500ppm

1000ppm



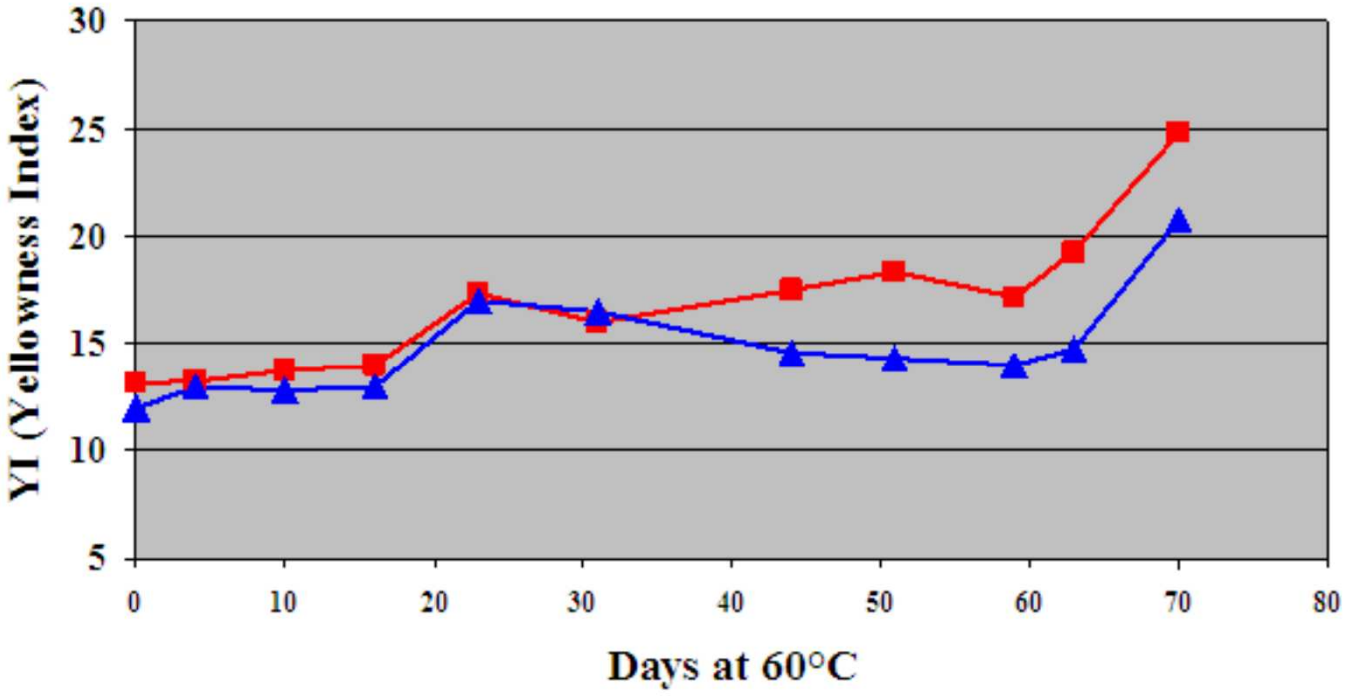
1500ppm

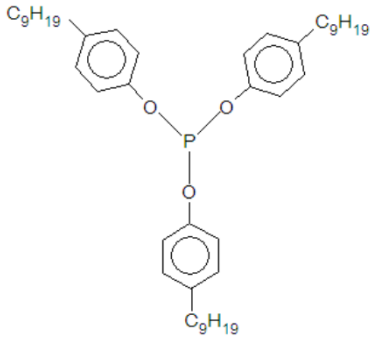
1000ppm

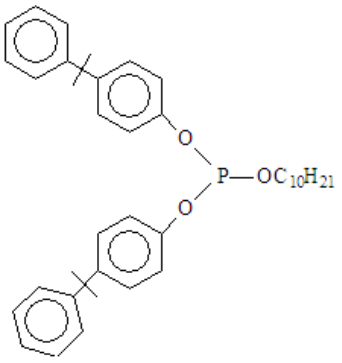


NOx Aging – 60°C

Yellowness Index - YI







New High MW Liquid Phosphite (LGP-11)

- No alkylphenols
  - It is possible to design a phosphite that meets all the required performance attributes, without the use of alkylphenols
- High molecular weight
  - Reduction in plate-out during processing and no exudation/bloom post-processing
  - Reduced volatility
  - Reduced migration and exposure

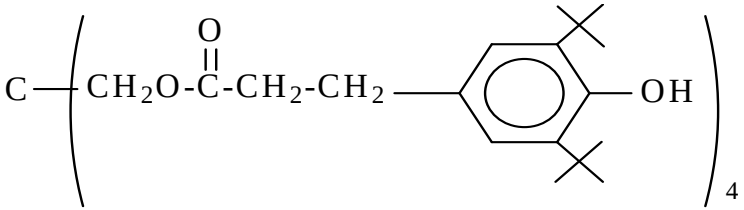
Process Stability

- Percent phosphorus correlates with the performance of the phosphite in terms of melt index (MI) control during melt processing.
  - LGP-11 (4.9% phosphorus)
  - TNPP (Trisnonylphenyl phosphite, 4.5% phosphorus)
  - SP-1 (Tris-2,4-Di-t-butylphenyl phosphite, 4.8% phosphorus)
- Color control (YI) is dependent upon ligand choice. High performance "fast" phosphites, which display facile kinetics for scavenging hydroperoxides, result in good color hold.
- Color control is also significantly improved when the phosphite is not based on alkylphenols.

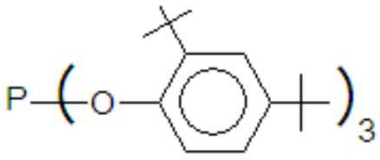
Performance Evaluation - PP

- Performance measured with multiple pass extrusion in homo-PP, MI and YI retention
- Co-rotating twin screw extruder, 260°C
- 2:1 and 1:1 blends of phosphites:AO-2. All formulations also contained 500ppm of calcium stearate

AO-2

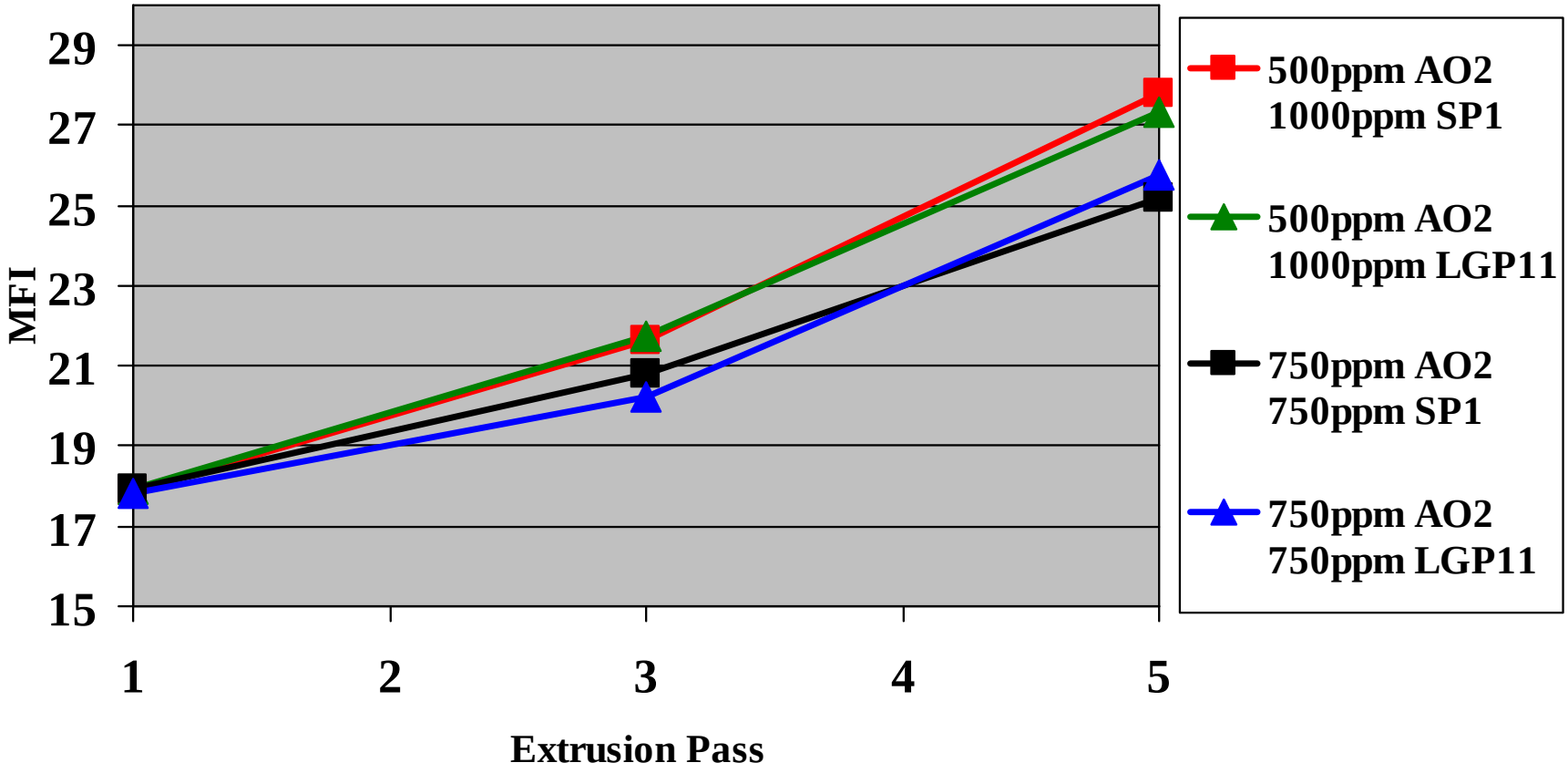


SP-1

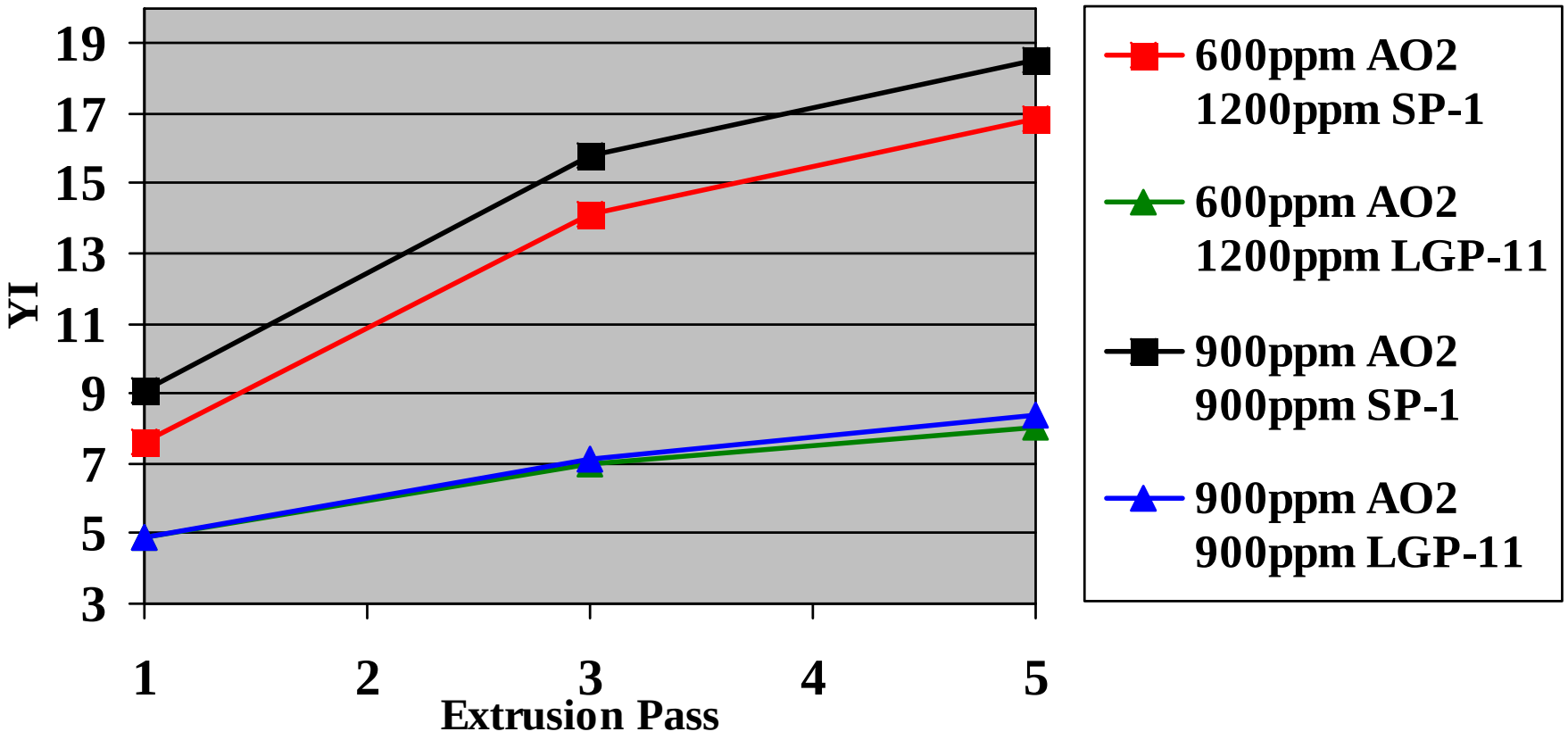


MFI (PP at 260°C)

2.16kg/230°C



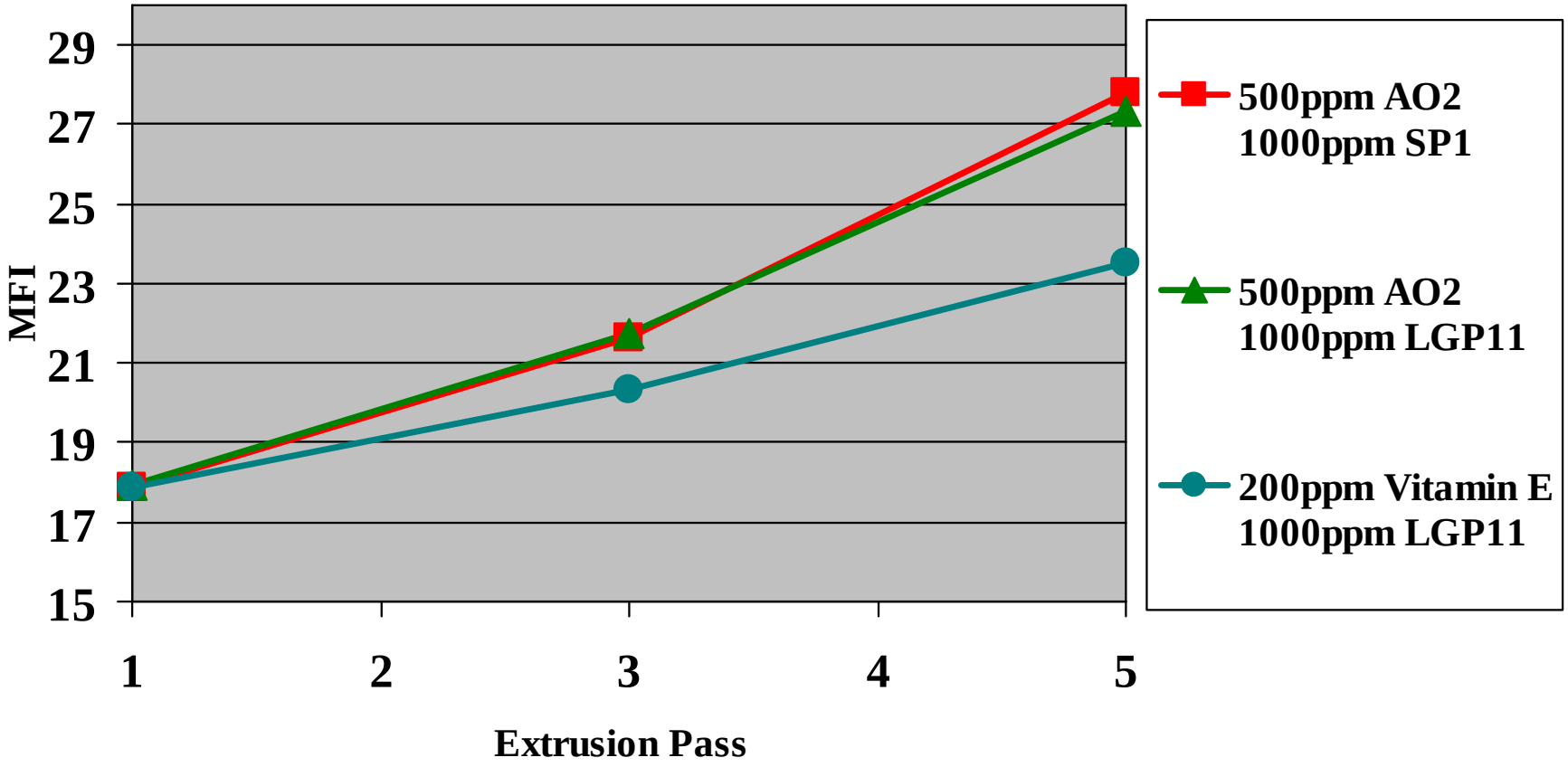
Yellowness Index (PP at 260°C)



MFI

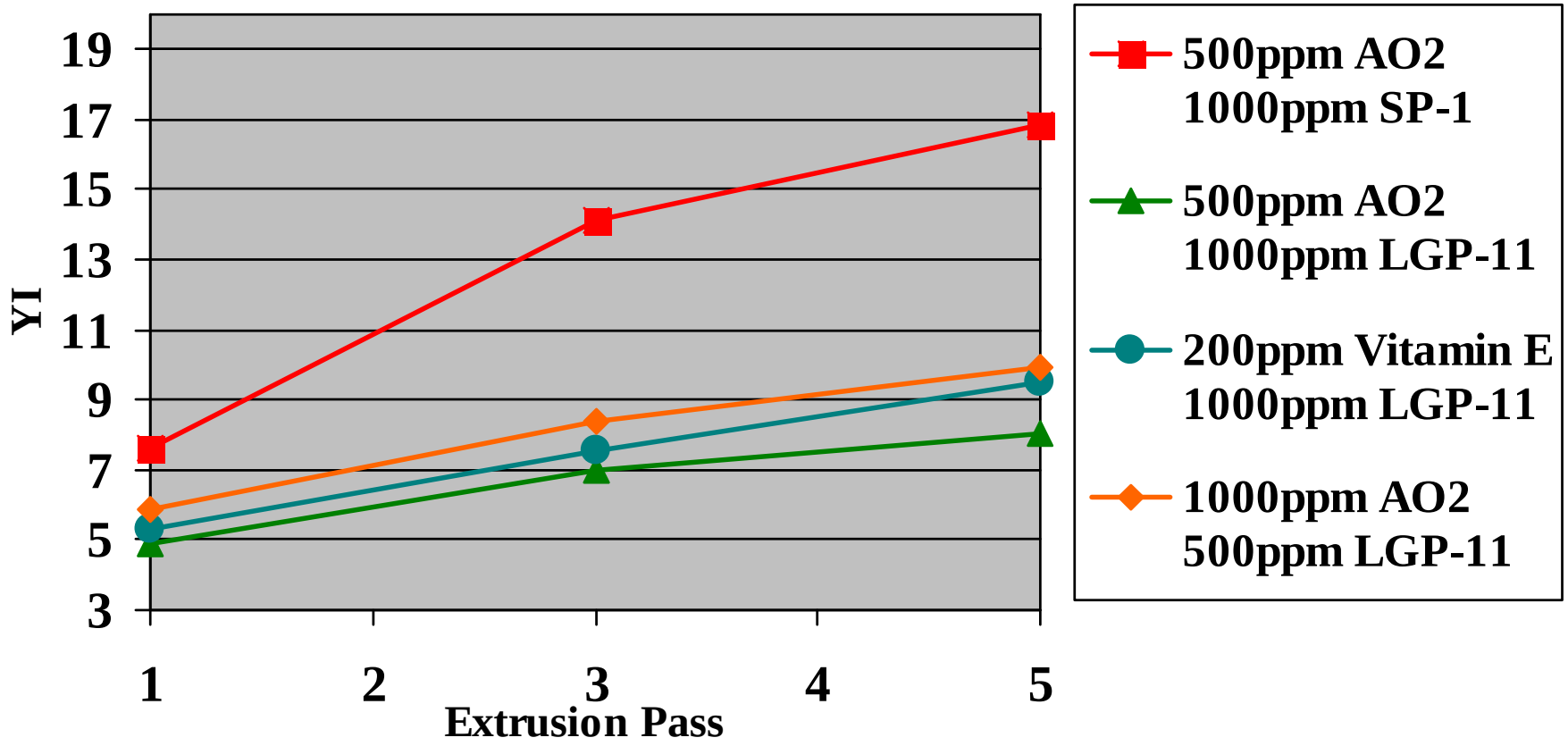
(LGP11 with Vitamin E)

2.16kg/230°C



Yellowness Index

Vitamin E and 1:2 ratio of LGP11/AO2



Ancillary Benefits of a High MW Phosphite

- In addition to performance (MI/YI), and cost performance, increasing the MW of a liquid phosphite has several benefits
- Compatibility
  - Reduced plate-out during extrusion and exudation/bloom post processing, also depends on the chemical structure of the phosphite ligands.
- Migration/exposure
  - Increasing MW decreases migration
- Consumer packaging benefits
  - Reduced or "no" migration, (organoleptics)
  - No alkylphenols
  - Non-toxic, biodegradable raw materials

Phosphite Compatibility

- The structure and choice of ligand(s) on the phosphite controls its compatibility in the resin
- The compatibility of a phosphite can be measured during processing and also post-processing
  - Plate-Out
    - Incompatibility during melt processing
    - Results in material "plating out" or leaving deposits on equipment such as calendaring mills or the cooling drum/roll during cast film production
  - Bloom/Exudation
    - Post processing
    - Over time, incompatible phosphites can bloom to the surface of LLDPE film after it has been compounded/processed. This results in either dusting/powder or a sticky surface

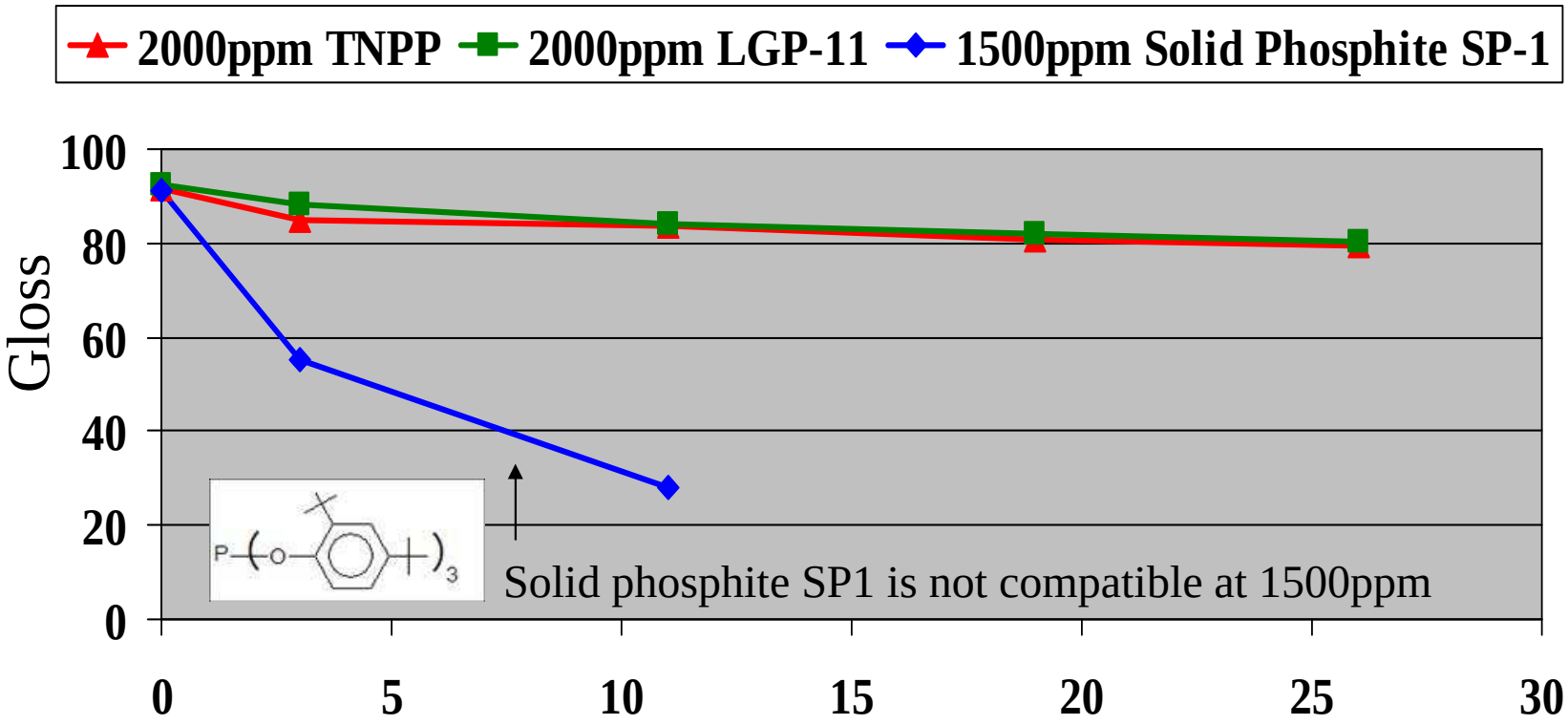
Bloom/Exudation in LLDPE

- Additive bloom in cast film LLDPE applications can be a problem because of the amorphous nature of the film.

- The compatibility of a phosphite can be measured by Brabender-Bowl (torque rheometer) compounding of LLDPE formulation 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.

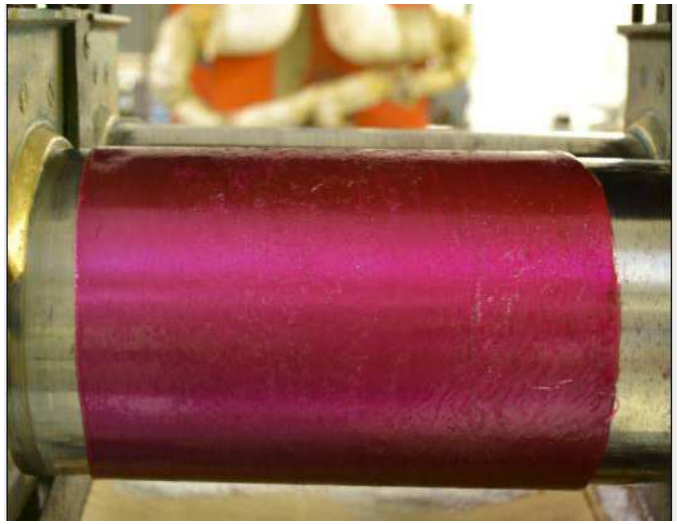
- Bloom can be monitored visually or by measuring the surface gloss. If the phosphite blooms, the surface gloss of the plaque will be reduced. The composition of the bloom can be identified by surface ATR-FTIR.

Compatibility at 2000ppm in LLDPE



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. Any migration of the additives will also carry the pigment to the surface of the rolls.
- The pigmented formulation is melt processed for a specific period of time and then removed.



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.

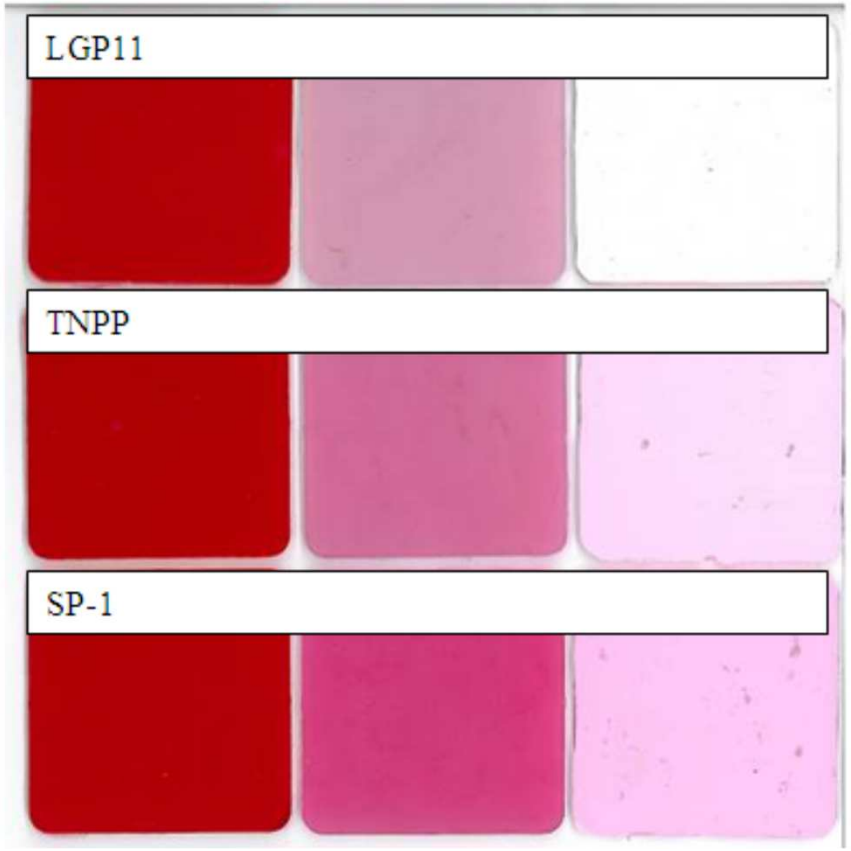
Formulations

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		

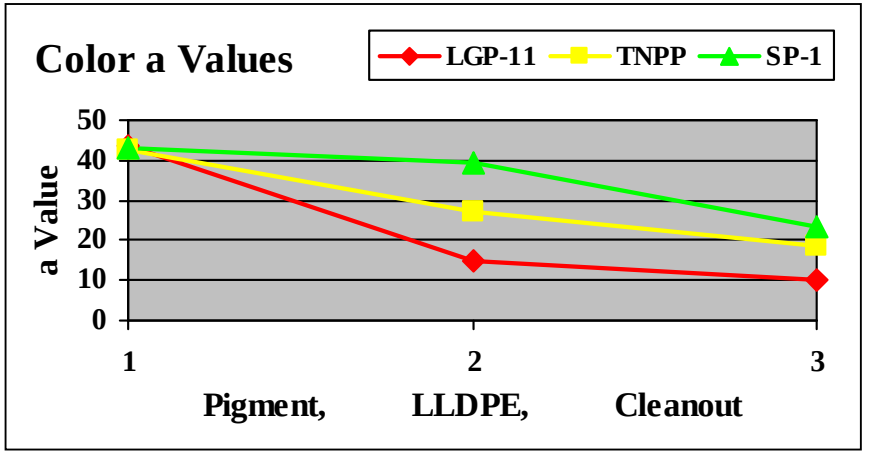
Blank LLDPE = No phosphite or AO

Plate-Out Results

Pigmented Formulation → Blank LLDPE → Purge/Cleanout



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



Color Measurements

	L	a	b	YI
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

Conclusion

- LGP-11 is very compatible in LLDPE, and will not bloom/exude even in applications that result in highly amorphous LLDPE such as cast film.
- Also, its high MW has the potential to reduce plate-out on equipment during cast film production, compared to typical monophosphites such as TNPP and SP-1.

Consumer Exposure

- Media is increasingly placing the spotlight on "chemicals" that consumers are indirectly exposed to. Much of the emphasis has been on alkylphenols:
  - Food and beverage containers
  - Packaging such as food films and can coatings
  - Water pipes
  - Detergents, cosmetics, diapers…
- Analytical techniques have become sensitive enough to measure concentrations below parts-per-billion

Ideal Approach…

- Design a stabilizer that is not based on alkylphenols, but rather from biodegradable, non-toxic materials
- Increase the molecular weight to reduce or eliminate migration and thus consumer exposure
- It is generally assumed that migration from polymers is controlled by Fickian diffusion, which is related to the molecular weight of the additive.
  - MW LGP-11 is >> than TNPP or SP-1

Fickian Diffusion

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

- $M_t = 2C_{po}(D_p t/\pi)^{1/2}$ *
  - M_t = Migration at time t
  - C_{po} = Concentration in the polymer
  - D_p = Polymer diffusion coefficient

Molecular Weight

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

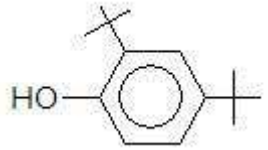
** A.Baner, J.Brandisch, R.Franz, O.G. Piringer, *Food Additives and Contaminants*, 1996, **13(5)**, 587-601

FDA-Type Migration Study of Additives Into Food

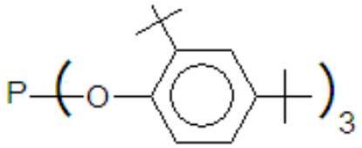
- Selected additives were compounded into LLDPE using a Brabender torque rheometer at a concentration of 1000ppm. Formulations were then compression molded into plaques.
- Plaques were exposed to 95% ethanol at 70°C for 2 hours. 95% ethanol is considered a fatty food simulant. Solutions were then analyzed for additive content.
- Additive migration was measured as µg of additive that migrated per inch squared surface.

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

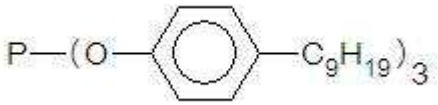
Additive Migration (Molecular Weight)



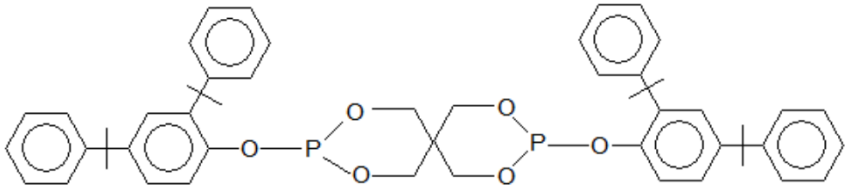
DTBP (MW = 206)



SP-1 (MW = 646)



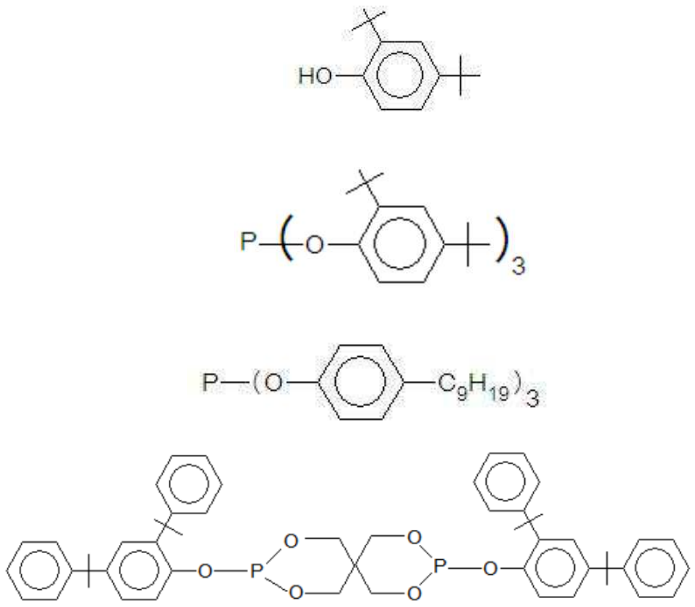
TNPP (MW = 688)



SP-2 (MW = 852)

LGP-11 (MW > 1500)

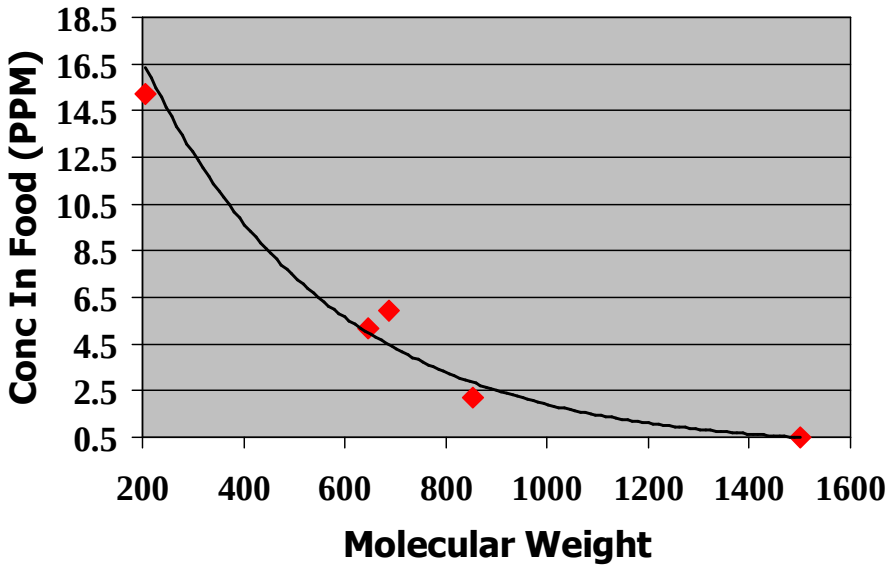
Migration of Additives - Fatty Food Simulant



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**

Migration and Molecular Weight

- Amount of migration decreases with MW
  - Relationship is not linear
  - At a given time and temperature:
    - $D_p \sim \text{Constant} * \exp(-0.01 * M_w)$
    - $\text{Migration} = \text{Constant} * C_{PO} * (D_p)^{1/2}$



LGP11 > 1500 Mw

Migration and Resin Concentration

- However, migration <u>is</u> directly proportional to the concentration of the additive in the polymer (C_{PO})
  - Migration = Constant * C_{PO} * $(D_p)^{1/2}$

- 500ppm of SP-2 performs similar to 1000ppm of SP-1. Thus, migration can be reduced significantly by using a high performance/high MW stabilizer, at a lower loading level.

Additive	Loading Level in Polymer	Ppm in Food
SP-2	0.1%	2.2
SP-2	0.05%	1.4
SP-1	0.1%	5.2

} Equal Performance but ¼ the Migration

Migration and Compatibility

- If an additive does not bloom or exude after the polymer has been processed, it is labeled as "compatible" at that concentration.
- Compatibility is not strictly related to migration into food simulants. A compatible phosphite will still migrate. Migration will be controlled by the MW of the additive (at a constant time/temperature/loading level).

More Compatible in LLDPE ⟷ Less Compatible in LLDPE

TNPP > SP-1 > SP-2

- Migration into food (ppm)

TNPP ≅ SP-1 > SP-2

(5.9ppm) (5.2ppm) (2.2ppm)

Conclusions

- LGP-11 is a high MW liquid phosphite that offers better performance than typical commodity phosphites such as TNPP and SP-1. Color hold is exceptional.

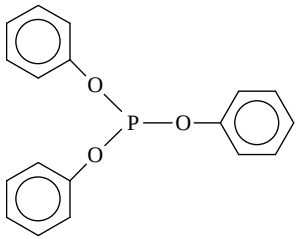
- Increasing the MW has additional ancillary benefits. These include:
  - Decreased plate-out and exudation/bloom
  - Decreased volatility
  - Decreased migration from the polymer

- LGP-11 is an example of "GREEN CHEMISTRY".
  - No alkylphenols
  - Significantly decreased consumer exposure versus other additives
  - Raw materials are non-toxic and readily biodegradable, thus no long term environmental effects

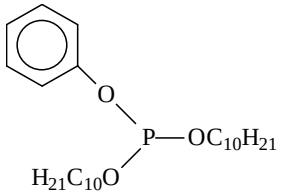
Stabilizer Challenges in PVC

- The property-structure relationships of phosphites still hold true (thermal and hydrolytic stability, volatility, etc.)
- However, PVC has much different selection rules than polyolefins due to its decomposition mechanism.
- The role of stabilizers in PVC is to scavenge thermally labile chlorines (tertiary/allyic), HCl and Lewis Acids ($ZnCl_2$) and to also act as an antioxidant.

General Phosphite Selection Rules

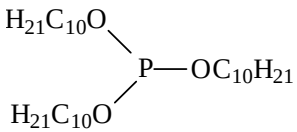


- All-aryl phosphites generally cannot be used as the sole phosphite, no ability to participate in Arbusov reactions. They can be used at small levels with other phosphites.

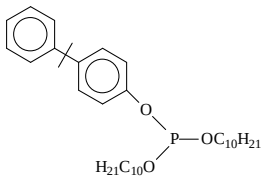


- Phenyl-alkyl based phosphites give best cost performance and overall properties. However, they are based on phenol and can generate phenol during and post processing. Phenol is a VOC.

General Phosphite Selection Rules



- All-alkyl phosphites give improved early color at expense of long term process stability/char. Reduced hydrolytic stability. Hydrolysis can liberate free alcohols, which are also VOCs. Excellent clarity and long term heat aging.



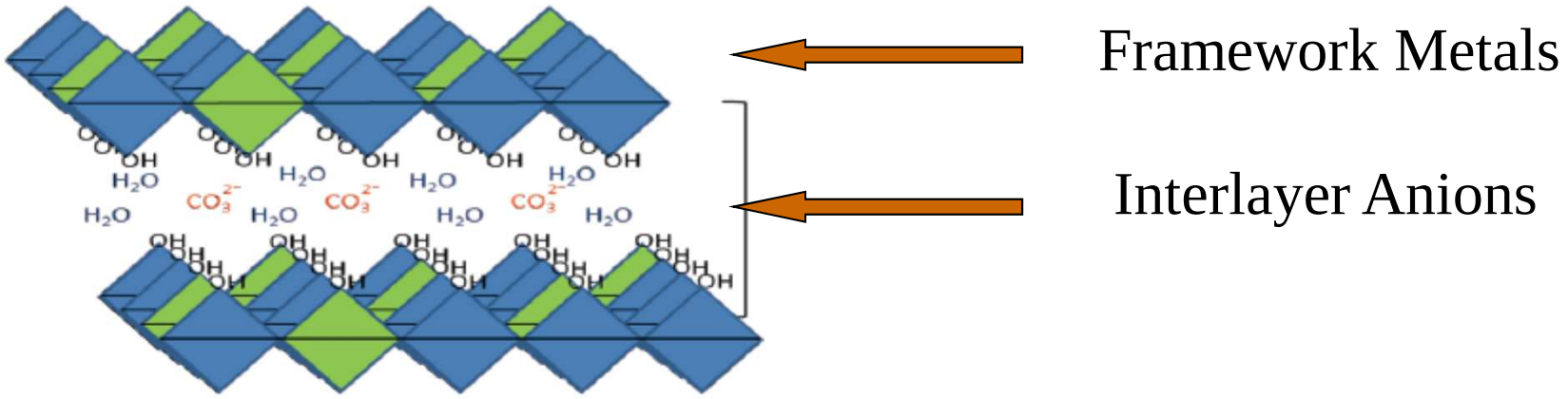
- Hindered phenolic-alkyl phosphites can be designed to give optimum overall properties, but at added expense.

Developments in Rigid PVC Stabilizers

- In the US, tin stabilizers dominate the market and represent state of the art.
- Europe has traditionally used lead based stabilizers for PVC. However, they will completely switch away from lead in the next several years. The most common replacement are solid Calcium/Zinc stabilizers.
- One of the critical components of these stabilizers is Layered Double Metal Hydroxides (LDHs).

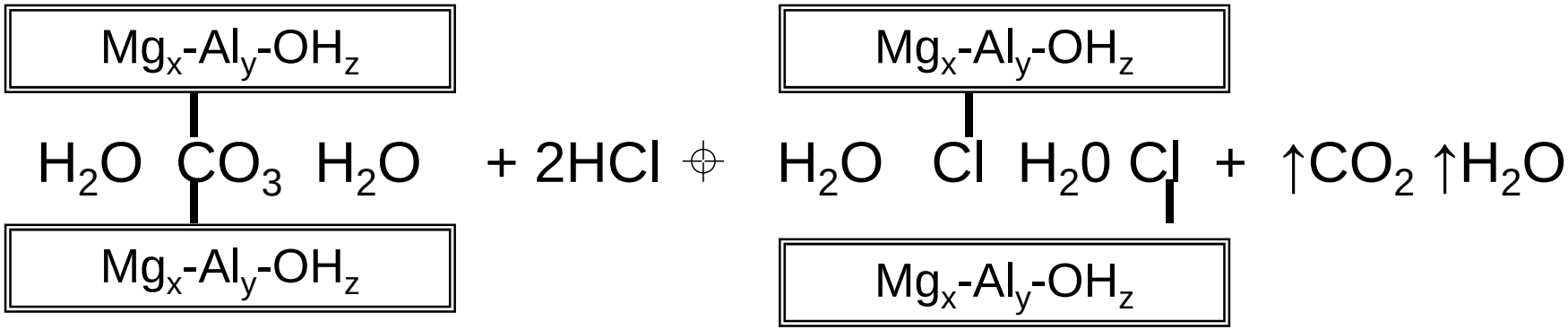
Layered Double Metal Hydroxides (LDHs)

- LDHs are synthetic crystalline materials similar in structure to hydrotalcite.
- They are layered materials that contain various metals in the framework, surrounded by hydroxyl groups. The ratio of the metals-hydroxyl groups results in a positive charge. This charged in not localized but rather dispersed across the framework.
- The anion is present is the interlayer region. Many different anions can be used, although the most common is carbonate.



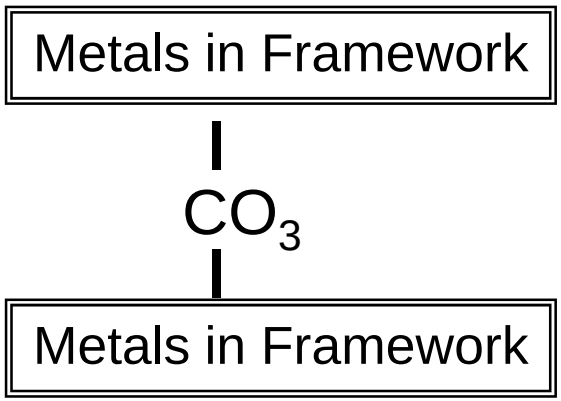
Layered Double Metal Hydroxides (LDHs)

- LDHs are used in PVC as acid scavengers.
- They are very effective at scavenging HCl, and are efficient at extending the long term process stability.
- When the LDH scavenges HCl, the chloride anion is trapped in the framework and not released. Thus the resultant chloride is not soluble. This is similar to lead, and a reason why LDHs are used in wire and cable applications. A water soluble product, such as Calcium chloride (from calcium stearate) has a negative effect on wet electricals.



Layered Double Metal Hydroxides (LDHs)

- Various metals and ratios can be used in the framework. Choice of metals has significant effect on PVC stability.
- The interlayer anions can also be changed. The most common/effective is carbonate. The outer framework can also be coated to improve dispersibility (PVC, Polyolefins).



Ex. Metal Combinations

MgAl

MgAlZn

CaAl

CaAlZn

Developments in Flexible PVC Stabilizers

- Early liquid mixed metal stabilizer were based on barium and cadmium. Because of the negative perception of cadmium, the industry has moved to mainly barium-zinc stabilizer systems.
- Recently there has also been an increase in the use of calcium-zinc stabilizers especially in less shear intensive applications such as plastisols.

Ba/Cd ⌖ Ba/Zn ⌖ Ca/Zn

Current Challenges – Mixed Metal Stabilizers

- Growing concern over nonylphenol in stabilizer packages including polyolefins, rubber and PVC.
- Reduction of VOCs and phenol in liquid mixed metal stabilizers.

Alternative to TNPP in Food Contact PVC

- TNPP is used mainly in food contact PVC applications. It was the only liquid phosphite with FDA indirect food contact approvals for PVC.
- Recently tri-lauryl phosphite (TLP) has received FDA clearance. It also offers much better performance than TNPP in PVC applications.

626	Trilauryl phosphite (CAS Reg No. 3076-63-9).	Dover Chemical Corporation Dover Chemical Corporation	As an antioxidant in vinyl chloride polymers and linear low density polyethylene.	Limitations/ Specifi-cations	August 3, 2006	CAT. EXCL. 21 CFR 25.32(i) and (j)

626	As an antioxidant in vinyl chloride polymers and linear low density polyethylene.	(1) For use at levels not to exceed 1 percent by weight of finished vinyl chloride polymers in contact with all food types under Conditions of Use B through H, as described in Table 2. (2) For use at levels not to exceed 0.25 percent by weight in linear low density polyethylene complying with 21 CFR 177.1520 (c), items 3.1 and 3.2, where the density of the polymer is not greater than 0.94 gram per cubic centimeter. Linear low density polyethylene articles containing the FCS may be used in contact with dry (with no free surface fat or oil), aqueous, acidic, and alcoholic food (up to 15 percent alcohol), under Conditions of Use B through H, as described in Table 2. The food contact substance may contain no more than 1 percent by weight triisopropanolamine (CAS Reg. No. 122-20-3).

Barium Nonylphenate

- Nonylphenol is present in most overbased Barium intermediates and Ba/Zn stabilizers.
- It is unknown whether these stabilizers will also be placed under EU focus.
- There are currently only a few alternatives that are globally registered that could directly replace Barium Nonylphenate.
- Focus is mainly Asia and partially EU. The use of BaNP in North America is generally accepted.

Current Challenges – VOCs

- One of the current challenges for liquid mixed metal stabilizers, and PVC in general, has been the reduction of VOC's.
- The EU market in particular has been focused on VOCs, in addition to phenol content.
- Two main areas of focus have been:
  - Wallcovering (US)
  - Plastisol Top Coat Flooring

Challenge: Reduce VOCs and Phenol

- The wall covering industry has shifted towards low VOC stabilizer packages.
- The stabilizer industry can now offer stabilizers that meet Greenguard certified low emissions.

Liquid Mixed Metal Stabilizers

- Typical Barium/Zinc Stabilizers include:
  - Ba salt (Barium Carboxylates or Nonylphenates)
  - Zn salt (Zinc Carboxylates)
  - Liquid Phosphite
  - Solvent (used to compatibilize Ba salt)
  - Antioxidant (BPA, BHT, etc.)
  - Costabilizers (*DBM, betadiketones and others)
    - Betadiketones were a critical development in Ba/Zn stabilizers and allowed them to match the performance of Ba/Cd stabilizers

Liquid Stabilizer Components

- Ba/Zn salts [$Ba(OOR)_2$, $Zn(OOR)_2$]
  - Conjugate acids commonly used include
    - Benzoic, t-butylbenzoic, 2-ethylhexanoic, decanoic, oleic acid, (nonylphenol)
- Compatibilizing Reagents
  - Aliphatic Solvents, glycols
  - Keep the mixed metals in solution with the phosphite (solubilize metal salt, lower viscosity of liquid stabilizer)

Phosphites are a critical component, and in some cases may be present at >60%

- There are many commercial phosphites available for use in PVC

Aryl Phosphites
Trisnonylphenyl phosphite (DP4)
Triphenyl phosphite (DP10)

Bisphenol A (BPA) Phosphites
Alkyl (C_{12-15}) BPA phosphite (DP613)
Alkyl (C_{10}) BPA phosphite (DP675)

Alkyl Phosphites
Triisodecyl phosphite (DP6)
Trisisotridecyl phosphite (DP49)
Trilauryl phosphite (DP53)
Triisooctyl phosphite (DP74)

Dipropylene Glycol Phosphites
Tetraphenyl DPG diphosphite (DP11)
Poly DPG phenyl phosphite (DP12)

Dialkyl/aryl Hydrogen Phosphites
Diphenyl phosphite (DP213)
Diisoctyl phosphite (DP298)

Alkyl-Aryl Phosphites
Phenyl diisodecyl phosphite (DP7)
Diphenyl isodecyl phosphite (DP8)
Diphenyl ethylhexyl phosphite (DP9EH)

Pentaerythritol Phosphites
Diisodecyl PE Diphosphite (DP1220)

Common Solvents and Diluents

(Boiling Points)

- Mineral Spirits ~140-210°C
- Mineral Oils ~180-300°C
- 2-Ethylhexanol ~184°C
- Isodecyl Alcohol ~220°C
- Dipropylene glycol ~230°C
- Dipropylene glycol, methyl ether ~190°C
- Tripropylene Glycol ~273°C
- Dioctyl Phthalate ~384°C

Metal Conjugate Acids

(Boiling Points)

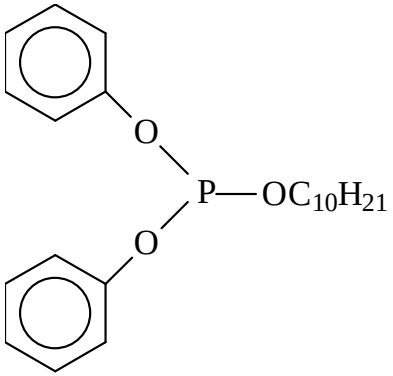
- 2-Ethylhexanoic acid ~228°C
- Benzoic acid ~249°C
- Neodecanoic acid ~275°C
- Nonylphenol ~290°C
- Oleic acid >330°C

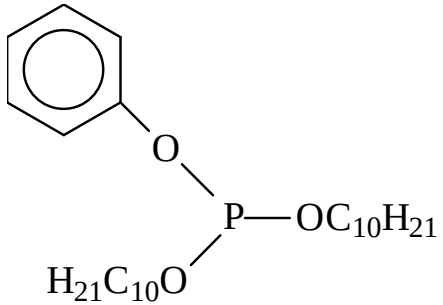
Phosphite Components
(Boiling Points)

Phenol	~182°C
2-Ethylhexanol	~184°C
IDA	~220°C
Dipropylene Glycol	~230°C
Nonylphenol	~290°C
Bisphenol A	>270°C

*Proper Choice of a Phosphite Can Help **Ba/Zn** and **Ca/Zn** Stabilizers Meet Greenguard Emissions*

- Besides solvents and 2-ethylhexanoic acid, phosphites contribute to VOC's.
- The VOC components are mainly phenol and the alcohol ligands.
- Most of the commonly used phosphites have phenol as one of the ligands.





Phosphite Reactions in PVC

- Peroxide decomposition

$$P(OR)_3 + R'OOH \longrightarrow O{=}P(OR)_3 + R'OH$$

- Arbuzov and related reactions

$$P(OR)_3 + Cl\text{-}R' \text{ (labile)} \longrightarrow (RO)_2P(O)\text{-}R' + RCl$$

$$P(OR)_3 + HCl \longrightarrow (RO)_2P(O)H + RCl$$

$$2P(OR)_3 + ZnCl_2 \longrightarrow Zn[OP(OR)_2]_2 + 2RCl$$

- Hydrolysis

$$P(OR)_3 + H_2O \longrightarrow (RO)_2P\text{-}OH + ROH$$

- Addition reaction

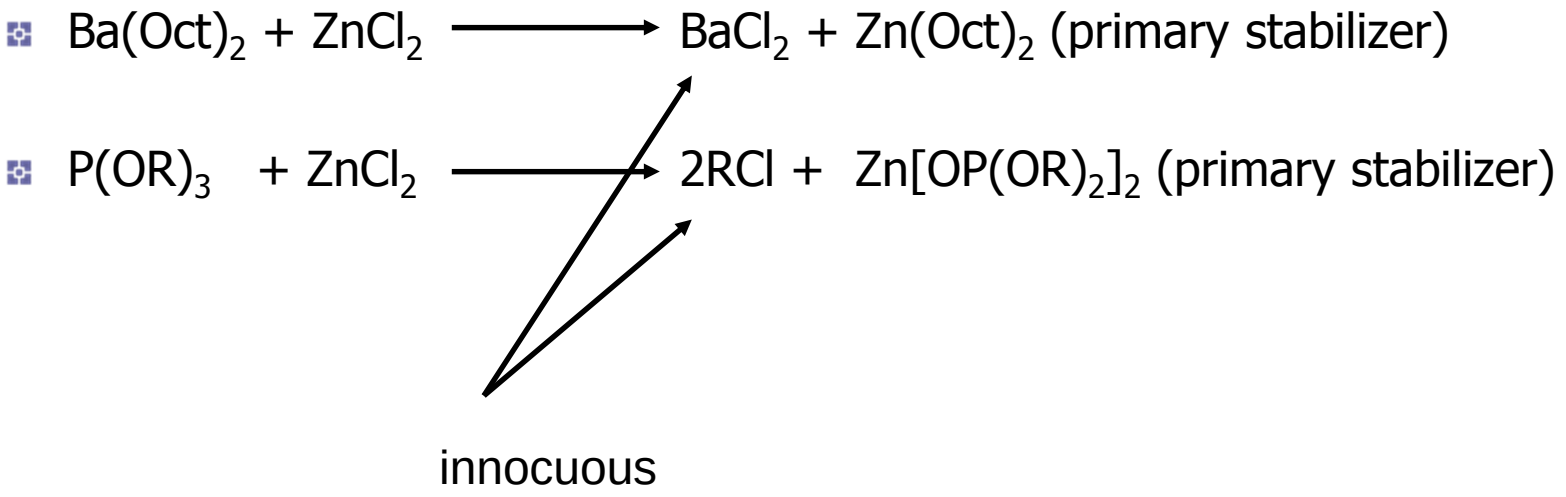
$$P(OR)_3 + -C{=}C- \longrightarrow O{=}P(OR)_2\text{-}C\text{-}C\text{-}R$$

Phosphite Chemistry

- In order to participate in the Arbusov reactions, the phosphite must contain at least one alkyl group.
- All-aryl phosphites cannot react with HCl, $ZnCl_2$ or labile chlorines, thus they are not as efficient as PVC stabilizers and result in poor early and mid-term color.

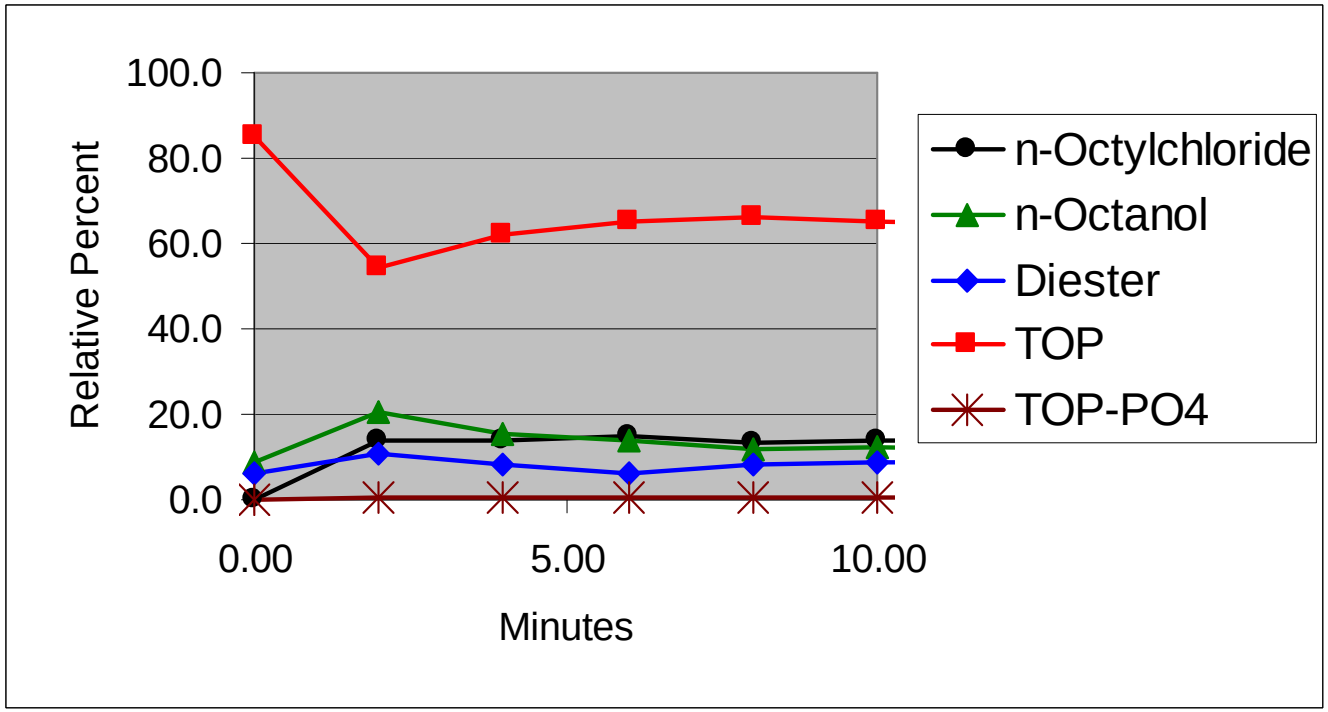
Phosphites and $ZnCl_2$

- Phosphites with at least one alkyl groups can regenerate a primary zinc stabilizer much the same way barium components regenerate zinc in a mixed metal stabilizer according to Frye-Horst Theory:



TOP (Trioctyl Phosphite)

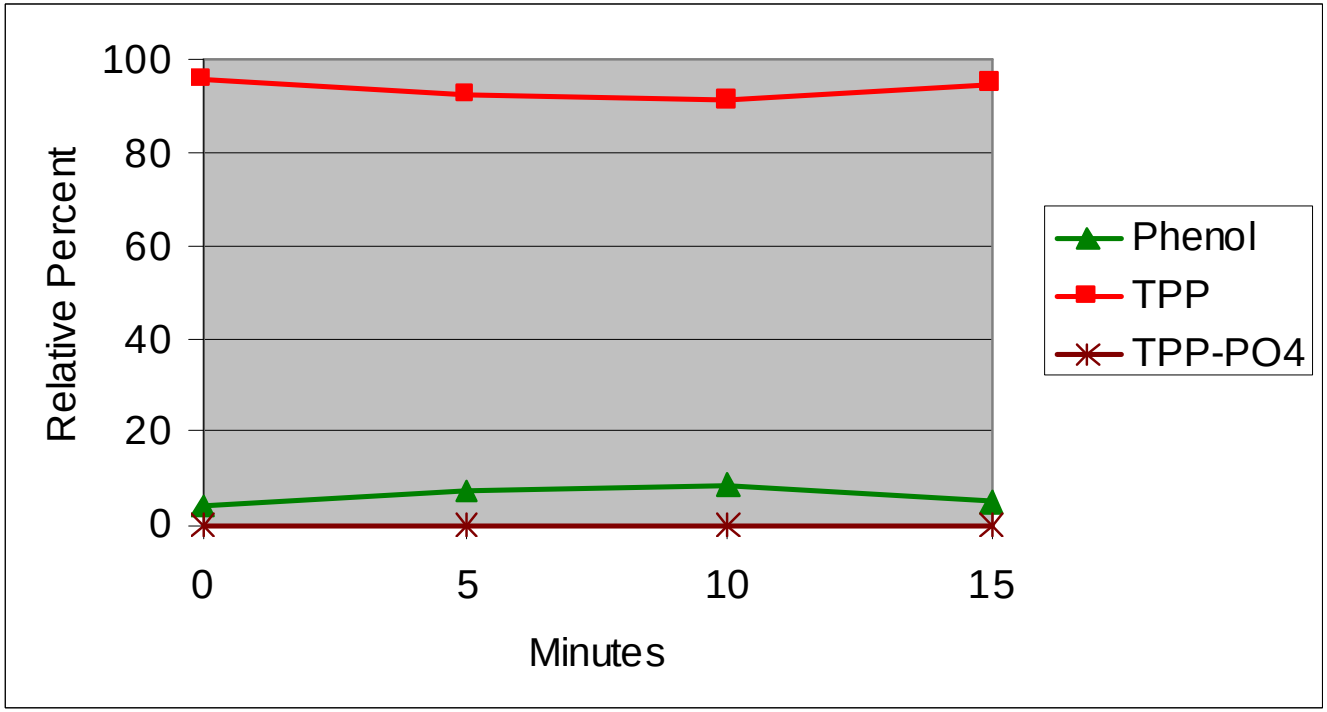
Alkyl Phosphites React with $ZnCl_2$ at 180°C



TOP reacts quickly with $ZnCl_2$ to form a salt

TPP (Triphenyl Phosphite)

Aryl Phosphites do not react with $ZnCl_2$ at 180°C



No Reaction Occurs

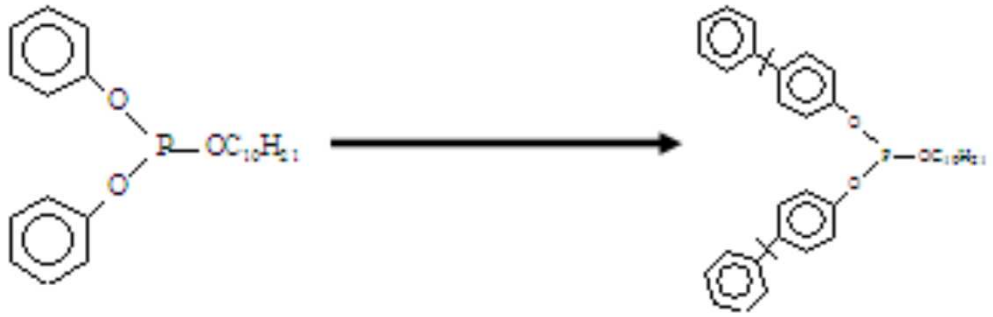
Phosphite Selection for Mixed Metal Stabilizers

- Aryl phosphites are not effective by themselves.
- Alkyl phosphites offer excellent early color, long term aging and compatibility. However, they do not have the "guts" of alkyl-aryl phosphites, their long term stability is not as good. Also, they are not as hydrolytically stable. It is the aryl group that gives hydrolytic stability.
- Mixed alkyl-aryl phosphites offer the best solution.

Replace The Phenol Ligand With An Alkylphenol

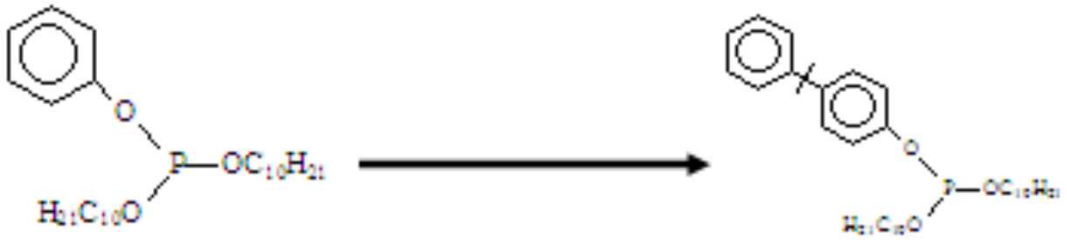
- Phenol replaced by para-cumylphenol (**PCP**)

"DPDP"



"PCP2"

"PDDP"



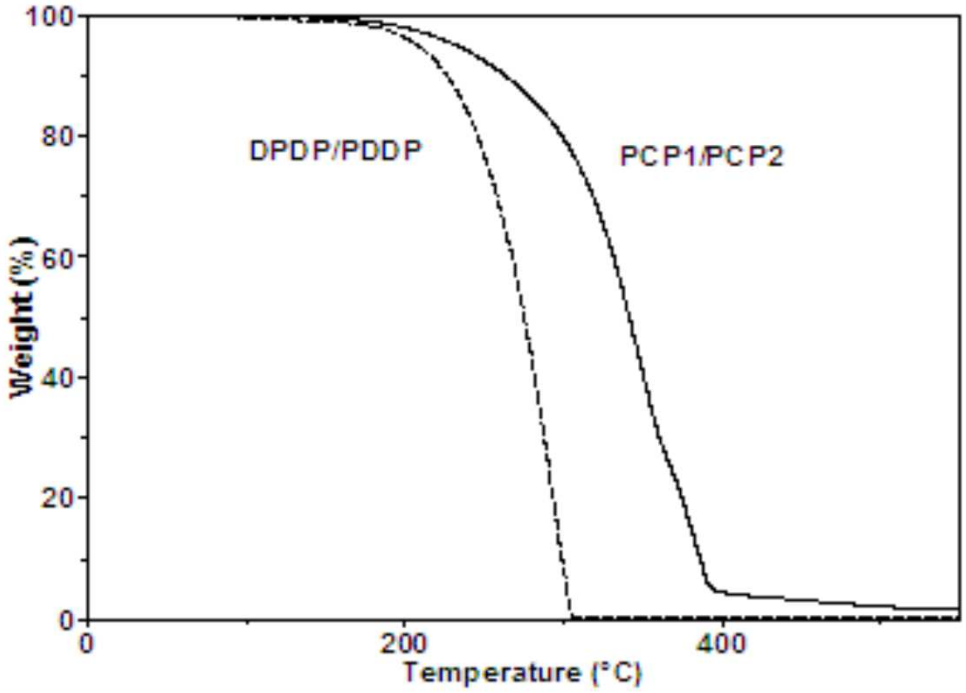
"PCP1"

Reduced Water Solubility

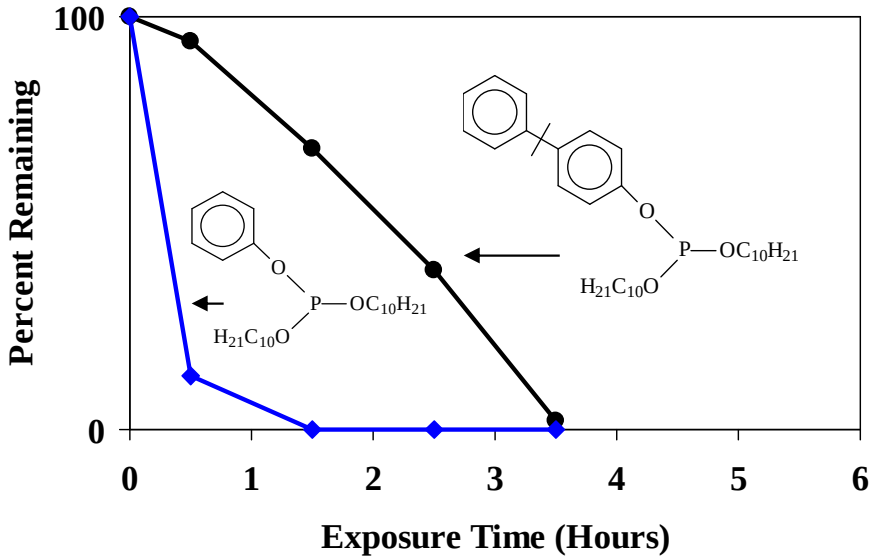
Material	FW	MP (°C)	BP (°C)	Solubility in Water
Phenol	94.1	41	182	Solubility (~1g/15mL)
Paracumylphenol (PCP)	212.3	70	335	Insoluble

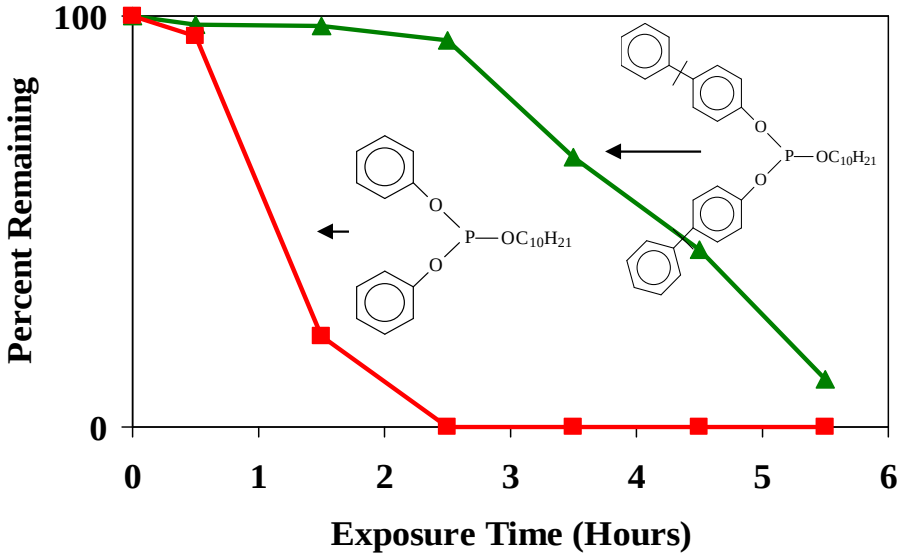
Improved Thermal Stability

Thermal Gravimetric Analysis (TGA)



Improved Hydrolytic Stability



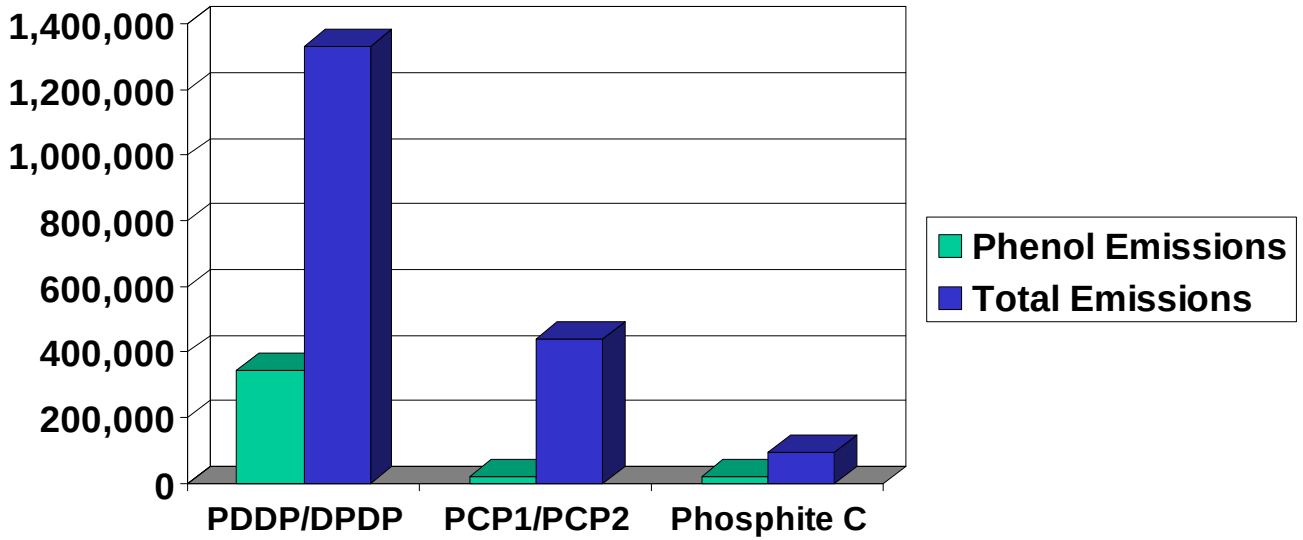


Phosphites exposed to 60°C, 85% Humidity

Reduced Volatiles, No Phenol

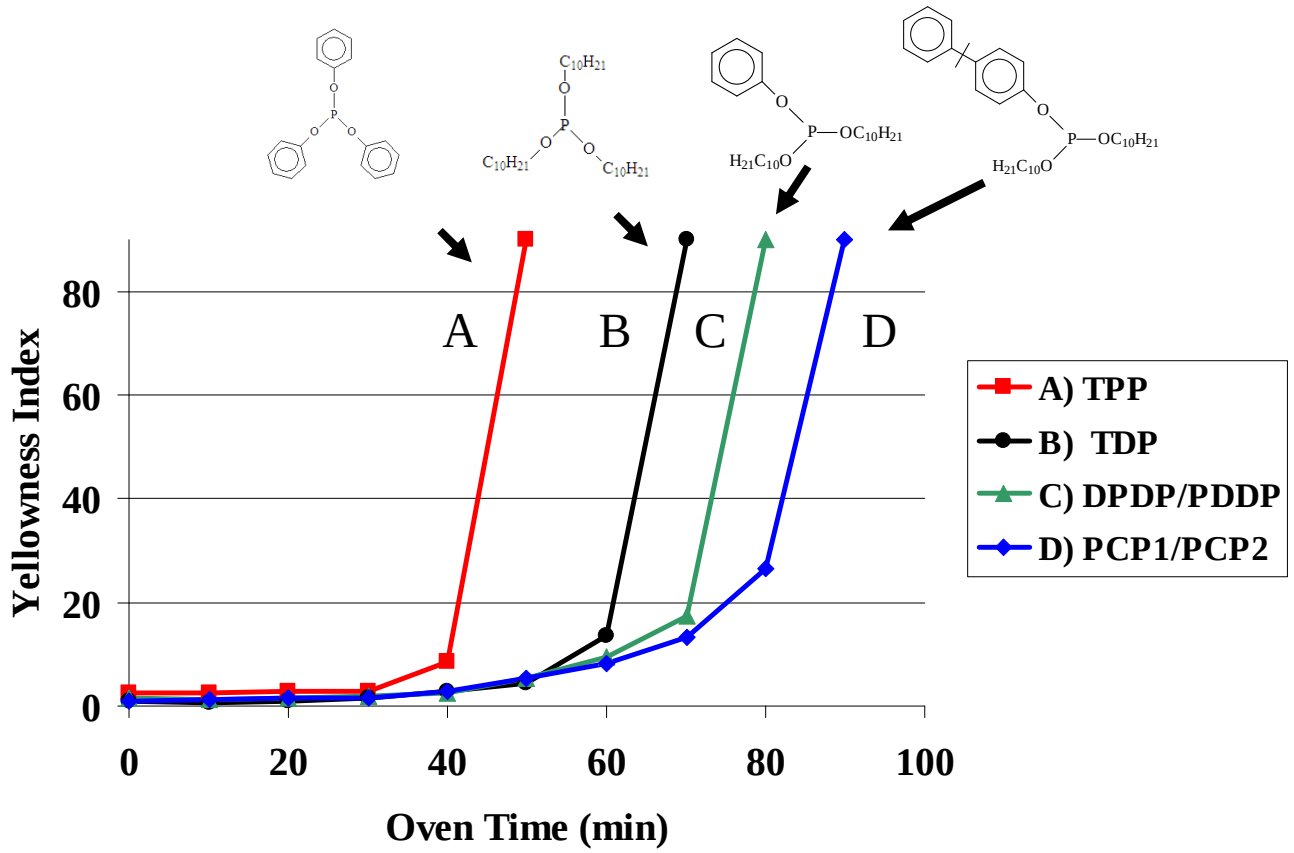
- PCP is less volatile than phenol
- Improved hydrolysis means less alcohol generated and thus lower VOCs

Total Integrated Emissions (SPME-GCMS)



Improved Process Stability

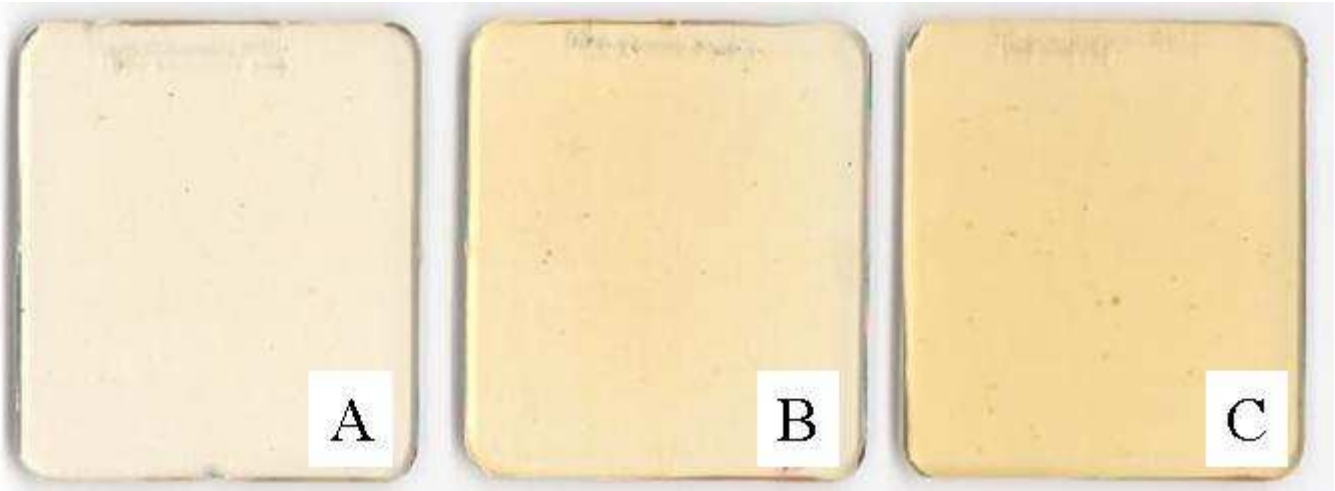
Static Stability
Mathis Oven
@ 185℃



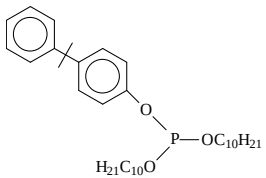
PCP Phosphites display the best stability

Long Term Heat Aging

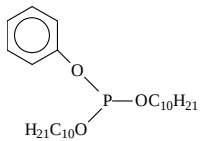
60°C Oven Aging 3 Weeks, Ambient Humidity



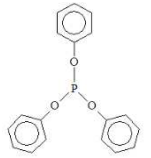
PCP1/PCP2



PDDP/DPDP

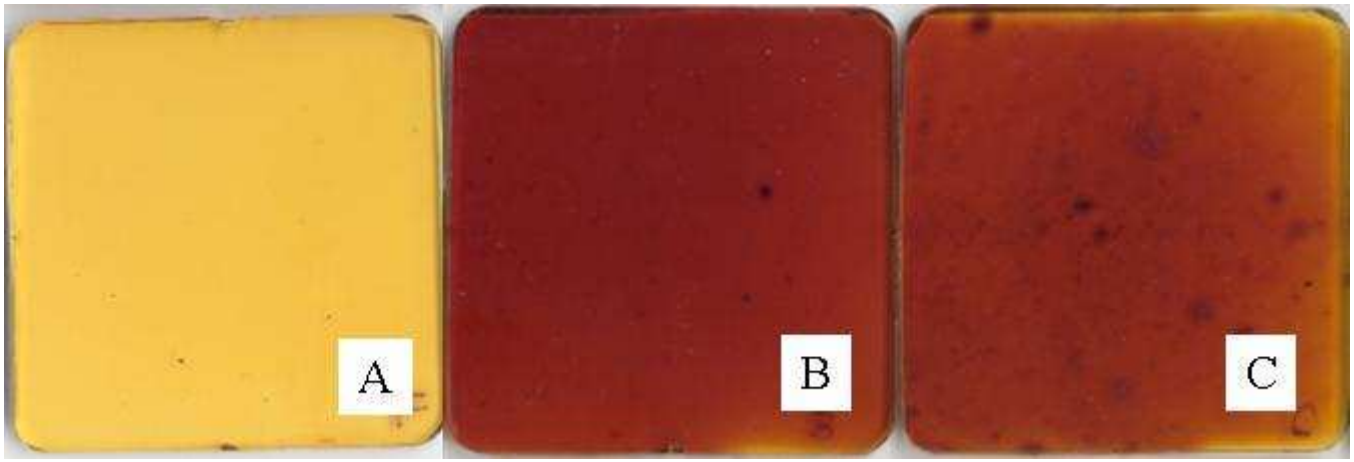


TPP

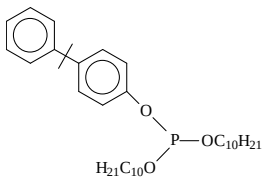


Improved Accelerated Heat Aging

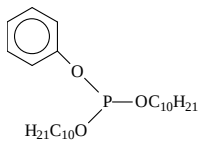
100°C Oven Aging 1 Week, Ambient Humidity



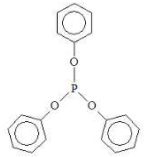
PCP1/PCP2



PDDP/DPDP



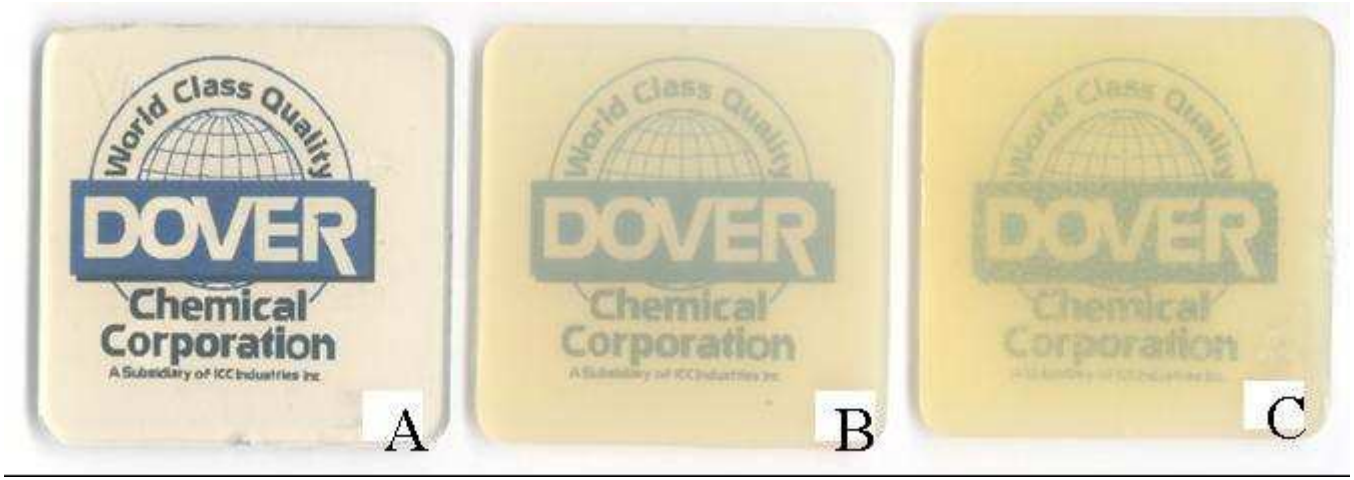
TPP



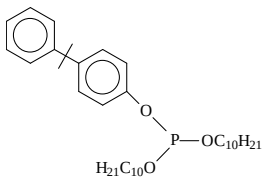
Improved Heat/Humidity Aging

60°C 72 hours, 85% Humidity

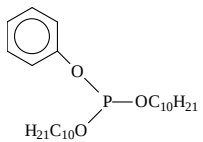
(Improved Hydrolytic Stability)



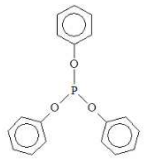
PCP1/PCP2



PDDP/DPDP



TPP



Conclusions

- There are many challenges in the current stabilizer market. Besides improvement in performance and ancillary properties, a main driver for new technology is the environmental focus.
- Continued focus will be placed on lowering the VOC and phenol content of all stabilizers.

Conclusions

- Products that contain nonylphenol will remain under focus, especially in Asia and the EU. There are no government mandated restrictions on any of these products. However, product de-selection may continue due media focus.
- Research will continue on additives to replace TNPP, BaNP and other stabilizer components.
- One of the biggest hurdles in new product development is the increasing cost of global registration, especially if indirect food contact clearance is needed.

Conclusions

- The design of new stabilizers in general will address the issue of biodegradation. Development of ultra sensitive analytical instrumentation allows analysis of <1ppb.
  - If you look hard enough, you can find anything.
  - BPA, brominated flame retardants, etc.
- This challenge will be difficult to meet, since most antioxidants including hindered phenolics, phosphites and UV stabilizers are not readily biodegradable.
- Future research will be directed at finding alternate structures to alkylphenols to improve their biodegradation, while maintaining cost-performance, hydrolysis and other ancillary properties.

Thank You!

Questions?