

**“New stabilizer solutions for polyolefin film grades”**

by

Dr. Florian Stricker  
Ciba Specialty Chemicals  
Basel, Switzerland  
[florian.stricker@cabasc.com](mailto:florian.stricker@cabasc.com)

Murray Horton  
Ciba Specialty Chemicals  
Macclesfield, Cheshire, UK  
[murray.horton@cabasc.com](mailto:murray.horton@cabasc.com)

European Tappi PLACE Conference  
May 12 - 14, 2003  
Rome, Italy



# NEW STABILIZER SOLUTIONS FOR POLYOLEFIN FILM GRADES

Dr. Florian Stricker and Murray Horton; Ciba Specialty Chemicals Corporation

## ABSTRACT

Over the years the plastic industry is launching a variety several new polyolefin products, including metallocene-based and bimodal polyethylenes and polypropylenes. Nevertheless the industry has matured quite considerably over the past 30 years. In such a mature industry, there are still many incumbent products which have established positions in existing markets. These products have been successful in meeting the most important needs in their markets but there still remains areas where performance can be improved or where deficiencies exist. These opportunities could encompass processing improvements, reduction of defects, reduced discoloration, or product stewardship concerns. Successful attempts to make improvements upon these incumbent products seem to depend from a technical stand point on two factors: a wide spectrum of products from which to choose (toolbox) and people with knowledge of the chemistries and the technologies they will be applied to. This paper will describe two examples of new approaches to base stabilization of polyolefins.

## INTRODUCTION

Base stabilization of polyolefins is necessary to protect the polymer from degradation during melt processing and conversion. Beside processing stability base stabilizers provide long-term thermal stability in use. But today's requirements in polyolefin applications demand more and many other constraints must be taken into account in real world situations. Figure 1 shows some of the constraints, which may apply to specific situations. In any given situation, some of the considerations listed may impose limitations on the chemistries which can be applied.

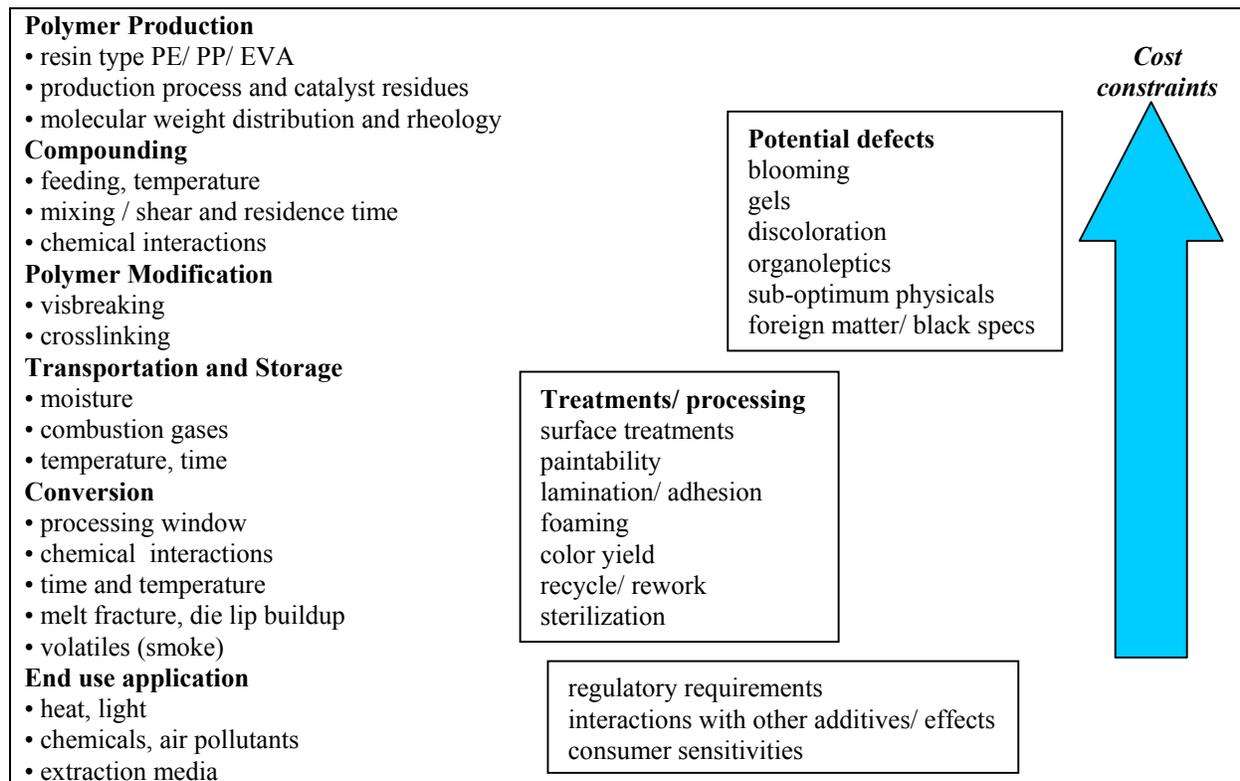


Figure 1: Aspects relevant to optimize stabilization systems for a given polymer grade

Stabilizers are by nature reactive chemicals and sometimes tend to give undesired reactions and effects. Examples are blooming or die build up as well as the tendency of phenolic antioxidants to discolor when exposed to active catalyst residues and exhaust gasses from combustion processes.

Two factors are key in being able to optimally formulate base stabilization packages. One is having access to a diverse toolbox of additives from which to choose. Having several degrees of freedom in the selection and combination of additives allows for a much greater possibility of meeting primary requirements and constraints. Fortunately, there exists a quite broad portfolio of stabilizers from which to choose. In particular, new chemistries like hydroxylamine and lactone or recently available ones like vitamin E, significantly improve the ability to reach a peak performance in a given situation. Perhaps even more important is having the knowledge and experience to apply the use of additives to different situations. This experience comes over many years as customer problems are worked through and needs are recognized. Many of the new chemistries which are now available came about via attempts to meet more demanding needs.

Some of the important constraints are listed in the Figure 1. With regard to the resin, certainly the amount and type of catalyst residue that remains after production and catalyst deactivation are known to have an effect on the stabilization of the polymer during melt processing. In addition, other trace constituents like free radicals or oligomers can have an influence on the type and degree of molecular weight changes which are likely to occur during subsequent processing.

Compounding is usually the most straightforward step however issues can still arise. For instance, accurate feeding of all additives can sometimes be a challenge. In such cases, preblends can often improve the situation but care must be taken to insure proper stability of the blend. Other parameters such as processing temperature 'window' can constrain the stabilizer selection.

Often polymer modification such as PP visbreaking or PE crosslinking is practiced. These free radical initiated processes can be very sensitive to additive selection. Stabilizers will in general interact with the radicals and care is needed in selecting appropriate additives for specific situations. Some representative examples of pitfalls that can occur include degradation of properties like color or organoleptics, reduction of physical integrity or interference with the cross link density. In addition, a poor selection of stabilizers can result in increased cost for chemicals or treatment needed to achieve the desired property.

### Stabilization Principles

As a brief review [1], the autoxidation cycle for olefin polymers is shown in Figure 2. In this cycle, which is representative of various stages of the life cycle of the polymer, the polymer is subjected to a variety of damaging stresses. This includes high temperatures and shear rates from the multiple melt compounding steps as the product is transformed from reactor powder (melt) → pelletized product → formulated compound → finished article. In addition to temperature and shear, catalyst residues, entrapped oxygen, and other types of impurities might also play a role in promoting further degradation of the polymer.

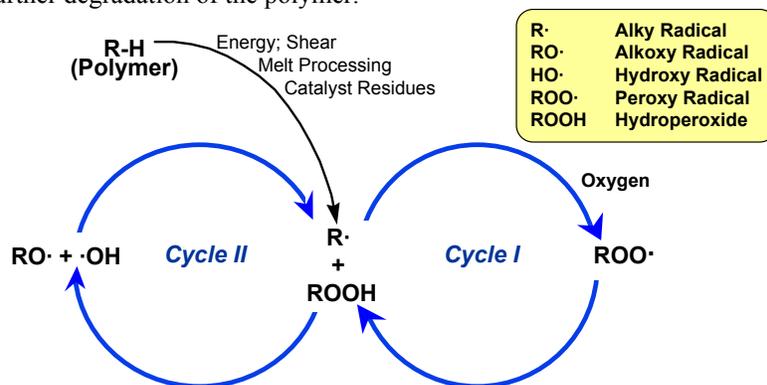


Figure 2: Auto-oxidation cycle for polyolefins. During these repeated heat histories, free radicals are initiated via C-C and C-H bond scission. Once the free radical

cycle is initiated, the resultant carbon centered free radicals not only react with other polymer molecules, but also feed on the oxygen that is entrapped in the system, leading to the formation of peroxy radicals. The peroxy radicals react with the polymer generating hydroperoxides; concomitantly, a new carbon centered free radical site is formed. The carbon centered free radical feeds back into Cycle I.

The formation of unstable hydroperoxides, which can be decomposed by heat, UV light, catalyst residues, or other metallic impurities, ultimately leads to the formation of alkoxy and hydroxy radicals, as depicted in Cycle II. Oxygen centered radicals can react further with the polymer, leading to the formation of more carbon centered free radicals, which feed back into Cycle I. The reactions leading to free radicals being formed on the polymer backbone results in chain linking and/or chain scission reactions in an effort to quench the free radicals.

These chain linking and chain scission reactions result in fundamental changes to the molecular architecture of the polymer in regard to molecular weight (MW), MW distribution (MWD), as well as the nature of chain branching on the polymer backbone. Most, if not all of these changes are unwelcome in that they can change the physical properties, melt processability and the final utility of the polymer during its life cycle. Considering the costs associated with the design put into the development of the polymer (catalyst; polymerization process; etc.), it is undesirable for indiscriminate changes in the molecular architecture of the polymer (remodeling) to take place.

In an effort to eliminate these type of negative reactions that lead to the unwelcome “remodeling of the molecular architecture of the polymer”, a variety of stabilization chemistries have been developed [2,3] and commercialized over the last four decades. A phenolic antioxidant, typically in combination with a phosphite melt processing stabilizer, can be used at various loadings and ratios to meet most requirements of a given end-use application. The role of the phenolic antioxidant is to scavenge oxygen centered free radicals, such as alkoxy, hydroxy and peroxy type species, while the role of the phosphite is to decompose the hydroperoxides into relatively inert products (before they can split back into oxygen centered free radicals); see Figure 3.

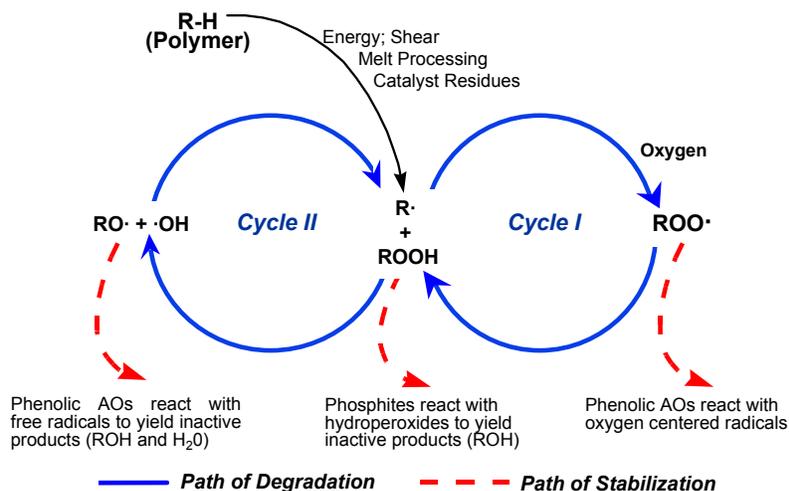


Figure 3: Traditional inhibited auto-oxidation cycle for polyolefins.

Where limitations have been encountered regarding the desired level of stabilizer performance, the judicious re-selection of the phenolic antioxidant and/or phosphite, combined with adjustments in the concentration and ratio of the stabilizers could usually resolve the problem. In addition, acid acceptors can be used to fine tune the performance of the stabilizers, and work to assure a synergistic functioning of the stabilizers [4].

### Trends in Polymers and Stabilization

Over the last few years, a variety of new catalyst systems and polymerization processes have been developed. The relative performance of the polymers derived from these recent developments has shown a path of continuous

improvement. New polymers have been, and continue to be, developed for a variety of new end-use applications that give improved performance and often serve as replacements for metal, paper and glass.

In addition, subtle features (not necessarily associated with the intrinsic physical properties of the polymer), such as initial color, color maintenance, compatibility, resistance to discoloration due to pollution, clarity, cling, taste and odor, have also become key measures with regard to specific applications. Thus, there always seems to be room for improvement in the field of stabilization, whether it is associated with maintaining or improving physical properties (MW and MWD), or with the subtle aesthetic features as described above.

Along with these technology driven developments, the demands and expectations being made on the polymer and the stabilizer system have been significantly increased as well. In order to address these more demanding applications, antioxidant systems have been improved through the development of new and novel chemistries for polymer stabilization. The primary objective for bringing these new stabilizers forward to commercialization was to provide new solutions for polymer stabilization based on the escalating demands being made on the polymer during melt processing; such as high temperature or high shear.

Representative examples of these new chemistries are based on traditional functional groups, such as phosphites. [5] In one sense phosphites are traditional, since they are based on P(III)  $\rightarrow$  P(V) hydroperoxide decomposition chemistry which is well known. However, it must be made clear that each phosphite is not “just a phosphite”. Upon more careful analysis, these individual molecules have specific properties that have a positive effect on important ancillary properties in various polyolefin substrates. These can be, improved initial color and color maintenance; enhanced long term thermal stability; improved compatibility in linear lower density olefin copolymers; excellent hydrolytic stability and inhibition of discoloration during hot water contact. They also possess low melting points as well as outstanding solubility in process solvents. Therefore, beyond the traditional retention of MW & MWD via hydroperoxide decomposition chemistry, the ancillary properties of the new phosphorus based stabilizers can be translated into real end use applications. Stabilizer performance can be optimized based on key measures, such as: good color maintenance for color critical applications; better maintenance of cling properties; improved handling in hot/humid environments, better color maintenance in hot water contact applications; as well as molten systems for the topical addition of additives.

In 1997, a fundamentally new chemistry was introduced, that not only inhibits the autoxidation cycle, but attempts to shut it down as soon as it starts [6,7,8]. The exceptional stabilizer activity of L-1 is due to the ready formation of a stable lactone (benzofuranyl) radical by donation of the weakly bonded benzylic hydrogen atom; see Figure 4.

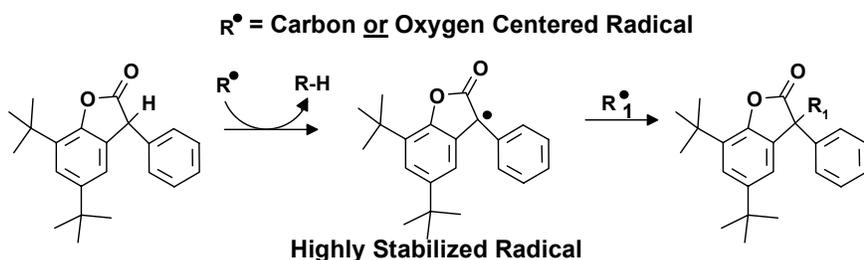


Figure 4: Proposed stabilization mechanism of arylbenzofuranones.

The resonance stabilized lactone (benzofuranyl) radicals can either reversibly dimerize or react with other free radicals. Model experiments have demonstrated that this class of chemistry behaves as a powerful hydrogen atom donor and are also effective scavengers of carbon centered and oxygen centered free radicals [9]. While the sterically hindered phenols react preferentially with oxygen centered radicals like peroxy and alkoxy rather than with carbon centered radicals, lactones (benzofuranones) can scavenge both types of radicals. Accordingly, the lactone, can be repeatedly positioned at key locations around autoxidation cycle to inhibit the proliferation of free radicals. The combination of phenolic, phosphite and lactone represents an extremely efficient stabilization system since all three components provide a specific function.

In Figure 5, the hindered phenolic antioxidant functions as a scavenger of oxygen centered radicals and provides

melt processing and long term thermal stability. The phosphite functions as a hydroperoxide decomposer and provides melt processing stability and color maintenance. The lactone and its radical intermediates persistently inhibit the propagation of polymer radicals. It has also been observed that the lactone can also donate hydrogen atoms to the phenoxy radical to regenerate the phenolic AO [9]. This mechanism allows the phenolic to extend its use as a long term thermal stabilizer.

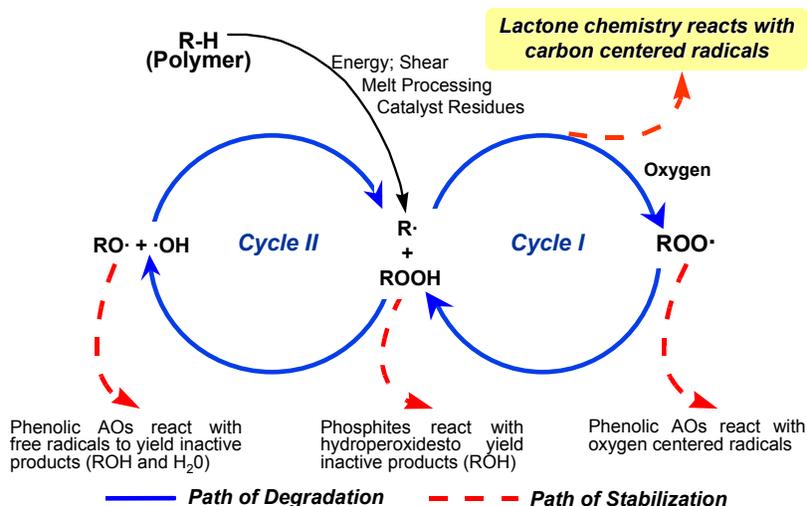


Figure 5: Revised inhibited auto-oxidation cycle for polyolefins

## Film Converting

Producers of polyolefin film grades, as well as the downstream film converters, often look for new developments in polymer stabilization technology to make sure that they can provide the best products with the most value while minimizing costs. Additives, or combinations of additives, represent tools that can be used for adjusting product performance (improved physical and aesthetic properties). Examples of such improvements might include better maintenance of melt flow rates, lower YI color, improved long term thermal stability, inhibition of gas fade discoloration, enhanced additive compatibility, reduced taste and odor, resistance to irradiation induced oxidation, as well as the suppression of 'gels' and other extrusion related imperfections [10]. More difficult to demonstrate, but of significant economic value, stabilization can often influence the processing window. Processing window refers to the range of machine parameters over which acceptable quality parts can be produced. Generally speaking, a polymer and additive formulation that yields a wider processing window will translate into a more robust process at the converter. One which will be less sensitive to small perturbations in the system. Improvements in processing window might translate to higher onstream time, faster line speeds, better quality, less sensitivity to process upsets, etc. Identification and exploitation of these kinds of opportunities usually requires cooperation between the converter, resin producer, and additive supplier.

The identification of new stabilizing additives that can deliver these type of desirable improvements usually begins with the development of novel molecules; or clever ways to use known, but under-utilized molecules. New stabilizer chemistries are compared to "established" systems. Unfortunately, acceptance of new stabilizer chemistries takes a long time from initial concept to commercial success. Qualification begins with standard lab scale extrusion experiments, where typical measures such as a) melt flow rates and b) color maintenance are the key measures. As the qualification moves forward, key measures are shifted to ones that are considered to be more relevant in the final end-use application. There are many steps between initial lab testing and final qualification. Nevertheless, if the new chemistries solve real problems, the implementation process is usually accelerated.

Regarding traditional measures of stabilization, improvements in melt flow rate control can be achieved using a variety of approaches. For example, higher concentrations or the use of more powerful additives (per unit weight)

are two representative examples. Over the last several decades, a variety of phenolic AO and phosphite melt processing stabilizers have been developed to meet new opportunities. Used in different ratios and concentrations, blends of phenolic AO and phosphites can provide optimal performance based on the nature of the polymer, the extrusion temperatures, and shear rates experienced during various types of extrusion processes.

### TNPP FREE STABILIZATION OF LLDPE FILM GRADES

Tris-nonylphenylphosphite (TNPP) is a successful phosphite stabilizer for LLDPE due to its excellent price/performance ratio and its good compatibility in PE. As a response to ecological concerns surrounding some chemistries with similarities to nonylphenol, some organizations that serve the consumer market have taken the cautious step of removing stabilizers based on nonyl phenol from their products. This has created a need for resin producers and additive suppliers to devise new environmentally friendly formulations which are able to meet the requirements of these markets without containing TNPP.

The data shown below in Figures 6 and 7 gives the results of an alternative stabilization system to replace an existing formulation based on P-2. Any of these formulations could potentially replace the base formulation containing P-2. The melt flow data shows that some of the formulations containing lower levels of phosphite are not able to maintain melt flow control as well as the base formulation at the fifth extrusion pass. This may or may not be a problem for a specific application. The situation could be improved by increasing the phosphite level. All of the formulations are equivalent or better performing in terms of the resistance to discoloration during processing, but also during oven aging and regarding gas fade. Any of these formulations could potentially be replacements for the control formulation.

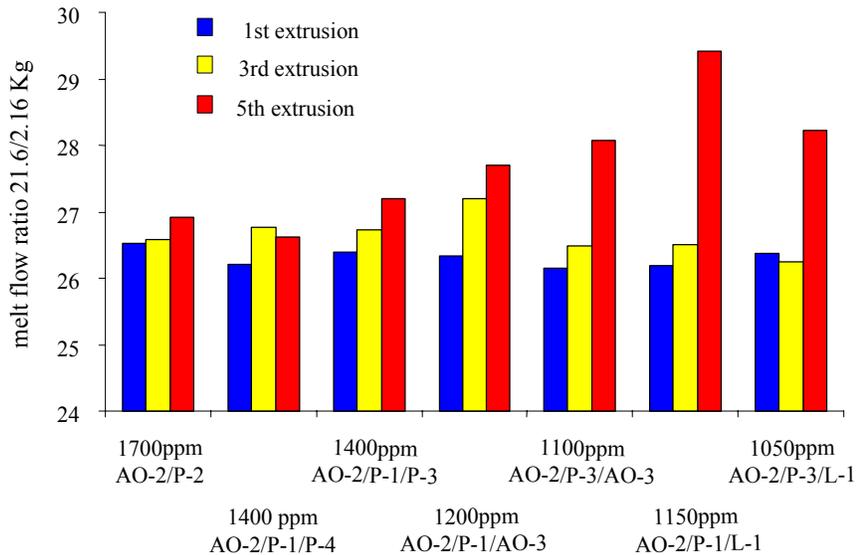


Figure 6: Melt flow ratio (melt flow index obtained with a 21.6 kg weight divided by the MFI obtained with a 2.16 kg weight) during multiple pass extrusion of LLDPE. Melt flow ratio is usually a good indication of melt processing stability in PE. Both melt flow readings were obtained at 190°F.

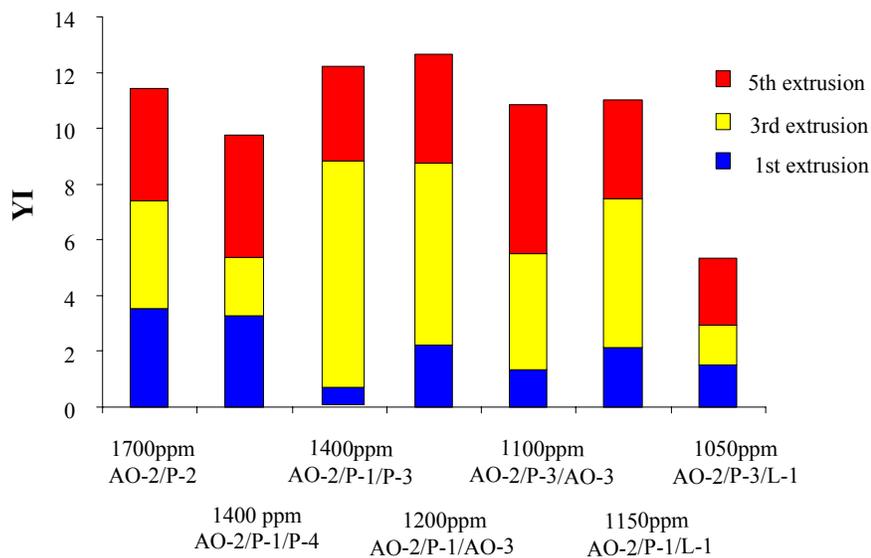


Figure 7: Color during multiple pass extrusion (compression molded plaques)

Solubility and compatibility are important features of stabilizers as they have a strong influence on final product performance. This is mainly related to migration behaviour of the additives and can result in blooming effects as well as gel formation. Density and crystallinity of the polymer are two factors influencing the migration behaviour as they have impact on solubility of the stabilizers. Solubilities of different phosphites are illustrated in figure 8, showing significant differences. Common loadings of phosphites are in the range of 700 to 1500ppm but can be even higher. P-1 has a solubility limit, which is significantly below these common loadings of phosphites and consequently can result in blooming effects and gel formation. The other phosphites investigated all have a very good solubility.

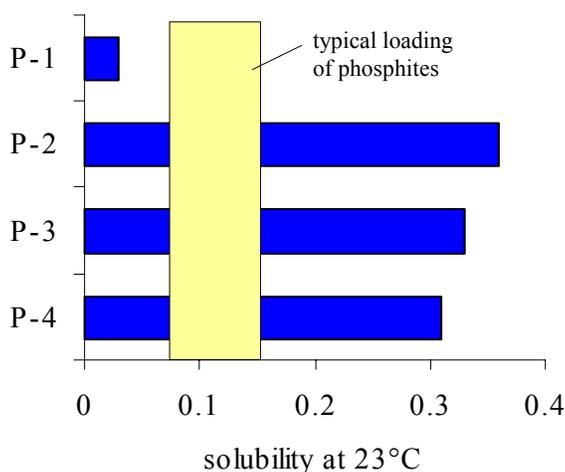


Figure 8: Solubility of phosphites in LLDPE (0.92 g/cm³)

Selection of formulations for further studies will most likely depend upon cost as well as some of the other factors listed in Figure 1 like resistance to gel formation or processing window. The data shown in this study give sufficient indication that there are solutions available with attractive performance in terms of processing stability and film

properties. Depending on process-specific demands on the stabilizer package further fine-tuning might be required in order to fulfill all requirements on LLDPE film grades.

### BOPP FILM STABILIZATION

BOPP film converters have an interest in improving the base stabilization of PP resins used in film production. Film plants recycle trim strips to improve efficiency. The amount of recycle may vary from time to time and there is value in having a robust stabilization system in order to reduce sensitivity to different amounts of recycle. Also, process improvements to increase throughput have resulted in higher temperatures in the extruder and increased thermal stress on the polymer. At the slitting end and in the warehouse, there is an interest in improving color of the film in order to provide a good-looking product.

Results of multiple pass extrusion experiments on polypropylene homopolymer are shown in Figure 9. The blend containing the lactone L-1 is superior both in terms of maintaining melt flow rate and color. The new lactone chemistry, L-1 has been shown to synergize very well with traditional phenol/ phosphite systems. In this case as well as in the previous example, the ability of a new system to control melt flow and maintain color during multiple pass extrusion is an indication that the molecular structure is being preserved, but does not directly imply that the polymer will be better fit for use.

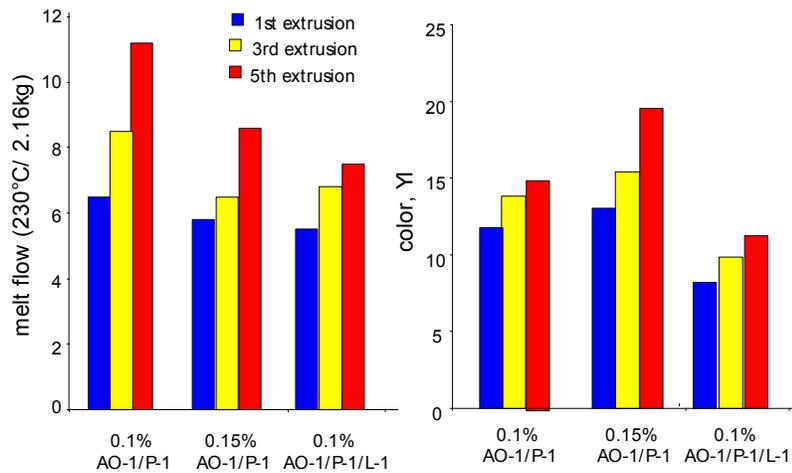


Figure 9: Changes in melt flow rate and color of polypropylene homopolymer during multiple pass extrusion

Similar formulations have been tested on a Brückner pilot film line. This line uses the tenter process with a two-step orientation: first the film is stretched in the machine direction, and then in the transverse direction. Table 1 describes the conditions run on the line. In addition to measuring physical and optical properties of the films, the machine direction orientation stretching ratio and the web temperature in the transverse direction orientation section were independently varied in order to determine the influence of stabilization on the processing window.

Table 1: Operating parameters for the Brückner pilot BOPP film line

Parameter	Varied or Constant?	Standard Value
Extrusion temperature	Constant	250°C
Line Speed	Constant	85 m/min
MDO Ratio	Varied	4.5:1
TDO Ratio	Constant	8:1
TDO Temperature	Varied zone temps	172-172-159-150°C

Coex Film Thickness	Constant	20 micron (1/18/1)
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Three formulations were compounded and cast into film on the Brückner pilot line. 1500ppm of a conventional phenol/ phosphite blend of AO-1/ P-1 (1:2) was compared with lesser amounts of phenol phosphite blends boosted with the lactone L-1. One of the new formulations uses the phosphite P-1 and the other uses the high performance phosphite P-3. Table 2 shows the results of the processing window part of the study. It is interesting that even in the case of this commercial resin, the improved stabilization shows a discernable improvement in the processing window. These differences can be of significant value to converters for instance, a few extra degrees C of tolerance on the transverse orientation can make a lot of difference when the line is being brought up and is not yet fully under control.

Table 2 The influence of lactone blends on the processing window for BOPP film production

Formulation	Machine Direction Orientation (highest ratio before break)		Transverse Direction Orientation (high/low before break)	
	Range	% Increase	Range (°C)	% Increase
1500 ppm AO-1/ P-1	5.1:1	-	14	-
1000 ppm AO-1/ P-1/ L-1	5.7:1	12%	16	14%
800 ppm AO-1/ P-3/ L-1	5.4:1	6%	17	21%

Figure 10 shows another way of visualizing the processing window. In this graph, the difference between the upper and lower data points for each formulation represent the variation in thickness that across the web from the thinnest to thickest part of the sheet. The data point farthest to the right represents the last viable stretching ratio before the film broke.

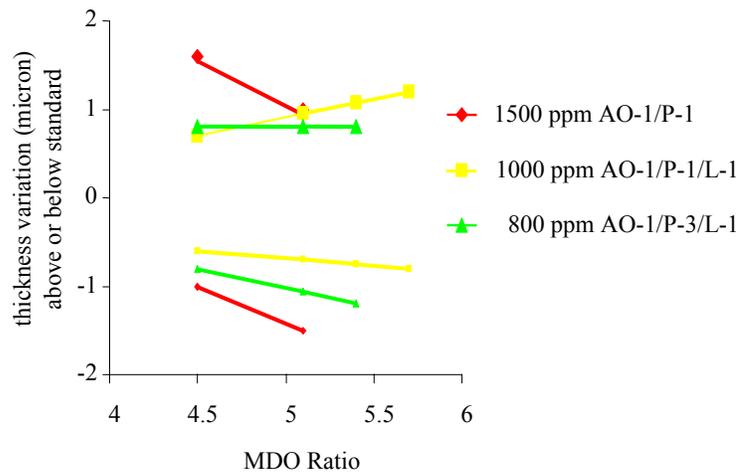
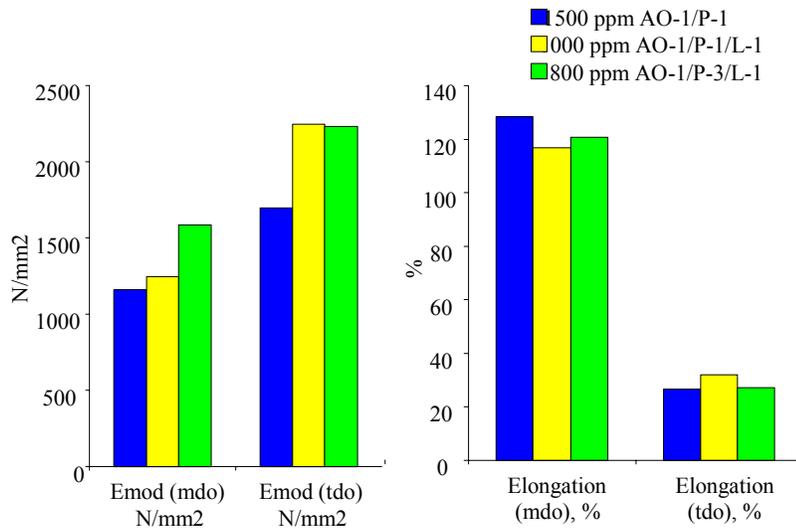


Figure 10: Maximum thickness variation measured by the thickness gauge on the Brückner line versus the MDO stretching ratio

Figure 11 shows some physical properties of the films produced in the trial. All the formulations show approximately the same elongation to break. However, the elastic modulus on the lactone-boosted formulations is significantly higher than the control. This may be due in part to the better thickness control, which is achieved with the lactone-boosted formulations. Optical properties were also measured on the films. For this resin, there was no significant difference between the formulations. All films had haze values of 1% and clarity values of 98%.



**Figure 11:** Elastic modulus and elongation data from the Brückner pilot trial.

It is known that the lactone boosted systems are better at suppressing polymer chain scission especially the longer ones which are the most likely to be attacked. During drawing, the number and complexity of tie molecules between crystallites is important to good performance. These tie molecules insure that as the film is drawn, there is a compensating factor for the tendency of the film to neck down at weak points leading to stress concentration and failure. When these tie molecules or crosslinks between crystallites are present during drawing, the resin will strain harden, resulting in a more stable drawing process. It seems likely that the lactone boosted stabilization packages are better able to preserve the rich web of tie molecules present in the resin and that this accounts for the improvements observed in thickness uniformity and processing window.

By this study it has been able to demonstrate improvements in processability which result from optimizing the base stabilization for this BOPP grade. Since this work was completed, commercial experience with the system has borne out the suitability of the lactone boosted systems for this application. For instance, on stream time at high line speeds has reportedly been increased. In addition, experience has shown that other operations like metallizing, flame treatment, and printability are not adversely affected by the new system.

## CONCLUSION

Two examples of development of new stabilization systems have been discussed. In both cases, an incumbent stabilization system has existed and a new stabilization system has been found which better meets the needs of the polyolefin producer and their markets. These success stories have each involved a clear set of needs expressed by the converters or end users. They have also included direct involvement from the additive supplier and the resin producer in attempting to identify new opportunities.

Within the area of base stabilization there are many opportunities for improving on incumbent products. These improvements in stabilization have the potential for improving economics at converters and for improving the properties and appeal of the final articles. In order for these possibilities to become realized, it requires good communication between additives suppliers, resin producers, converters and end users. This is sometimes a tall order, but there are representative examples in which it has been done successfully.

Key elements for success can be summarized:

- The converter or end user must be motivated to make an improvement
- The additive supplier and resin producer need to be aware of the opportunity
- The existence of chemistries which can meet the needs
- Knowledgeable scientists who are able to make the connection between needs and available technologies.
- Commitment on all sides to drive the project through to completion

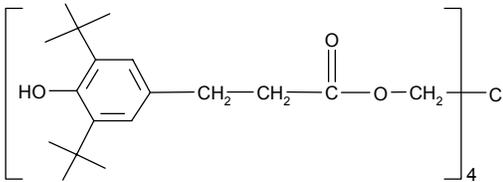
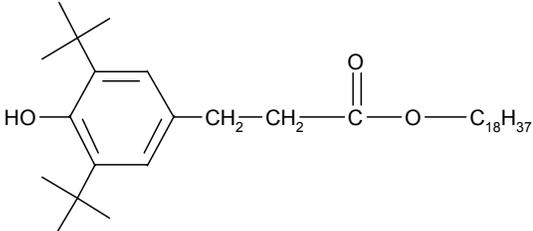
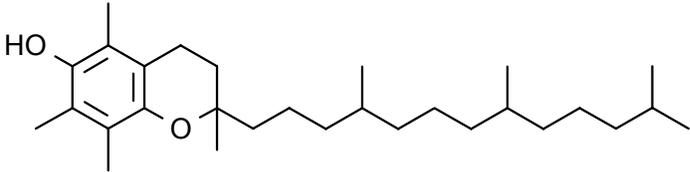
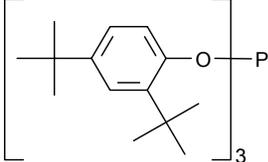
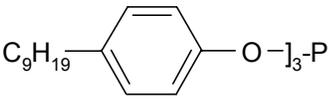
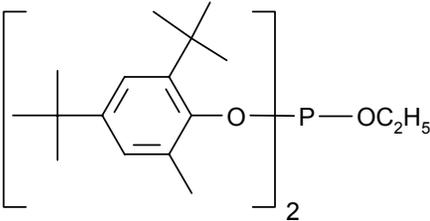
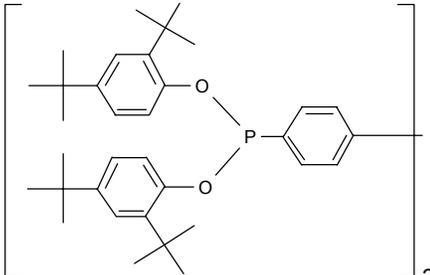
## ACKNOWLEDGEMENTS

The authors wish to thank the following scientists and their teams for completing these projects and for sharing their results: Dave Horst, Dr.Jay Ghosh, Dr.Doris Eisermann, Andreas Thuermer, Dr.Rick King. Also to be thanked are customers, converters, and end users who have partnered with Ciba Specialty Chemicals in these and other projects.

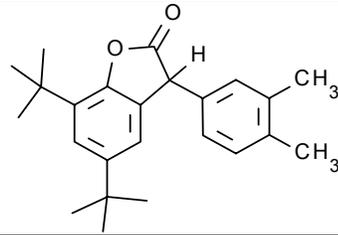
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**APPENDIX 1. Description of Stabilization Chemistries.**

Code Class Tradename	Molecular Structure	Stabilizer Function
AO-1 Phenolic <b>Irganox® 1010</b>		Melt Processing Stability; Long Term Thermal Stability; Oxidative Induction Time;
AO-2 Phenolic <b>Irganox 1076</b>		Melt Processing Stability; Long Term Thermal Stability;
AO-3 Phenolic <b>Irganox E201</b>		Melt Processing Stability; Long Term Thermal Stability;
P-1 Phosphite <b>Irgafos® 168</b>		Melt Processing Stability; (secondary enhancements to the performance of the phenolic AO)
P-2 Phosphite <b>Irgafos TNPP</b>		Melt Processing Stability; (secondary enhancements to the performance of the phenolic AO)
P-3 Phosphite <b>Irgafos 38</b>		Melt Processing Stability; (secondary enhancements to the performance of the phenolic AO)
P-4 Phosphite <b>Irgafos PEPQ</b>		Melt Processing Stability; (secondary enhancements to the performance of the phenolic AO)

L-1  
Lactone  
**Irganox HP-136**



Melt Processing Stability;  
(secondary enhancements to  
the performance of the  
phenolic antioxidant and  
phosphite)

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- 
- Introduction
  - TNPP-free stabilizer formulations for LLDPE film grades
  - BOPP film stabilization

# Base stabilization of polymers

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protects polymer during compounding and conversion  
provides long-term thermal stability

Additional aspects:

- no undesired side effects
- no interference with other components in the formulation
- no interference with operations later in the life of the polymer
- can provide application-specific benefits
- must be commercially viable ....



## **Polymer Production**

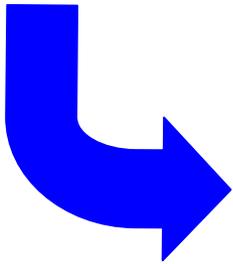
- resin type PE/ PP/ EVA
- production process
- catalyst residues
- molecular weight distribution
- rheology

## **Compounding**

- feeding
- temperature
- mixing / shear
- residence time
- chemical interactions

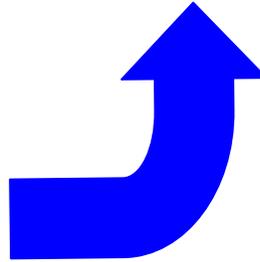
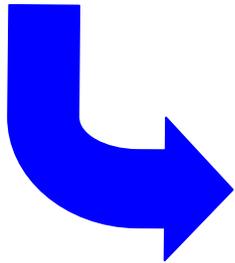
## **Polymer Modification**

- visbreaking
- crosslinking



## Transportation and Storage

- combustion products (gas fading)
- incidental light exposure
- moisture
- temperature/ time

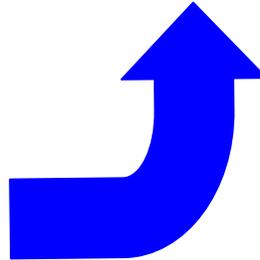
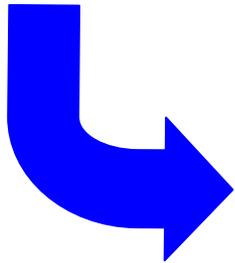
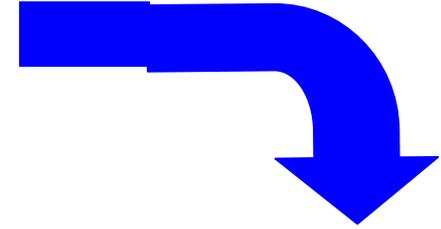


## Conversion

- processing window
- start-up transients
- time and temperature
- melt fracture, die build-up
- water carry over
- volatiles (smoke)
- build-up

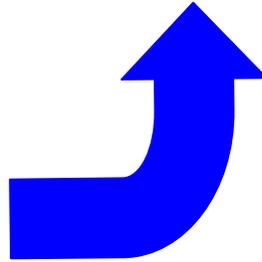
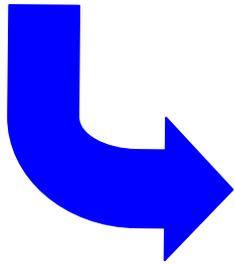
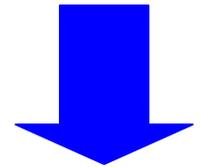
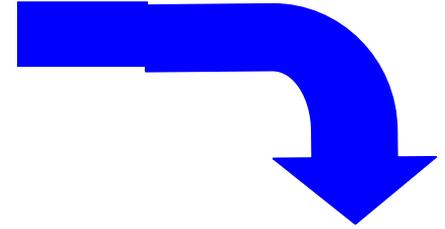
## Treatments/ Processing

- flame/corona treatment
- paintability/ printability
- lamination/ adhesion
- foaming
- color yield
- recycle/ rework
- sterilization



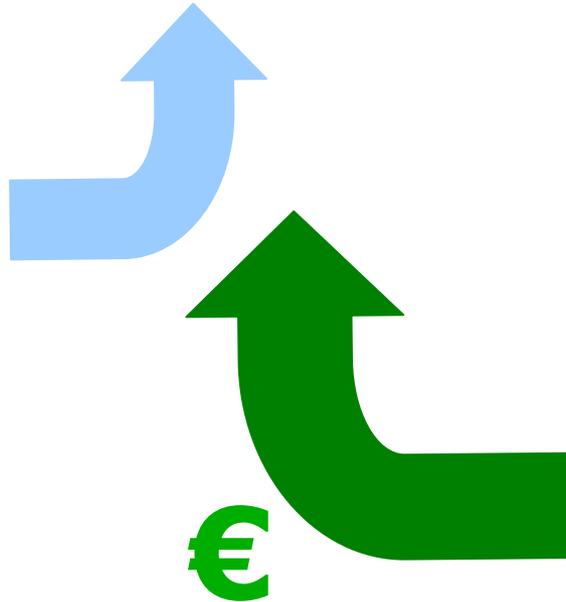
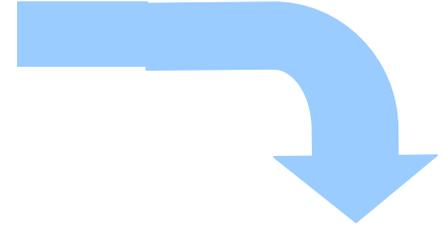
## Transportation and Storage

- combustion products (gas fading)
- incidental light exposure
- moisture
- temperature/ time



DIN

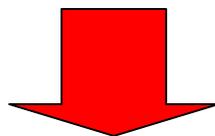




# Base stabilizers as part of successful applications

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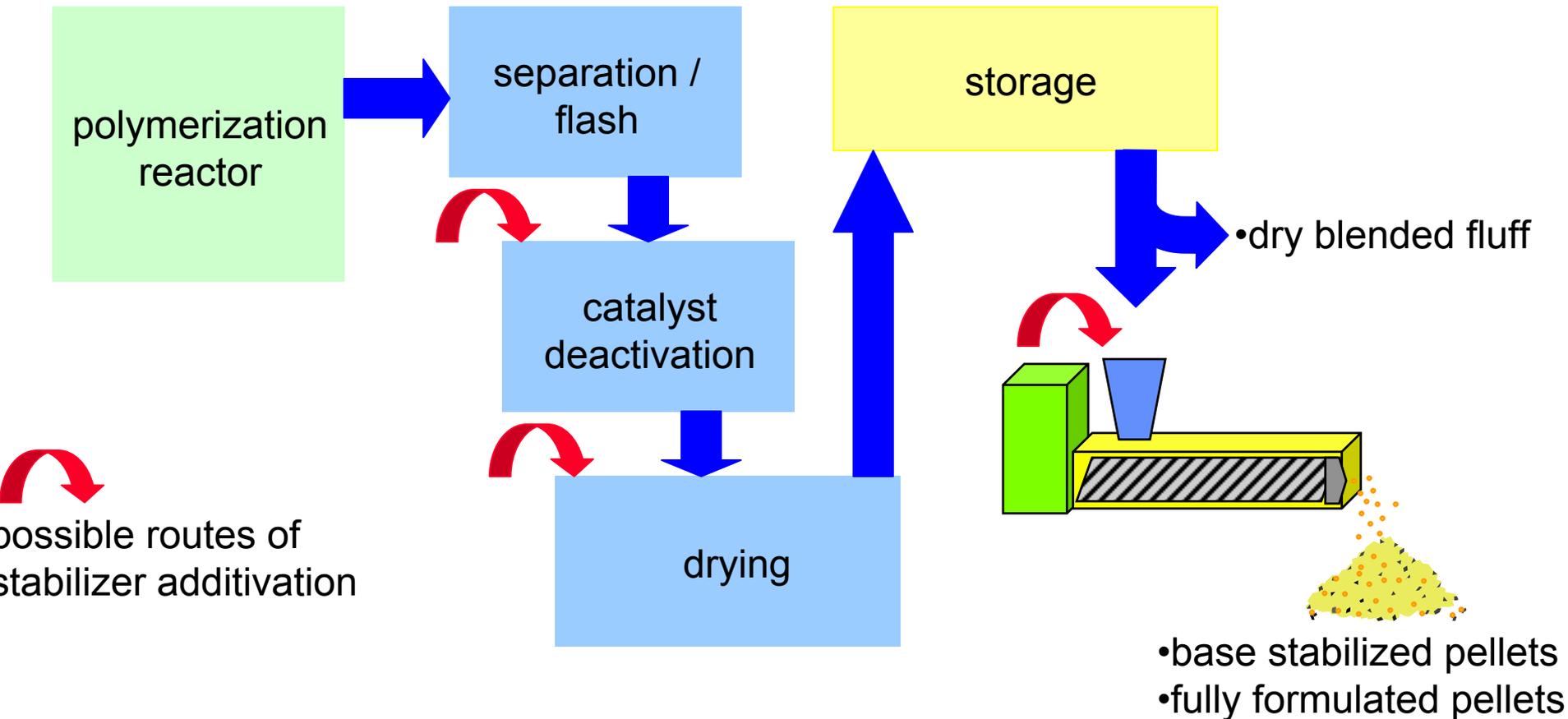
- Market need
- Knowledgeable people
- Communication
- Database of experience
- Toolbox of additives
- Business commitment
- Considerable patience
- Good fortune



Innovative stabilizer solutions meeting requirements defined by

- production technology (dosing, compounding)
  - molecular structure
  - converting process
  - end-use application

# Adding stabilizers during resin production



***Ultimate goal: Keep Molecular Architecture Intact***

# Impact of stabilizers in the film value chain



- **Polymer manufacturer**

- reactor product
- finishing step and pelletization
- fill & ship railcars, trucks, boxes, etc.

**Consistency**  
**Ease of use**



- **Film producer**

- blown & cast film blowing
- conversion to commercial products (print; seal; fold)
- recycle ( edge trim; wide spec)

**Processability**



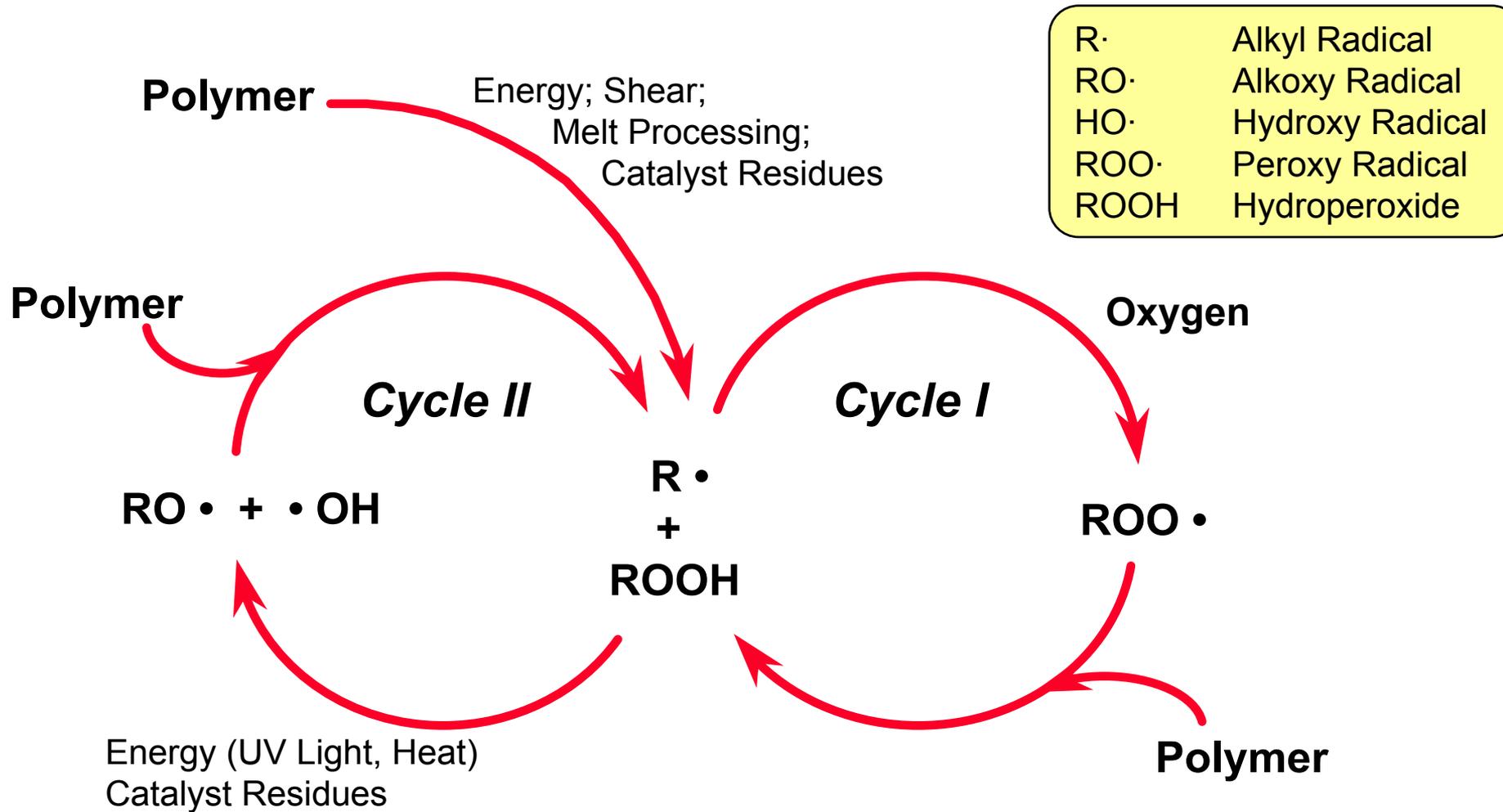
- **Distribution**

- storage stability
- performance in application

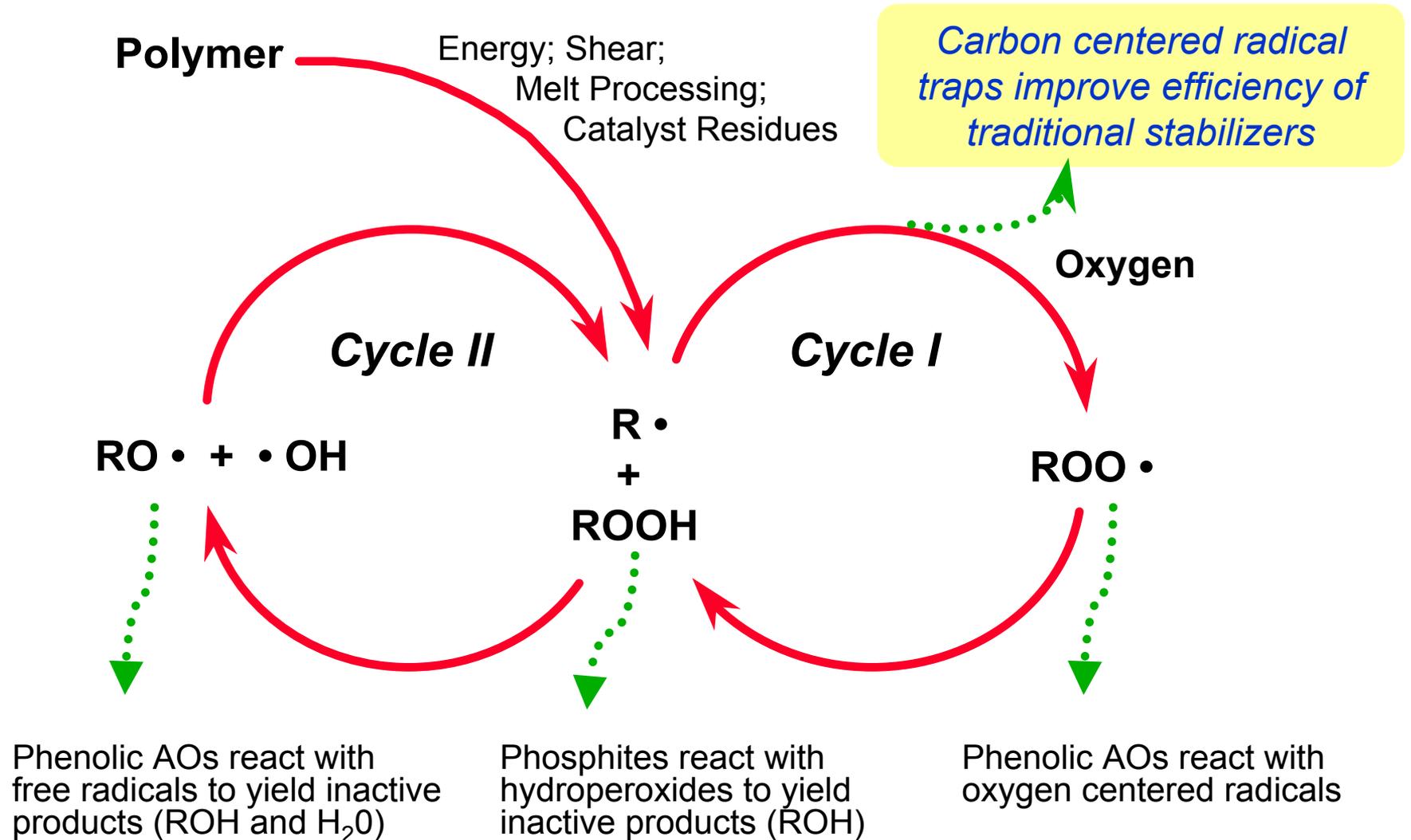
**Durability**  
**Aesthetics**



# Autoxidation cycle of polyolefins



# Revised inhibited autoxidation cycle



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# **TNPP-free stabilization of LLDPE film grades**

# Requirements on LLDPE film grade stabilization

## Film processing requirements:

- processing stability
- low gels and black specs
- sealability



## Film performance requirements:

- optical properties / color
- mechanical properties
- organoleptics
- regulations
- environment/health



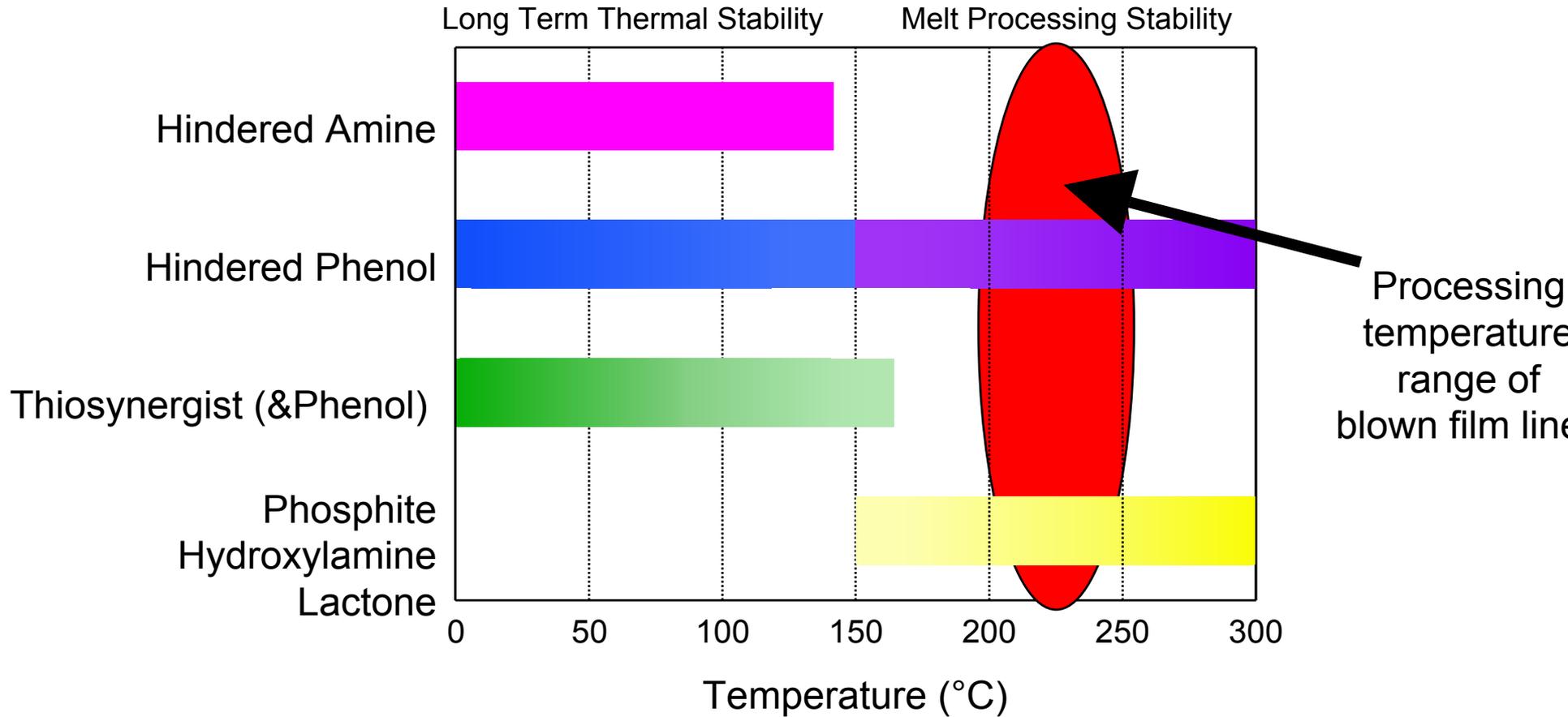
**LLDPE**  
*film*  
*grades*

## Relevant resin production requirements:

- additive handling
- additive and resin stability
- formulation costs and availability



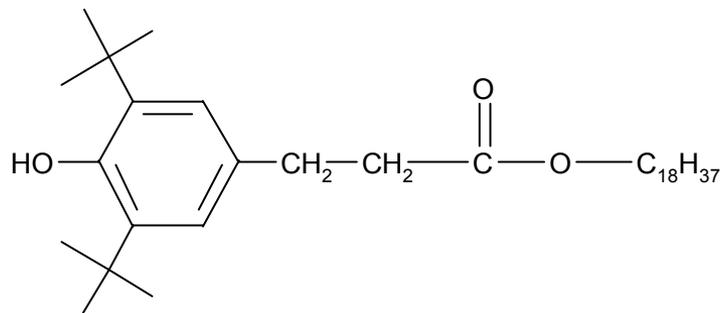
# Process stability essential for LLDPE film grades



# Common LLDPE stabilization based on AO-2/P-1 or P2

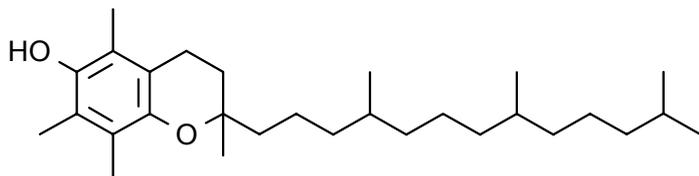
## Scavenger of oxygen centered radicals

AO-2

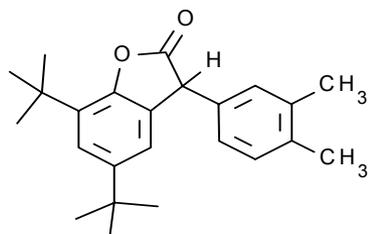


## Scavenger of carbon centered radicals

AO-3

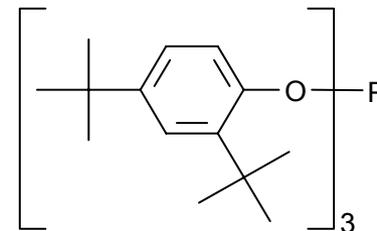


L-1



## Hydroperoxide decomposers

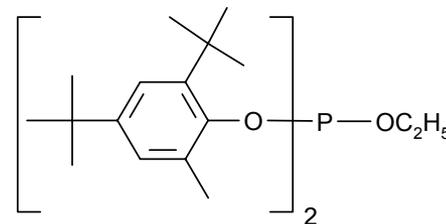
P-1



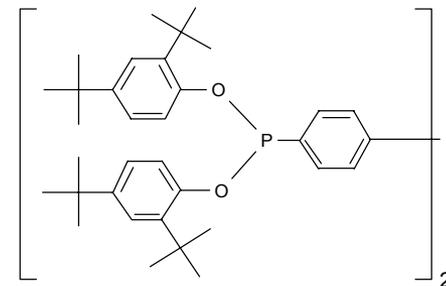
P-2



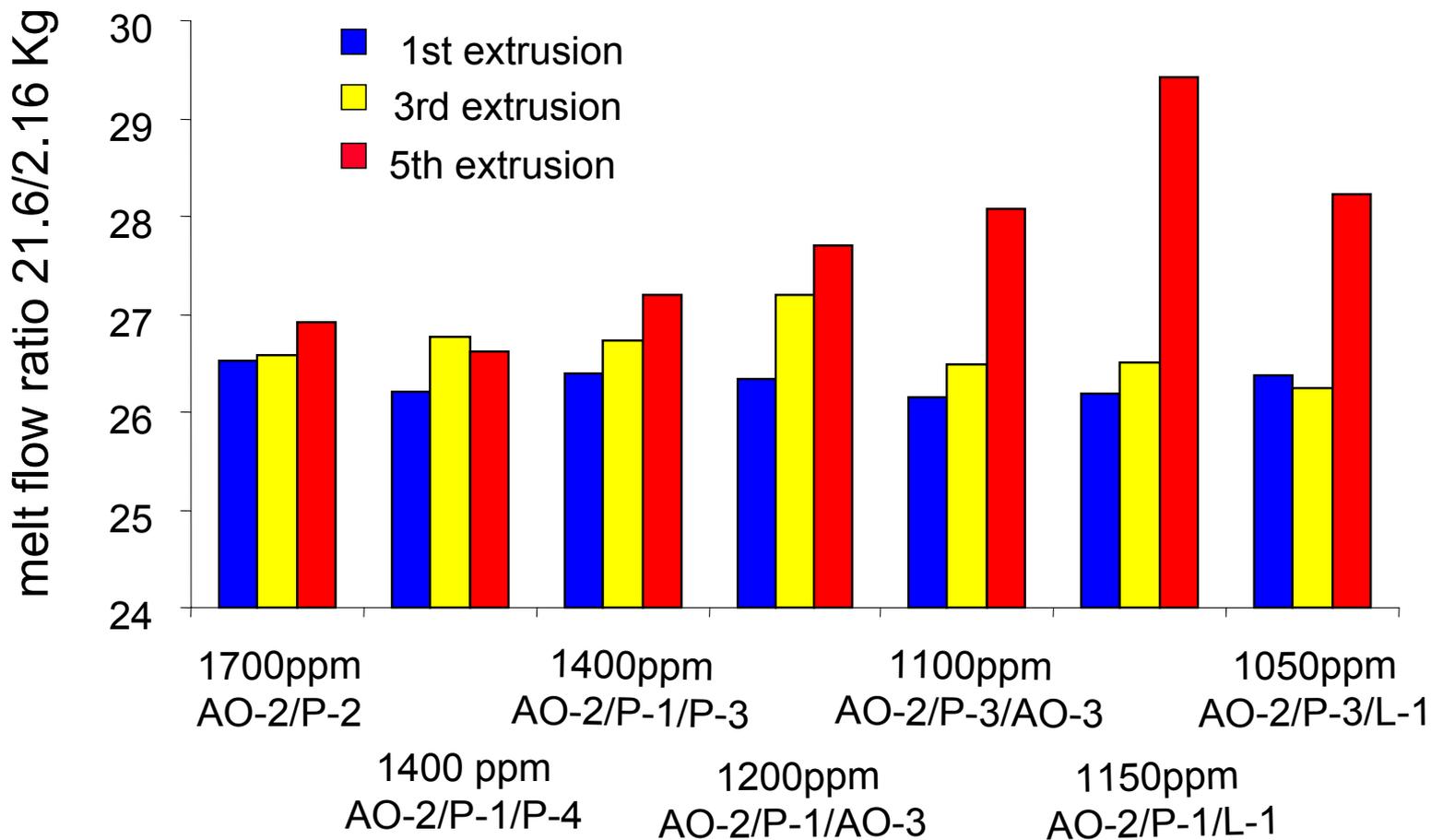
P-3



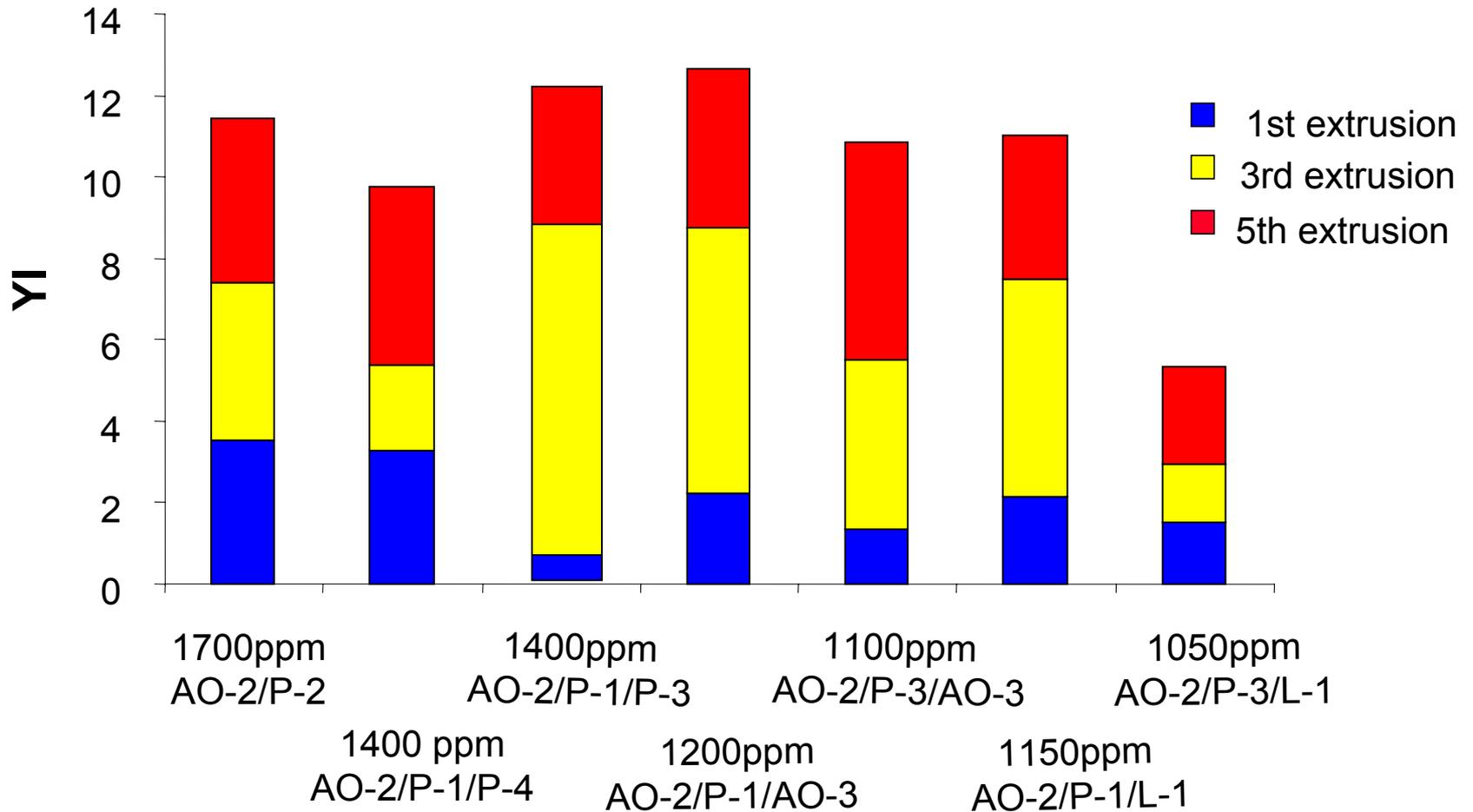
P-4



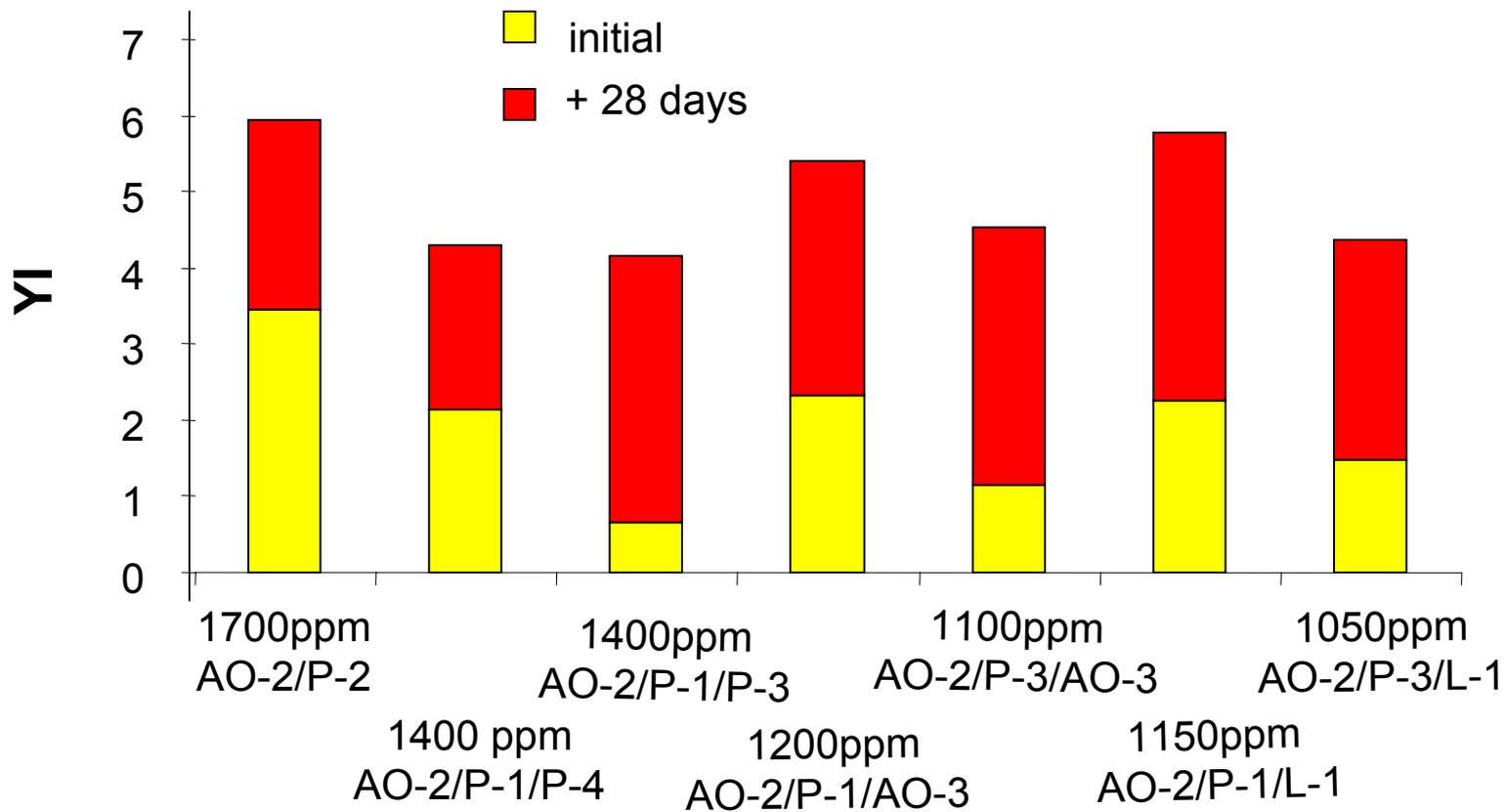
# Processing stability during multiple pass extrusion



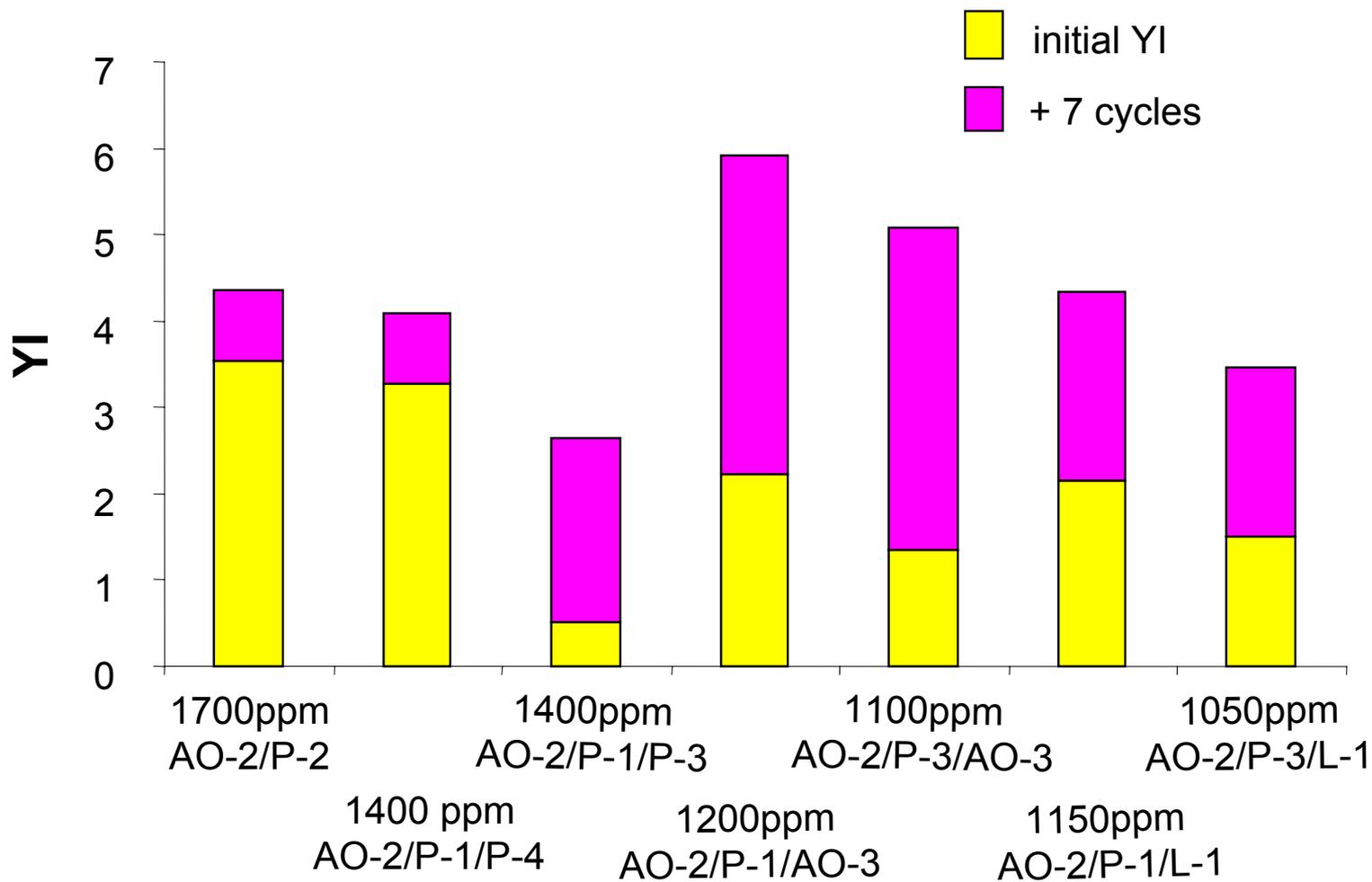
# Color generation during multiple pass extrusion



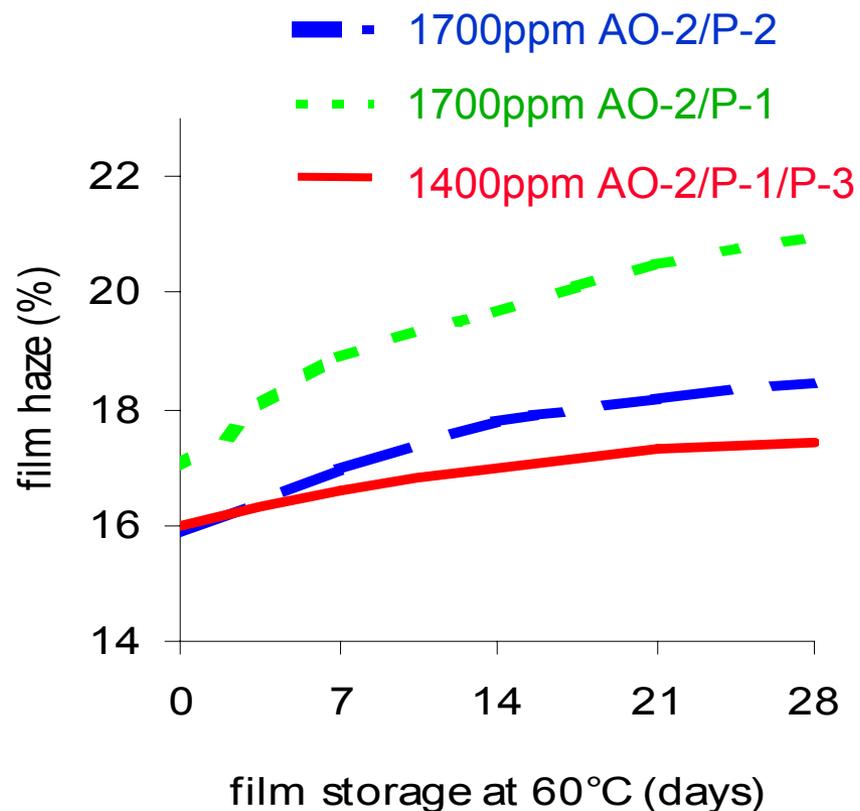
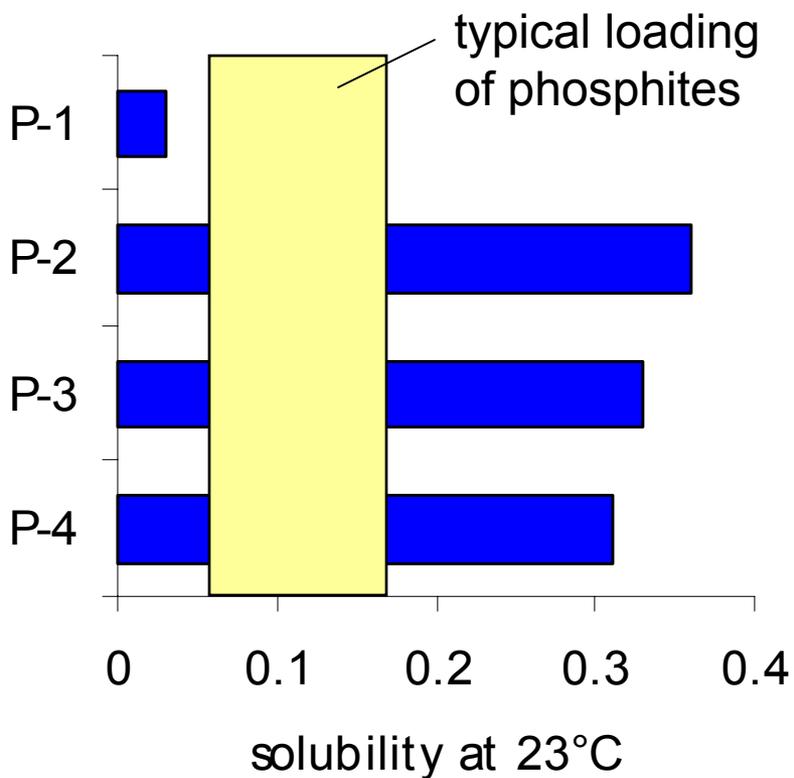
# Color development during aging at 80°C



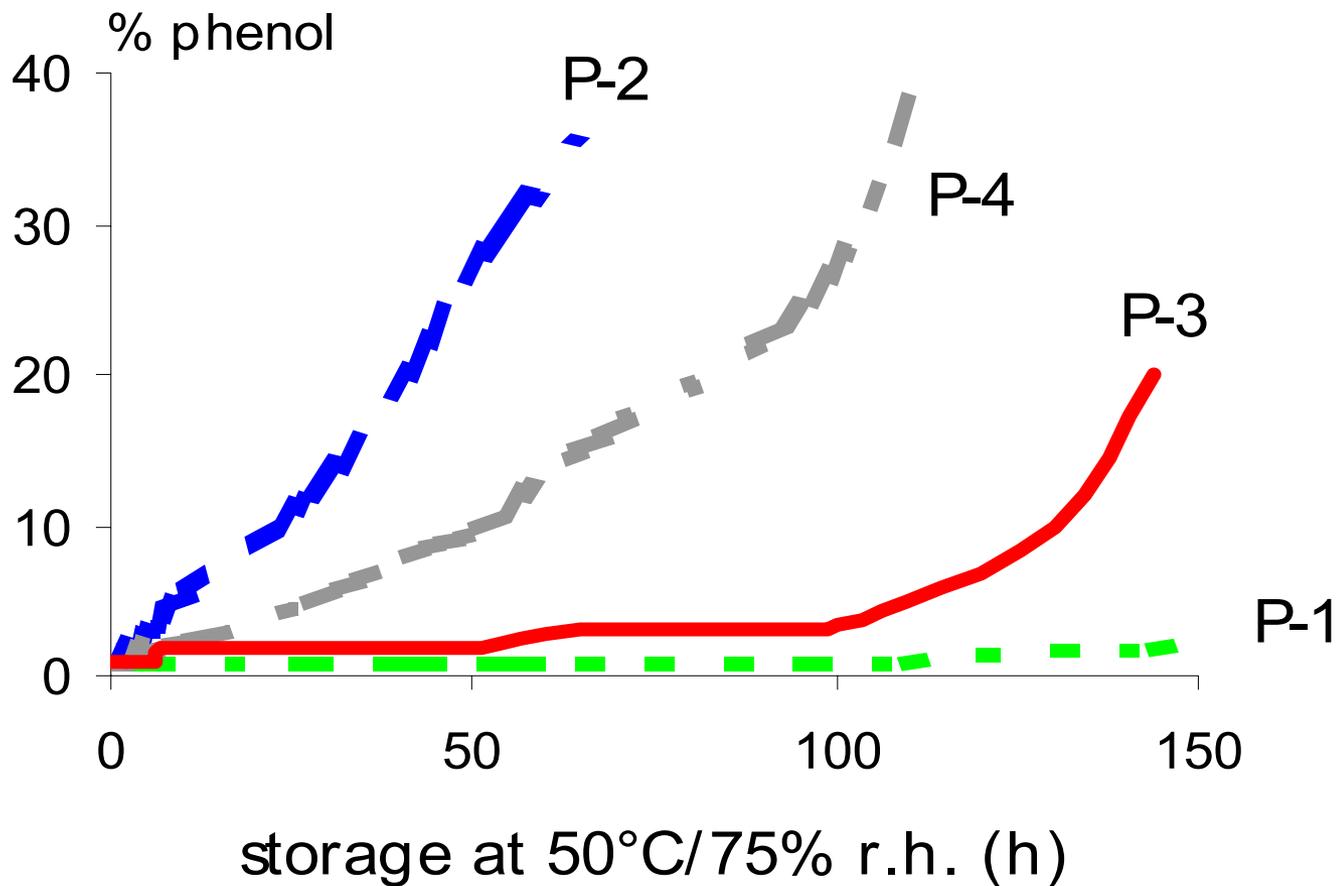
# Gas fading performance



# Solubility of stabilizers effects blooming



# Hydrolytic stability of phosphites



# TNPP-free stabilization of LLDPE film grades

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## **Processing stability:**

- equivalent melt flow control
- better color performance possible

## **Film performance:**

- compatibility issues can be avoided
- hydrolytic stability can be improved
- improved gas fade resistance possible

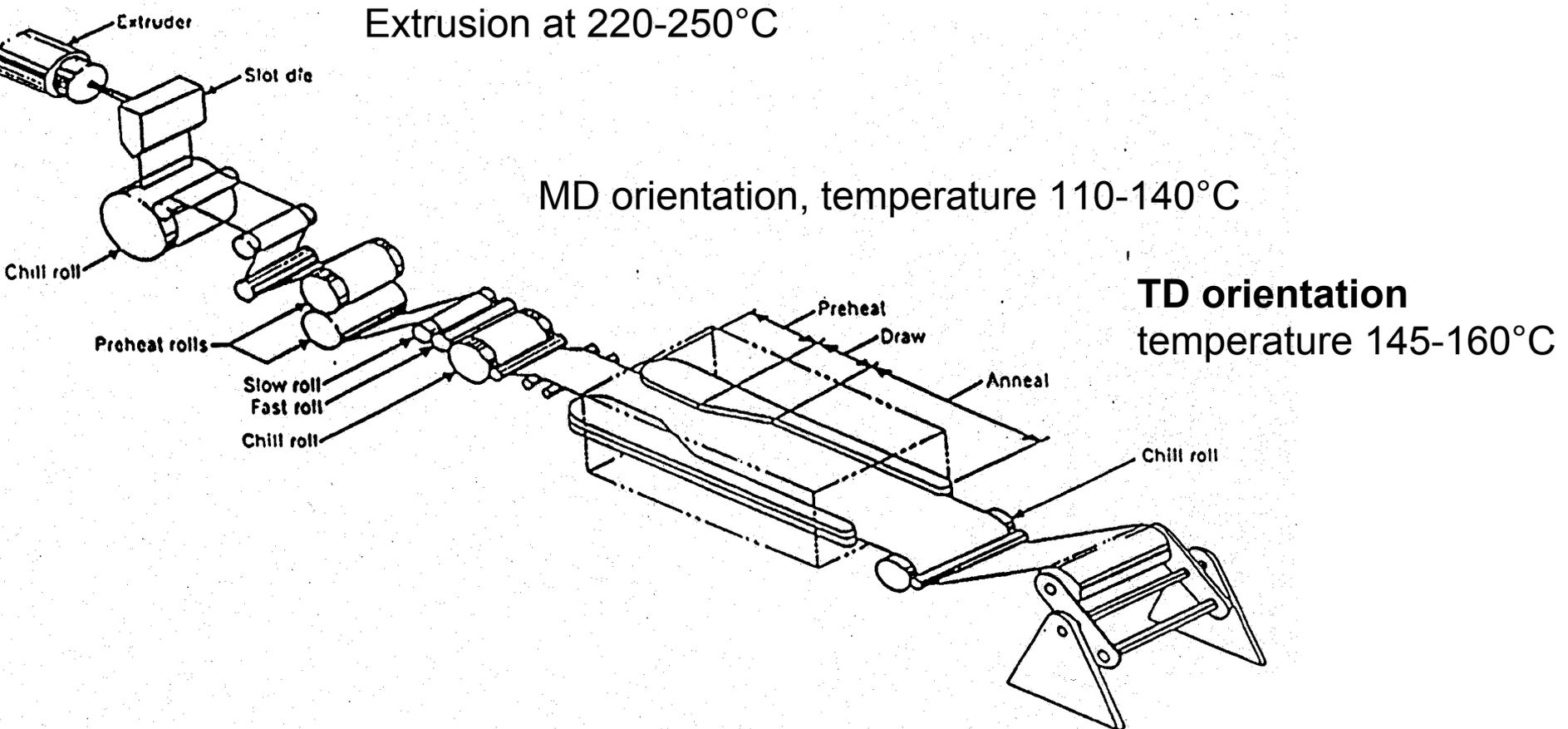
 **Attractive cost-performance alternatives possible**

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# **BOPP film stabilization**

# Influence of temperature of the BOPP process

## *Stenter frame process* (sequential stretching)



# BOPP Film Stabilization

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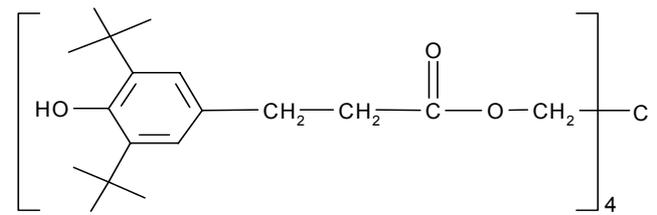
## Major requirements on stabilizers:

- broad processing window
- low color
- excellent optical properties (transparency, gloss)
- maintain mechanical properties (stiffness) and shrinkage performance
- excellent organoleptic performance
- rework quality
- no negative impact on printing, flame/corona treatment, metallization
- formulation costs

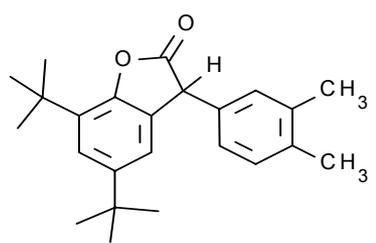
# Conventional BOPP stabilization based on AO-1/P-

1

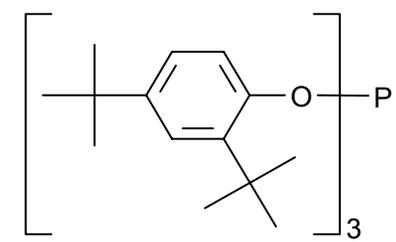
AO-1



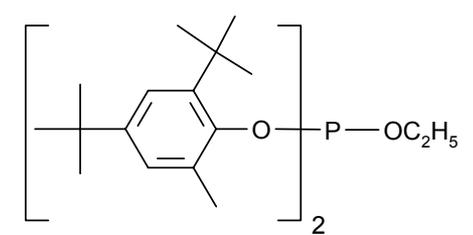
L-1



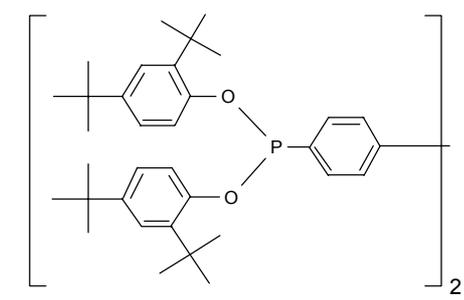
P-1



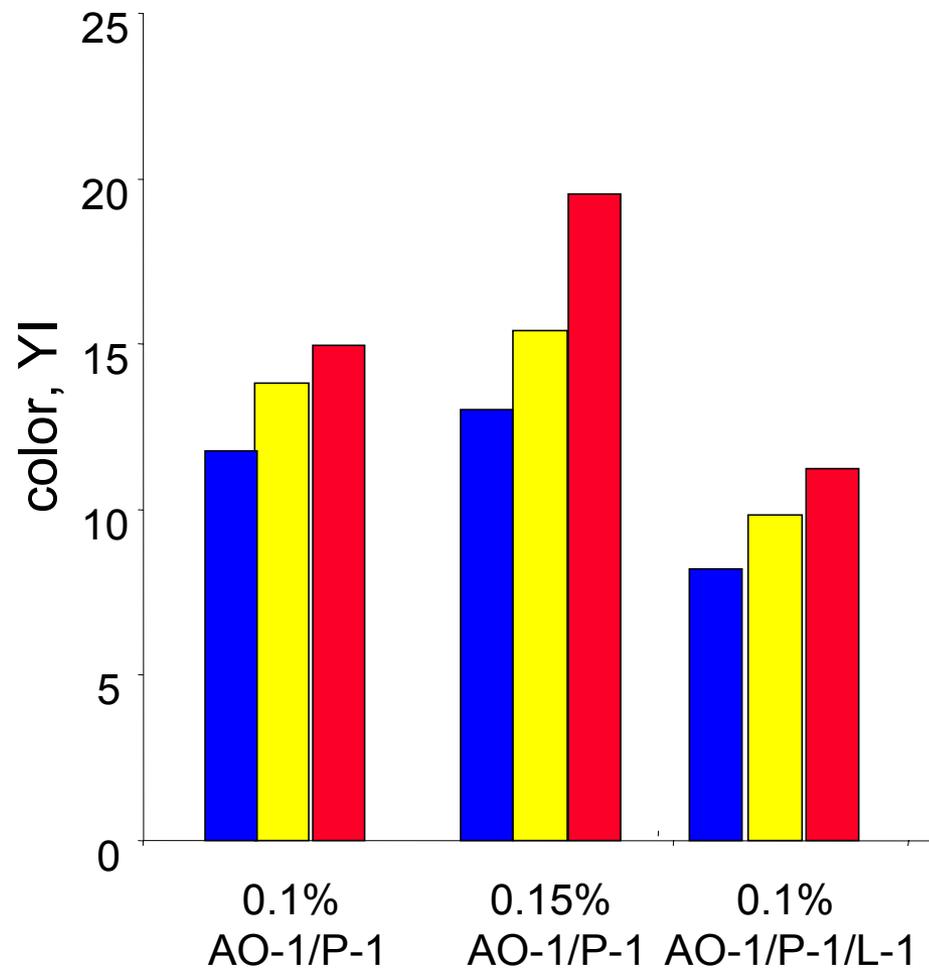
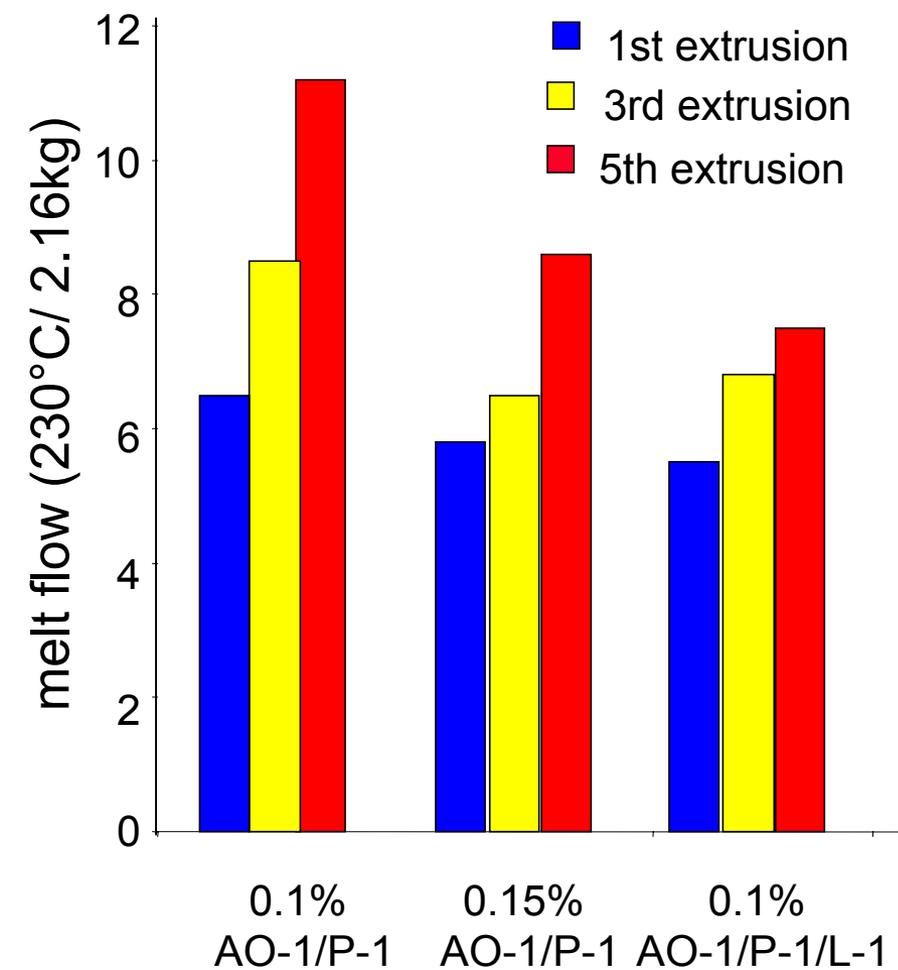
P-3



P-4



# Effect of lactone chemistry on BOPP film grades



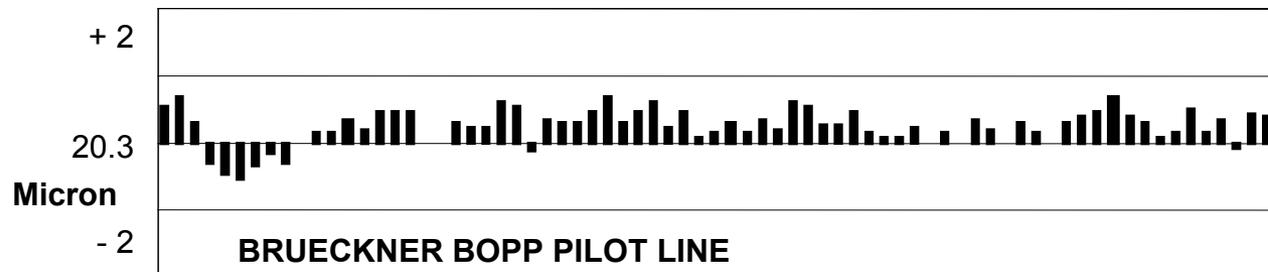
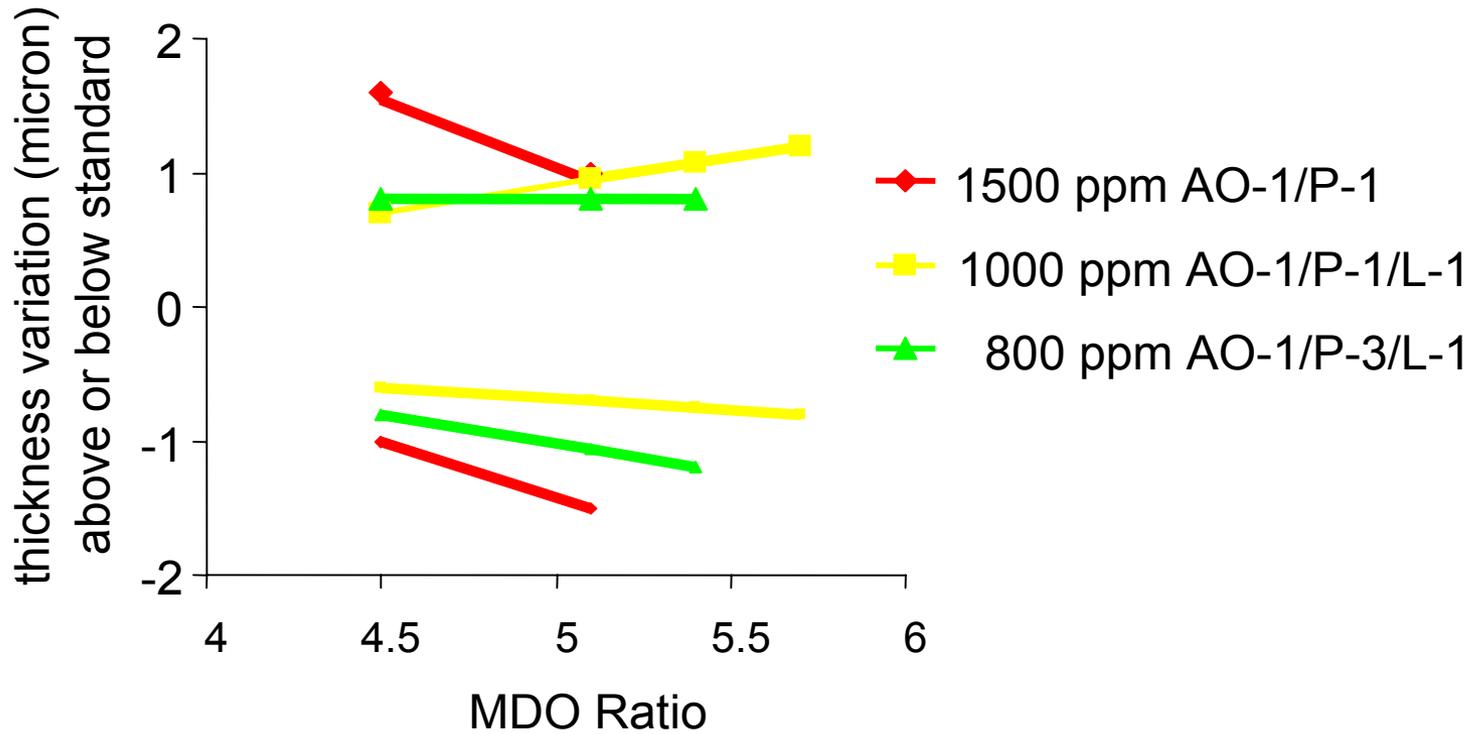
# Operating parameters for Brückner pilot BOPP line

Parameter	Varied or Constant?	Standard Value
Extrusion temperature	constant	250°C
Line Speed	constant	85 m/min
MDO Ratio	varied	4.5:1
TDO Ratio	constant	8:1
TDO Temperature	varied zone temps	172-172-159-150°C
Coex Film Thickness	constant	20 micron (1/18/1)

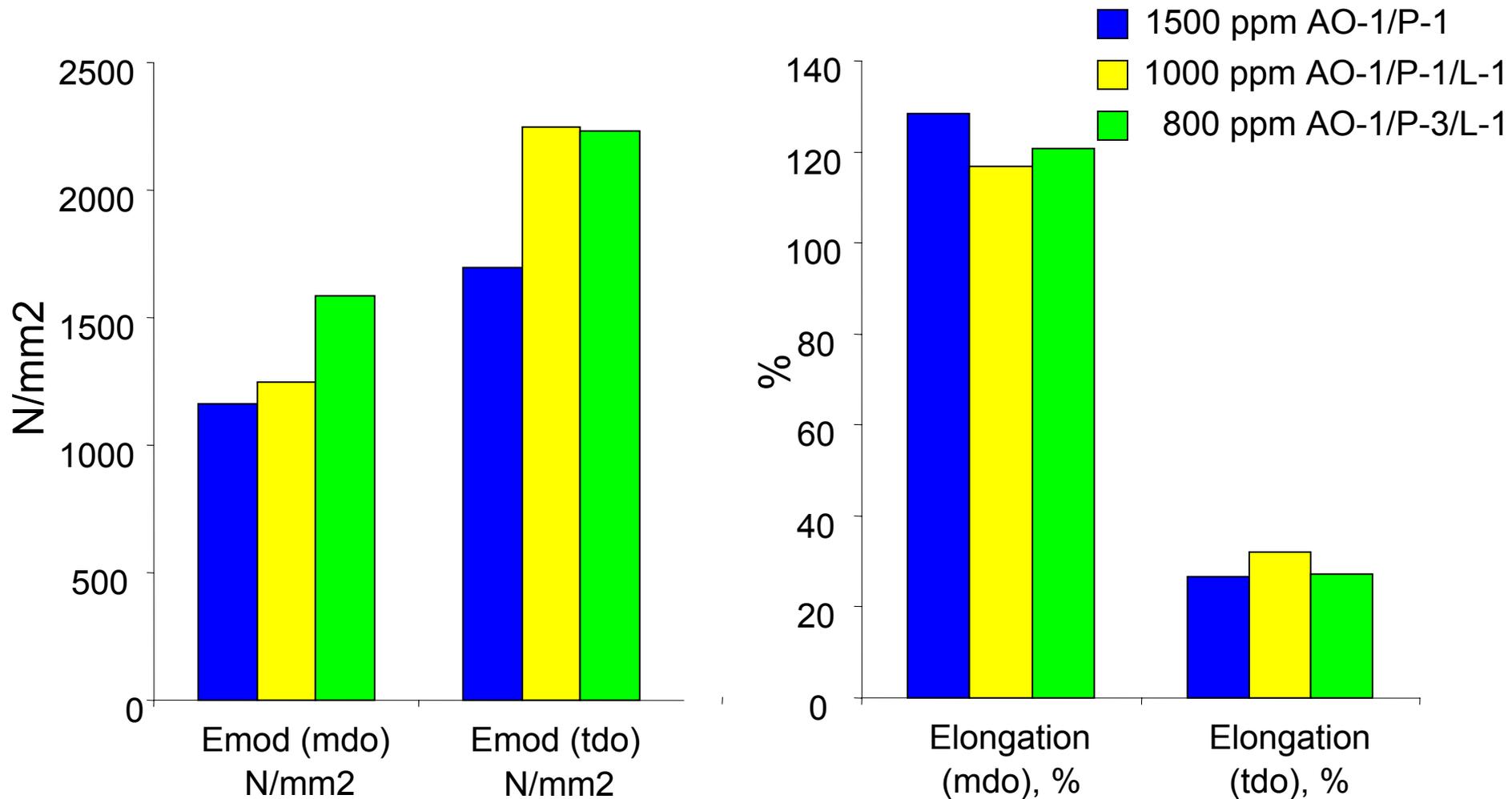
# Effect of stabilization on BOPP processing window

Formulation	Machine direction orientation (MDO) - highest ratio before break		Transverse direction orientation (TDO) - high/low before break	
	Range	% Increase	Range (°C)	% Increase
1500 ppm AO-1/P-1	5.1 : 1	-	14	-
1000 ppm AO-1/P-1/L-1	5.7 : 1	12%	16	14%
800 ppm AO-1/P-3/L-1	5.4 : 1	6%	17	21%

# Stabilizer impact on thickness uniformity of BOPP films

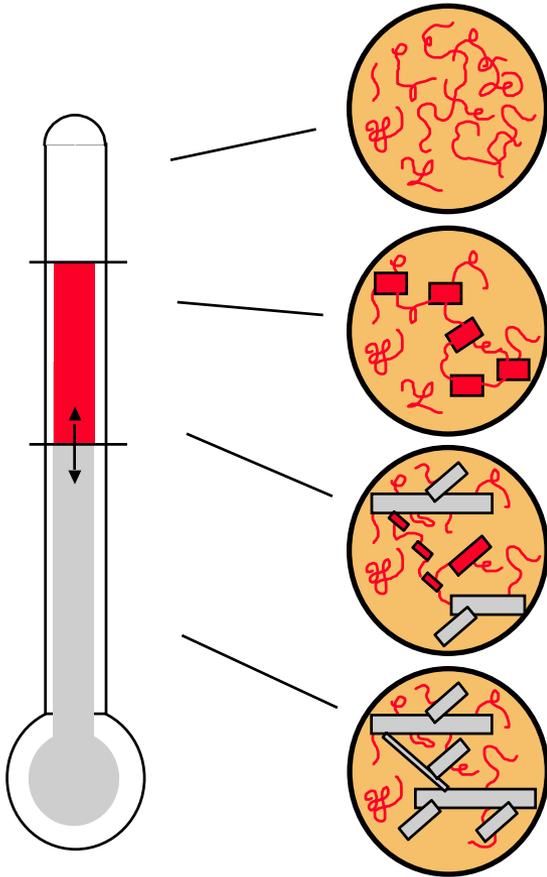


# Physical properties of BOPP films



# BOPP Film Stabilization

✓ extended processing window



- ✓ improved color
- ✓ equal or better optical properties
- ✓ improved mechanical properties
- ✓ cost equivalent
- ✓ no difficulties with treatments, printing and metalization
- ✓ improved onstream time observed

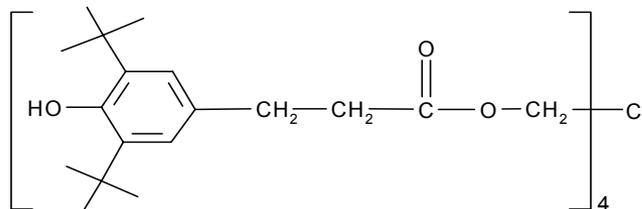
# In Summary

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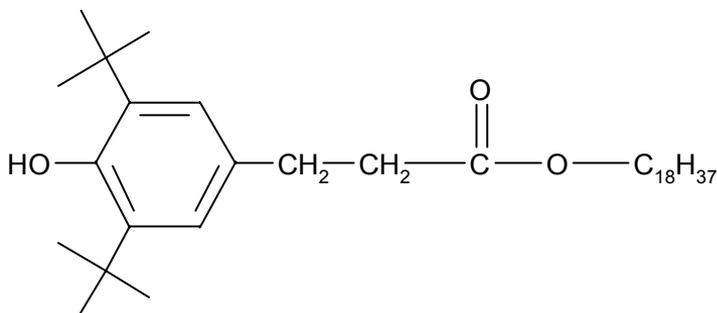
- base stabilization is easy
- base stabilization is complex
  
- opportunities for improvement
- taking into account requirements of
  - end-use application
  - resin production
  - polymer type and molecular structure

# Stabilizers presented in this paper

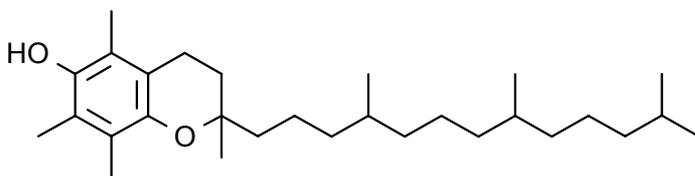
**AO-1**  
**IRGANOX® 1010**



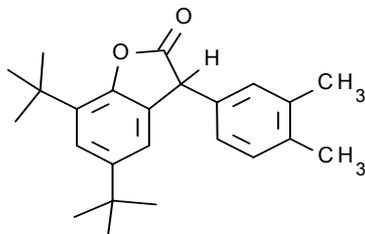
**AO-2**  
**IRGANOX 1076**



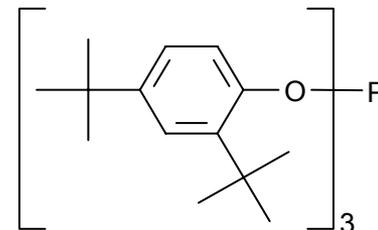
**AO-4**  
**IRGANOX E**



**L-1**  
**IRGANOX HP-136**



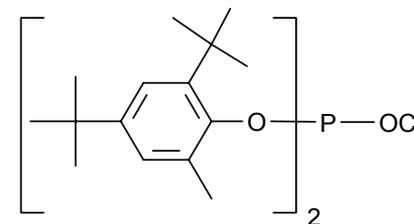
**P-1**  
**IRGAFOS® 168**



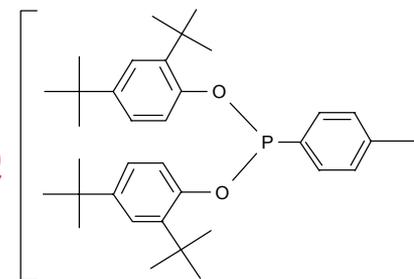
**P-2**  
**IRGAFOS TNPP**



**P-3**  
**IRGAFOS 38**



**P-4**  
**IRGAFOS PEPQ**



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Thanks for your  
attention!