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### BREAKTHROUGH CHEMISTRY FOR PROCESSING STABILIZATION OF POLYPROPYLENE

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## **BREAKTHROUGH CHEMISTRY FOR PROCESSING STABILIZATION OF POLYPROPYLENE**

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### **ABSTRACT**

Traditional stabilization systems for polypropylene are typically based on a binary combination of a phenolic antioxidant and a phosphorus based melt processing stabilizer. The phenolic antioxidant provides melt processing stability as a hydrogen atom donor and free radical scavenger; it also provides the polymer with some desired level of short-term or long-term thermal stability, simply for storage or throughout the lifetime of the final article. The phosphorus based melt processing stabilizer, usually a phosphite or phosphonite, functions as a hydroperoxide decomposer above the melting point of the polymer, during melt compounding and processing. Both chemistries work together synergistically to help maintain the original molecular architecture of the polymer.

Recently, a new class of additives, 3-aryl-benzofuranones (lactones) has been introduced and adopted commercially. Lactones are highly efficient at scavenging both carbon and oxygen centered radicals during melt processing of polyolefins. Investigations have been underway to examine the impact of low concentrations of lactone in regard to enhancing the performance of traditional stabilization systems. The presumed stabilization mechanism of a lactone and the optimum composition of ternary stabilizer blends for polypropylene are discussed.

### Processing Stabilization of Polyolefins

The constant need to improve the technical performance of existing polyolefin grades in a highly competitive environment, where the advent of new catalyst technology is leading to new applications requires ever more effective stabilizer systems. The additive supplier has to provide producers, converters and end-users of polyethylene and polypropylene, stabilizer solutions which improve performance, enhance productivity and decrease costs.

Polyethylene or polypropylene undergoes several melt processing steps from the reactor material to the final article. Each of those steps causes degradation, a result of the combined action of shear, heat and oxygen. Thermo-oxidative degradation takes place by a free radical mechanism which leads to a variety of oxidative reactions that either cause chain scission (decrease in molecular weight) or molecular enlargement due to recombination reactions. Both types of reactions take place simultaneously, but one or the other will be predominate depending on the processing conditions, the molecular structure and molecular imperfections. The latter is highly dependent on the polymerization catalyst technology used.

The C-centered polymeric radicals play a paramount role during the degradation in the extruder. Normally, under processing conditions very little oxygen is available for the reaction with C-centered polymeric radicals. As a result, significant concentrations of C-centered polymeric radicals can prevail in the extruder. The traces of oxygen still present in the extruder react very fast with the C-centered polymeric radicals to give peroxyradicals and subsequently hydroperoxides. The hydroperoxides decompose yielding the very reactive RO• and •OH radicals which produce new C-centered polymeric radicals R•. Therefore, the ideal processing stabilizer should trap the C-centered polymeric radicals R• before they can react with oxygen.

The oxidative degradation of polyolefins during melt processing can efficiently be inhibited through the use of small quantities of stabilizers. The traditional, binary processing stabilizer systems are comprised of properly selected ratios of phosphites and sterically hindered phenols and dosed for the optimum final concentration [1, 2, 3]. For specific applications requiring phenol free stabilization packages, synergistic mixture of hindered amines and hydroxylamine can be used [4]. The phenolic antioxidant scavenges the oxygen centered radicals (alkoxy and peroxy). The phosphite decomposes the hydroperoxides to yield inert products. Acting on different species in the degradation cycle, phenolic and phosphites function synergistically.

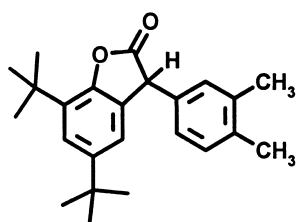
Unfortunately, none of these processing stabilizers are C-radicals scavengers.

The traditional binary systems have some shortcomings. Increasing processing temperature and demanding end-use applications generally result in the need to increase the concentrations of stabilizers. The result is a negative shift in the cost performance profile, possible additive incompatibilities, limitation due to indirect food contact regulations and potential for increased additive interactions. New high performance stabilizer systems are available to address these challenges.

### A New Alternative - A Revolutionary Stabilizer Chemistry

Several new high performance products have been introduced as alternatives to the traditional binary systems [5]. These high performance products offer superior performance and increased productivity while maintaining the performance of the polymer in demanding applications. These new products are synergistic mixtures of sterically hindered phenol and phosphite processing stabilizers boosted by a small amount of a lactone (3-arylbenzofuran-2-one) stabilizer (Figure 1). The latter (code HP-136) is a revolutionary new processing stabilizer for polyolefins.

The exceptional stabilizing activity of HP-136 is due to the ready formation of a highly stabilized benzofuranonyl radical, formed by easy donation of the weakly bonded benzylic hydrogen atom (Figure 2). The stabilized benzofuranonyl radical can either reversibly dimerise or react with other free radicals.



**HP-136**

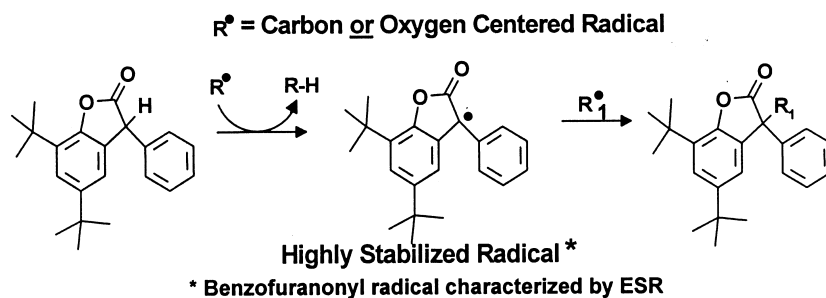
Name: 5,7-di-*t*-butyl-3-(3,4 di-methylphenyl)-3H-benzofuran-2-one

Physical Characteristics

- Free flowing white powder
- Melting range : 97°-130°C
- Molecular weight : 351
- Not prone to Hydrolysis
- Solubility at 20°C (g/100g solvent)
 

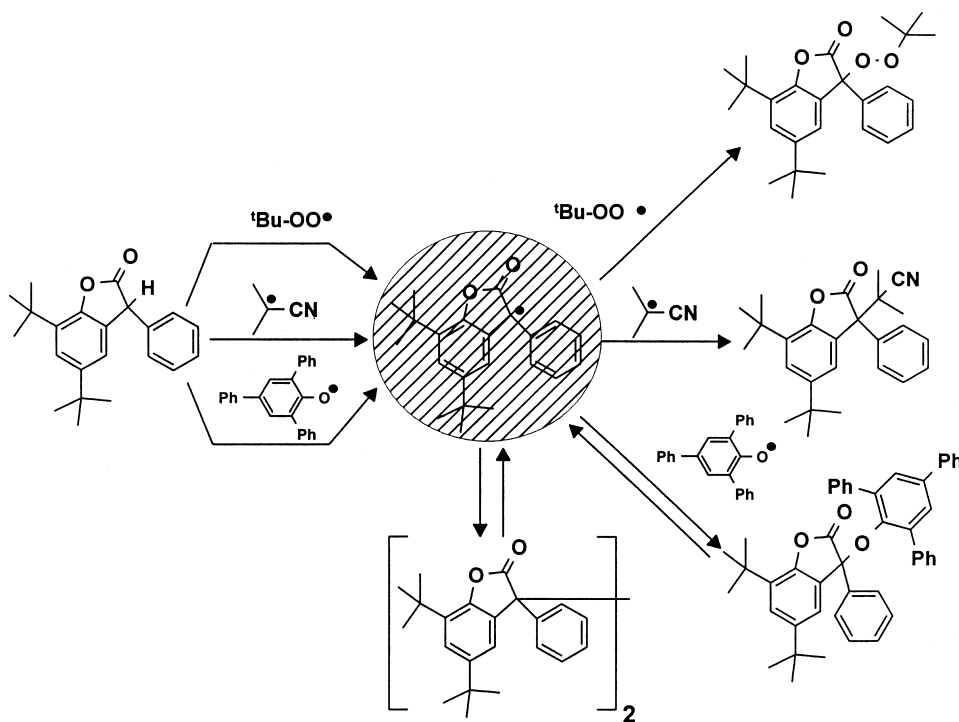
- methanol	0.96
- acetone	15.3
- hexane	2.5

**Figure 1.** A new high performance processing stabilizers.



**Figure 2.** Stabilization mechanism of arylbenzofuranones.

Sterically hindered phenols react preferentially with oxygen centered radicals like peroxy and alkoxy rather than with carbon centered radicals, while arylbenzofuranones scavenge both classes of radicals. The model experiments depicted in Figure 3 demonstrate that lactones act as powerful hydrogen donors and effective scavengers of many free radicals [5]. Lactones easily donate hydro-



**Figure 3.** Model radical scavenging reactions of arylbenzofuranones.

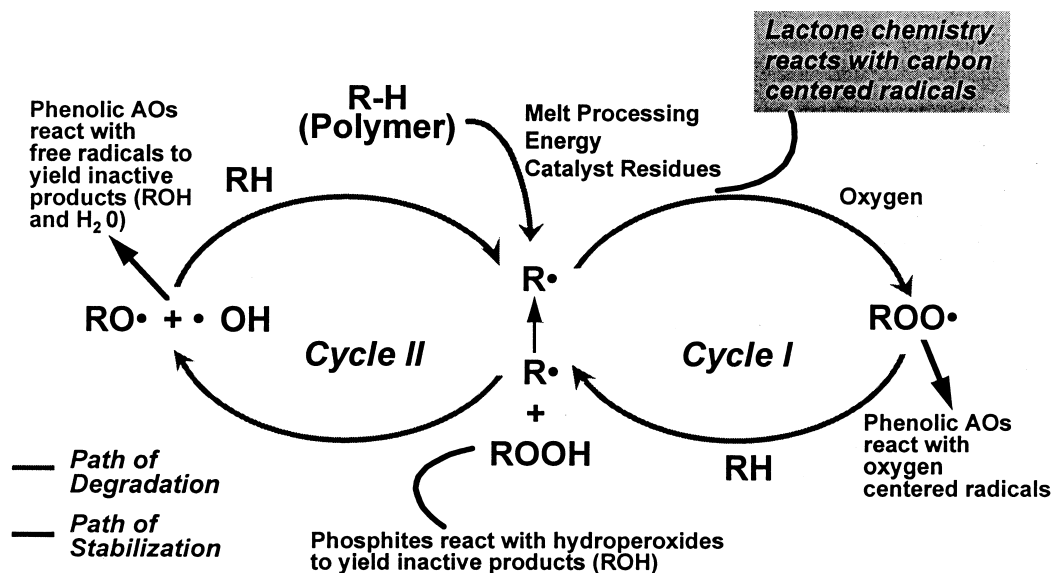


Figure 4. Revised Autoxidation Cycle for HP products.

gen to sterically hindered phenols, thus potentially regenerating the phenolic antioxidant.

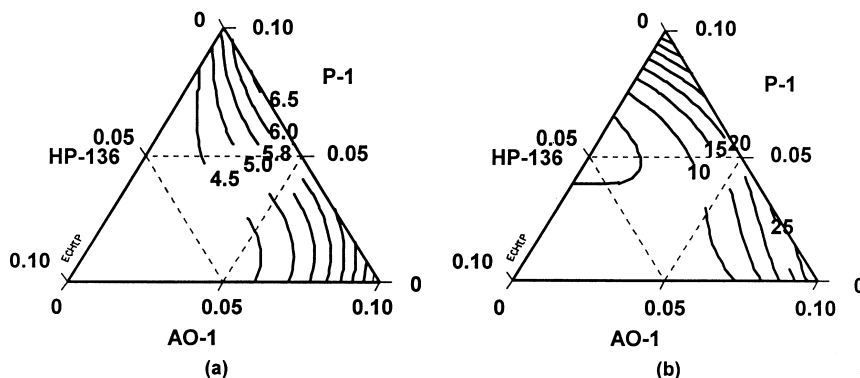
The new high performance products are extremely efficient since each of the three components provides a specific activity (Figure 4). The function of hindered phenolic antioxidants is to scavenge oxygen centered radicals and provide processing and long-term thermal stability. The alkarylphosphites function as hydroperoxide decomposers and provide processing stability and color maintenance. Finally the lactone, HP-136, functions as a carbon centered radical scavenger inhibiting auto-oxidation as soon as it starts. Additionally, HP-136 can potentially regenerating the phenolic antioxidant.

### Processing Stability Performance of Hp Products

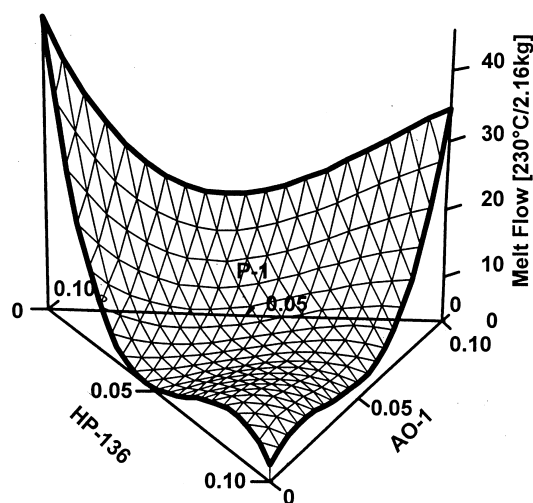
The selection of appropriate processing stabilizers is an integral part of the development and optimization of commercial polypropylene grades. The first step in formulation development is usually completed on lab scale equipment. Multiple pass extrusion experiments are very useful in the evaluation of processing stabilizers. These tests gives the relative performance of stabilizers under defined experimental conditions.

The theoretical considerations on the stabilization cycle suggest that the highest efficiency in preventing oxidation during processing should be achieved by a combination of the three types of stabilizers. The question then arises about the optimum ratio of the three components. To answer this important question, a series of experiments was run using the experimental design software package ECHIP. A partial cubic model was used for a mixture design with three variables: the phenolic antioxidant AO-1, the phosphite P-1 and the lactone HP-136. The concentration of the mixture was 0.1% in a polypropylene homopolymer (gas phase process) of nominal melt flow ( $230^{\circ}\text{C}/2.16\text{kg}$ ) = 3.5 g/10 Min. The individual stabilizers in the mixture vary between 0 and 0.1%. Ca-stearate was used at 0.05% in all the formulations as an acid scavenger. A total of nineteen multiple extrusion experiments were run on a Goettfert 20 mm lab extruder of  $L/D = 20$  and the maximum temperature of  $280^{\circ}\text{C}$  at the die. Five pure replicates were included to estimate the reproducibility (standard deviation) of the tests. The melt flow ( $230^{\circ}\text{C}/2.16\text{kg}$ ) and the yellowness index were determined after the first, third and fifth extrusion passes. The yellowness index was measured with spectrophotometer (Datacolor; C illuminant,  $2^{\circ}$  observer) on 2 mm compression molded plaques. Compression molded plaques of 1mm thickness were prepared with pellets of the first extrusion and exposed at  $150^{\circ}\text{C}$  and  $135^{\circ}\text{C}$  in a draft air oven until embrittlement.

The mixture diagrams for the melt flow after the first and fifth extrusion are shown in Figure 5. The lowest melt flow values (the least polymer degrada-



**Figure 5.** Melt flow after the first (a) and the fifth (b) extrusion of PP homopolymer at  $280^{\circ}\text{C}$ .



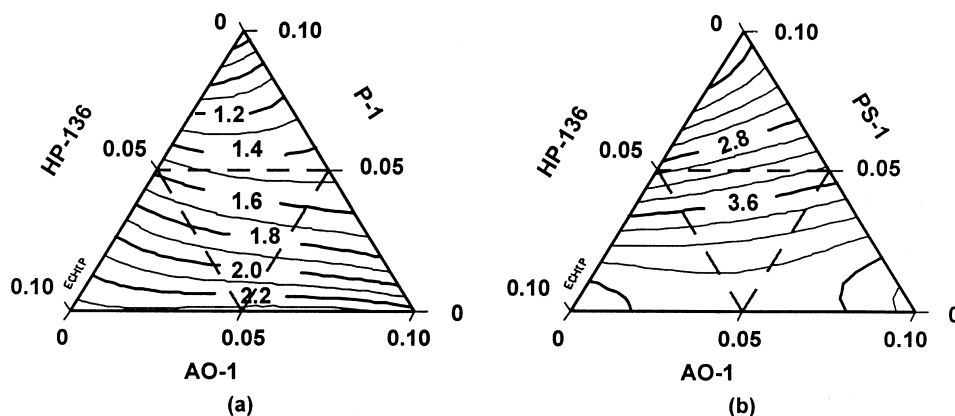
**Figure 6.** Melt flow after the fifth extrusion of PP homopolymer at 280°C.

tion) were obtained with mixtures having a high content of lactone. Mixtures with lactone concentration higher than 0.03% did not differentiate. These results confirm the high activity of the lactone as a processing stabilizer.

The same data can be presented in a three dimensional plot as shown in Figure 6 on the results of the fifth extrusion. From this graph, two observations are of particular interest. First, if the concentration of HP-136 equals zero, there is a distinct minimum in the curve representing the binary mixture AO-1 and P-1. This is a confirmation of results obtained by Drake *et al.* [3] for these binary mixtures. Secondly, the curve obtained for AO-1 equal to zero represents the results obtained with a *phenol free* processing stabilizer systems. Such systems gain increasing importance in the polypropylene fiber industry, where phenolic antioxidants are no often longer acceptable, because of the tendency to discolor when exposed to oxidative environments (gas fading). A lactone concentration of 0.03% in the mixture is sufficient to control the melt flow during melt processing. In such phenol free systems, a high molecular weight hindered amine stabilizer (HAS) is used to provide the required long-term thermal stability.

Figure 7 shows the mixture diagrams for color (yellowness index) measured on the samples after first and fifth extrusion. Color is mainly controlled by the concentration of phosphite P-1 in the mixture. The lowest color is obtained for mixtures with high P-1 content. At a given phosphite concentration, varying

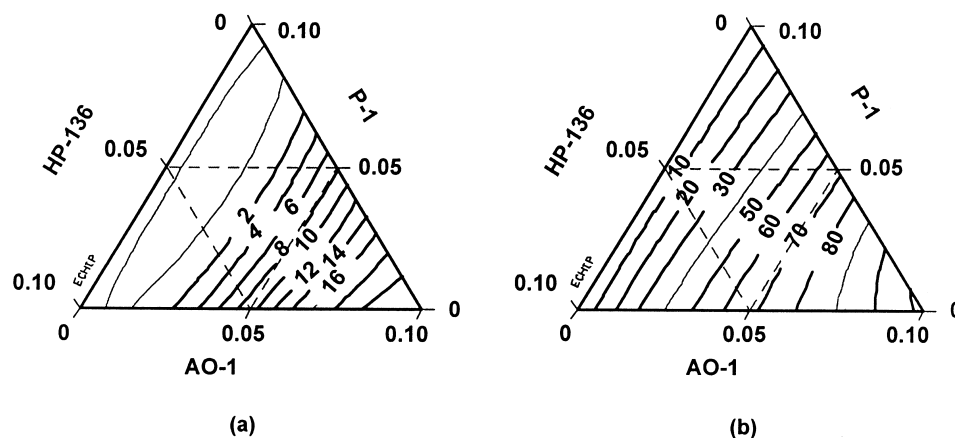




**Figure 7.** Yellowness Index after the first (a) and the fifth (b) extrusion of PP homopolymer at 280°C.

the ratio lactone HP-136 to phenolic antioxidant AO-1 has no significant impact on color.

The results of the long-term thermal stability as determined by aging experiments are plotted in Figure 8. Long-term thermal stability is mainly a function of the concentration of phenolic antioxidant in the stabilizer mixture, the lines of identical time to embrittlement being parallel to the left axis. The longest lifetime is obtained with 0.1% AO-1 alone.



**Figure 8.** Days to embrittlement at 150°C (a) and 135°C (b) of PP homopolymer stabilized with a mixture of AO-1, P-1 and HP-136.

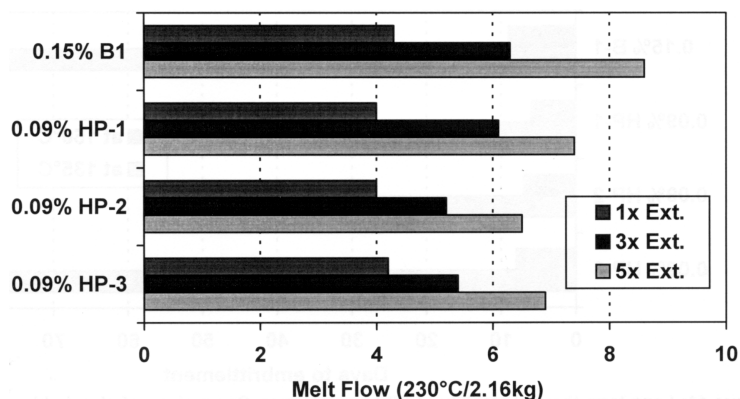
The ideal stabilization system for polypropylene should have the best melt flow retention, the lowest color and the longest lifetime. The results above, show that only combinations of the three stabilizers will approach the performance of such an ideal system. Some compromises will be necessary and will vary depending on the final application. Ternary processing stabilizer systems with 15% of lactone HP-136 are commercially available. They guarantee a high performance in melt flow control by maintain a low color. Different ratio between AO-1 and P-1 are used depending on the long-term thermal stability requirements of the final product.

The validity of the model has been checked by checkpoints experiments in the same polypropylene grade.

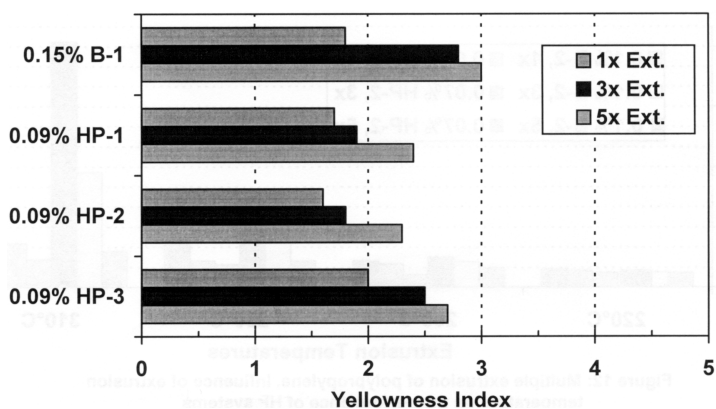
The conclusions or general principles derived from the model have also been verified in other polypropylene grades. Figures 9 to 11 show such multiple extrusion results obtained on a different polypropylene (liquid phase) and using a different extruder (30 mm; L/D = 25). Melt flow (Figure 9) and color (Figure 10) are significantly better for the high performance systems with the lactone than for the conventional binary phenol/phosphite blend.

The results show that by using the appropriate composition, the long-term thermal stability can be maintained (Figure 11).

One critical parameter in the stabilization of polypropylene is the processing temperature. A major advantage of the high performance systems (those

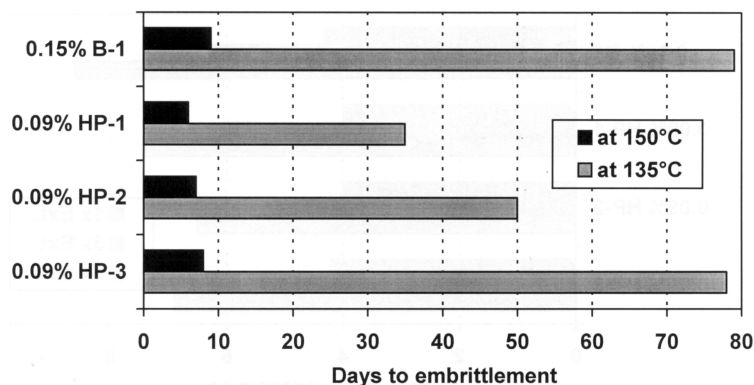


**Figure 9.** Melt flow after multiple extrusion of PP homopolymer. Comparison of classic binary blend and high performance systems with HP-136.

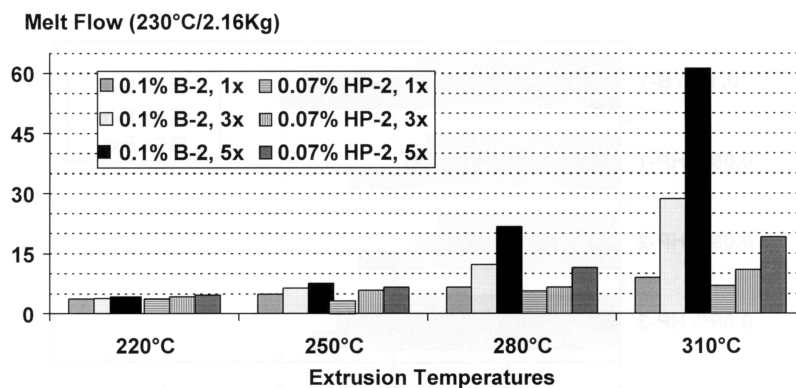


**Figure 10.** Color after multiple extrusion of PP homopolymer. Comparison of classic binary blend and high performance systems with HP-136.

containing HP-136) is their unique performance at very high processing temperatures and under high shear conditions. The influence of the extrusion temperature on the performance of systems with HP-136 in polypropylene is illustrated in Figure 12. Although used only at 0.07% they perform similarly to 40% more of an equivalent binary system for melt flow retention. Polypropylene stabilized with the high performance systems is less sensitive to changes in extrusion temperature thus broadening the processing window of the polymer quite signifi-



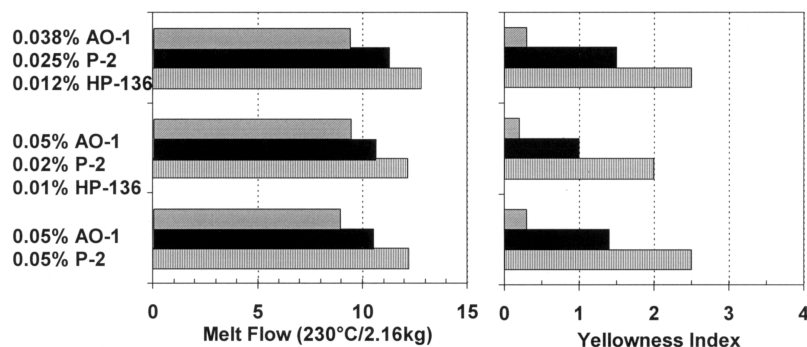
**Figure 11.** Long-term thermal stability of PP homopolymer. Comparison of classic binary blend and high performance systems with HP-136.



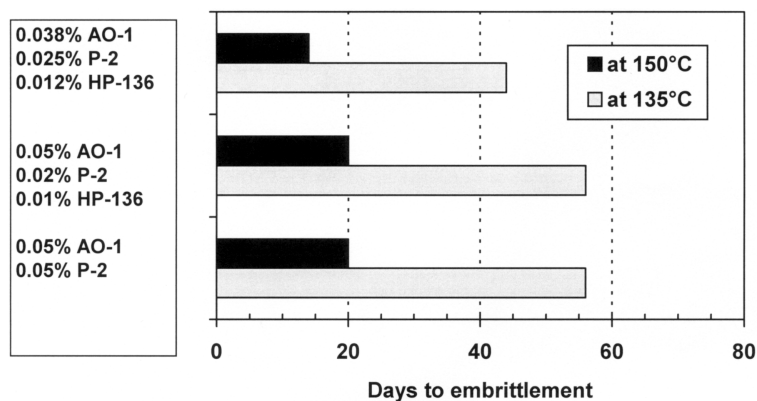
**Figure 12.** Multiple extrusion of polypropylene. Influence of extrusion temperature on the performance of HP systems.

cantly. From these results the potential for high performance systems to make significant productivity increases in polyolefin processing without affecting polymer properties can be observed.

The new lactone stabilizer HP-136 can also be combined with the high performance phosphite (P-2) to benefit from their ability to better maintain the color under critical conditions. Figure 13 shows the results obtained with P-2 in combination with the phenolic antioxidant AO-1. Identical melt flow retention



**Figure 13.** Multiple extrusion at 260°C of polypropylene. Combination of HP-136 with a high performance phosphite P-2 and AO-1.



**Figure 14.** Long-term thermal stability of polypropylene. Combination of HP-136 with a high performance phosphite P-2 and AO-1.

can be achieved using 20 to 25% less stabilizer while maintaining the good color performance of the initial system.

The long-term thermal stability here is also a function of the concentration in phenolic antioxidant AO-1 as demonstrated in Figure 14.

A practical consideration for any polymer stabilizer is the regulatory status. The lactone HP-136 is regulated by FDA in USA, BgVV in Germany, in France and Belgium for food contact applications in polypropylene and polyethylene. The application for regulation in all polyolefins has been submitted to the European authorities.

## CONCLUSION

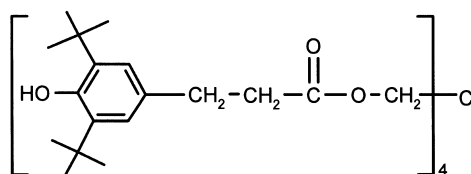
The new high performance systems, based on HP-136, offer an absolutely new performance profile. These systems are composed of synergistic mixtures of a novel C-centered radical scavenger, conventional hydroperoxide decomposers and long-term thermal stabilizers. High performance systems are intended to up-grade today's state-of-the-art stabilization systems in a revolutionary sense. The key benefits of lactone based stabilization systems combine excellent processing stability at low concentrations with particularly pronounced results

under severe conditions such as high processing temperatures even above 300°C, providing unparalleled melt flow retention and color maintenance improvements.

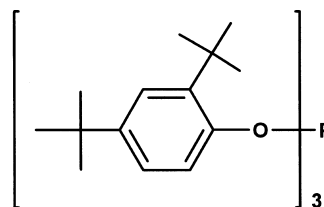
## APPENDIX

AO-1	IRGANOX <sup>®</sup> 1010	
P-1	IRGAFOS <sup>®</sup> 168	
P-2	IRGAFOS 126	
B-1	IRGANOX B215	(33% IRGANOX 1010/67% IRGAFOS 168)
HP-1	IRGANOX HP 2215	(85% IRGANOX B 215/15% HP136)
HP-2	IRGANOX HP 2225	(85% IRGANOX B 225/15% HP 136)
HP-3	IRGANOX HP 2251	(57% IRGANOX 1010/28% IRGAFOS 168/15% HP 136)

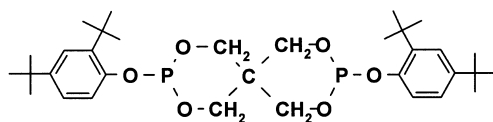
## CHEMICAL STRUCTURES



AO-1



P-1



P-2

## ACKNOWLEDGEMENTS

The development of the lactone and the high performance stabilizer systems is the results of hard work by many people. The authors wish to thanks all colleagues and technicians for their contributions.

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