Phenol vs. Phenol Free Stabilization and the Impact of Selected Grades of TiO_2:

Can we make non-discolored white LLDPE film by adding phenol-free masterbatch to phenolic AO stabilized resin?

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Abstract

The preservation of physical properties and aesthetics are two key measures for film products. As such, one needs to be selective in terms of choosing the polymer and stabilization systems that are used to derive robust and attractive film products. For most applications, traditional stabilization systems provide the appropriate level of physical property retention, good processability, and long term thermal stability without compromising the overall aesthetic appearance of the film product. In selected applications, however, it is desirable to have film products that do not discolor during processing; and more importantly, while the product is kept in storage. Under a selected set of circumstances, certain types of phenolics have been shown to be susceptible to discoloration, due to various factors; some of which can be controlled, others not. For example, inadequate stabilizer concentrations, harsh processing conditions, improper selection of white pigments (TiO_2), and/or prolonged storage of the films in an environment containing oxides of nitrogen (pollution).

To deal with these discoloration issues, a phenol free stabilization concept was developed and studied extensively. However, there are only limited numbers of film grade resins that are phenol free. Some film manufacturers are attempting to solve the discoloration issues by adding phenol free stabilization masterbatches to minimally phenol stabilized resins.

We will report the experimental results by using the masterbatch approaches to prevent discoloration. Overall, "phenol free" stabilization systems are highly recommended for color critical polyolefin film applications.

Introduction

Manufacturers of film grade polyolefins, as well as the downstream fabricators of film products, always look for new advances in polymer stabilization in order to make sure that they can provide the best products with the most value while minimizing costs. Additives, or combinations of additives, are tools that can be used for adjusting film 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, improved UV resistance, inhibition of gas fade discoloration, enhanced additive compatibility, reduced taste and odor, as well as the suppression of 'gels' and other extrusion related imperfections. [1]

Over the last several decades, a variety of phenolic AO and phosphite melt processing stabilizers have been developed to meet these 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. [2] These traditional phenol based systems have been successfully utilized in a variety of polyolefin applications for the last 20 years, and are well known for providing good melt flow control and acceptable maintenance of color in routine film applications.

As new applications for polyolefins have developed, there have been opportunities where "higher" performance stabilization systems are necessary. "Higher" performance may be described as better melt flow maintenance under more demanding extrusion conditions (high temperatures; shear). For these higher performance applications, one can use a substitution strategy; e.g., change the phenolic AO and/or, the phosphite, and fine tune the system by changing the ratio of these components. For the most demanding applications, new stabilizer chemistries based on hydroxylamine have been developed to supplement the performance of the base stabilization system. Each approach

has been proven in the field, and most demands have been addressed; at least in regard to controlling molecular weight and molecular weight distribution of the polymer.

There have also been opportunities where "higher performance" stabilization was needed to provide improved maintenance of color. The "improved maintenance" of color can be expressed as, lower color during repeated heat histories (recycle of edge trim; scrap); minimizing discoloration during warehouse storage (gas fading); maintaining low color during railcar shipment during the hot & humid time of year; or resistance to discoloration from oxidizing environments, i.e., corona treatment or gamma irradiation. Over the last few years, this has been the subject of various inquiries into our labs. It should be noted that each of these higher performance stabilization systems, described above, were based on the concept of using a phenolic AO as one of the stabilization building blocks. While phenolic AO's have a proven track record, they can also be prone to discoloration when they are over-oxidized. For an increasing number of "color critical" film applications, especially in while films, this has become an issue. The next section will provide details on several approaches we have used to minimize discoloration.

Minimizing Discoloration

For improved initial color and color maintenance, a variety of approaches can be used, such as:

1) Change the nature (propensity to discolor) of the phenolic antioxidant;
2) Change the phosphite (color inhibition by alleviating the workload on the phenolic);
3) Change the phenolic (lower) : phosphite (higher) ratio;
4) Examine "hyperactive" stabilizers (hydroxylamines) as a booster for traditional binary blends;
5) Change the acid acceptor (create a more "pH neutral" environment in the matrix);
6) Eliminate the phenolic antioxidant ("phenol-free" stabilization).

(1) In regard to changing the nature of the phenolic antioxidant, certain types of phenols provide excellent melt flow control, but may be more prone to discolor. Establishing a tradeoff between melt flow control and less discoloration can be used to deliver adequate melt processability with lower overall color.

(2) When changing the type of phosphite, various issues must be taken into consideration since each phosphite has its own unique set of attributes; such as total phosphorus content, steric hindrance, hydrolytic stability, compatibility in the matrix, as well as its intrinsic reactivity towards decomposing hydroperoxides.

(3) By adjusting the concentration and ratio of the phenolic antioxidant/phosphite blend components, melt flow rates can be maintained, while systematically minimizing the overall color of the system.

(4) Hydroxylamines and tocopherols (Vitamin E) and are representative examples of "hyperactive" stabilizers that can supplement the performance of traditional phenol/phosphite blends. Using this type of approach, the workload on phenolic and phosphite components can be alleviated and/or enhanced.

(5) Acid neutralizers (also known as acid acceptors; acid scavengers) can be surprisingly effective in regard to buffering the environment of matrix, which is important for phenolic antioxidants. This is noteworthy since certain types of "acidic" or "alkaline" species can promote discoloration of phenols (by accelerating the oxidation process). Neutralizers can be used to create more of a "pH neutral" environment in the polyolefin matrix.

(6) If the phenolic is considered to be the reagent that is most susceptible to discoloration (via over-oxidation), the most simple-minded approach to minimize discoloration would be to eliminate the phenolic AO. Unfortunately, this simple-minded approach of removing the phenol is not that simple, since the phenolic AO makes such a key contribution to melt processing stability of most LLDPE's. Phenolic AOs also provide a significant amount of long term thermal stability. Consequently, removal of the phenolic requires the use of other types of stabilizers to make up for the significant contribution to melt processing and long term thermal stability.

Ciba pioneered the concept of "phenol free" stabilization, and several products have been developed and commercially introduced over the last decade. [3] These "phenol free" stabilization systems are usually based on a combination of

hindered amines (which provide light stability and good long term thermal stability) in combination with powerful melt processing stabilizers, such as phosphites, hydroxylamines, tocopherols or selected combinations of these melt processing stabilizer chemistries.

Since their introduction in 1995, "phenol free" systems have been successfully used in applications where melt flow control is important; but where the initial color and maintenance of color is critical. [4] The most prevalent use has been in fiber applications (polypropylene; high density polyethylene), [5] where any type of discoloration is unacceptable. Recently there have been other color critical applications where this approach has also been used; again, most often in PP homo - and copolymers. [6, 7] Our last several papers by King on this subject focused on the utility of this concept in HDPE [2,4] and LLDPE [8a; 8b; 8c; 8d] films. Even though the "phenol free" systems have consistently solved most discoloration problems, adoption of this product concept in HDPE and LLDPE films has been slow in comparison to PP and HDPE fiber.

Stabilization Principles: Traditional phenol based systems and phenol free systems

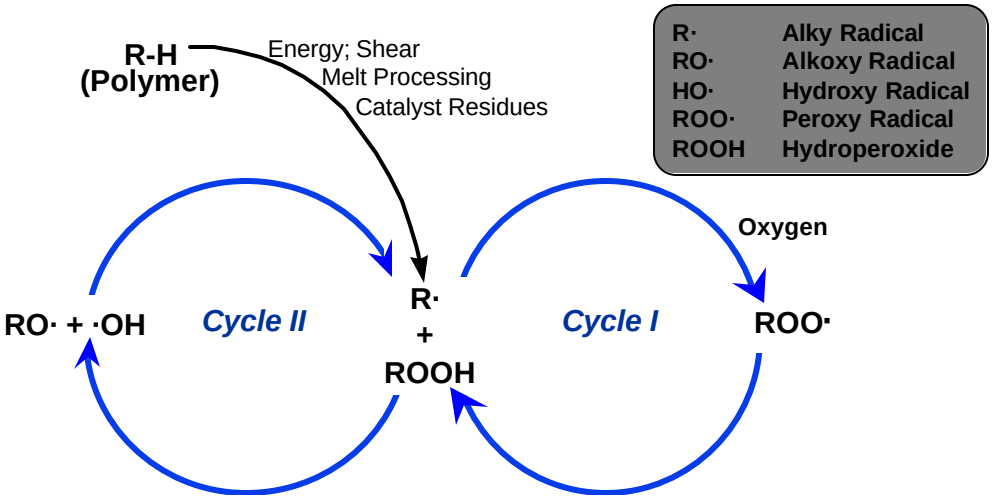

Figure 1: Auto-oxidation cycle for polyolefins.

As a brief review [9], the autoxidation cycle for olefin polymers is shown in **Figure 1**. 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) → pelleted product → formulated compound → finished article. In addition to temperature and shear, catalyst residues, entrained oxygen, and other types of impurities might also play a role in promoting further degradation of the polymer.

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 entrained 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 [10,11] and commercialized over the last four decades. A hindered phenolic antioxidant, typically in combination with an organic phosphite melt processing stabilizer, can be used at various loadings & 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 2**.

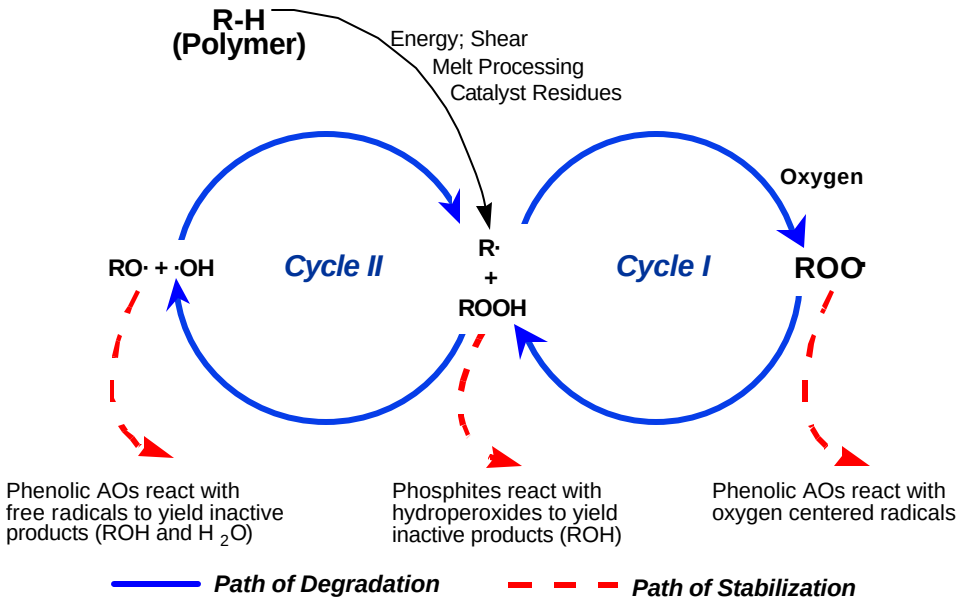

Figure 2: Traditional Inhibited Auto-oxidation Cycle for Polyolefins.

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. [12]

There have also been entirely new approaches to polymer stabilization. One new stabilizer chemistry, which is based on the hydroxylamine functionality, can serve as a very powerful hydrogen atom donor and free radical scavenger [13] and hydroperoxide decomposer [14] as shown in **Figure 3**. For color critical applications, synergistic mixtures of hindered amines (UV; Long term thermal stability) and hydroxylamine (melt processing), with or without a phosphite, can be used to avoid discoloration typically associated with the over-oxidation of the phenolic antioxidant [3].

In **Figure 2**, 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.

"Phenol free" stabilization concept is based on the elimination of the phenolic AO from **Figure 2**, and the addition of hindered amine to provide the long term thermal stability afforded by the phenolic AO. In addition, the scheme would be modified to illustrate how hydroxylamine chemistry with or without traditional phosphites is used to stabilize the

polymer during the melt processing of the polymer, and the hindered amines are used for long term thermal (as well as UV) stabilization of the polymer; see **Figure 4**.

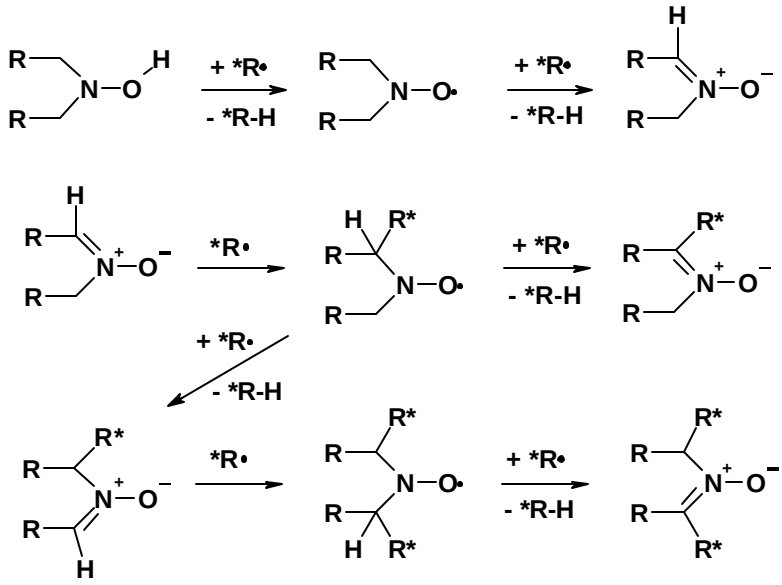

Figure 3a. Free Radical Decomposition Mechanism for Hydroxylamines.

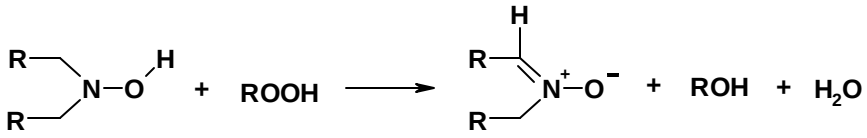

Figure 3b. Hydroperoxide Decomposition Mechanism for Hydroxylamines.

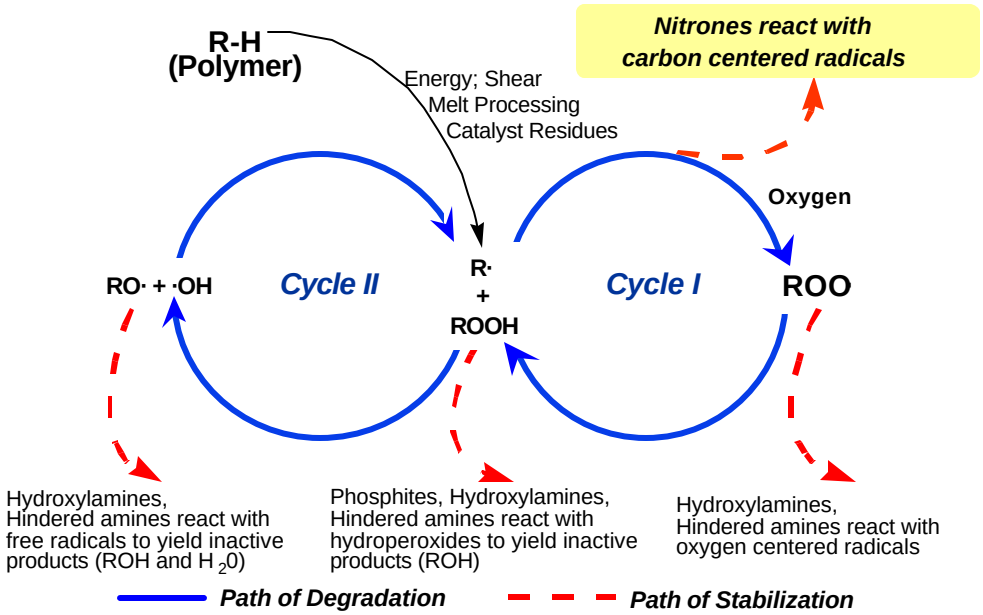

Figure 4: "Phenol free" Inhibited Auto-Oxidation Cycle for Polyolefins.

"Phenol" vs. "Phenol Free" vs. "Almost Phenol Free" Stabilization: Review

As discussed earlier, over the last several years, there have been many inquiries to our labs regarding "lower color" stabilization systems for LLDPE. The primary dissatisfaction with conventional stabilization systems (phenol/phosphite blends) has centered on the propensity of phenol based systems having a tendency to discolor over time. It should be noted that this tendency to discolor has not necessarily been observed at the reactor during polymer pelletization, nor has it been noticed during loading of the railcar. The inclination to discolor has mostly been seen at the fabricators, or downstream from the fabricators, where certain types of end use articles undergo a color shift over a relatively short period of time; typically in less than two to four weeks.

To address these concerns, a series of studies were conducted in LLDPE, both without and with TiO_2, in an effort to sort out a premier discoloration resistant stabilization system. **[8a, 8b, 8c, 8d]** In these studies, it was clearly demonstrated that phenol free stabilization systems are capable of providing excellent melt flow control, good initial color and superior resistance to gas fade discoloration; both without, and then with two different types of TiO_2.

We also examined the impact of low levels of phenol, which represent a compromise between the traditional phenol based approach vs. going phenol free. This approach was necessary to make the technical solution of going phenol free more feasible to film manufacturers who rarely use one type of film grade LLDPE to make their film products. We looked at the impact of 0, 50, 100, 250 and 500 ppm of AO-1 to determine the limit of phenol that could be tolerated in a film product that needed to be used in a color critical application. It was demonstrated that even low levels of phenolic antioxidant could be tolerated in a phenol free system, as long as the adventitious amounts introduced by another resin did not exceed 100 – 200 ppm.

As a follow up to earlier work in LLDPE, the work described below examines some of our most recent studies where we examined the impact of "phenol" vs. "phenol free" stabilization systems in LLDPE. The driving force for this additional work was based on recent inquires from customers. Because there are only limited numbers of film grade resins that are phenol free, some film manufacturers are attempting to solve the discoloration issues by adding phenol free stabilization masterbatches to minimally phenol stabilized resins. We will report the experimental results by using the masterbatch approaches to prevent discoloration.

Experimental

The base polymer chosen for this work was a commercially available ethylene-octene-1 copolymer LLDPE (2.3 MI). Analysis showed that the stabilization system of this LLDPE contains about 170 ppm AO-1, 240 ppm AO-2 and 1200 ppm Phosphite-1. Masterbatches were made using LDPE (12 MI) which was devoid of stabilization. Three grades of TiO_2 used from a well known and respected major producer of white pigments.

In the first step of this work, seven masterbatches were prepared:

- 70% TiO2 -1 in LDPE
- 70% TiO2 -2 in LDPE
- 70% TiO2 -3 in LDPE
- 1% AO PF-1 in LDPE
- 2.5% AO PF-2 in LDPE
- 1% PPA in LDPE
- LDPE passed through one heat history

Using the above phenol free masterbatches, blown film (1.5 mil in thickness) and compression molded film (12 mil) were made with the phenol based LLDPE resin. The final additives concentrations of the film are shown in **Table 1**. All the white films had 10% TiO2 masterbatches and 83% LLDPE film resin.

For comparison, same set of experiments (16 formulations) were repeated using a phenol free LLDPE film resin in replacement of the phenol based LLDPE and the final compositions are in **Table 2**.

	No TiO2		TiO2-1		TiO2-2		TiO2-3
P00	No TiO2 300 ppm PPA No stabilizers 83% LLDPE-phenol	P10	7% TiO2-1 300 ppm PPA No stabilizers 83% LLDPE-phenol	P20	7% TiO2-2 300 ppm PPA No stabilizers 83% LLDPE-phenol	P30	7% TiO2-3 300 ppm PPA No stabilizers 83% LLDPE-phenol
P01	No TiO2 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol	P11	7% TiO2-1 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol	P21	7% TiO2-2 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol	P31	7% TiO2-3 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol
P02	No TiO2 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol	P12	7% TiO2-1 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol	P22	7% TiO2-2 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol	P32	7% TiO2-3 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol
P03	No TiO2 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol	P13	7% TiO2-1 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol	P23	7% TiO2-2 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol	P33	7% TiO2-3 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol

The balance is an unstabilized LDPE passed through one heat history

Table 1: Final additive concentration in film: Phenolic AO stabilized LLDPE

	No TiO2		TiO2-1		TiO2-2		TiO2-3
PF00	No TiO2 300 ppm PPA No stabilizers 83% LLDPE-PF	PF10	7% TiO2-1 300 ppm PPA No stabilizers 83% LLDPE-PF	PF20	7% TiO2-2 300 ppm PPA No stabilizers 83% LLDPE-PF	PF30	7% TiO2-3 300 ppm PPA No stabilizers 83% LLDPE-PF
PF01	No TiO2 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-PF	PF11	7% TiO2-1 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-PF	PF21	7% TiO2-2 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-PF	PF31	7% TiO2-3 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-PF
PF02	No TiO2 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-PF	PF12	7% TiO2-1 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-PF	PF22	7% TiO2-2 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-PF	PF32	7% TiO2-3 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-PF
PF03	No TiO2 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-PF	PF13	7% TiO2-1 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-PF	PF23	7% TiO2-2 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-PF	PF33	7% TiO2-3 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-PF

The balance is an unstabilized LDPE passed through one heat history

Table 2: Final additive concentration in film: Phenol-free AO stabilized LLDPE

We examined four film stabilization systems where they were incorporated by means of masterbatch. The first was a blank without stabilizers, which is often overlooked, but is considered to be an important control experiment. The second was the phenol free stabilization system based on a hydroxylamine, PF-1. The third was a 1:1 blend of

hydroxylamine (PF-1) and phosphite (Phosphite-1); denoted as "PF-2". The fourth was the same as the third but the loading level was doubled.

1. No stabilizers
2. 250 ppm PF-1
3. 500 ppm PF-2
4. 1000 ppm PF-2

For all the sample names in **Table 1** and **Table 2**, the first letter or two letters denotes the stabilization systems of the LLDPE resin: phenol (F) or phenol-free (PF). The first number represents the TiO2 being incorporated by masterbatch (0: no TiO2-not a white film; 1: TiO2-1; 2: TiO2-2; 3: TiO2-3, all at 7% in film). The second number represents the stabilization incorporated through masterbatch (0: no stabilizers; 1: PF-1 250ppm; 2: PF-2 500ppm; 3: PF-2 1000ppm).

The color development of the film was examined by gas fade aging and oven aging at the same temperature. This involves running two sets of parallel exposures, where one set of film samples is exposed to oxides of nitrogen in a circulating oven held at 60°C, while the other set of film samples is heat aged at the same temperature, but in the absence of oxides of nitrogen. Color was monitored over time. (AATTC control ribbons that turn from blue to pink were used to calibrate the gas fade chamber; the cycle time was about 24 hours.) We monitored color development every few days for up to twenty weeks for the thick film.

Chemistry of Phenolic Over-Oxidation. The stepwise transformation of a phenolic antioxidant is shown in **Graph 1**. The oxides of nitrogen facilitated transformation is shown in **Graph 1B,** whereas the thermally induced transformation is depicted in **Graph 1A.**

Results and Discussions

Gas Fade Aging at 60°C; 1.5 mil film: The results for 1.5 mil white film using phenolic AO LLDPE are depicted in **Graph 2A** (gas fade aging; 60°C). As can be seen, all the film samples, weather there were TiO2 or not, had a sharp color development at the beginning. The color reached the peak after about 20 days of exposure and started to decrease very slowly. On the other hand, by design, the phenol free system simply does not discolor; it is truly discoloration resistant. (**Graph 2B)**

We examined different stabilizations systems that were incorporated into the film by masterbatch. As showed in a typical graph with TiO2-1 (**Graph 3**), the addition of phenol free stabilizations did not change the discoloration. There were no improvements if we added PF-1 or PF-2 or even doubled the concentration of PF-2.

The fact that addition of hydroxylamine to phenolic AO stabilized LLDPE via masterbatch did not prevent the discoloration is not surprising because the phenolic antioxidants are still present in the final film formulation. This is consistent with the previous work by King **[8a, 8b, 8c, 8d]** that after phenolic antioxidant concentration reaches certain level, phenol free stabilization systems cannot stop the discoloration associated with the presence of phenolic antioxidants. In this study, we used an LLDPE resin with over 400 ppm phenolic antioxidant (170 ppm AO-1 and 240 ppm AO-2) and 1200 ppm phosphite. The final concentration of ~340 ppm phenol was too high to prevent discoloration.

The discoloration reached a maximum after three weeks, and then declined thereafter. Similar phenomenon is observed by film manufacturers as well. It can be explained that during gas fading, a color body was first developed but the color body is unstable under the experimental conditions. Upon further oxidation, the color body is consumed and eventually results in the decline of the discoloration.

Upon examining the different TiO2, we found that with the phenolic AO stabilized LLDPE, TiO2-1 showed the least discoloration. TiO2-3 appeared better than TiO2-2 but these two lines crossed at about 28 days. However, the discoloration differences between the different TiO2's were relatively small. (**Graph 4**)

Gas Fade Aging at 60°C; 12 mil film: We have also examined gas fade discoloration of the thicker film. **Graph 5A** depicted the results for 12 mil white film using phenolic AO LLDPE. As can be seen, all the film samples had a sharp color development at the beginning. The color reached the peak after about 3 days of exposure and started to decrease quite sharply. After about 7 days, the decrease started to level off. The discoloration reached a minimum at about 40 days and started to increase again. After reaching a peak at about 80 days, the YI began to decrease slowly again. On the other hand, similar to thin film, the phenol free system discoloration was small. (**Graph 5B)**

It is interesting to see that the discoloration of the thick film had two YI maximum peaks. It behaved as if it consisted of two independent thin films. It was well known that the warehouse discoloration of film typically occurs on surfaces/edge exposing to the air. This suggests that it is difficult for the NOx gases to diffuse into the interior of the film. The thick film in our study was made by compression molding several layers of thin film together. It is possible that there are small gaps between the layers and with time the NOx gases diffuse between the layers, causing the discoloration of the interior film layers. We should be able to confirm experimentally if this phenomenon is characteristic of thick film discoloration with a different sample preparation method.

We could also conclude that the effects of different stabilizations systems and different TiO2's on discoloration were similar to the thin film.

Oven Aging at 60°C: We ran a parallel control experiment in a circulating air oven at 60°C, without the oxides of nitrogen. The results are illustrated in **Graphs 6A and 6B**. As can be seen in these experiments, the significant color development that was observed with the gas fade aging is not observed during the oven aging studies (run at the same temperature/time frame). This clearly demonstrates how removing one of the variables (NO_x) out of the equation can result in significant reduction of discoloration.

However, small degree of discoloration still existed for film made from phenolic AO based LLDPE. Over all the yellowness index change of 12 mil film after 70 days was about 2-4 compared to about 1 when the film was made from phenol free LLDPE.

One interesting observation was that when the stabilization changed from no stabilizers, to PF-1 250 ppm, to PF-2 500 ppm, and to PF-2 1000 ppm, the discoloration reduced accordingly. This was true with all TiO2's when phenolic AO stabilized LLDPE was used. However, the difference was quite small. (**Graph 7**)

We also found a consistent trend of TiO2's effect on oven aging discoloration. TiO2-1 appeared more prone to oven aging discoloration than the others and TiO2-2 had the least discoloration. The difference, however, was again very small. (**Graph 8**)

Conclusion

Gas fading experiments of the films showed that the addition of hydroxylamine to phenolic AO stabilized LLDPE via masterbatch did not prevent discoloration. This is not surprising, since the phenolic antioxidants are still present in the formulation and is consistent with the previous work by King **[8a, 8b, 8c, 8d]** that after phenolic antioxidant concentration reaches certain level, phenol free stabilization systems cannot stop the discoloration associated with the presence of phenolic antioxidants. On the other hand, we found that when phenol free LLDPE was used (totally phenol free), the film does not discolor; it is truly discoloration resistant.

This work demonstrated that by blending phenol-free masterbatch with a phenolic AO stabilized LLDPE (at 10/90 ratio for example) will not solve the film discoloration problem. Therefore, we can conclude that one cannot make non-discolored white film by adding phenol-free masterbatch to phenolic AO stabilized LLDPE resin. For color critical applications, "phenol free" stabilization systems are highly recommended.

It was also found that the selection of different titanium oxide grades did not lead to significant differences in terms of discoloration.

Acknowledgments

The authors wish to thank the colleagues and technologists for their direct and indirect contributions from Ciba Specialty Chemical and Ampacet Corporation. Special thanks go to Florian Stricker, Dave Horst, Anna Bassi, Carolyn Pressley and Peter Solera for their help and support, and to Maurice Gray for the Tarrytown lab work. Additionally, we thank both companies for the opportunity to publish the paper.

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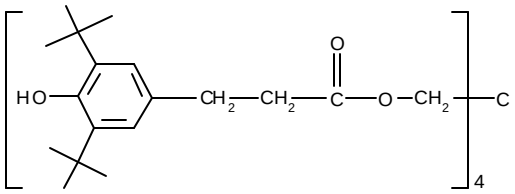
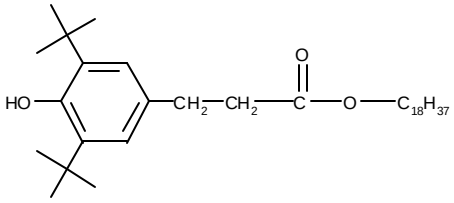
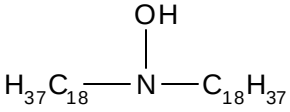
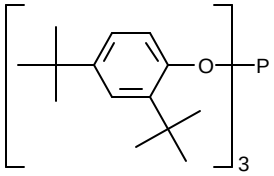
[11] Zweifel, H., Moss, S., "Degradation and Stabilization of High Density Polyethylene during Multiple Extrusion", Polymer Degradation and Stability, 25 (1989), 217-245.

[12] Pauquet, J.R., King, R., Kröhnke, C., “Revolutionary Stabilizer Systems for Polyethylene”, Polyethylene ‘97 Maack Conference, Milan, May 1997.

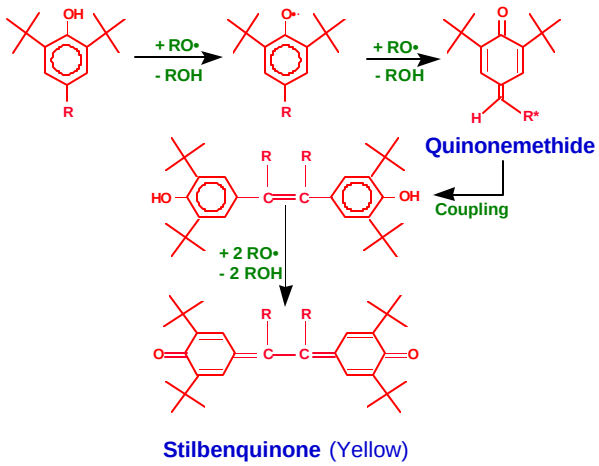
[13] Smith, P.A., Gloyer, S.E., J. Org. Chem., 40 (1975), pp. 2508-2512.

[14] DeLaMare, H.E., Coppinger, G.M., J. Org. Chem., 28 (1963) p. 1068-1070.

Appendix: Description of Additives.

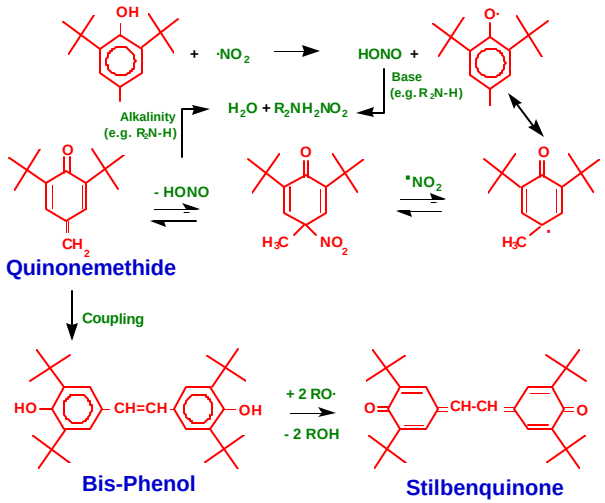
Code Class Tradename	Molecular Structure	Stabilizer Function
AO-1 Phenolic AO Irganox® 1010		Melt Processing Stability; Long Term Thermal Stability; Oxidative Induction Time;
AO-2 Phenolic AO Irganox® 1076		Melt Processing Stability; Long Term Thermal Stability; Oxidative Induction Time;
PF-1 Hydroxylamine Irgastab® FS-042		Melt Processing Stability; (secondary enhancements to the UV stability afforded by the hindered amine)
Phosphite-1 Phosphite Irgafos® 168		Melt Processing Stability; (synergistic performance booster with phenolic AO)
PF-2 Hydroxylamine/Phosphite Irgastab® FS-301	1:1 Blend of NOH-1 / P-1	Melt Processing Stability; (secondary enhancements to the UV stability afforded by the hindered amine)
TiO_2-1 Titanium Dioxide	Coated TiO_2	White pigment
TiO_2-1 Titanium Dioxide	Coated TiO_2	White pigment
TiO_2-3 Titanium Dioxide	Coated TiO_2	White pigment
PPA	FX-5920A (Dyneon)	Polymer Processing Aid

Phenolic AO Oxidation Chemistry

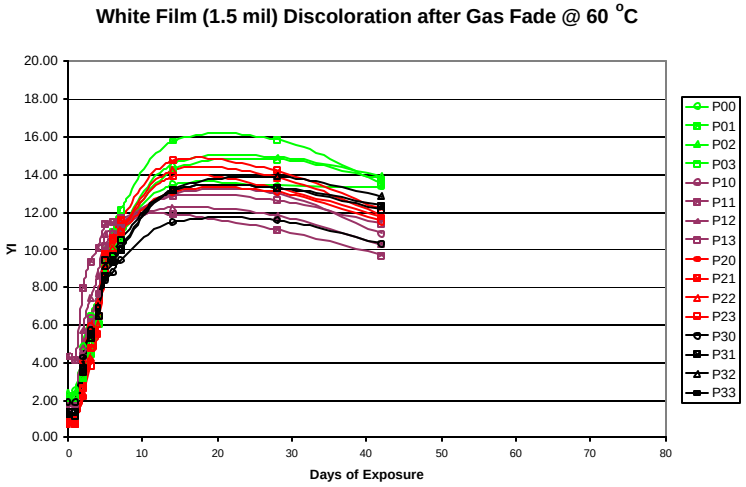


Graph 1A: Over-oxidation of phenolic AO via Heat/O_2 (e.g., oven aging)

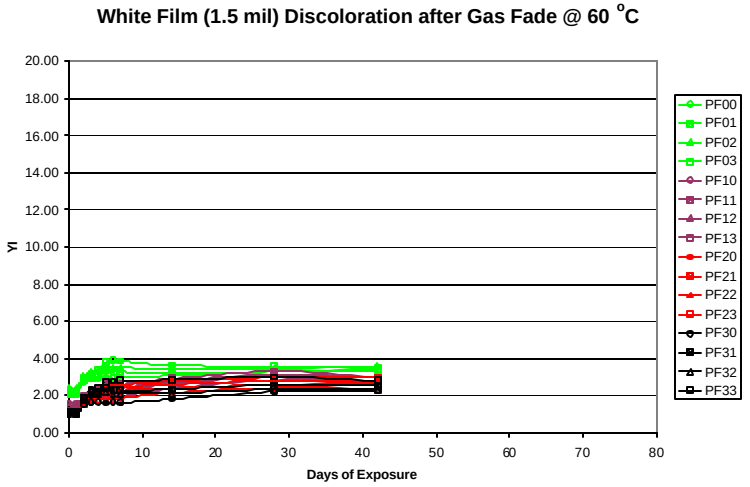
Gas Fade / Gas Yellowing Chemistry



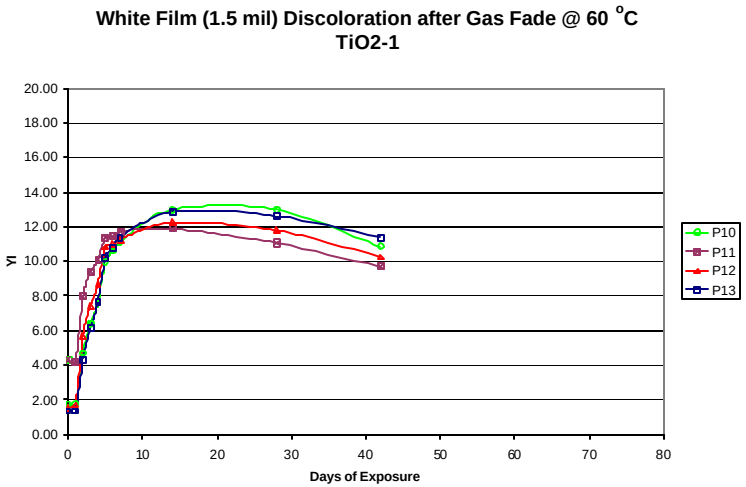
Graph 1B: Over-oxidation of phenolic AO via NO_x (e.g., gas fade aging)



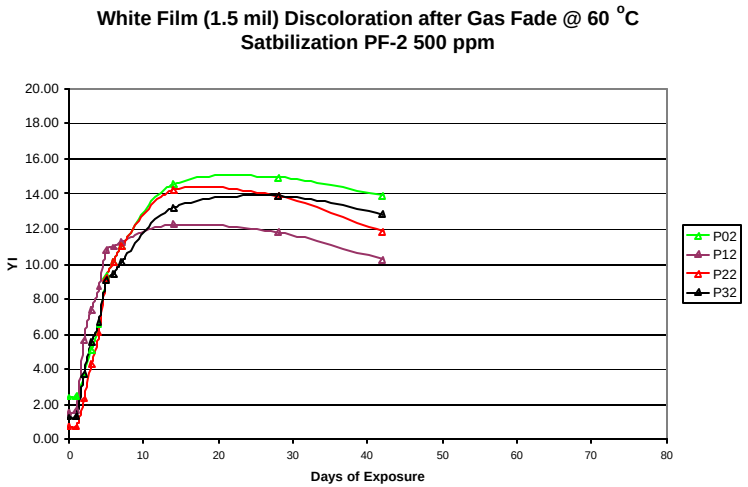
Graph 2A: Gas fade discoloration: Phenol based LLDPE



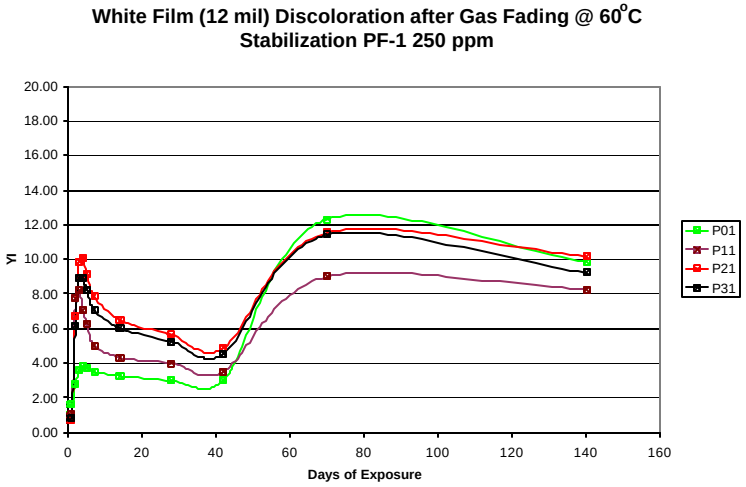
Graph 2B: Gas fade discoloration: Phenol free LLDPE



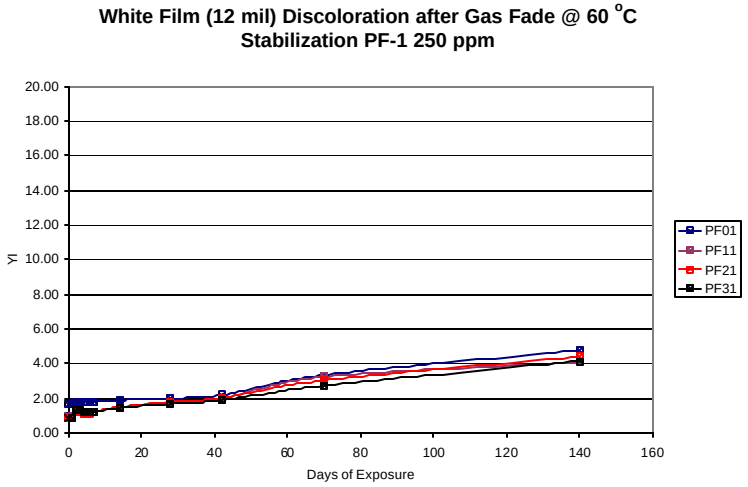
Graph 3: Gas fade discoloration: different PF MB stabilizations



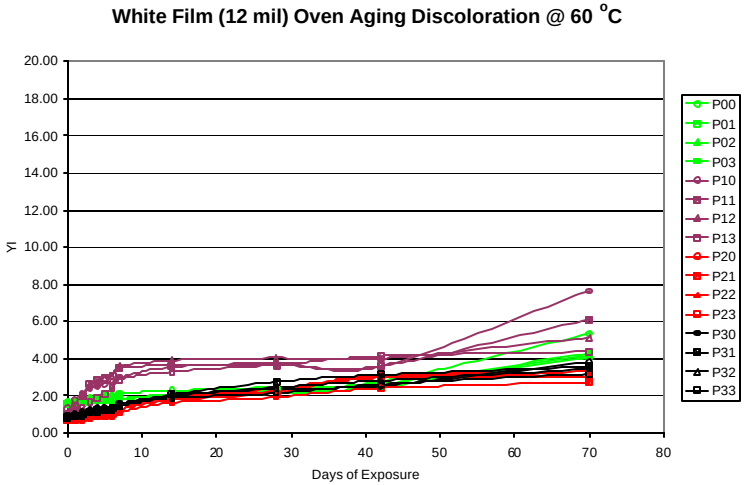
Graph 4: Gas fade discoloration: different TiO2



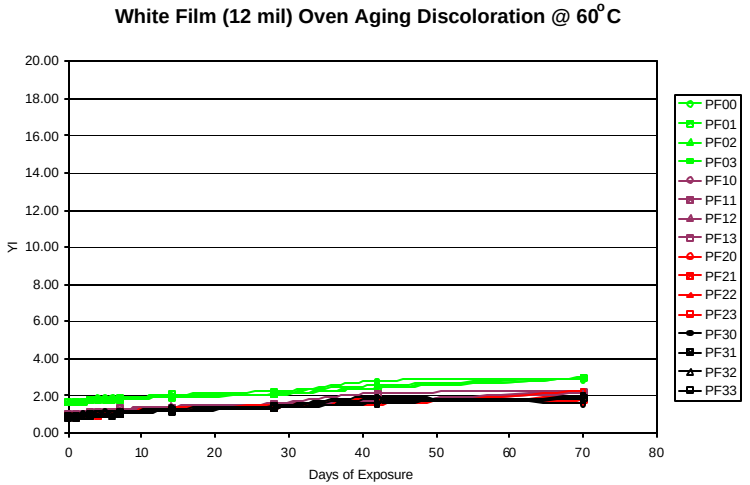
Graph 5A: Gas fade discoloration: Phenol based LLDPE



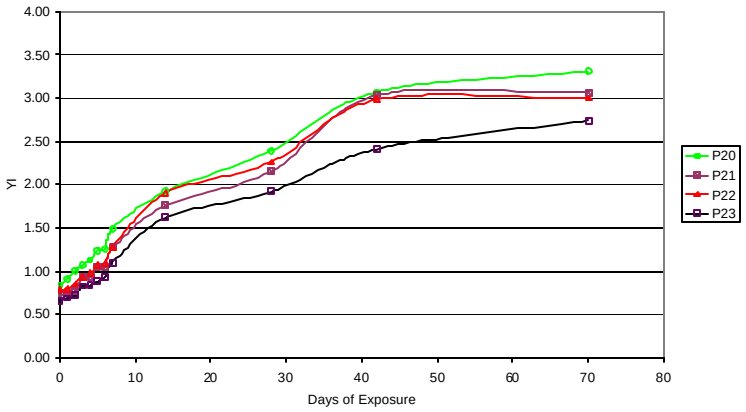
Graph 5B: Gas fade discoloration: Phenol free LLDPE



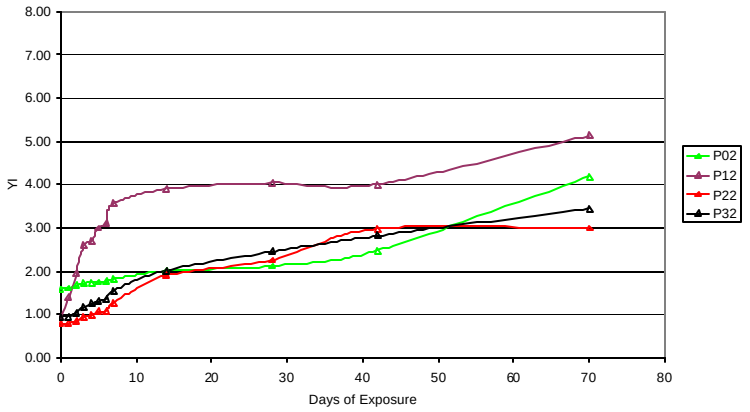
Graph 6A: Oven aging discoloration: Phenol based LLDPE



Graph 6B: Oven aging discoloration: Phenol free LLDPE



Graph 7: Oven aging discoloration: Phenol based LLDPE



Graph 8: Oven aging discoloration: Phenol based LLDPE

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Phenol vs. Phenol Free Stabilization and the Impact of Selected Grades of TiO_2:

Can we make non-discolored white LLDPE film by adding phenol-free masterbatch to phenolic AO stabilized resin?

Presented by:

Yijun Ye

Ciba Specialty Chemicals

Ciba

Outline of Presentation

- Background:
  - Review of Previous Work
  - Phenol vs. Phenol Free
  - Overview of Stabilization
  - Discoloration Mechanism
- Experimental Results and Discussion
- Conclusion
- Acknowledgments

Background: Review of previous work

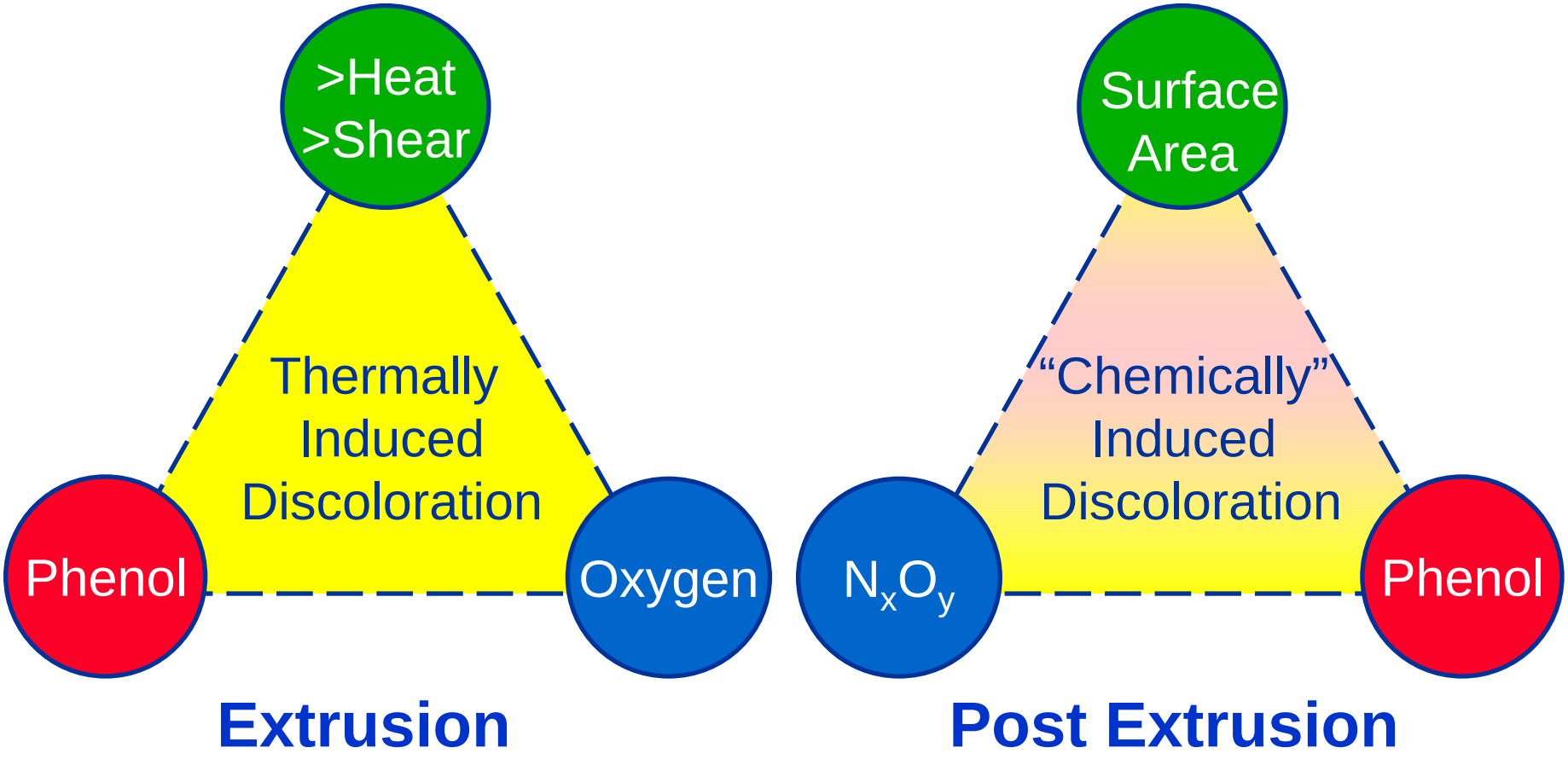
- **Situation:** Plethora of film grade LLDPEs having:
  - Excellent physical properties
  - Superior melt processability
  - Attractive cost effectiveness
- **Concern:** Some films tend to discolor either:
  - Some time after film blowing
  - After harsh / ionizing radiation
  - During shipping / transportation
  - Upon prolonged storage / inventory
  - After beta or gamma irradiation
- **Challenge:** Maintain physical properties, melt processability and cost effectiveness and somehow avoid this post processing discoloration

Phenol Based Stabilization

- **Industry Standard** (Entrenched ~ last 25 Years)
  - **Recognized Advantages**
    - Excellent Melt Flow Control
    - Good Initial Color
    - Long Term Thermal Stability
    - Relatively Easy to Analyze
  - **Potential Disadvantages**
    - Some Tendency to Discolor
      - → After Prolonged Melt Processing
      - → During Exposure to Oxides of Nitrogen
      - → After Exposure to Gamma Irradiation
      - → Sensitive to Catalyst Residues

“Triangles” of Polymer Discoloration

- Polymers stabilized with phenolic AO’s can be susceptible to discoloration if the system is “over-used or abused”



How to Deal with Phenol Based Discoloration

1. **Change the Phenol to Phosphite Ratio**
   - Less phenol 1:1 ⇨ 1:2 ⇨ 1:4
2. **Change the Phenolic Antioxidant**
   - Chose a more color stable phenol
3. **Change the Phosphite Stabilizer**
   - Use a higher performance phosphites
4. **Use a Hyperactive Process Stabilizer**
   - Hydroxylamine; Benzofuranone
5. **Change the Acid Neutralizer**
   - Somewhat surprising, but true

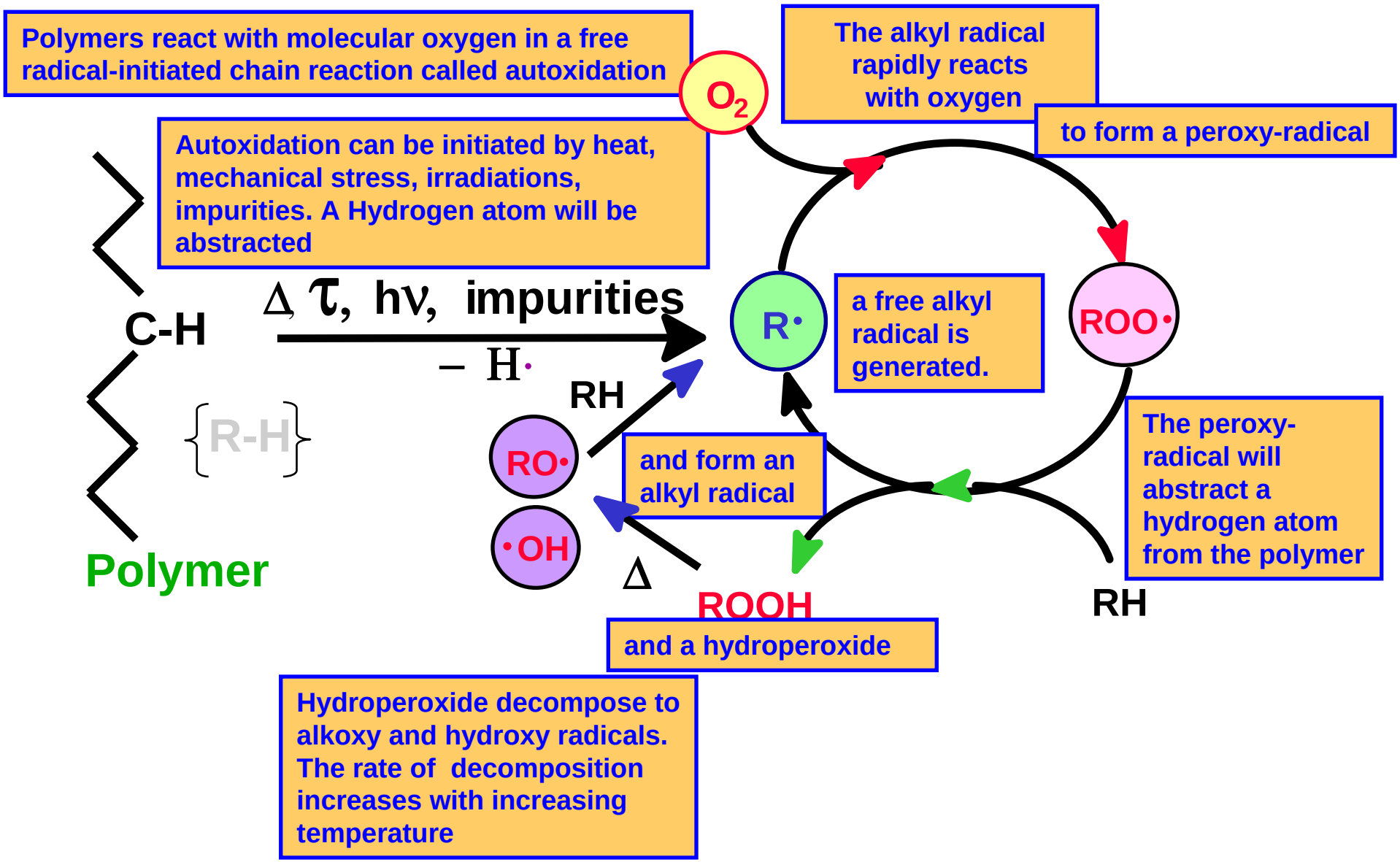
Note: Incremental steps lead to incremental improvements. Therefore, if a more robust improvement is necessary, then:

6. **Switch to a Phenol-free Stabilization System**

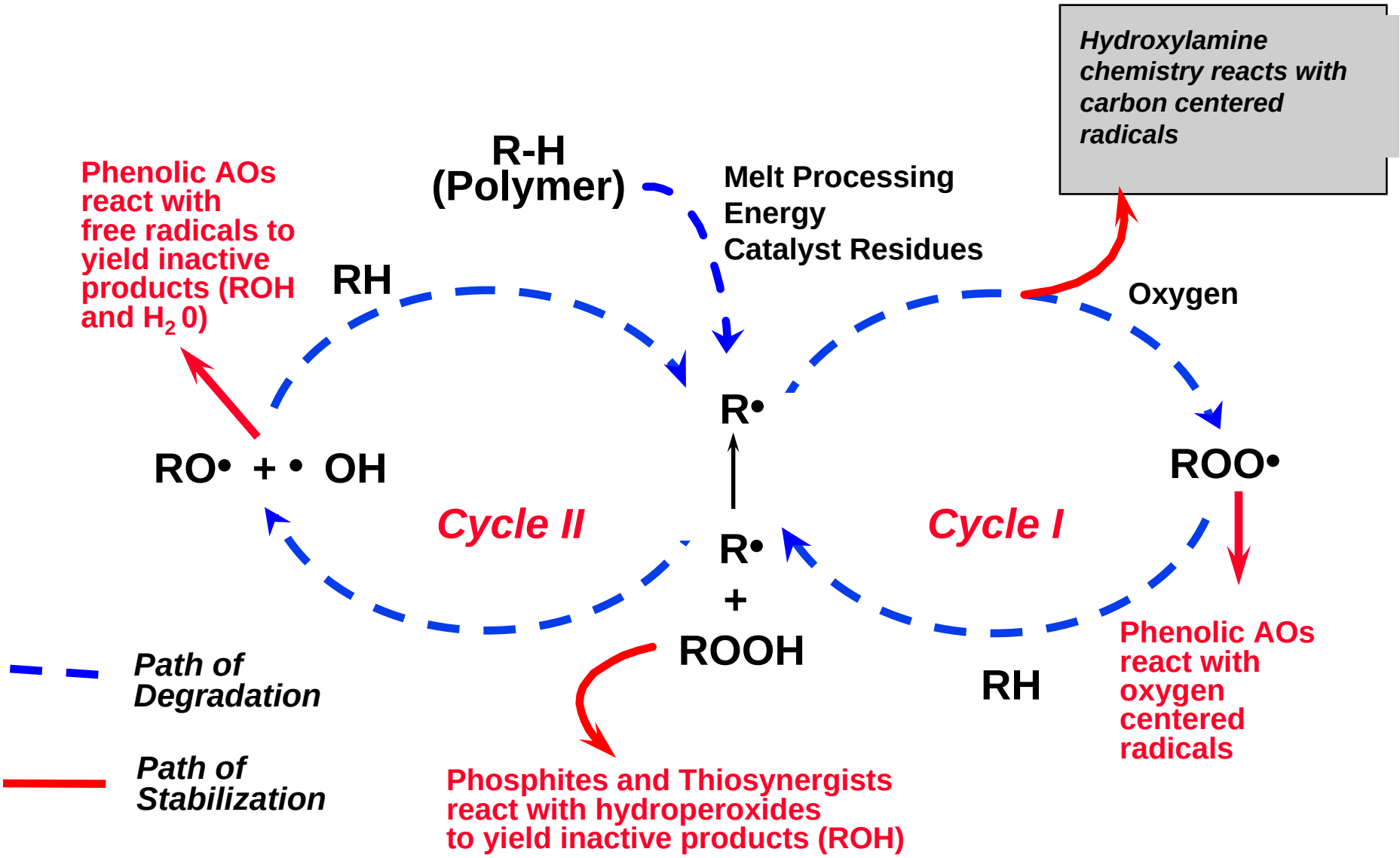
Phenol Free Stabilization Systems

Continue to Gain Acceptance (~ last 5-10 years)

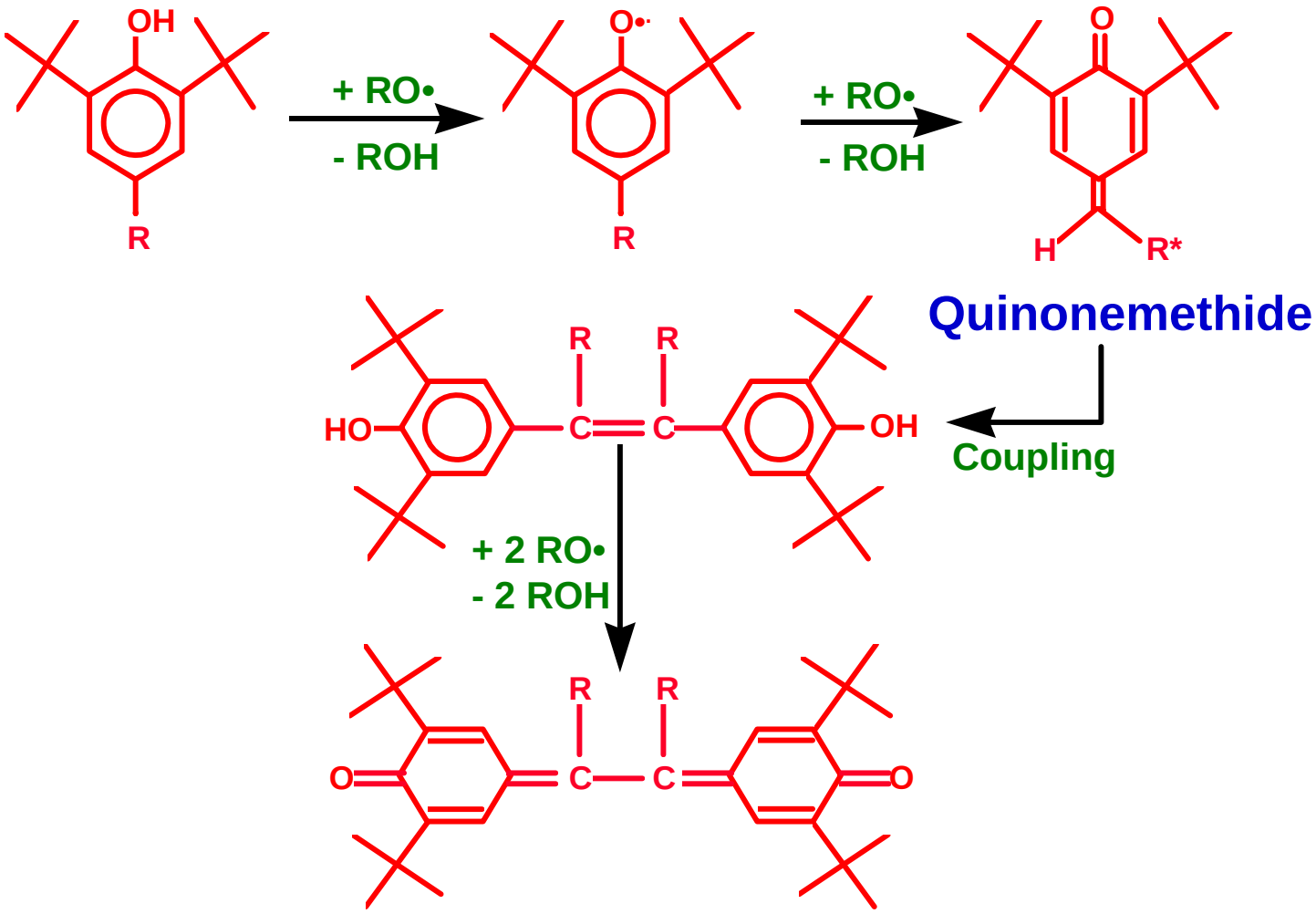
- **Recognized Advantages of Phenol Free Systems**
  - Good Melt Flow Control
  - Excellent Initial Color
  - Good Color Maintenance
  - Excellent Gas Fade Discoloration Resistance
  - Low Discoloration after Gamma Radiation
  - Long Term Thermal Stability (< 120^{o}C)
- **Potential Challenges of Phenol Free Systems**
  - It is different (vs. entrenched AO/P standard)
  - Resin availability for down stream customers
  - Method of Analysis (vs. Phenol / Phosphite)


Polymers react with molecular oxygen in a free radical-initiated chain reaction called autoxidation
O2
The alkyl radical rapidly reacts with oxygen
to form a peroxy-radical
Autoxidation can be initiated by heat, mechanical stress, irradiations, impurities. A Hydrogen atom will be abstracted
C-H
Δ τ, hν, impurities
– H·
R·
a free alkyl radical is generated.
ROO·
R-H
RH
RO·
and form an alkyl radical
The peroxy-radical will abstract a hydrogen atom from the polymer
·OH
Δ
Polymer
ROOH
RH
and a hydroperoxide
Hydroperoxide decompose to alkoxy and hydroxy radicals. The rate of decomposition increases with increasing temperature

Autoxidation Cycle

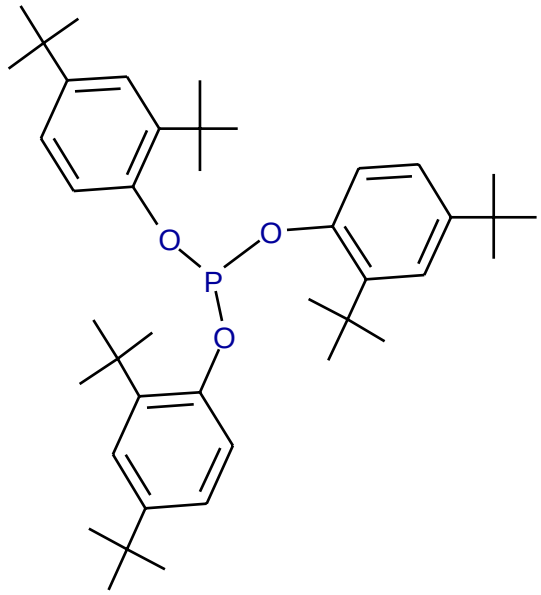


Phenolic AO Oxidation Chemistry



Stilbenquinone (Yellow)

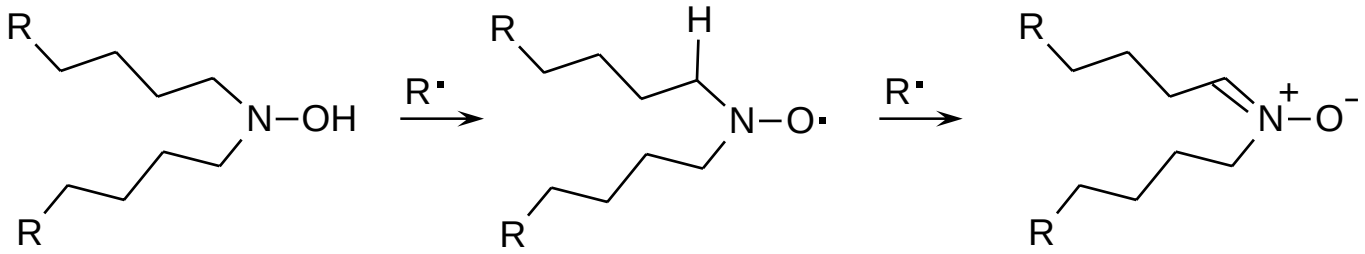
Phosphite - Process Stabilizers



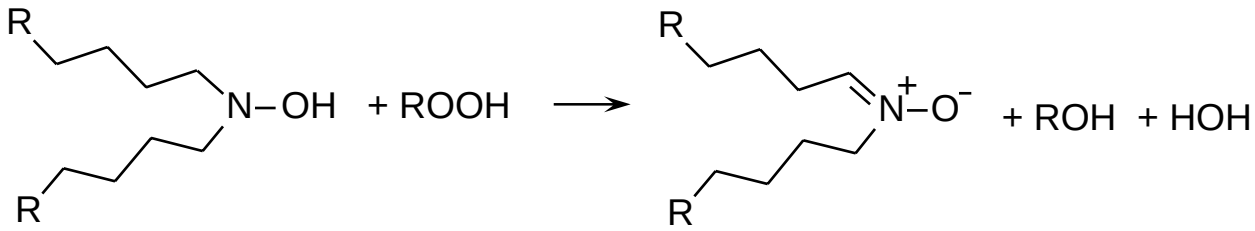
$(RO)_3P$ + $R'OOH$ ⟶ $(RO)_3P{=}O$ + $R'OH$

Phosphite	Alkyl peroxide	Phosphate	Alcohol

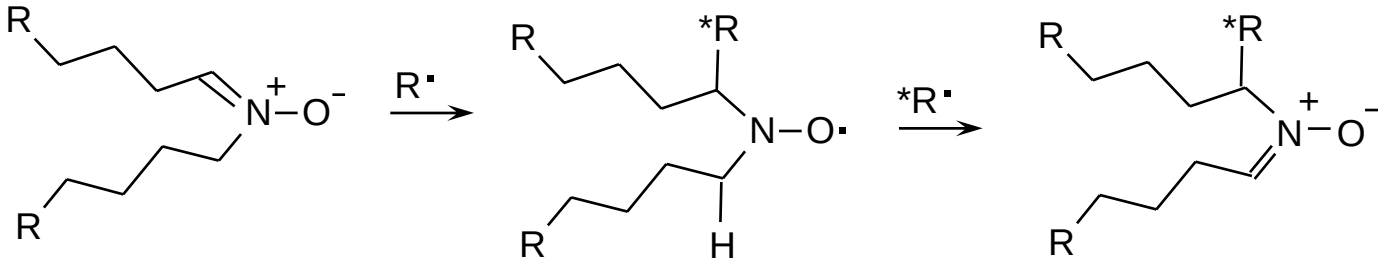
Stabilization Chemistry of Hydroxylamines



Hydroxylamine **Nitroxyl Radical** **Nitrone**

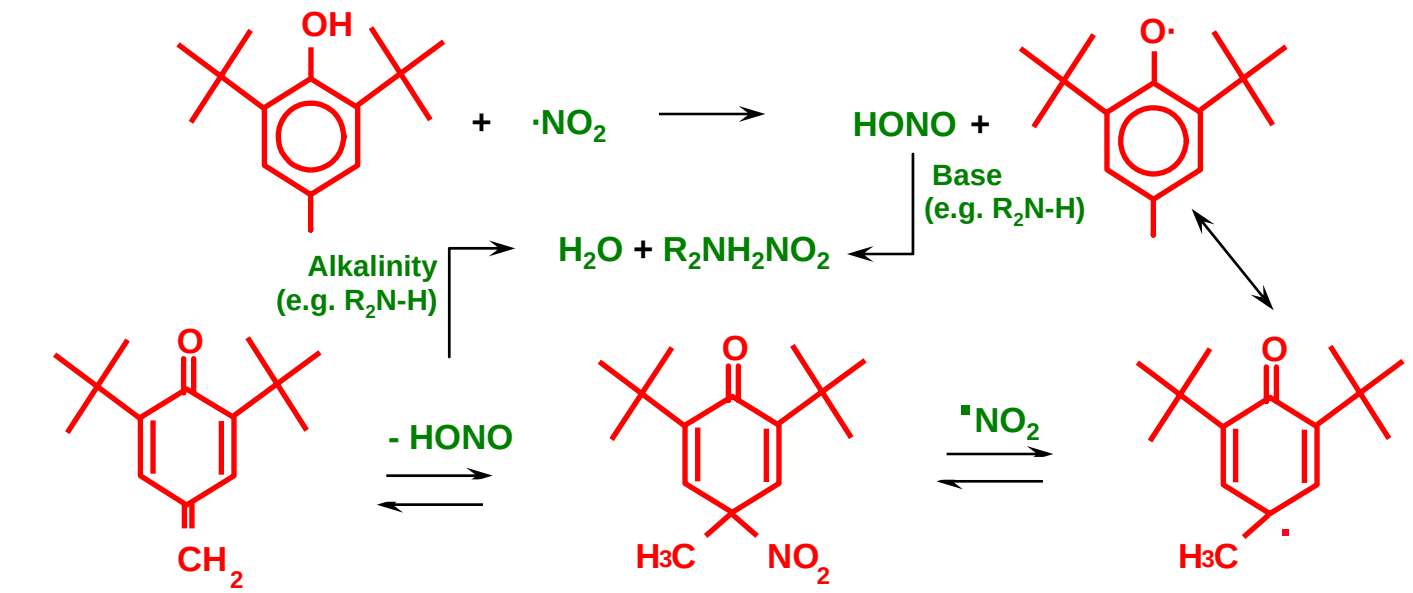


Hydroxylamine **Nitrone**



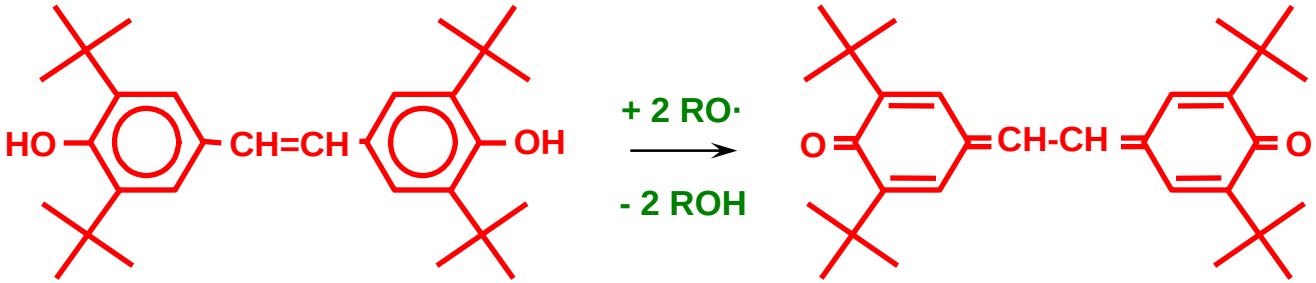
Nitrone ***Nitroxyl Radical** ***Nitrone**

Gas Fade / Gas Yellowing Chemistry



Quinonemethide

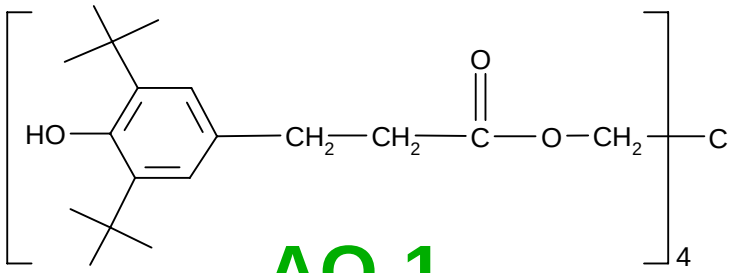
Coupling



Bis-Phenol

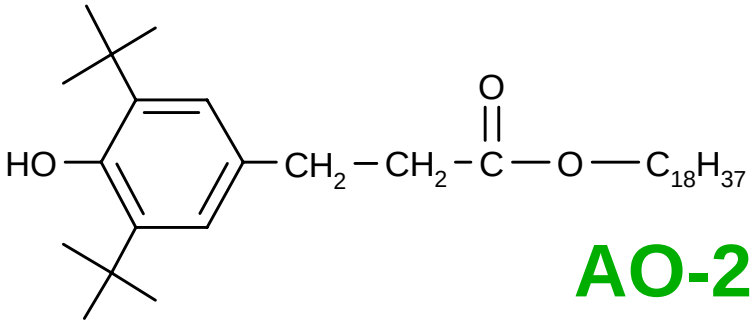
Stilbenquinone (bright yellow)

Structure Codes



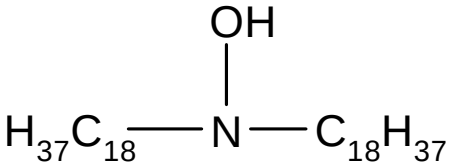
AO-1

Irganox 1010



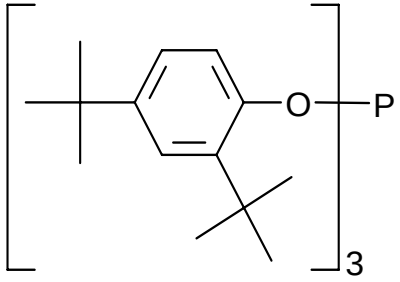
AO-2

Irganox 1076



PF-1

Irgastab FS-042



P-1

Irgafos 168

- **PF-2:** 1:1 blend of PF-1 & P-1
- **PPA:** FX-5920A (Dyneon)

Experimental Procedure

- Masterbatches in phenol free LDPE: TiO2, PF stabilizers, PPA
- Blown film (1.5 mil in thickness) and compression molded film (12 mil):
  - 83% LLDPE phenolic AO stabilized resin
  - 83% LLDPE phenol free stabilized resin
- Color development of the film:
  - Gas fade aging at 60^{o}C, expose to oxides of nitrogen in a circulating oven per AATCC Method 23
  - Oven aging at the same temperature

Experimental Formulations

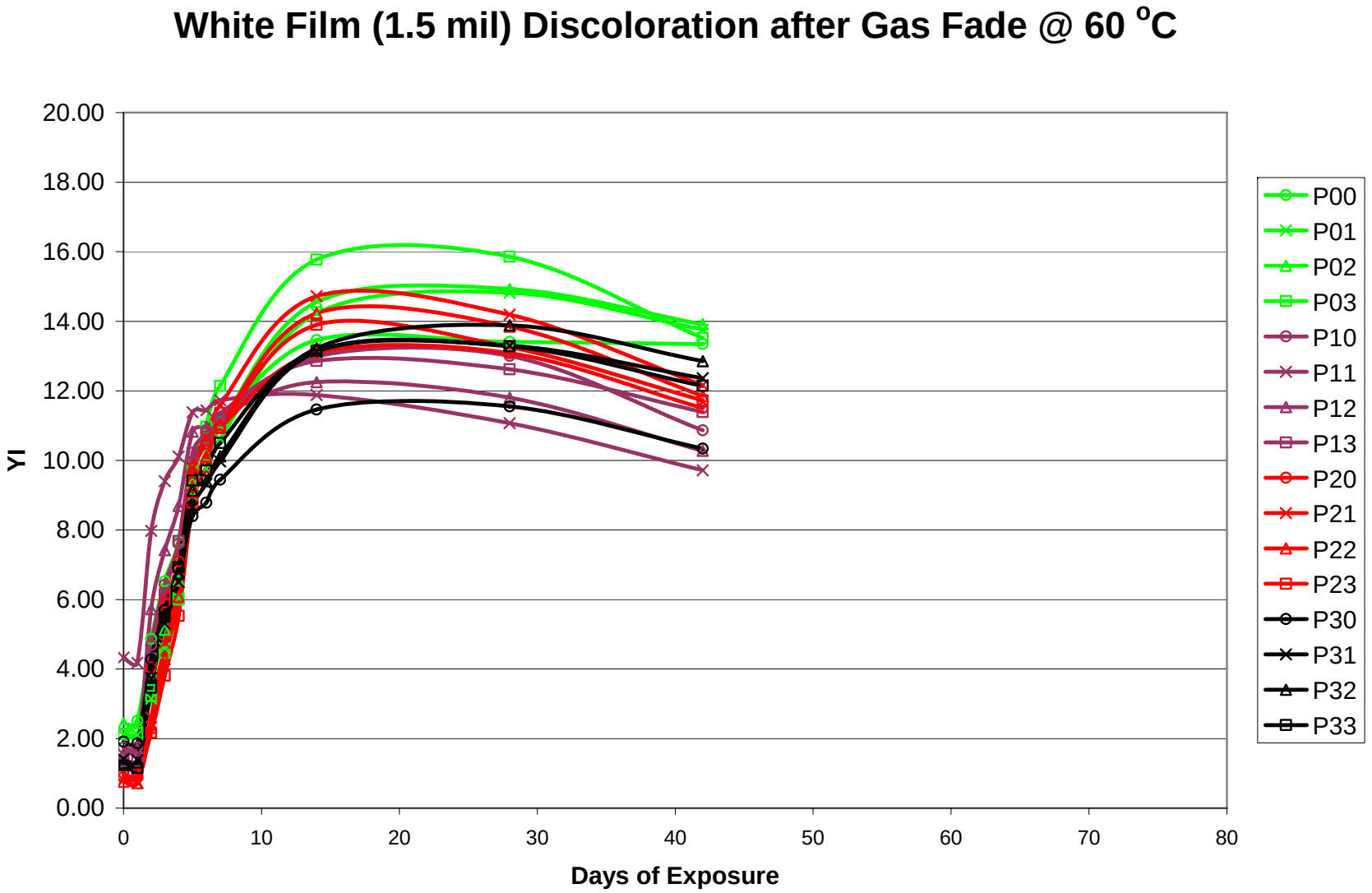
- (Additional) Stabilizers Introduced by Masterbatches
  - No stabilizers
  - 250 ppm PF-1
  - 500 ppm PF-2
  - 1000 ppm PF-2
- White Film with Different TiO_2
  - No TiO2-not a white film
  - TiO2-1, 7 wt% in film
  - TiO2-2, 7 wt% in film
  - TiO2-3, 7 wt% in film
- Note: When using phenolic AO stabilized LLDPE, the film still contains ~340 ppm phenolic AO

Formulations

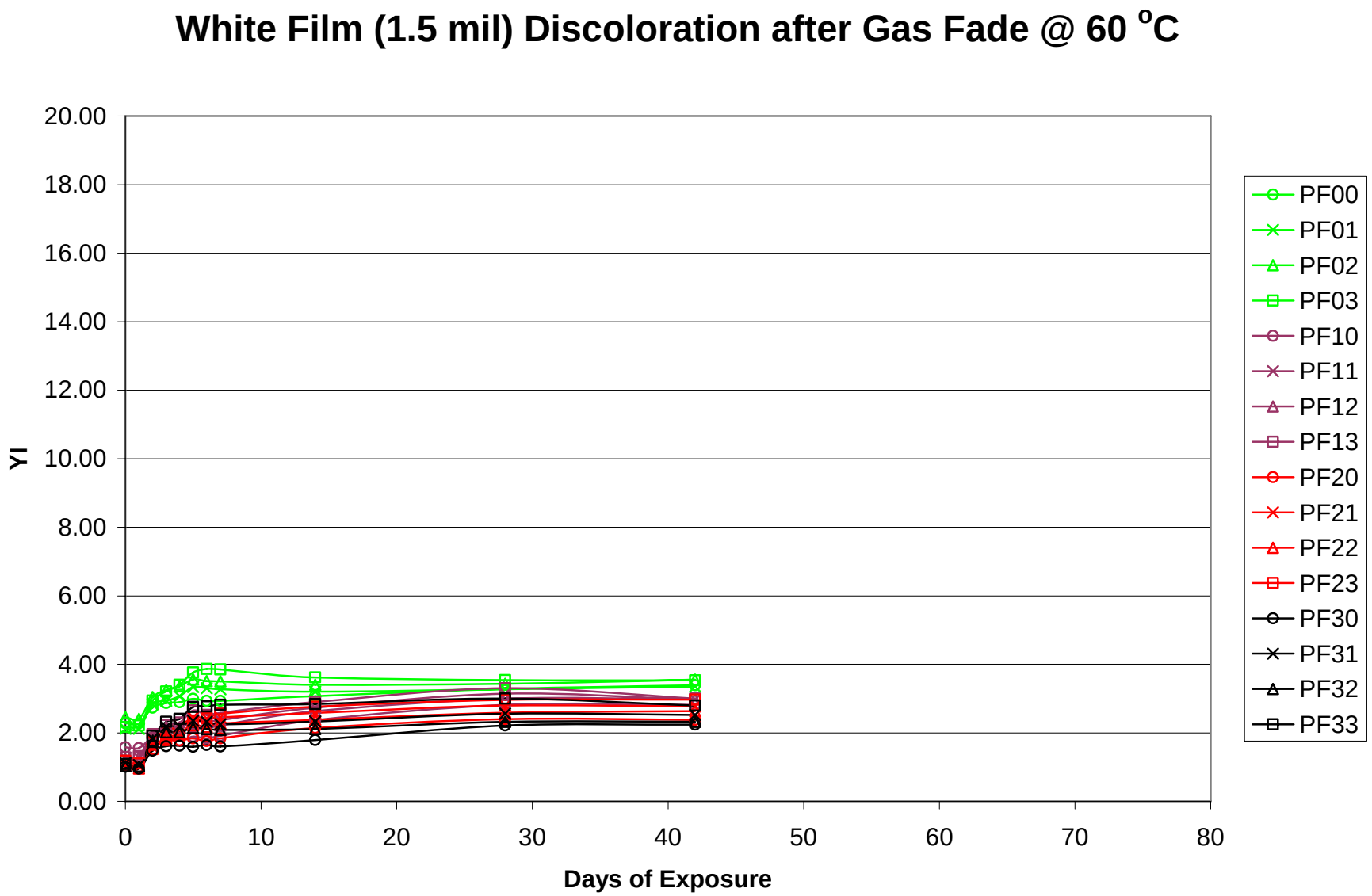
	No TiO2		TiO2-1		TiO2-2		TiO2-3
P00	No TiO2 300 ppm PPA No stabilizers 83% LLDPE-phenol	P10	7% TiO2-1 300 ppm PPA No stabilizers 83% LLDPE-phenol	P20	7% TiO2-2 300 ppm PPA No stabilizers 83% LLDPE-phenol	P30	7% TiO2-3 300 ppm PPA No stabilizers 83% LLDPE-phenol
P01	No TiO2 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol	P11	7% TiO2-1 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol	P21	7% TiO2-2 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol	P31	7% TiO2-3 300 ppm PPA 250 ppm AO PF-1 83% LLDPE-phenol
P02	No TiO2 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol	P12	7% TiO2-1 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol	P22	7% TiO2-2 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol	P32	7% TiO2-3 300 ppm PPA 500 ppm AO PF-2 83% LLDPE-phenol
P03	No TiO2 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol	P13	7% TiO2-1 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol	P23	7% TiO2-2 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol	P33	7% TiO2-3 300 ppm PPA 1000 ppm AO PF-2 83% LLDPE-phenol

The balance is an unstabilized LDPE passed through one heat history

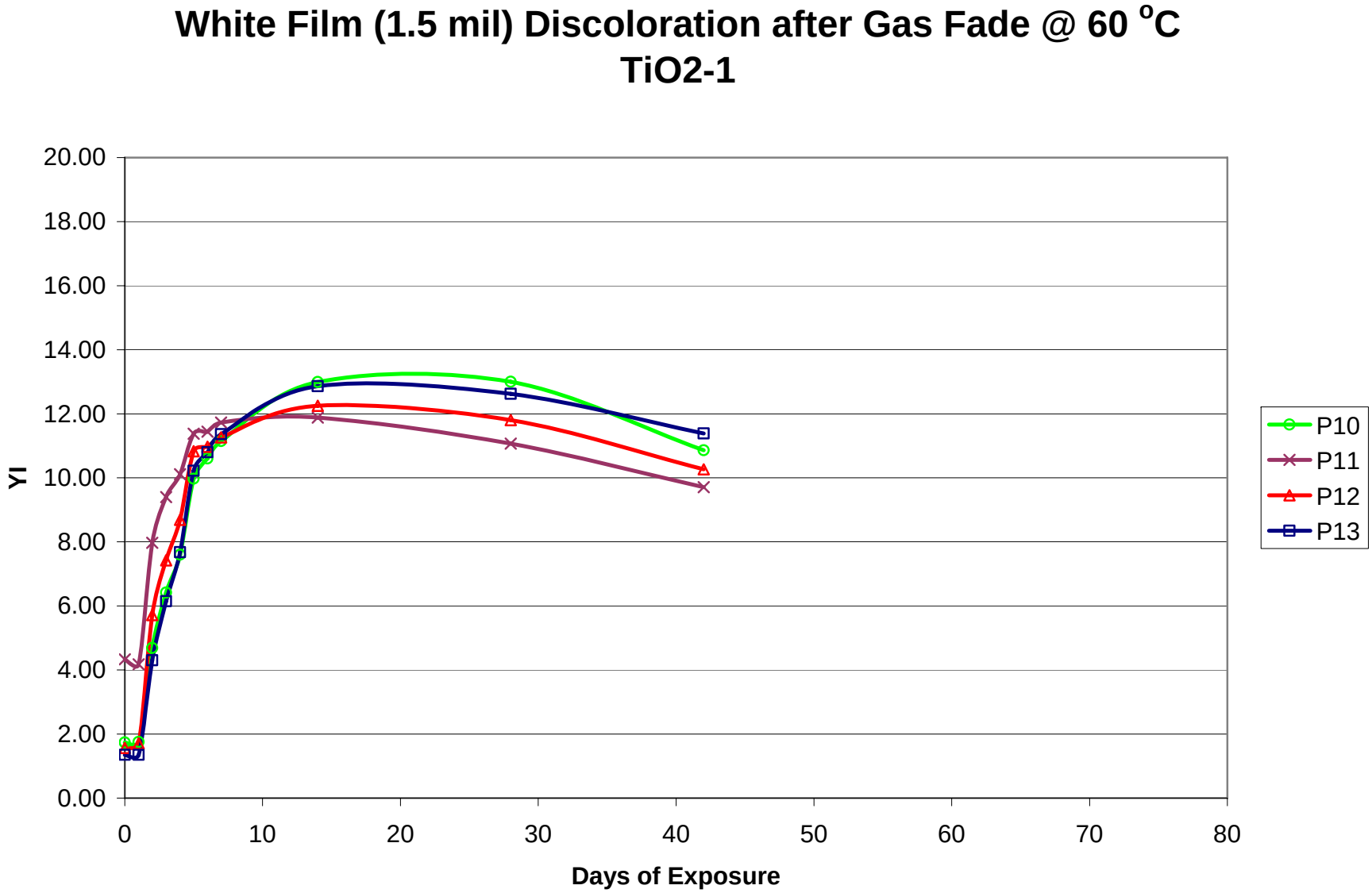
Gas fade discoloration: Phenol based LLDPE



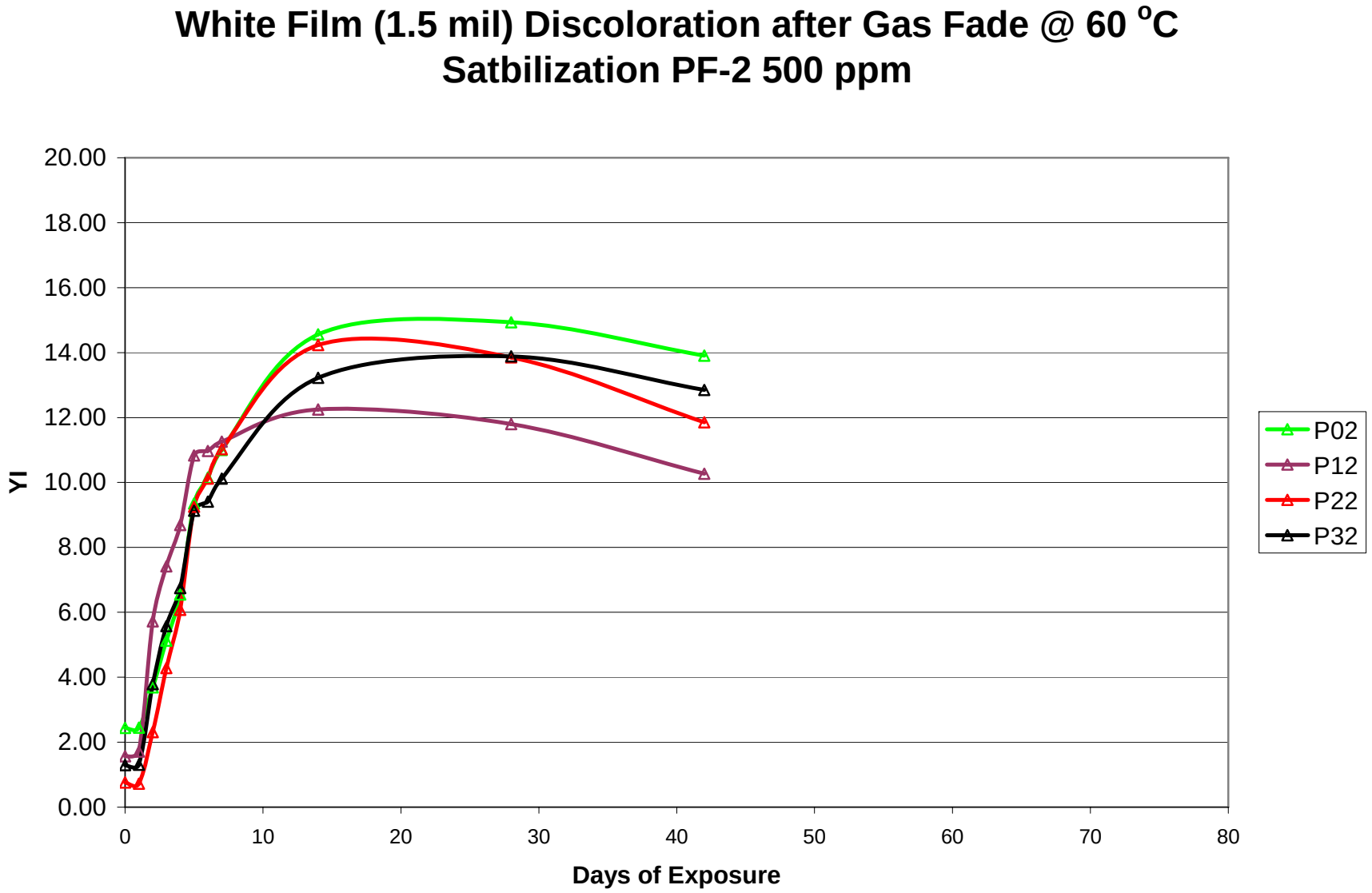
Gas fade discoloration: Phenol free LLDPE



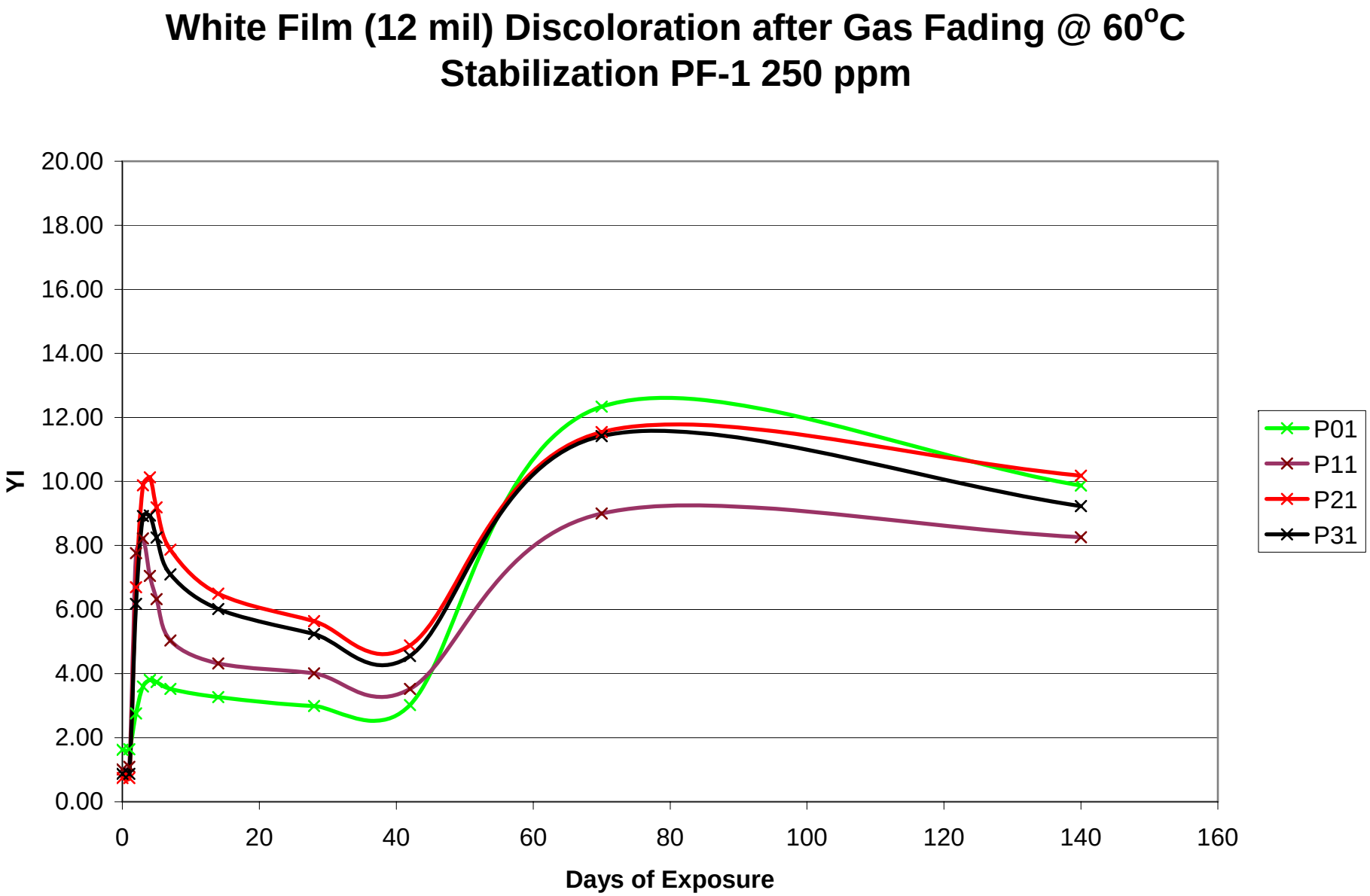
Phenol free LLDPE Gas fade discoloration: different PF MB stabilizations



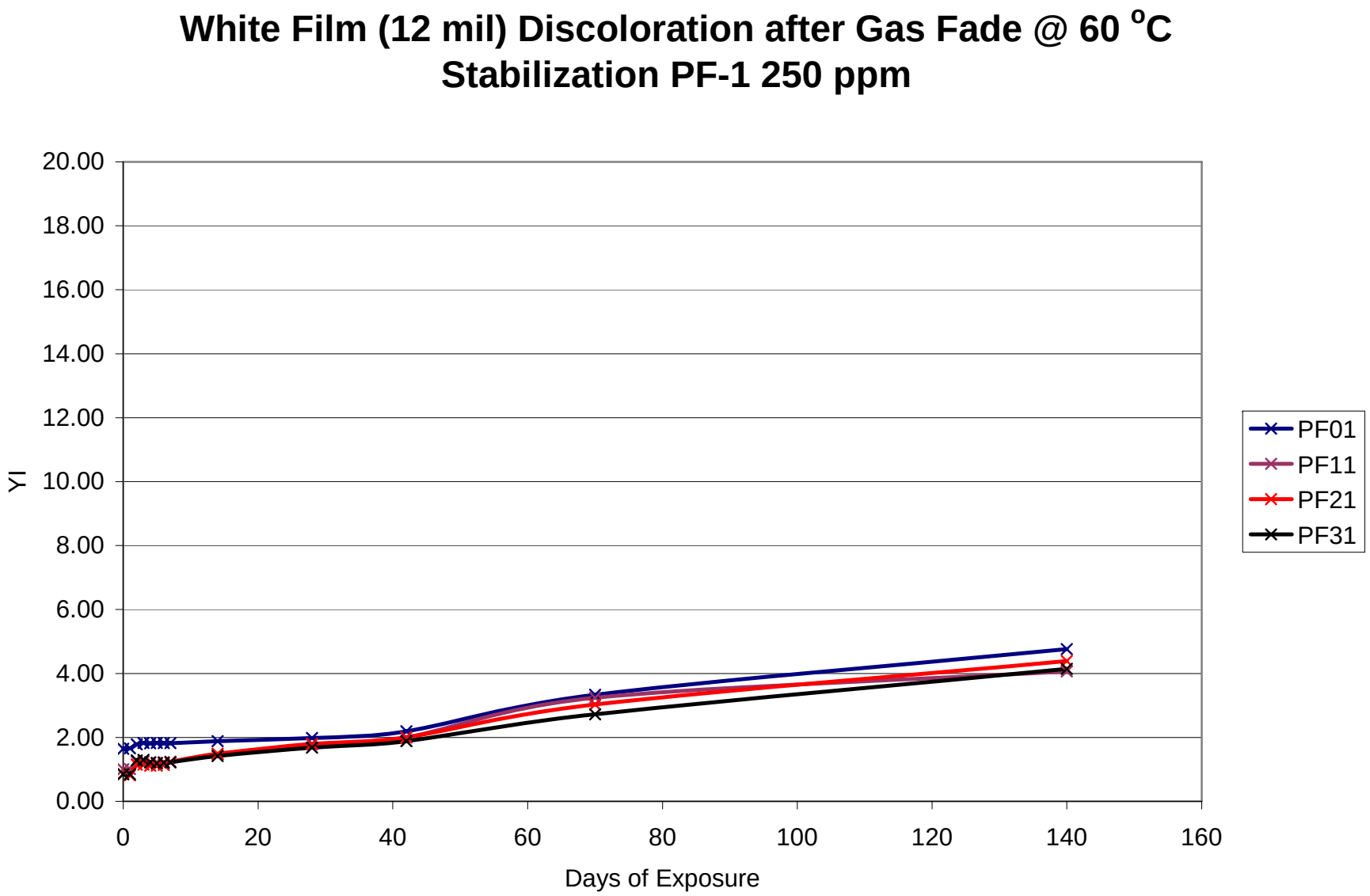
Gas fade discoloration: different TiO2



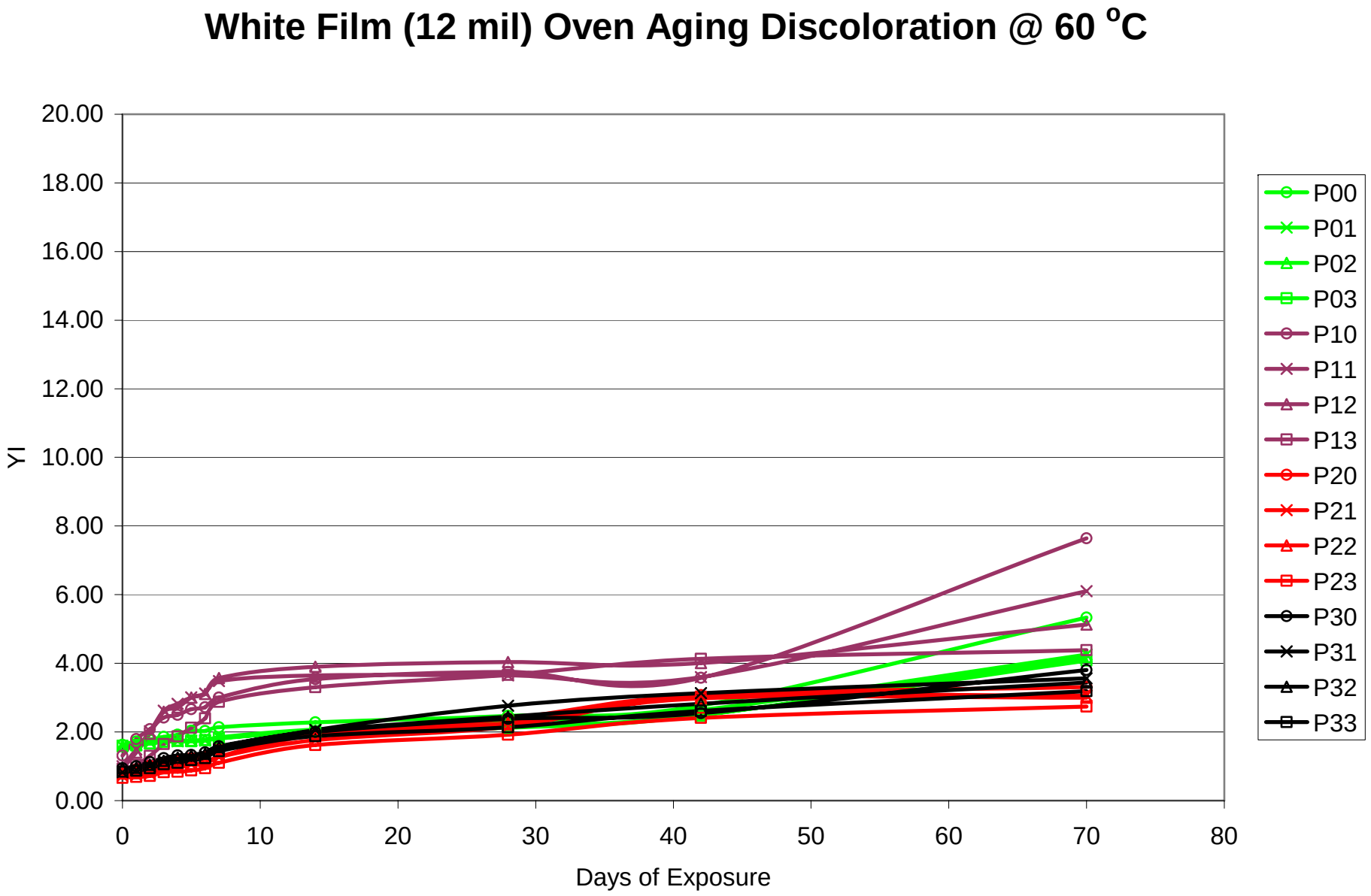
Gas fade discoloration: Phenol based LLDPE



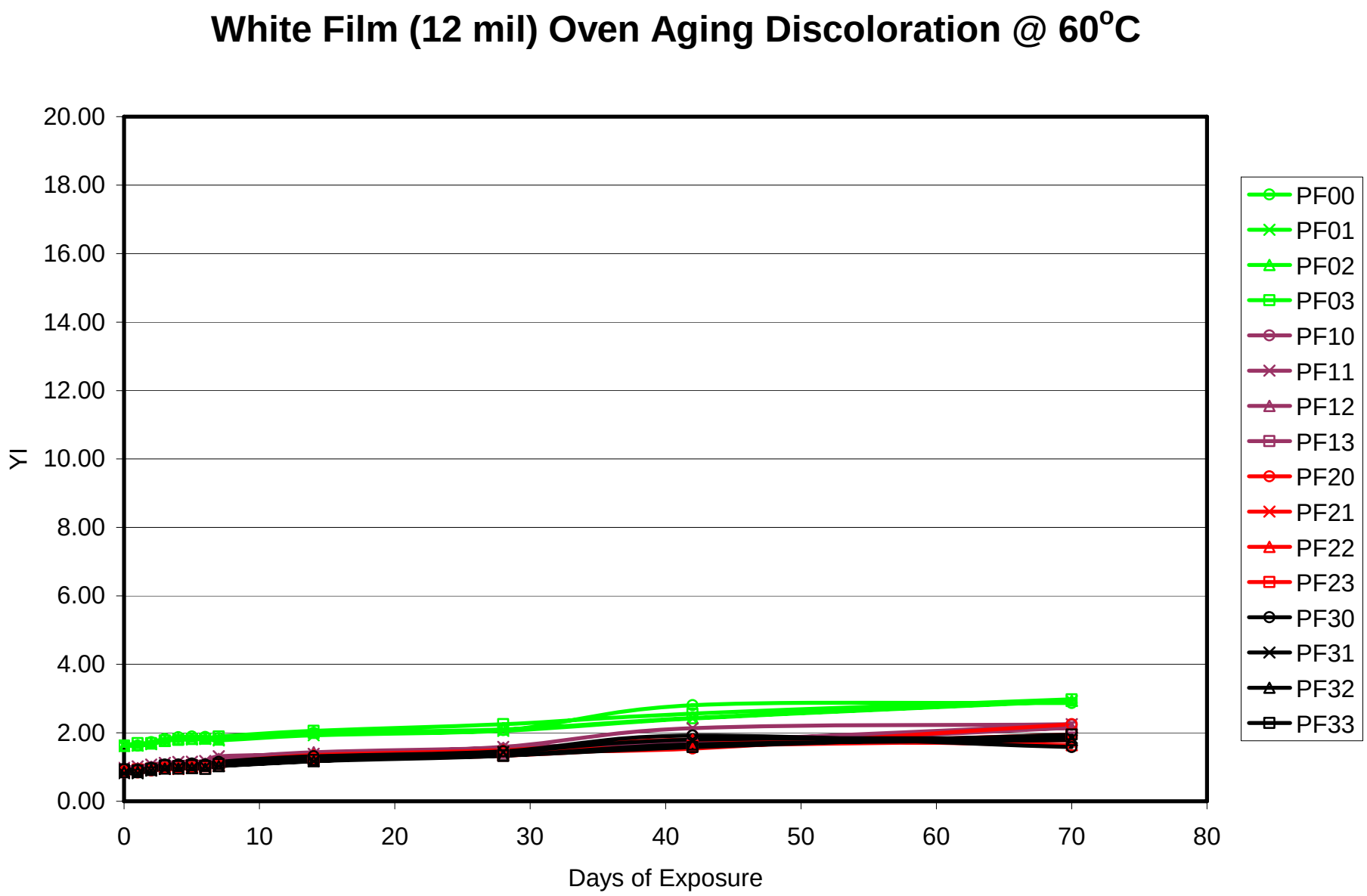
Gas fade discoloration: Phenol free LLDPE



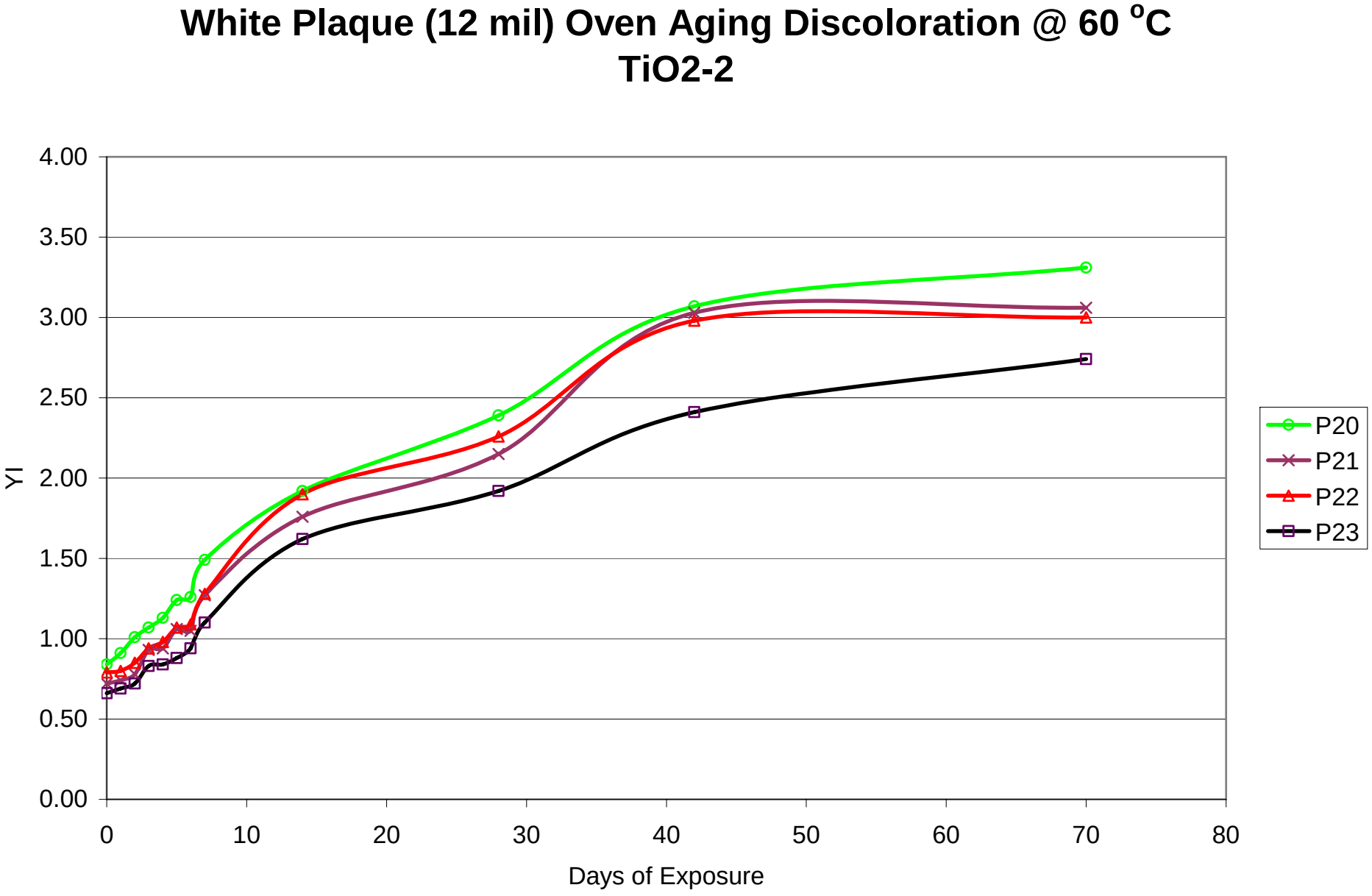
Oven aging discoloration: Phenol based LLDPE



Oven aging discoloration: Phenol free LLDPE



Oven aging discoloration: Phenol based LLDPE



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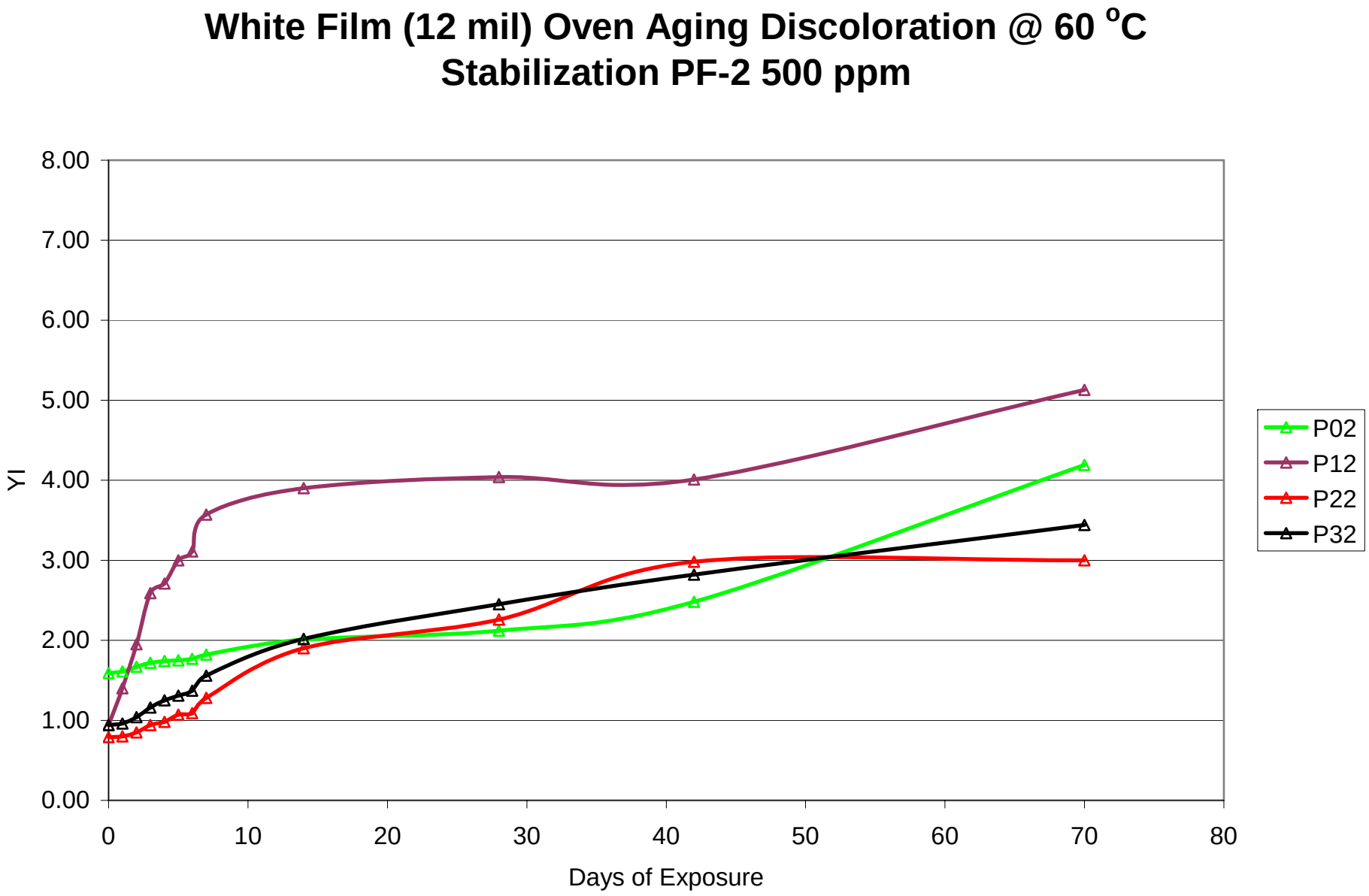

Conclusions and Recommendations

- **Summary:**
  - Addition of hydroxylamine to phenolic AO stabilized LLDPE via masterbatch did not prevent gas fading discoloration
  - Film made from phenol free LLDPE resin (totally phenol free in film) is truly discoloration resistant
  - Selection of different titanium oxide grades did not lead to significant differences in terms of discoloration
- **Overall Conclusion:**
  - One cannot make non-discolored white film by adding phenol-free masterbatch to phenolic AO stabilized LLDPE resin
- **Recommendation:**
  - If the final application is considered to be color critical, phenol free systems provide the best overall performance

Acknowledgments

The authors would like to thank the following helpful people:

- **Ciba Specialty Chemicals**
  - Maurice Gray, Anna Bassi, and Florian Stricker
- **Ampacet Corporation**
- **Thank you for your attentions!**

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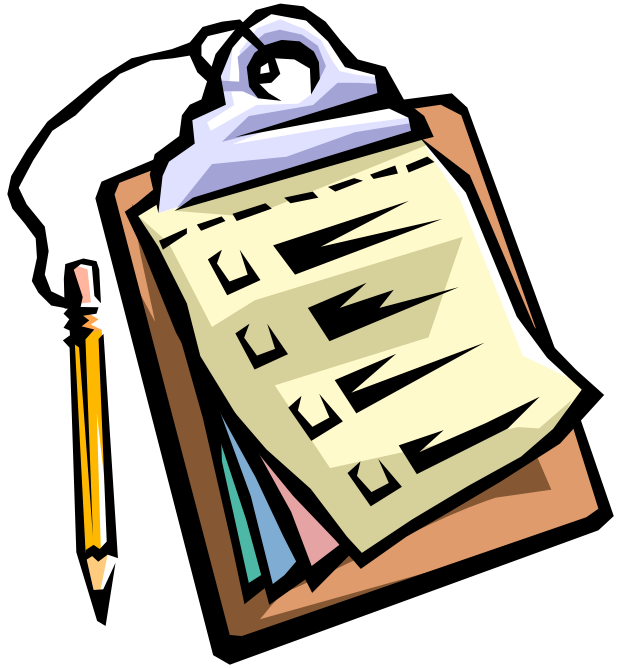

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