

Additives for Polyolefin Film Products: An Overview of Chemistry and Effects

Yijun Ye and R.E. King III, Ciba Specialty Chemicals, Tarrytown NY 10591

Abstract: Polyolefin film products are in a state of continuous improvement in regard to their physical properties, aesthetic features, durability during processing, weatherability, and various types of special effects. Accordingly, the polymer producers of these film grade products, as well as the manufacturers of the downstream films are always interested in new developments in additive technology these type of properties. This presentation will begin by providing an overview of stabilization fundamentals, and recent advances along those lines. It will end with new directions that are being taken, above and beyond stabilization, into new additive technologies that provide innovative effects to the plastic articles in specific end use applications.

Introduction

Thermoplastic materials are processed in the melt at high temperatures and under high shear. The final product has to survive exposure to conditions such as heat, light and humidity, without changes in appearance or premature mechanical failure during their service life. Suitable additives, such as antioxidants, processing and heat stabilizers, processing aids, nucleating agents and light stabilizers are required. [1]

Other effects provided by additives, such as color, flame retardant, antistatic, antimicrobial or antifogging properties are attracting increasing interest. The use of fillers and reinforcement materials allows new applications involving plastics. Recycling of used plastic materials is also an area of major interest, which is only possible with appropriate additives.

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.

In this paper, we will review the fundamentals of stabilization and the latest development in stabilization technology. It will end with two examples of new approaches that provide innovative effects to polyolefin films.

Stabilization Principles

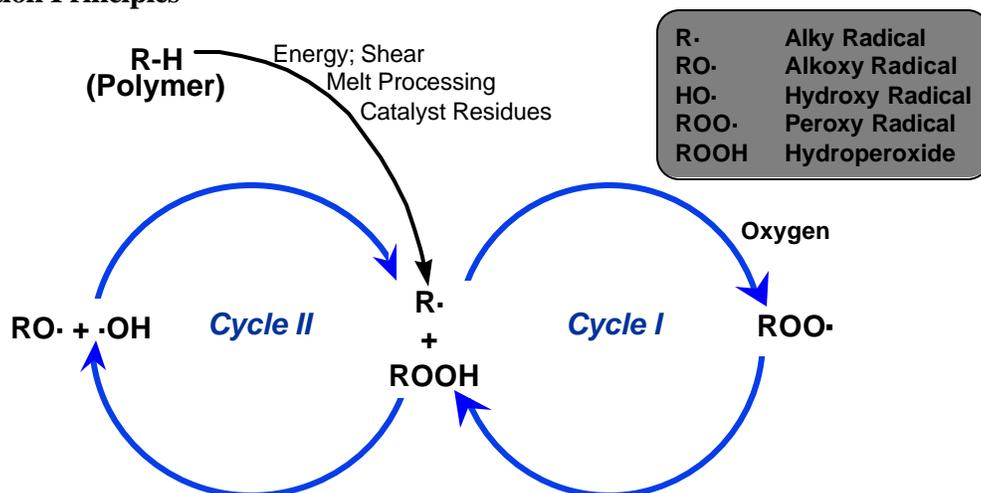


Figure 1: Auto-oxidation cycle for polyolefins.

As a brief review [2], 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 [3,4] 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**.

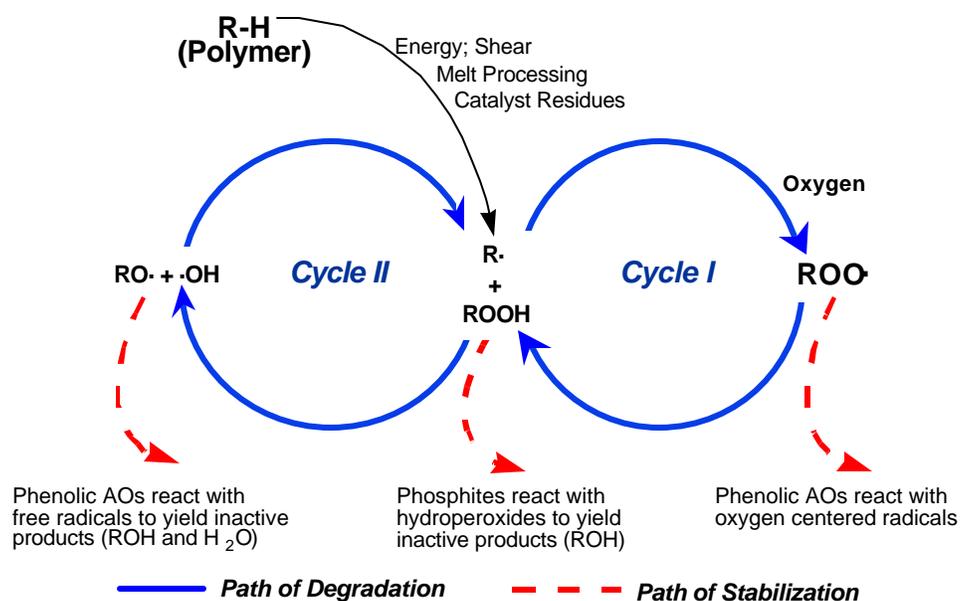


Figure 2: Traditional Inhibited Auto-oxidation Cycle for Polyolefins.

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. [5]

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 experienced a path of continuous improvement. New polymers have been, and continue to be, developed for a variety of new end-use applications that not only include improved performance, but also the development of polymer products that can 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 phosphorus, such as P-2 and P-3. [6,7]. In one sense both P-2 and P-3 are traditional, since they are based on P(III) \rightarrow P(V) hydroperoxide decomposition chemistry (as with the well know phosphite, P-1). 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, such as: improved initial color and color maintenance (P-2, P-3); enhanced long term thermal stability (P-2); improved compatibility in linear lower density olefin copolymers (P-2, P-3); excellent hydrolytic stability and inhibition of discoloration during hot water contact (P-2); and low melting point as well as outstanding solubility in process solvents (P-3). 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 and humid environments or hot water contact applications; and molten systems for topical addition of additives.

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 [7] and hydroperoxide decomposer [8] 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 [9].

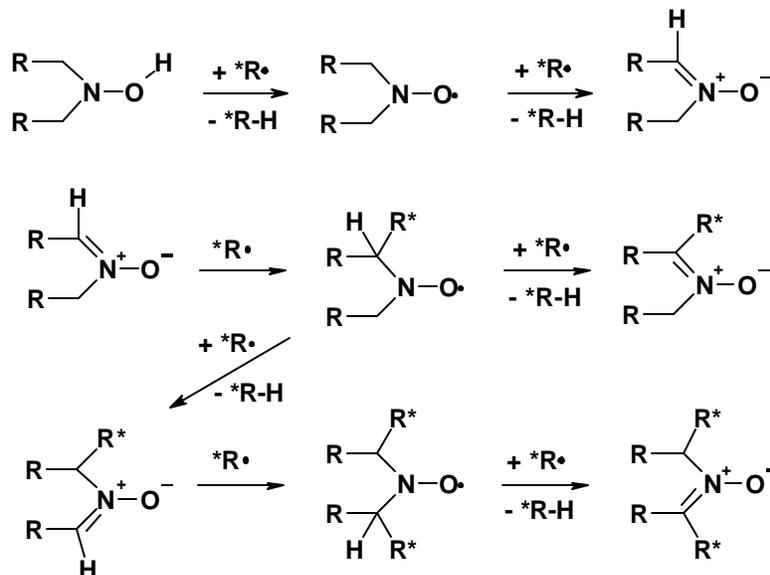


Figure 3a. Free Radical Decomposition Mechanism for Hydroxylamines.

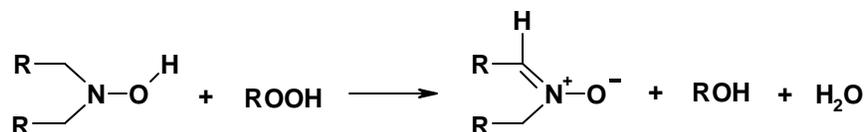


Figure 3b. Hydroperoxide Decomposition Mechanism for Hydroxylamines.

The use of “phenol free” stabilization systems has been found to be very effective in color critical products such as polypropylene & polyethylene fibers, and selected TPO applications.

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.

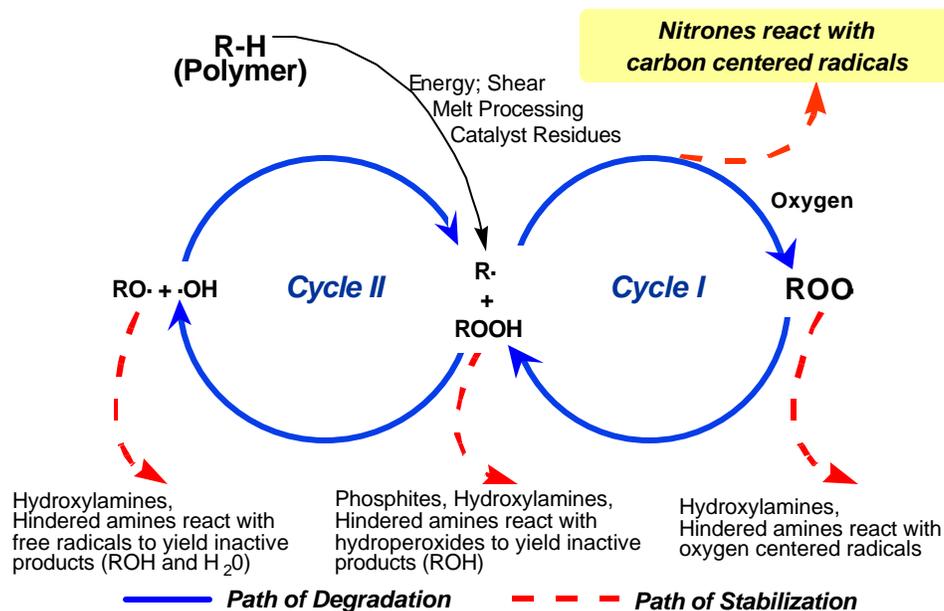


Figure 4: “Phenol free” Inhibited Auto-Oxidation Cycle for Polyolefins.

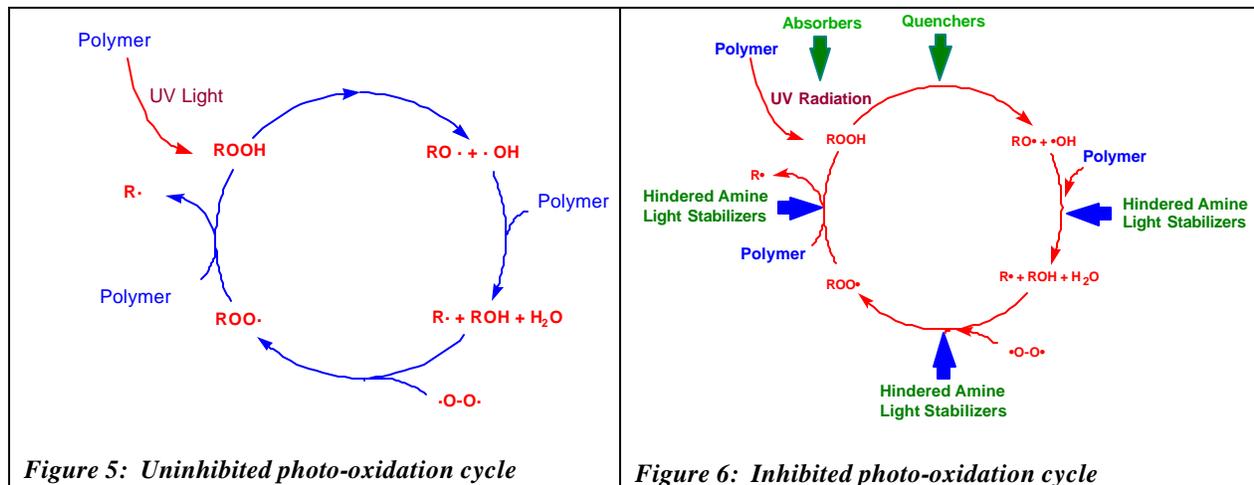
UV Stabilization

The ultraviolet component of sunlight is known to contain the energy necessary to break covalent bonds that comprise organic polymers; see **Figure 5**. To combat the destructive effect of UV radiation in the early days of long term outdoor film applications, polymers either needed to be chosen due to their intrinsic resistance to degradation, or co-additives needed to be added, such as carbon black or titanium dioxide, which were used to preferentially absorb or reflect the UV light. As can be imagined, this tended to limit the market appeal or attractiveness of plastics in broader markets. In order to facilitate the growth of plastics in outdoor applications, a variety of non-pigmenting stabilizer chemistries have been developed over the last several decades. Each of these chemistries works in its own unique way to inhibit the degradation afforded by the ultraviolet (UV) component of solar radiation. These technologies can be broken down into three classes:

- 1) UV Absorbing (e.g., hydroxyphenylbenzotriazoles, hydroxyphenyltriazines, or hydroxybenzophenones);
- 2) Excited State Quenching (primarily based on nickel chelates); and,
- 3) Free Radical Scavengers (hindered amine light stabilizers, HALS)

Without going into details about mechanisms, “UV Absorbers” prevent polymer degradation by preferentially absorbing the UV component of the radiation, and releasing that energy as vibrational energy or heat. The effectiveness of UV Absorbers is fundamentally based on the Beer-Lambert equation; $A=[e][B][C]$; (where A = Absorbance, $[e]$ = absorption coefficient, $[B]$ = path length, and $[C]$ = concentration of the absorbing species). Accordingly, as the path length decreases, higher concentrations of the UV Absorber are necessary to provide a similar degree of absorbance. UV Absorbers are not only effective at stabilizing polymers, but also enhance the lifetime of organic pigments. [10] “Quenchers” take the excited state energy states induced in the polymer from UV radiation and dissipate that energy via lower frequency light. “Free Radical Scavengers” react with the radicals that are generated by the UV induced decomposition of hydroperoxides that build up in the polymer.

As shown below in **Figure 6**, the UV Absorbers and Quenchers need to provide effectiveness before free radicals are created in the matrix. If these types of stabilizers cannot soak up the UV energy or deactivate the excited states, the consequence is the generation of free radicals. From this point on, Hindered Amines bear most of the burden for protecting the polymer via free radical scavenging.



Each of these UV stabilizers has something to offer in regard to cost and/or effectiveness for a particular end use application. Over the last two decades, it has generally been recognized that hindered amine light stabilizers afford the best balance of properties, since they address the key aspect of UV degradation, i.e., free radical scavenging. This is especially an issue when the substrate is thin section, such as film, where the UV absorbers reach a limit of effectiveness due to concentration limits. On a separate note, some of the nickel based excited state energy quenchers have fallen out of favor due to the potential environmental impact (not to mention that most film products containing nickel based excited state quenchers are light green). Accordingly, for most thin films (0.4 - 20 mils; 100-500 microns) used in outdoor applications, hindered amines have gained a superior position based on their overall effectiveness, and lack of color generation.

However, as mentioned earlier, not all types of co-additives are compatible with hindered amine light stabilizers. As a representative example, antagonistic relationships between higher concentrations of thiosynergists in hindered amine containing formulations have already been documented. [11] The antagonistic relationship is due to the fact that an over-oxidized thiosynergist can lead to sulfenic and sulfonic type acids, see **Figure 7**, which can partially deactivate the hindered amine as shown in **Figure 8** below. The partial deactivation of the hindered amine, via acidic by-products, can lead to a partial reduction in the overall light stability (or long term thermal stability) afforded by the hindered amine, see **Chart 1**.

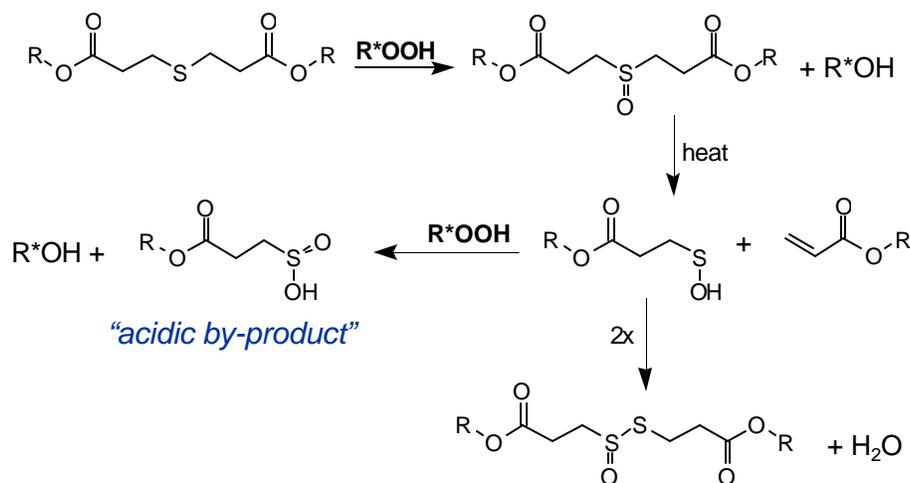


Figure 7. Generation of Acidic by-Products via Overoxidation of Thiosynergists.

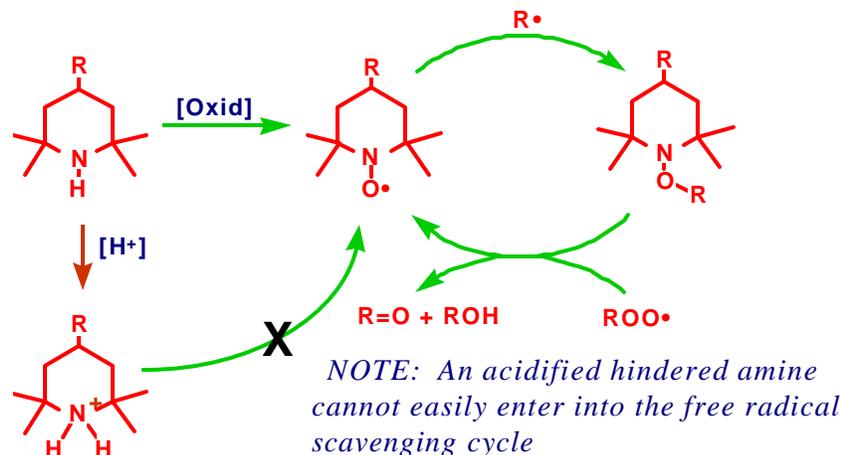


Figure 8. Partial Deactivation Inhibited photo-oxidation cycle.

As such, in selected outdoor film markets, which require light stability, efforts are made to formulate around the use of thiosynergists when hindered amines are used as the reagent for providing UV stability. This acid/base type chemistry can also affect hindered amine containing formulations in other ways. For example, there are other sources of acidic by-products that a film can come into contact with, such as certain types of oxidized and/or degraded pesticides. Since most of the early hindered amines are alkaline due to the relatively higher content of nitrogen in the molecule, these acid/base type interactions could lead to diminished activity in the field. As such, a variety of hindered amines have been developed with the goal of being less alkaline; a scheme for minimizing the interaction with acidic by-products. These include alkylated piperidines piperidine esters, and amino ethers as well as piperazinones or piperizinediones.

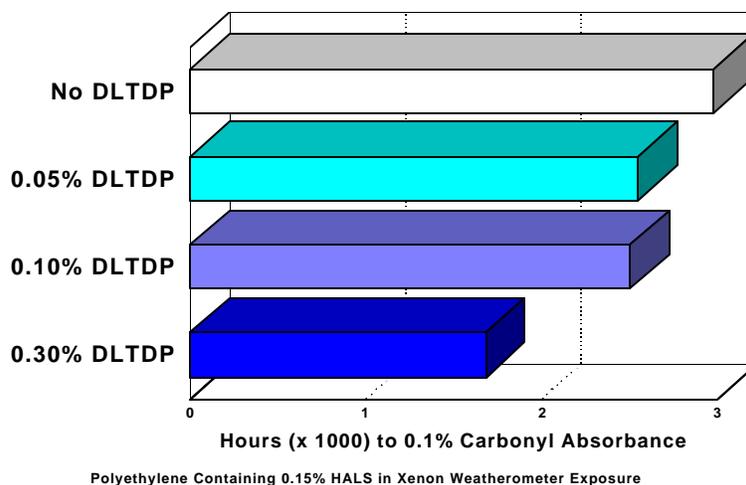


Chart 1. Partial Deactivation of UV Stability Afforded by HALS.

The “alkalinity” of various hindered amines is illustrated in **Chart 2**, where measuring the pKa of the hindered amine is an indirect way of quantifying the alkalinity. A technique has been developed where the hindered amines are titrated with buffered perchloric acid solution to elucidate the pKa. [12] Of greatest interest is the pKa of the piperidinyl group, since this is the most active component of the HALS type UV stabilizer. The alkalinity of the piperidinyl groups can be arranged into four subclasses: secondary amines (N-H), with higher alkalinity; methylated tertiary amines (N-CH₃), with similar alkalinity; alkylated tertiary amines (N-R), with intermediate alkalinity; and tertiary aminoethers (N-OR), with the least alkalinity. This type of acid/base interaction is only observed in selected applications; for example, with high loadings of brominated flame retardants, selected pesticides (acidic by-products)

in agricultural applications, or high chloride content (poor deactivation of the catalyst residues). For these valued added applications, HALS selection is an important step in the product formulation.

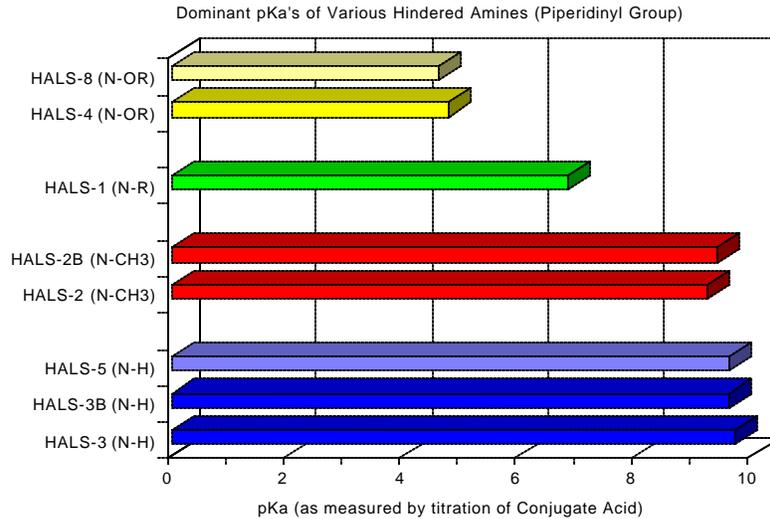


Chart 2. Dominant pKa's of the Piperinyl Group of Various Hindered Amines

Weatherability of Hindered Amine Light Stabilizers (HALS) in LLDPE and Impact of Polymer Processing Aids on the Performance of HALS

As we discussed before, Hindered Amine Light Stabilizers (HALS) are often used to create polyolefin film products that can endure prolonged contact with the damaging effects (UV radiation) of sunlight. On the other hand, Polymer Processing Additives (PPA) are often used in the LLDPE film production to improve the melt extrusion. Since HALS tend to interact with other additives, it is important to understand if the HALS/PPA additive chemistry is synergistic, neutral or negative so that we can choose the best combination of HALS and PPA for outdoor film applications.

PPA used in LLDPE blown films are typically based on fluoroelastomers, or mixtures of fluoroelastomers in combination with a high molecular weight polyethylene glycol. They are used to eliminate a phenomenon known as melt fracture during blown film extrusion of LLDPE, and to improve throughput rates for HDPE. They work by forming a coherent layer in the land region of the die, which prevents the molten polymer from stick / slipping while exiting the die.

On the other hand, additives that compete with the PPA for the metal surface, such as HALS, have been shown to prolong the amount of time necessary to eliminate melt fracture. To remedy this situation, higher concentrations of PPA are used, which solves the problem, but has a negative impact on the cost effectiveness.

A significant amount of work has been carried out to identify and quantify the impact of co-additives that can affect the PPA performance. [13,14] King et al. [13] examined the performance of 5 different hindered amines (HA-3, HA-5, HA-2, HA-1 and HA-4) as light stabilizers during Xenon weathering. They also studied the impact of three PPAs (PPA-1, PPA-2, and PPA-3) on these 5 hindered amines. The ranking of HALS performance was observed as follows:

Good **HA-1** (N-R) < Better **HA-2** (N-CH₃) < Best **HA-3** (N-H) ≤ Best **HA-5** (N-H) ≤ Best **HA-4** (N-OR)

The following impact of PPA on HALS performance (although quite subtle) was observed:

Good **None** < Better **PPA-1** (Fluoroelastomer + PEG) < Better **PPA-2** Fluoroelastomer < Best **PPA-3** Fluoropolymer

HA-3, HA-5 and HA-4 provide the best UV performance. It was also observed that HA-3 has the most negative interaction on the performance of their PPA products, and that HA-5, HA-4, and HA-2 have much less of an impact, with HA-1 having the least impact.

It was generally recognized that alkaline N-H type hindered amines, such as HA-3, have the most negative impact on PPA performance, measured by rate of elimination of melt fracture. Less alkaline, N-R type hindered amines, such as HA-1, have much less of a negative impact. There were few exceptions, however. For example, the alkaline N-H type hindered amine, HA-5 had much less of a negative impact in comparison to HA-3. On the other hand, the least alkaline hindered amine, HA-4, did not provide the least interference (most likely due to the N-H groups on the backbone).

Based on the above results, Woods et al. [14] examined more HALS effects on PPA and explored the two plausible interaction mechanisms between the PPA and HALS.

- Site competition (between the HALS and the PPA at the polymer metal interface)
- Potential for acid/base chemistry (chemical reaction between the HALS and PPA)

It was believed that the interaction mechanism is likely some combination of site competition and chemical reaction, and that depending on extrusion conditions one or the other may occur to different extents.

In this section, we examined a selection of HALS that reflect our most current recommendations, HA-6, HA-7 and HA-8 (HA-3 and HA-1 were used as controls) and one PPA (PPA-2). The ranking of HALS performance in LLDPE film was evaluated by Xenon weathering. The impact of the PPA on the effectiveness of HALS was evaluated. On the other hand, the impact of these HALS on PPA performance was reported separately by Woods et al. [14]

Experiment Design: Blown film experiments were carried out both without and with PPA for the Xenon weathering study. The film was ca. 90 μm in thickness. The base resin for these films was a Dowlex 2045 (1 MI, 0.92 density) ethylene/octene solution phase process zn-LLDPE. All PPA levels were kept constant at 900 ppm and HALS at 1500 and 3000 ppm.

HALS/PPA Results: As can be seen from the graphs below, in regard to the relative performance of the various HALS, we observed the following general trends in the Dow ethylene/octane zn-LLDPE (time to 50% retained physicals):

More Performance: HA-8 \geq HA-6 \geq HA-7 > HA-3 > HA-1 :Less Performance
(NOR) (NR+NH) (NR+NCH₃) (NH) (NR)

In regard to the impact of PPA on the performance of the HALS, we observed a slight negative impact of PPA on the performance of hindered amines (except HA-8); ~15-20% reduction in time to 50% retention of physical properties. We did not see this in the 1st study [13] suggesting that the variables involved in the work (base polymer; initial extrusion and blown film conditions, etc.) may have had more of an impact on the inherent error in the experiment than anticipated.

The blown film work by Woods et al. [14] clearly demonstrated the relative ranking in regard to the impact on PPA performance. The results were not too surprising; HA-6 fell between HA-3 and HA-1; HA-7 had slightly less interference, and fell between HA-2 and HA-1. HA-8 was once again not the least interacting HALS, but was still closer to HA-1 in terms of less interfering.

In addition to the experiments with 1500 ppm HALS (w/o and w/ 900 ppm PPA; PPA-2), we also looked at 1500 ppm vs. 3000 ppm HALS (w/ 900 ppm PPA; PPA-2). At first glance the results were initially disappointing; i.e., doubling the HALS did not result in a twofold increase in performance as measured by retention of physical properties during Xenon weathering. On the other hand, this observation is not really that unusual; we have never been able to see a twofold increase in the performance of HALS stabilized films by doubling the HALS loading. This claim is based on a variety of xenon weathering studies with LLDPE.

In the past, we have tried to justify the lack of twofold performance by using arguments based on Francois Gugumus, that the impact of the HALS on light stability in LLDPE type substrates is based on the square root of the

concentration. This would lead to roughly a 40% improvement. However, we only saw (on the average), a ~20% improvement in this study. Similar type of results were seen in the previous studies.

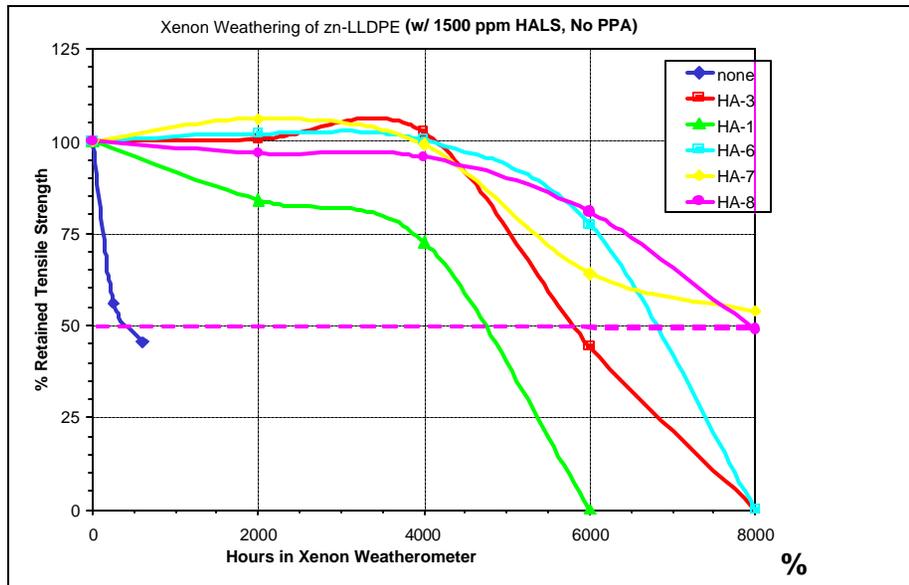
Post Extrusion Discoloration: We measured both gas fade induced discoloration and oven aging (as the control experiment) at 60°C in an effort to understand the impact of the various HALS on post extrusion discoloration. We found the following trend regarding gas fade color:

More Discoloring: HA-3 > HA-6 > HA-7 > HA-8 ≥ HA-1 ≥ Blank :Less Discoloring
(NH) (NR+NH) (NR+NCH₃) (NOR) (NR)

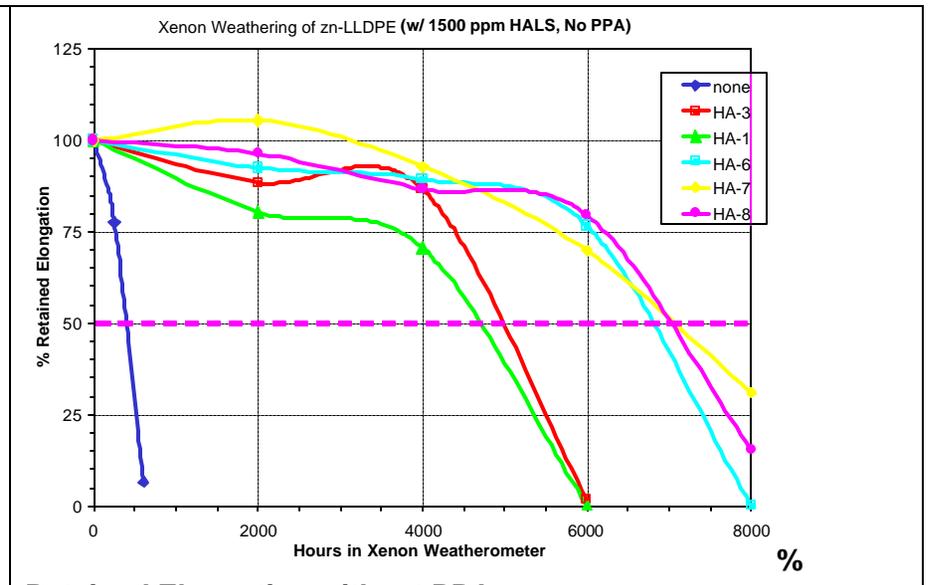
These results more or less confirm what is generally known about the impact of the various HALS on gas fade discoloration. As expected, there was not a significant impact on discoloration during oven aging at 60°C.

Summary of HALS/PAA work: Based on the two studies that we have run, the results suggest that there may, or may not, be a slight reduction in the performance of the HALS, as measured by Xenon weathering. Of greater importance is the general ranking of the various HALS in LLDPE. The performance of HA-6 and HA-7 is noteworthy in comparison to the traditional HA-3. The HA-8 performs the best.

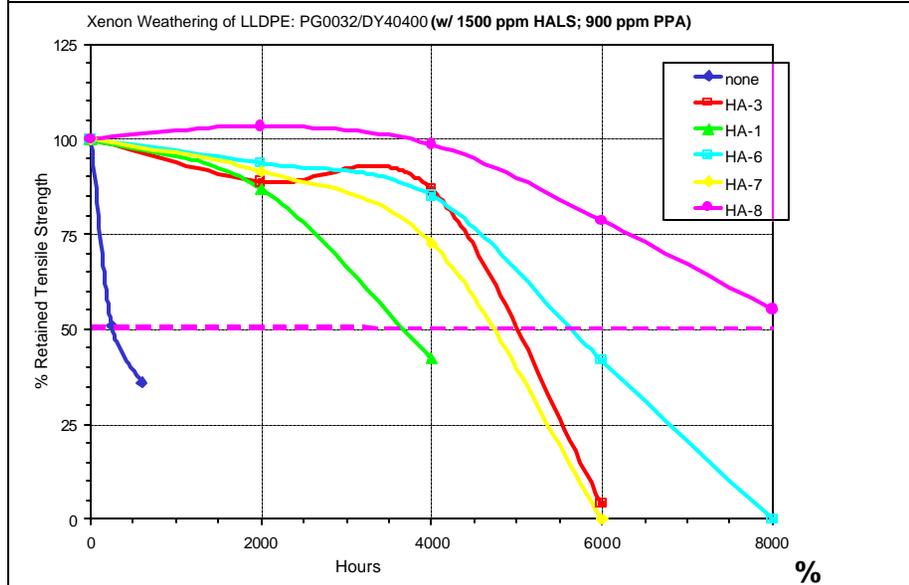
This work clearly demonstrates that selected PPAs and HALS can be used together **without** a significant interference on the rate of elimination of melt fracture *or* weatherability. This should lead to new outdoor film applications for z/n-LLDPE and m-LLDPE. This work should help to demonstrate the value of our HALS systems, especially HA-7 and HA-8 for agriculture film applications, which require defect free films with good weatherability.



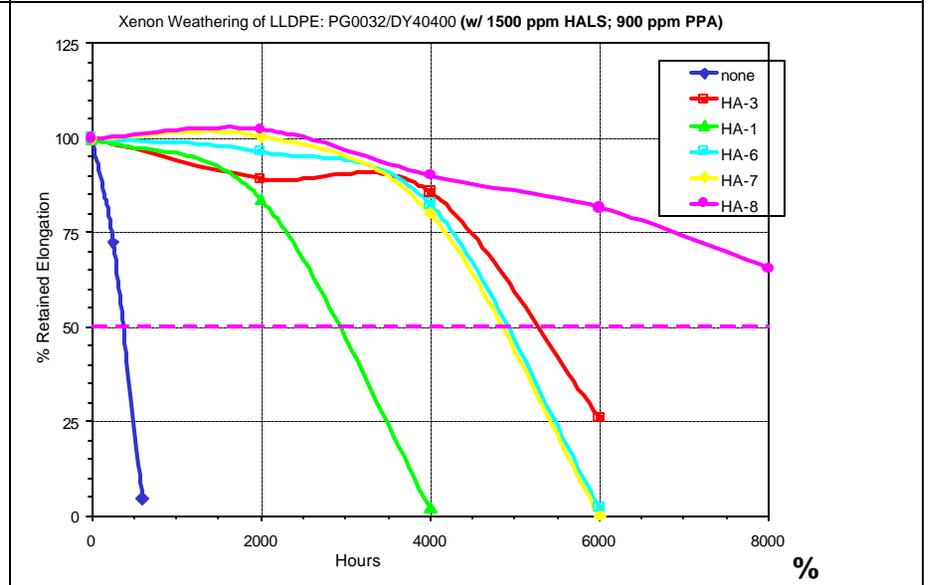
Retained Tensile Strength without PPA



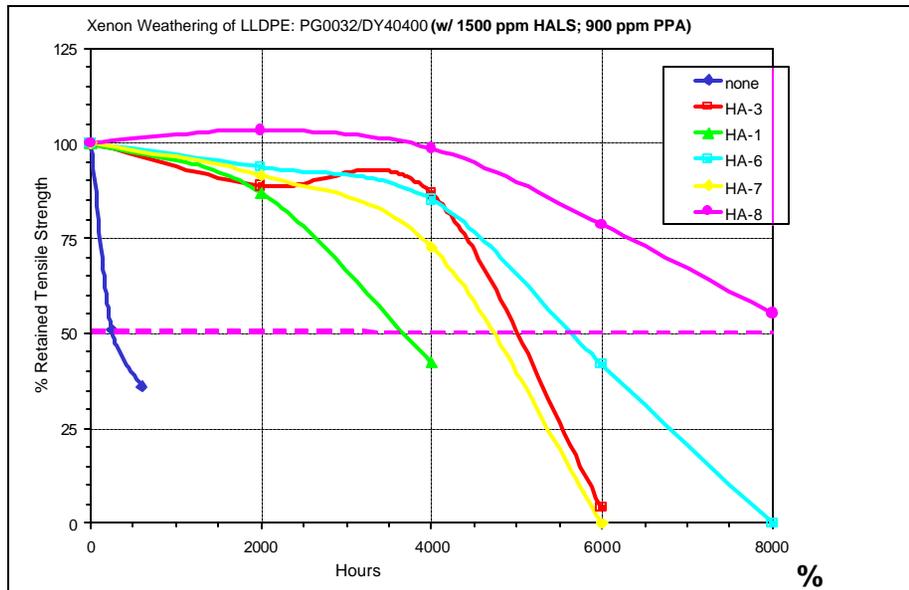
Retained Elongation without PPA



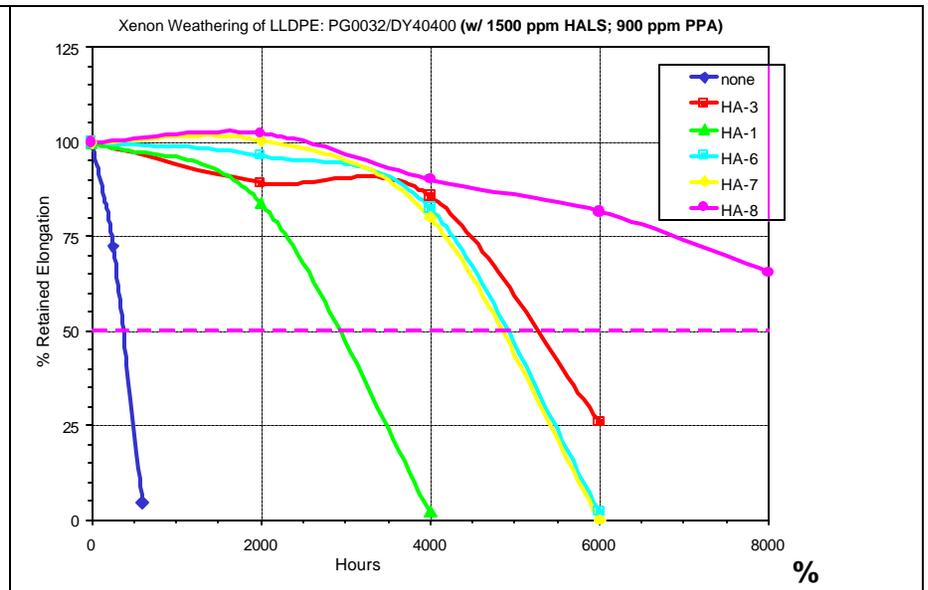
Retained Tensile Strength with PPA



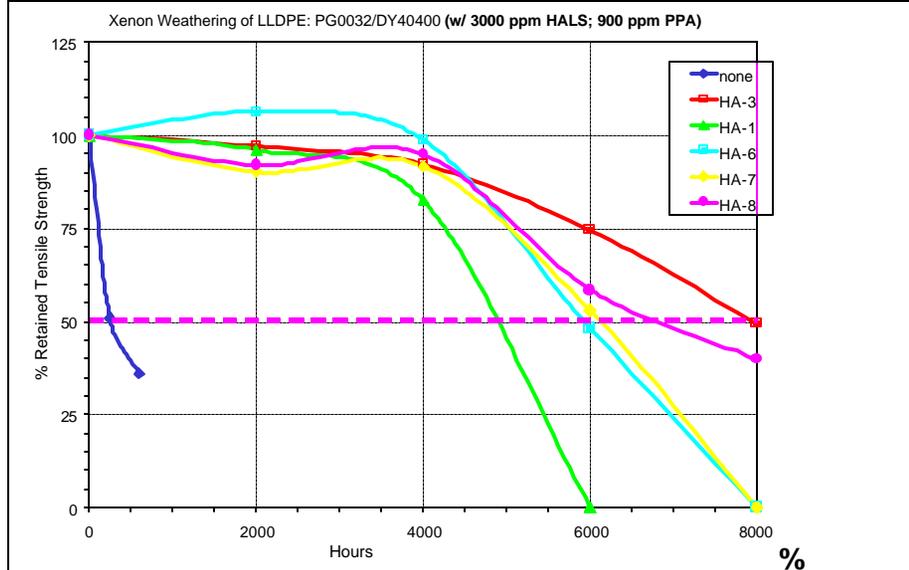
Retained Elongation with PPA



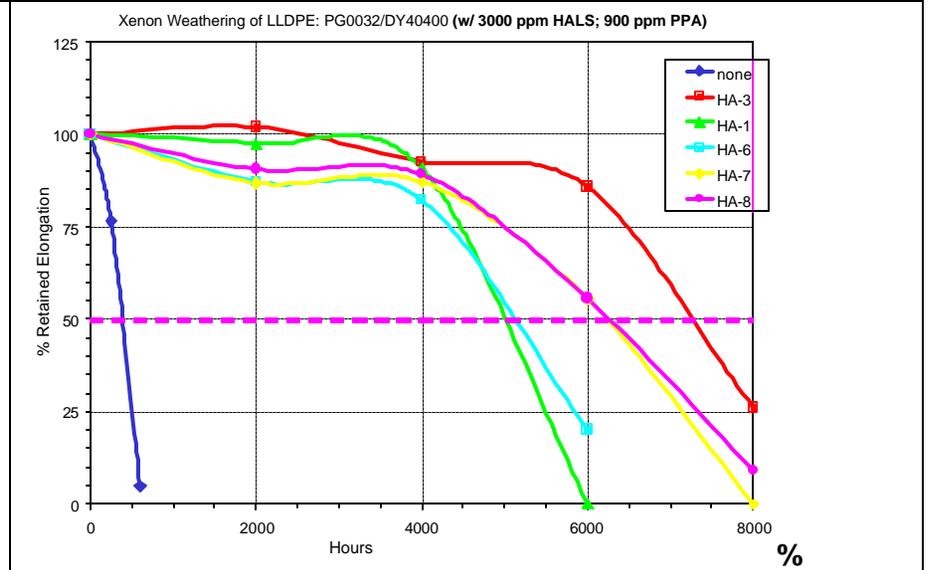
Retained Tensile Strength w/ 1500 ppm HALS



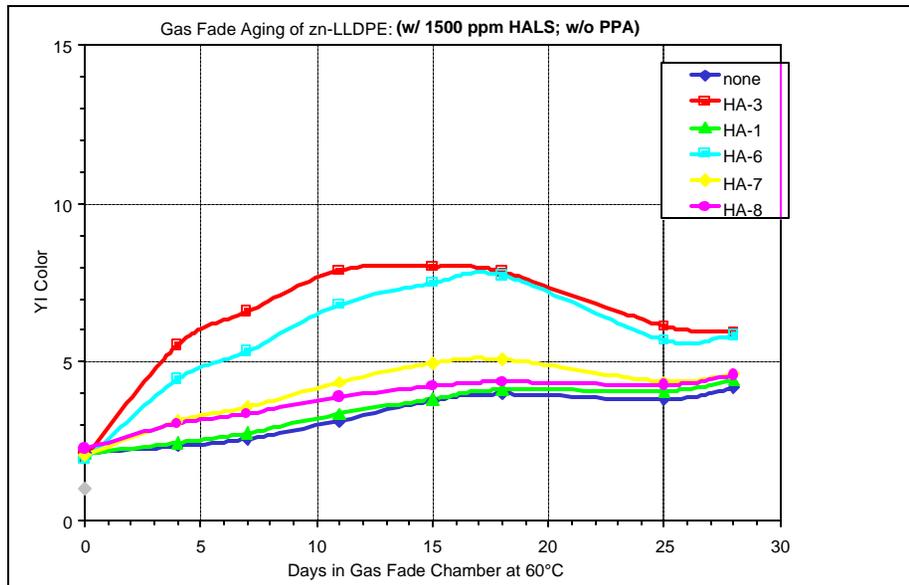
Retained Elongation w/ 1500 ppm HALS



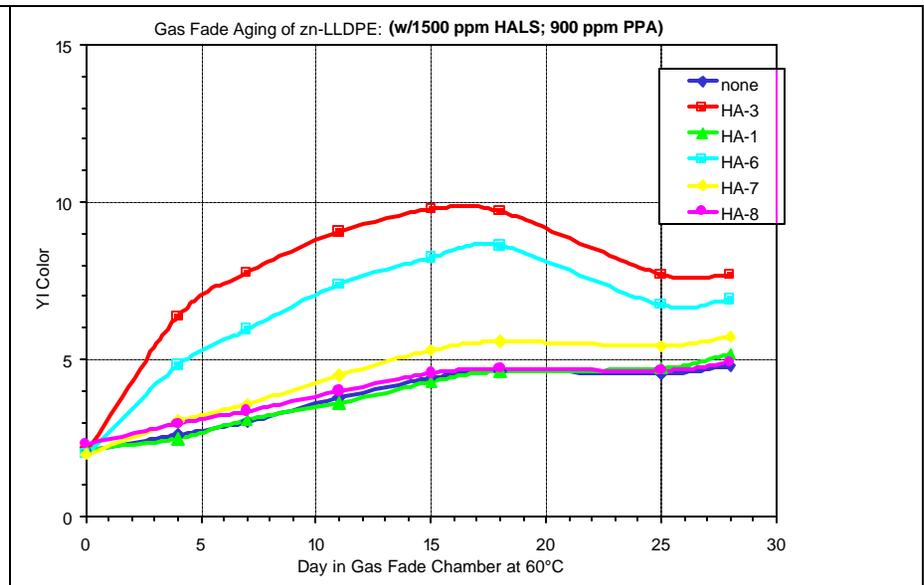
Retained Tensile Strength w/ 3000 ppm HALS



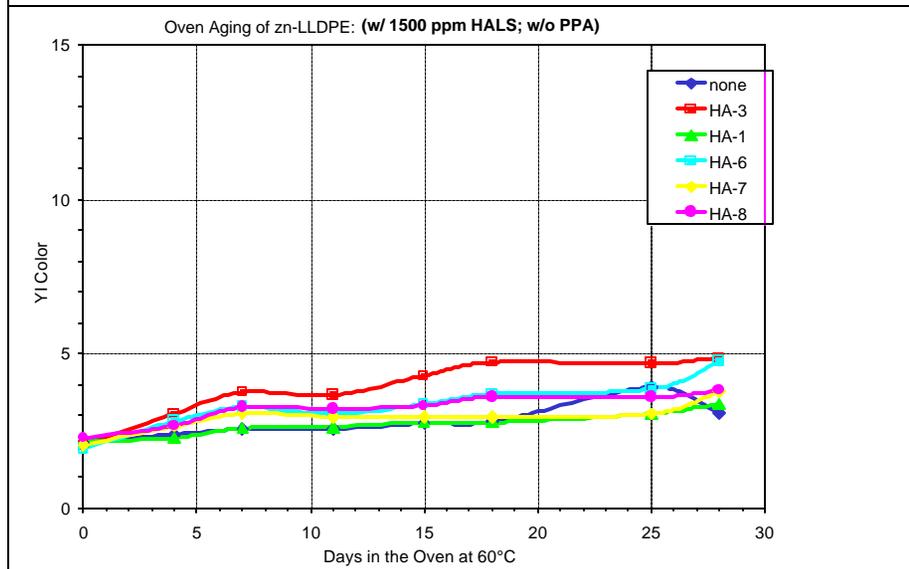
Retained Elongation w/ 3000 ppm HALS



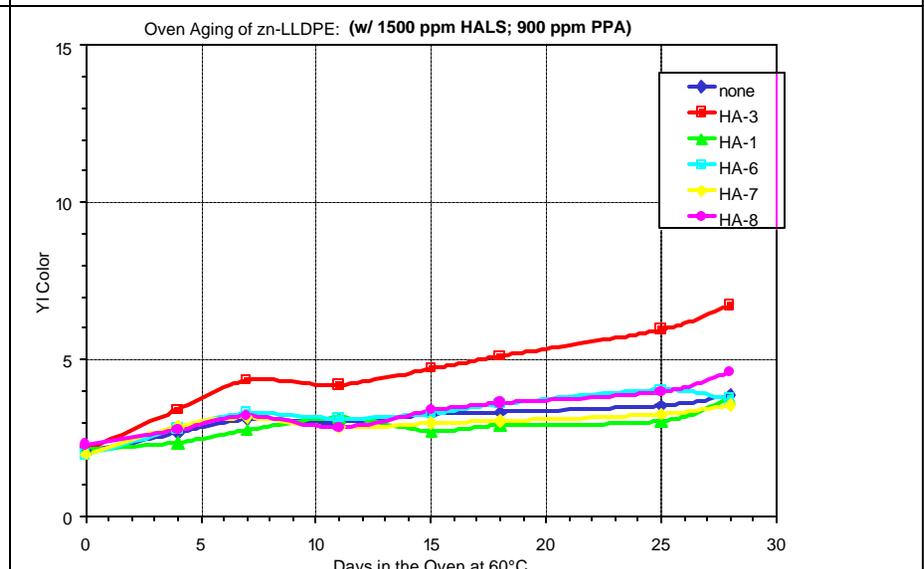
Gas Fade Discoloration w/o PPA



Gas Fade Discoloration with PPA



Oven Aging Discoloration w/o PPA



Oven Aging Discoloration with PPA

Active Food Packaging Materials – Oxygen Scavengers

Many packaged consumer goods are sensitive to oxygen degradation and therefore efforts have been made to reduce the oxygen inside the package. Methods that have been used over the years to combat the presence of oxygen in packages include the use of passive barrier layers (glass, metals, EVOH, Foil, PET, and nylons, etc.) to minimize permeation of oxygen into the package over time and the use of gas flushing to reduce oxygen initially present within the packaging headspace. However, even with these techniques, there can often be enough oxygen present within the package to adversely affect product quality and therefore limiting product shelflife. With the growing use of plastics in convenience packaging (metal/glass replacement and smaller packaging sizes), as well as increasing consumer demands for improved packaged product quality, this issue is one of increasing importance. Many companies are going to great lengths to improve product quality. It follows that improved packaging materials are necessary to maintain the optimum product presentation that meets these requirements. [15, 16, 17]

Oxygen scavenging technologies, in combination with other techniques, can meet the increasing performance demands being placed on the package. In this section, we will discuss how to best use scavengers in packaging applications and the factors one needs to consider when designing packaging incorporating this technology. One application example will be given utilizing SPO₂ oxygen scavengers.

Oxygen Scavenger Use: When dealing with oxygen in packaging, there are two different oxygen sources which one needs to address – the oxygen initially present within the package itself and the ingress of oxygen through the package walls with time. Previously, with the widespread use of metal cans and glass bottles that were essentially impervious to oxygen permeation, ingress over time was not necessarily a critical issue. However, with the increased use of plastic materials in packaging to meet convenience needs, there comes an increasing need to address the impact of permeated oxygen on product quality, particularly as smaller packaging units are utilized.

Regardless of the packaging material, oxygen trapped inside the package from the initial moment of packaging has been an issue. Sources of this oxygen include the headspace volumes of the package, as well as any oxygen dissolved within the product. When looking at the amount of oxygen brought in by the product, this can vary considerably depending on the nature of the product. For example, most liquid products have little dissolved oxygen, whereas bakery products, particularly breads, can contain a significant amount of oxygen. Technologies that have been used in the past to address this issue include vacuum packaging and gas flushing. However, these techniques have limitations as to which foods they can be used with or how much oxygen can be removed cost effectively with the net result being that a small amount of oxygen still remains inside the package.

For many food products, even a small amount of oxygen present can be sufficient to adversely affect product quality. It is in these instances that one would consider the use of oxygen scavenging technology.

Scavenger Form: Currently, scavengers can be introduced as either a separate entity (sachet) within the package or integrated as part of the package itself.

Sachets

Technologies to scavenge oxygen have been worked on now for over three decades. Some of the first uses of oxygen scavenging technology involved the use of sachets – small pouches placed in the interior of the package that contained a species that is highly reactive with oxygen. Formulations containing iron, typically with a metal halide salt are the most common, though other materials such as ascorbic acid have also found use in sachets. Such sachets can be very effective in meeting the goal of reducing residual oxygen within the package and maintaining an oxygen free environment. A significant strength of the sachet approach is the ability to size the sachet to oxygen absorption needs. As the demands for absorption capacity increase, a bigger sachet can be utilized.

However, there are some concerns that need to be considered when using sachets – mainly centered on the presence of a foreign object within the package. Also, sachets do not work in the packaging of any type of liquid product such as soups or gravies. Furthermore, the need to adjust packaging line speeds to place the sachet into the package and ensuring 100% placement can be a significant concern with this approach.

In-Package Systems

Because of the limitations of sachets, there has been a push to develop scavenging technologies that can be incorporated into the walls of the package. By incorporating the scavenger into the walls of the package, one can eliminate the concerns regarding the presence of a distinct object within the package. Additionally, such systems

should not significantly impact the physical characteristics of the package; thus allowing the converter the ability to run at normal line-speeds.

Systems which can be incorporated into the walls of the package include polymeric based materials which can be added as distinct layers within the structure or additives which can be incorporated into an existing layer within the package structure.

Scavenging Systems : Along with deciding the form of the scavenger to be used, one needs to decide which scavenging system chemistry can best meet the needs of the application. There are numerous systems currently on the market or are in the process of being commercialized. While these systems use a variety of materials as the scavenging component, they can be grouped into three broad categories based on their mode of operation.

Iron Based Systems

One of the first types of chemistry utilized in scavenging systems, and still a predominant chemistry utilized in sachets, fine particulate iron is introduced into the package where it reacts with oxygen in the presence of moisture. Iron based systems are characterized by high absorption capacity. In addition to iron, such systems typically incorporate a metal halide salt as a reaction promoter.

Since the reaction of iron with oxygen requires moisture, humidity within the package is often used as the trigger to initiate the scavenging reaction. Some sachets incorporate in-situ moisture sources such that they can work with dry products; however, most iron systems rely on product moisture to trigger the scavenging reaction. Prior to incorporation of the scavenger into the package, the system is kept dry, thus preserving the capacity of the system.

Oxidizable Polymers

In the late 80s, CMB Foodcan filed a patent application [18] which in general describes the use of an oxidizable organic component as an oxygen scavenger. Typically, the oxygen scavenging reaction is catalyzed by a transitional metal salt (very often cobalt). These systems may use a distinct additive as the oxidizable component, but they often utilize a polymer as the oxidizable component. Polymers which have been used as the oxidizable component include polybutadienes, polyamides, and copolymers incorporating unsaturated pendant groups. These systems may or may not require a triggering mechanism (such as UV radiation).

In the case of UV triggered systems, the scavenger capacity is preserved until a dose of actinic radiation is provided to the article as part of the packaging process. This system has the advantage of providing the scavenging reaction on demand, but requires the installation of activation equipment into your packaging line and may affect packaging operations.

Other systems in this category are active on production. In such systems, the catalyst and oxidizable components are typically brought together during the article fabrication process. After some initiation time, the scavenging reaction commences. While this approach has the advantage of not requiring a triggering step or related equipment, articles formed incorporating such scavengers have a defined shelf-life and must be utilized quickly or else a significant amount of the scavenging capacity of the article can be lost.

Photo Reducible Compounds

The third general category of oxygen scavengers involves the use of UV radiation to photo-reduce a susceptible compound to create an oxygen reactive species. An example of this type of system can be found in CSIRO's oxygen scavenging system [19] in which anthraquinones, upon UV exposure, form hydroxyquinones which can then react with molecular oxygen. One advantage to this type of system is that it does not require a catalyst for an effective scavenging rate to occur. Secondly, the oxygen reactive species is formed at the time of packaging, so there are no significant shelf-life issues for the scavenger.

Package Design Considerations: Oxygen scavengers are complementary technology to existing methods to minimize oxygen ingress in packages. As such, they are most cost effective when used in a well-designed package that incorporates other technologies such as a passive barrier layer and gas flushing.

Oxygen Absorption Requirements: The first step in designing a structure incorporating oxygen scavengers is to determine the amount of oxygen that will be absorbed over the intended shelf life of the package. Three main oxygen sources are typically considered: oxygen dissolved within the product, oxygen present in the headspace of the

package, and oxygen entering the structure over time. Once values for these factors have been determined, one can then determine how much scavenger needs to be incorporated into the structure.

Capacity

Regardless of the system used, all oxygen scavenger systems have a finite capacity. Thus, the amount of oxygen absorbed by a package is directly proportional to the amount of scavenger that is added to the structure. With sachets, capacity requirements define the size of the sachet.

When working with in-package scavenging systems, an additional factor needs to be looked at when considering the capacity of the scavenging system – namely, the amount of space or “real estate” available to incorporate the scavenger. There are practical considerations to how much scavenger can be incorporated into a structure. Two significant factors which can influence the amount of scavenger within the package include limitations on the amount of scavenger that can be incorporated into a given layer and the thickness of the scavenging layer.

Rate

Often, when one is determining the loading level for a given application, the tendency is to solely look at the amount of oxygen needed to be absorbed. Then, the minimum amount of scavenger needed to absorb that amount of oxygen is added. However, the rate of scavenging is an equally important consideration. If it takes several days for the scavenger to eliminate all of the residual oxygen from the package, yet it only takes a day or two for the oxygen to negatively impact product quality, the damage will have been done prior to the scavenger completing its work.

Depending on the scavenging system and the storage conditions used, the scavenging rate will vary. Thus, it is important to know the rate of the scavenging reaction at a given storage condition. Storage conditions that can affect scavenging rate include storage temperature, oxygen level within the package, and the relative humidity within the package.

Two additional factors that can affect the scavenging rate include scavenger concentration and diffusion rate of oxygen to the scavenging component.

Carrier resin

In order for the scavenger to begin to remove oxygen from the package interior, the oxygen has to first reach the scavenger. This situation is of particular importance when the scavenger is incorporated into a film or a tray. When the scavenger is incorporated into a polyolefin layer (or other resin with a high oxygen transmission rate, O₂TR) oxygen inside the package can be readily removed from the interior of the package. However, when the scavenger is incorporated as part of the barrier layer, the oxygen molecule has to travel through a portion of the passive barrier layer in order for scavenging to occur. Thus, such systems may not be best if the primary goal of the package is to remove headspace oxygen from the packages.

Package Construction: Scavengers are not selective – they will absorb oxygen from the outside of the package as readily as they will from the package interior. Therefore, to most cost effectively use oxygen scavengers they need to be used in concert with traditional barrier materials such as nylons, EVOH, foil, etc. The scavenger is typically placed to the interior of the passive barrier layer and may be in a distinct layer or added as part of an existing layer. This type of structure can be produced through common co-extrusion or lamination technologies.

Often, the scavenger layer will not be directly in contact with the contents of the package. Scavengers may need to be separated from the contents for regulatory reasons or they are separated from the contents to minimize any potential organoleptic interactions between the scavenger and the product.

Application Example: Our oxygen scavenger system, SPO2 (Scavenger Product for oxygen, O₂), is an active oxygen scavenger system based on iron. It is designed to be incorporated into a polyolefin packaging and to work in combination with a passive barrier. SPO2 is incorporated in a polyolefin layer within a multi-layer packaging structure during co-extrusion or lamination to form a self-contained oxygen-absorbent packaging system. This multi-layer barrier structure will decrease oxygen transmission by absorbing any oxygen permeating through the barrier layer of the film structure as well as removing any residual oxygen from the package interior. The carrier resin can be either polyethylene or polypropylene.

Typical packaging containing SPO2 can be rigid, multi-layer containers, flexible films, and cap liners. Potential applications can be soups and beverages, ready meals and snacks, fresh or processed meat and cheese, moist pet food, cosmetics and personal care products.

Retort Applications: An area of increased activity in the packaging arena is in the use of rigid polypropylene containers in the packaging of retort-processed food. Such containers are finding use in the packaging of soups, home meal replacements and pet foods and often use EVOH as the oxygen barrier layer in these multi-layer packages. However, the high temperature and moisture conditions found during the retort process saturate the EVOH leading to a drop in its barrier properties for a period of time after processing (see **Figure 9** blue lines). During the first month of storage after processing, up to half of the total oxygen ingress into a package (over its intended shelflife) can occur.

This “Retort Shock” effect is well known and a variety of solutions have been proposed and used over the years to address this problem. They include the use of a desiccant material in the layers surrounding the EVOH to moderate its moisture exposure, blends of EVOH with other barrier materials such as nylon, and the use of thicker EVOH layers to moderate the effect of retort shock. While these approaches can help to moderate the effects of retort shock on the barrier performance of the package, they also can negatively impact different package attributes.

Increasing the thickness of the EVOH barrier layer leads to increased raw material costs, can negatively impact the physical properties of the package due to the brittleness of EVOH and can also impact ones ability to recycle in-process scrap due to the higher level of EVOH. Use of a desiccant or blends can also lead to similar effects.

SPO2 is an iron-based scavenger designed to be incorporated into the walls of a multi-layer packaging structure. The oxygen scavenging activity can be triggered in this system by the moisture from the retort process and the scavenger system will be at its most active immediately after undergoing retorting.

When looking at the characteristics of the SPO2 scavenger system and EVOH under the retort process, there seems to be a very natural synergy between these two products. Namely, the scavenger is at its most active state when EVOH is at its weakest. As the structure “dries out” after retorting and the EVOH barrier properties return, the scavenger activity can be designed to tail off allowing the passive barrier properties of EVOH to protect the product at that point.

Figure 10 shows such a typical structure of a cup with retort applications. Here a polypropylene outer layer is bonded to a passive barrier layer which reduces permeation of oxygen, while the SPO2 active layer removes oxygen in the head space, dissolved in the food and permeating into the package. The final layer is a food contact layer. Adhesives join the layers.

The red lines in **Figure 9** show the oxygen permeation rate with SPO2 in such a structure. As can be clearly seen from this graph, the permeation rate data for the container changes dramatically with time after the retort process for tray without scavenger. On the other hand, the samples containing the scavenger shows consistent barrier performance through the retort process and over a long period of time. SPO2 compensates for the loss of EVOH barrier properties during and after retort until EVOH recovers its original barrier properties. Ultimately, we saw the permeation rates for the two samples approach one another as the scavenger is consumed and the barrier properties of the EVOH recover.

Summary of Oxygen Scavenger Work: Oxygen scavenging technology can be a valuable tool in meeting some of today’s toughest packaging demands. We have highlighted one area where the combination of active and passive barrier technologies can lead to a package with improved barrier performance. In long shelf-life retort applications, the use of SPO2 with EVOH can lead to a more optimum synergic performance versus barrier material alone.

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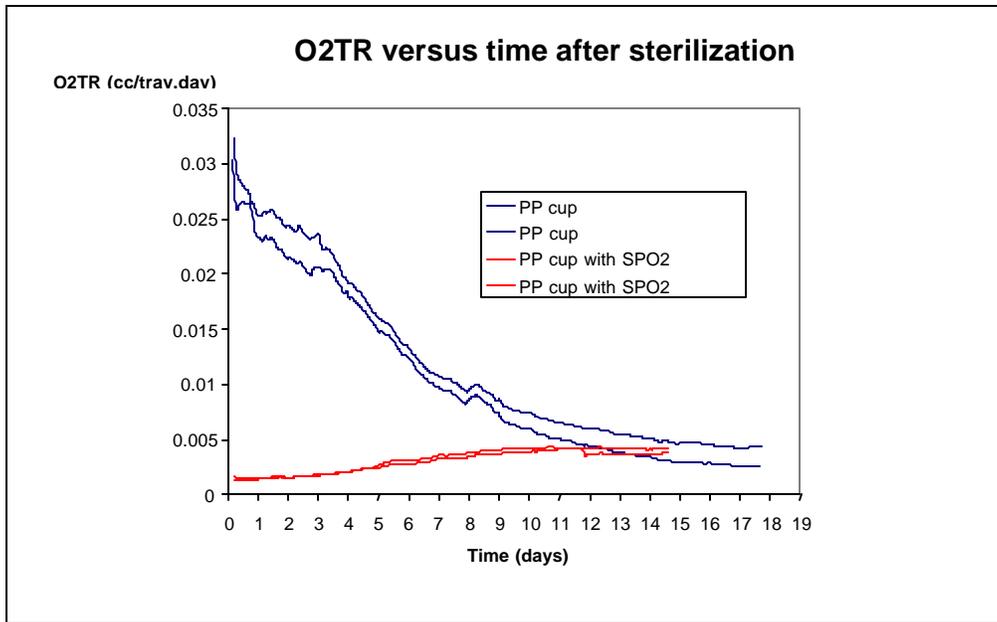


Figure 9. Oxygen Transmission Rate after Sterilization

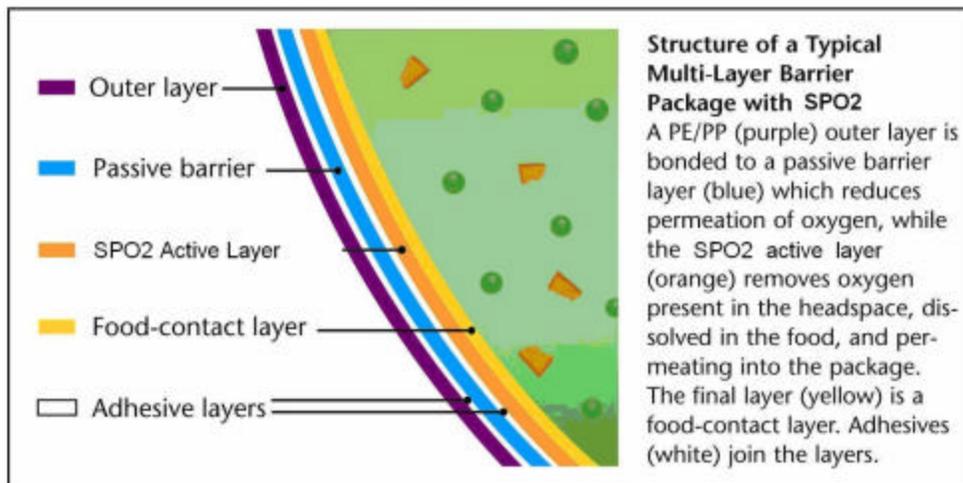
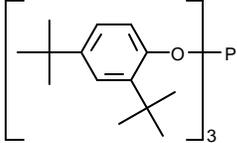
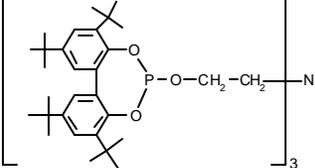
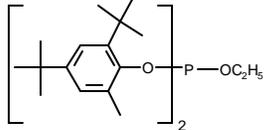
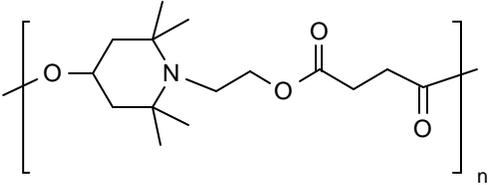
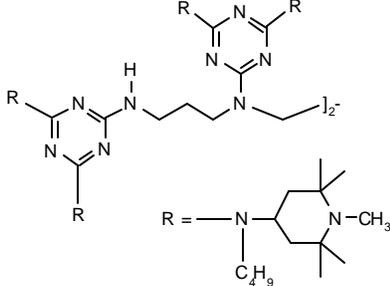
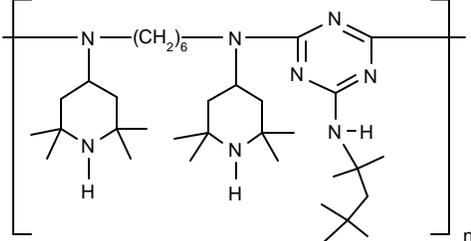


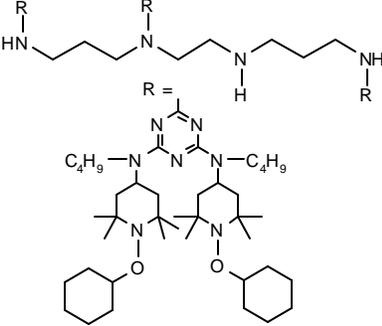
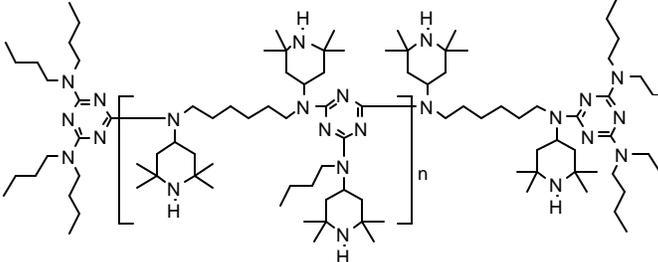
Figure 10. A Typical Multilayer Package Structure with SPO2 for Retort Applications

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Appendix: Description of Additives.

Code Class Tradename	Molecular Structure	Stabilizer Function
P-1 Phosphite Irgafos® 168		Melt Processing Stability; (secondary enhancements to the performance of the phenolic antioxidant)
P-2 Phosphite Irgafos® 12		Melt Processing Stability; (secondary enhancements to the performance of the phenolic antioxidant)
P-3 Phosphite Irgafos® 38		Melt Processing Stability; (secondary enhancements to the performance of the phenolic antioxidant)
HA-1 High Molecular Weight Tertiary (N- R) Hindered Amine Tinuvin® 622		UV Stability; Long Term Thermal Stability (<135°C);
HA-2 High Molecular Weight Tertiary (N-CH ₃) Hindered Amine Chimassorb® 119		UV Stability; Long Term Thermal Stability (<135°C);
HA-3 High Molecular Weight Secondary (N-H) Hindered Amine Chimassorb® 944		UV Stability; Long Term Thermal Stability (<135°C);

<p>HA-4</p> <p>High Molecular Weight Aminoether (N-OR) Hindered Amine</p> <p>NOR-116</p>		<p>UV Stability; Long Term Thermal Stability (<135°C);</p>
<p>HA-5</p> <p>High Molecular Weight Secondary (N-H) Hindered Amine</p> <p>Chimassorb® 2020</p>		<p>UV Stability; Long Term Thermal Stability (<135°C);</p>
<p>HA-6</p> <p>Hindered Amine</p> <p>Tinuvin® 783</p>	<p>1:1 HA-1 + HA-3</p>	<p>UV stabilization; Long term thermal stability (< 135°C)</p>
<p>HA-7</p> <p>Hindered Amine</p> <p>Tinuvin® 111</p>	<p>1:1 HA-1 + HA-2</p>	<p>UV stabilization; Long term thermal stability (< 135°C)</p>
<p>HA-8</p> <p>Hindered Amine</p> <p>Tinuvin® NOR® 371</p>	<p>Proprietary Structure</p>	<p>UV stabilization; Long term thermal stability (< 135°C);</p>

HALS-2B = Cyasorb UV-3529, HMW / Tertiary (N-CH₃) Hindered Amine; HALS-3B = Cyasorb UV-3346, HMW / Secondary (N-H) Hindered Amine.

PPA1 = Dynamar FX-5920A; PPA2 = Dynamar FX-9613; PPA3 = Dynamar FX-5911.

SPO2 = Scavenger Product for Oxygen O₂, ShelfPlus® O₂