UNDERSTANDING THE INFLUENCE OF ADDITIVES ON GAS FADE DISCOLORATION OF POLYETHYLENE RESINS

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Abstract

Discoloration of polyethylene resins can be induced by way of a number of different mechanisms. In particular, gas fading continues to be one of the most problematic sources of color afflicting the film packaging industry. While it is commonly understood that discoloration is strongly associated with the presence of phenolic (primary) antioxidants, there is significantly less understanding of the various parameters that impact this phenomenon. This paper seeks to provide an overview of the numerous factors which affect the extent and severity of gas fading while also offering insights towards mitigating, or eliminating, its onset.

Introduction

Polyethylene is inherently susceptible to degradation. The deteriorative reactions responsible for this degradation occur readily during processing, as a result of the polymer being exposed to combinations of oxygen, elevated temperatures, and mechanical stress, as well as throughout the lifecycle of the manufactured article. As a result, the incorporation of additives such as stabilizers has become critical in order to improve and maintain the properties of the final polymer [1]. While there are an abundance of stabilizers available to the polyethylene industry, the combination of a primary antioxidant (hindered phenolic) and a secondary antioxidant (organophosphite) is by far the most relevant and abundant. The reasoning for this is that primary and secondary stabilizers perform synergistically to protect the polymer from various degradants produced during the oxidation cycle (Schemes 1 and 2). The effect is that the combination is often greater than the sum of each individual species at a consistent loading level [2].

$$ROO\cdot + PhOH \rightarrow ROOH + PhO\cdot$$
and/or
$$RO\cdot + PhOH \rightarrow ROH + PhO\cdot$$
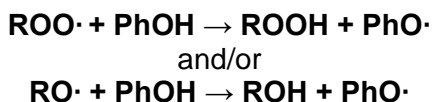
Scheme 1 Primary antioxidants quench radicals through an H-transfer mechanism [1]

$$ROOH + P(OR)_3 \rightarrow O=P(OR)_3 + ROH$$
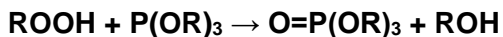
Scheme 2 Secondary antioxidants decompose hydroperoxides in a non-radical mechanism [3]

While this synergistic relationship can provide ideal processing and long-term stability to the polymer, a significant proportion of polymer discoloration can be directly attributed to the over-oxidation of primary antioxidants. More specifically, the oxidation of primary antioxidants is known to produce highly colored, multi-conjugated quinoidal species [4]. As the primary antioxidant stabilizes the polymer via Scheme 1, discoloration becomes evident immediately following extrusion. Alternatively, discoloration which develops slowly over time during storage is commonly referred to as gas fading. Gas fading is associated with the nitration and oxidation reactions of primary antioxidants with nitrogen oxide species (NO_x) found in atmospheric exhaust fumes (Scheme 3) [5].
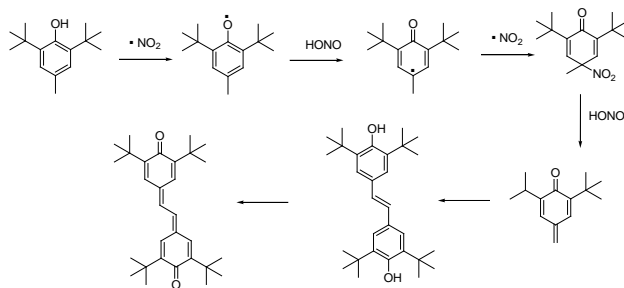
Scheme 3 Proposed gas fading mechanism

Gas fading continues to be one of the most problematic sources of color afflicting the film packaging industry. While there are a number of external factors which can be monitored and controlled in an effort to mitigate the gas fading reaction (i.e. limiting/restricting the use of gas/propane fueled forklifts and heating units, improving ventilation in storage facilities, use of over-wrap film, etc.) it is preferable to control the susceptibility of a polymer to gas fading through the use of an appropriate additive formulation. The selection of appropriate additive combinations, and ratios, can play a critical role in the onset and severity of discoloration associated with gas fading.

In this paper, we provide a few techniques for improving the gas fading performance of traditional stabilization systems containing primary antioxidants. Additionally, the benefits of phenolic-free stabilization systems are discussed.

Experimental

Materials

A Ziegler-Natta octene linear low density polyethylene (LLDPE) resin manufactured by NOVA Chemicals was used for the experimental work in this study. The resin had a solid density of 0.920 g/cm^3 and a melt index of 1.0 dg/min (190°C, 2.16 kg). A summary of antioxidants investigated in this study are compiled in Table 1.

Table 1 Summary of additives used in this study

Additive	CAS#
AO-1	2082-79-3
AO-2	6683-19-8
AO-3	40601-76-1
AO-4	27676-62-6
AO-5	1709-70-2
AO-6	203255-81-6
AO-7	10191-41-0
P-1	31570-04-4
P-2	154862-43-8
HALS-1	65447-77-0
HALS-2	71878-19-8
TiO$_2$-A	13463-67-7
TiO$_2$-B	13463-67-7

Small Scale Compounding

Polyethylene (PE) samples were blended with neat additives at 140°C under inert atmosphere for 5 minutes on a BRABENDER® mixing head blender using stainless steel roller blades.

Multiple Pass Extrusion Studies

Multiple extrusion pass studies were conducted using a LEISTRITZ® twin-screw extruder equipped with a 1.4″screw (33.5:1 L/D), and underwater pelletizing system. PE samples were first extruded at 190°C under inert atmosphere (nitrogen purge). Subsequent passes (one through five) were conducted at 225°C under air. Melt index and color measurements were collected for each extrusion pass. Physical property measurements (i.e. color and melt flow index) were conducted in accordance with standard ASTM test methods. High performance liquid chromatography (HPLC) was used to determine additive levels in each of the samples.

Gas Fading and Oven Aging Studies

Gas fading studies were conducted by exposing compression molded plaques in an atmospheric fume chamber at 60°C, consistent with AATCC Test Method 23-1999 "Colorfastness to Burnt Gas Fumes". PE samples were removed from the gas fading chamber at regular intervals and color measurements were taken.

Oven aging was conducted by exposing compression molded plaques in a Blue M® circulating oven at 60°C in the absence of burnt gas fumes. PE samples were removed from the oven at regular intervals and color measurements were taken.

Results and Discussion

Single Stabilizer Performance

Seven different primary antioxidants (AO-1 to AO-7) in LLDPE were evaluated for their susceptibility to gas fading. Each LLDPE sample was formulated with 250 ppm of primary antioxidant and 1000 ppm of P-1 secondary antioxidant. Figure 1 summarizes the change in yellowness index following 28 days exposure to an atmospheric fume chamber (~2-3 ppm NO$_x$).
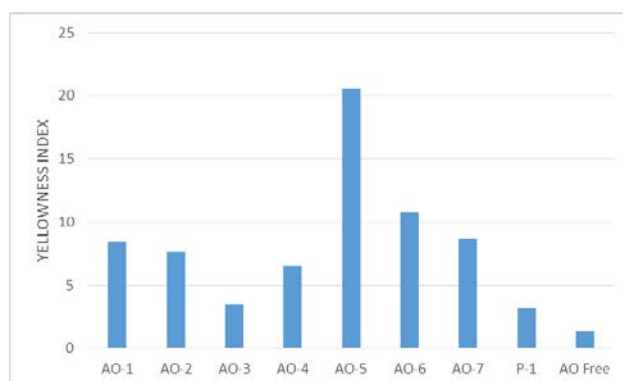

Figure 1 Propensity for gas fading of select primary antioxidants

It is relevant to note that all primary antioxidants are vulnerable to gas fading though some are less prone than others. In particular, AO-3 and AO-4 were less susceptible to gas fading as a result of the isocyanurate back bone in their structure which is more resistant to forming conjugated structures and thus colored species. In the case of AO-3, the gas fading performance was similar to that of a phenol-free system containing only secondary antioxidant P-1. Additional criteria, such as the steric hindrance of the phenolic moiety and molar activity (i.e. relationship between number of phenolic groups present per molecule of stabilizer and the molecular weight of the stabilizer) play a critical role in the severity of discoloration associated with gas fading. Previous literature has drawn conclusions to the fact that elevated melt stabilization performance is often associated with higher degrees of discoloration [6]. In other words, achieving the same level of stabilization with AO-3 as AO-1 may require higher levels AO-3 which could eventually off-set the color performance

advantage. Regardless, understanding the relationship between the type and usage levels of various primary antioxidants is a valuable strategy for mitigating gas fading. It is equally important to understand the potential interactions of a primary antioxidant with other additives in a given formulation.

Additive Interactions

As previously mentioned, primary and secondary antioxidants are commonly used in combination to provide a synergistic stabilization package. The combination of a secondary antioxidant with a primary antioxidant also provides substantial suppression to the severity of discoloration associated with gas fading. Figure 2 illustrates the gas fading performance of LLDPE resin samples prepared using a mixing head blender containing no antioxidant, 500 ppm of primary antioxidant only, 500 ppm of secondary antioxidant only, and a combination of 500 ppm primary and 500 ppm secondary antioxidant.
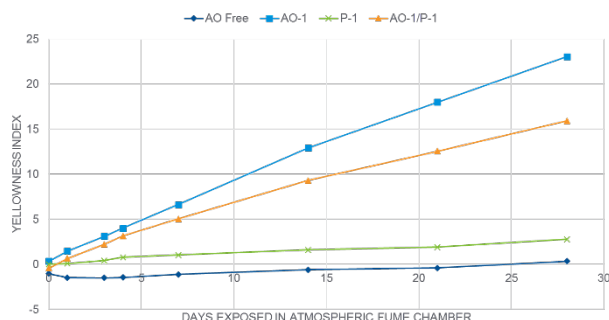
Figure 2 Comparison of gas fading performance of LLDPE resin containing various stabilization systems

While the incorporation of a secondary antioxidant in combination with a primary antioxidant does not completely alleviate the discoloration associated with gas fading, it was capable of significantly reducing the effect. Further improvements are made possible by varying the ratio of primary to secondary antioxidant, which will be discussed later in this paper.

Conversely, there are a number additives species which can exacerbate the discoloration associated with gas fading. One example are hindered amine light stabilizers (HALS). HALS are radical quenching stabilizers, similar to primary antioxidants, which all contain a similar piperidine-type active moiety. The functionality of this active moiety will not only control the stabilizing efficiency and kinetics of the stabilizer, but also its alkalinity and reactivity with other additives. The antagonistic interaction between HALS and primary antioxidants is well documented [7, 8, 9] and is commonly attributed to the formation of highly chromophoric species. Figure 3 compares effect of interactions between two different HALS with AO-1.

Small samples were blended on the mixing head blender and evaluated for gas fading performance. P-1/AO-1 contains 500 ppm P-1 and 500 ppm AO-1, HALS-1 and HALS-2 contain 5000 ppm of each additive respectively. All other samples contain 500 ppm AO-1, 500 ppm P-1 as well as the specified loading level of HALS
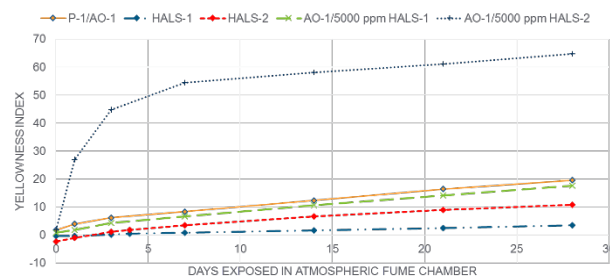
Figure 3 Influence of select HALS on gas fading performance.

Figure 3 illustrates that HALS on their own in LLDPE do not severely discolor via gas fading. In fact, HALS-1 performs similarly to P-1 in that almost no discoloration was observed after 28 days exposure in an atmospheric fume chamber, even at loading level of 5000 ppm. HALS-1, which is a less alkaline N-R type system, did not impart any antagonistic effect with regards to gas fading performance in a fully formulated resin regardless of loading level. Alternatively, when the highly alkaline HALS-2 (N-H type) was introduced in combination with a primary antioxidant (AO-1) and secondary antioxidant (P-1), the change in yellowness index was observed to have increased by 3-4 times. The rate and severity of discoloration was also found to be directly correlated with the concentration of HALS-2 present. It is also worth noting that a similar trend was observed when AO-2 and AO-3 were used in place of AO-1, though the overall severity of gas fading of AO-3 remained comparatively low. Figure 4 shows the change in yellowness index for LLDPE resin samples containing AO-1, AO-2, and AO-3, with and without 1500 ppm of HALS-2, following a simulated gas fading experiment.
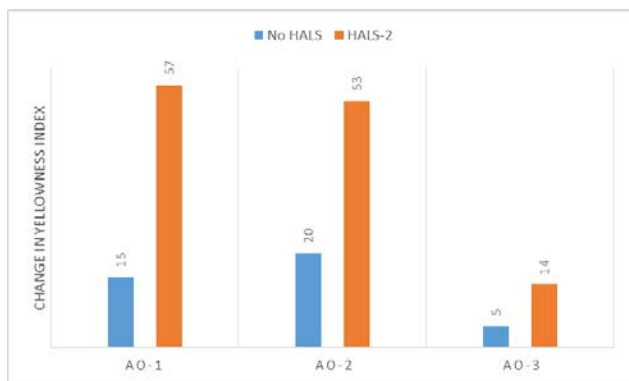
Figure 4 Change in yellowness index of LLDPE resins containing primary antioxidants only and primary antioxidants in combination with HALS-2 after 28 days exposure in an atmospheric fume chamber

Antagonistic interactions were also observed between primary antioxidants and select varieties of titanium dioxide (TiO_2). TiO_2 is one the most common white pigments used in the polymer industry. Surface coated varieties of TiO_2 are often used in the polymer industry as the coating provides improved dispersion, processing, weatherability, and discoloration resistance [10, 11]. Additionally, the surface coating of TiO_2 can prevent unwanted surface chemistry which can promote oxidation of primary antioxidants and accelerate the gas fading reaction [12].
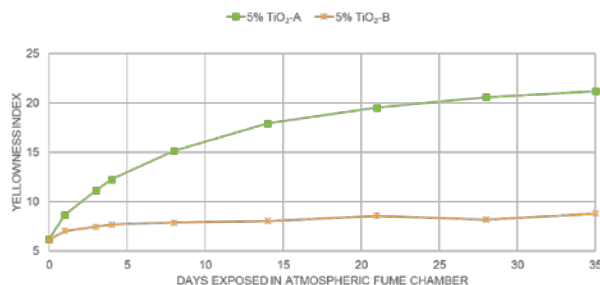

Figure 5 Influence of TiO_2 surface coating on gas fading performance

Two commercial varieties of TiO_2 with different surface coatings were compared for their contribution to gas fading discoloration (TiO_2-A and TiO_2-B). Mixing head blends of LLDPE resin containing 500 ppm AO-1 and 500 ppm P-1 were prepared along with 35,000 ppm TiO_2 (via 5% letdown of 70% commercial masterbatch) and subjected to accelerated gas fading conditions for 28 days. Figure 5 clearly illustrates the significant impact that the surface coating of the TiO_2 filler can have on gas fading discoloration.

Effect of Extrusion History

A polymer may be subjected to multiple heat histories throughout its life cycle. A multiple extrusion pass study can often be used to simulate this life cycle of a resin and compare the performance of various stabilization systems and the overall performance of a polymer [13]. The first extrusion (Extrusion Pass 0) mimics the pelletization of commercial resin by the PE producer and is typically conducted under mild conditions and nitrogen purge. Extrusion Passes 1-3 are often referred to as the commercial processing zone and are representative of the polymer state during extrusion at a PE converters facilities. Finally, Extrusion Passes 4-5 are often used to simulate the addition of re-processed material into the converters blend. A multiple extrusion pass study was conducted on an LLDPE resin containing 500 ppm P-1 and 500 ppm AO-2. The changes in color, melt flow index and antioxidant health were monitored for each pass and are summarized in Table 2.

Table 2 Multiple extrusion pass study of LLDPE resin

Extrusion Pass	I_2 (g/10 min)	Color (YI)	Active AO-1 (%)	Active P-1 (%)
0	0.98	-2.1	95	96
1	0.86	1.6	91	52
3	0.51	4.8	88	9
5	0.32	6.4	82	0

As would be expected, the melt index of the resin begins to decrease with successive heat histories as the polymer begins to cross-link. Additionally, the antioxidants are consumed in the process of protecting the polymer against thermo-oxidation. The secondary antioxidant is consumed most rapidly in an effort to preserve the longevity of the primary antioxidant. As the antioxidants are consumed, the polymer begins to discolor which is observed by an increase in the yellowness index of the resin. A gas fading study was conducted on samples from Extrusion Passes 0, 1, 3, and 5 to compare the rate of gas fading discoloration as a result of extrusion history (Figure 6).
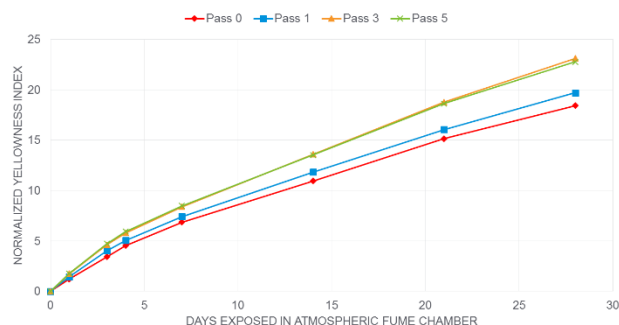

Figure 6 Gas fading correlation with extrusion pass

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The data presented in Figure 6 illustrate that the rate and severity of discoloration associated with gas fading is moderately dependent upon the extrusion history of the resin. With increasing number of passes through an extruder, and resulting consumption of antioxidants, the rate of gas fading increases. It is worth noting that the rate and severity of discoloration for Passes 3 and 5 are essentially equal. This observation suggests that the two key parameters which impact the gas fading reaction are the health of the secondary antioxidant as well as the total level of primary antioxidant available within the resin.

Often times an antioxidant masterbatch may be employed by converters in order to provide supplemental stabilization to a resin, particularly in situations where high levels of reprocessed material are being added back into the formulation. A study was carried out where the gas fading discoloration of an LLDPE resin was compared against samples in which additional stabilizer was added in the form of a masterbatch. A mixing head blender was used to deliver additional antioxidant to an LLDPE resin already containing 500 ppm P-1 and 500 ppm AO-1 which had previously been exposed to a heat history. The P-1 MB delivered an additional 1000 ppm of P-1, the AO-1 MB delivered an additional 1000 ppm of AO-1 and the P-1/AO-1 MB delivered an additional 500 ppm P-1 and 500 ppm AO-1. Figure 7 illustrates the normalized rate of change in yellowness index as a result of exposure to an atmospheric fume chamber.
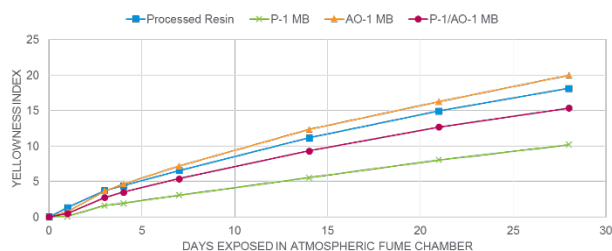

Figure 7 Effect of adding supplemental stabilizer on the rate of gas fading discoloration

These data show clearly that the rate of gas fading is directly related to the amount of primary antioxidant present as well as the health of the secondary antioxidant. The addition of an AO-1 only masterbatch provides additional melt stabilization to the polymer, but also increases the susceptibility of the final formulation to gas fading discoloration. Alternatively, the addition of a P-1 only masterbatch can significantly reduce the rate of gas fade discoloration while the addition of a blend of P-1 and AO-1 may also slightly reduce the rate of discoloration. These trends may be explained by examining the health of the antioxidants for each of the samples. A summary of the measured antioxidant activity levels is presented in Table 3.

Table 3 Measured antioxidant activity

Sample	Active AO-1 (%)	Active P-1 (%)	Ratio of Phenolic:Phosphite
Processed Resin	84	31	1:1
P-1 MB	87	73	1:3
AO-1 MB	81	58	3:1
P-1/AO-1 MB	84	74	1:1

The processed resin started with a relatively high level of active AO-1 antioxidant (84%) though P-1 was heavily consumed (31% active remaining). The addition of the AO-1 only MB increases the total amount of stabilizer present though the ratio of AO-1 to P-1 is now significantly higher than the original sample (3:1 rather than 1:1). The higher level of primary antioxidant is then also available to form colored species. Alternatively, the addition of P-1 only masterbatch not only increases the ratio of secondary to primary antioxidant, it also results in a higher overall activity of both AO-1 and P-1 antioxidants (87% and 73%, respectively). Finally, the combination of both AO-1 and P-1 yields the same ratio of primary and secondary stabilizer, but results in a significantly higher level of active P-1 (74%), which is then available to stabilize the primary antioxidant and suppress further discoloration. The observations made in this experiment support the hypothesis in the previous experiment whereby the gas fading reaction is strongly dependent upon the health of the secondary antioxidant, the amount of primary antioxidant available within the resin, and, to an extent, the ratio of primary to secondary antioxidant in the stabilization system.

Phenol-Free Stabilization Systems

While there are a number of different techniques and considerations for improving the gas fading performance of traditional stabilization systems, the most effective approach to prevent discoloration is to completely remove the primary antioxidant [14]. Figure 8 depicts a gas fading study that was conducted in order to compare the gas fading susceptibility of a traditional stabilization system (P-1/AO-1 loaded at 500 ppm each) against a phenol-free stabilization system (P-1/P-2 loaded at 750 ppm and 450 ppm, respectively).
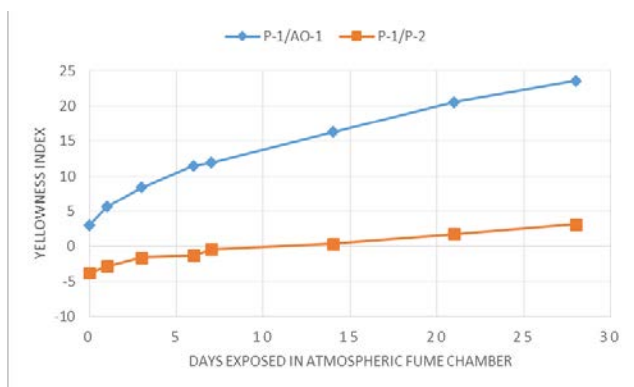
Figure 8 Gas fading performance of conventional primary / secondary AO system compared to phenol-free stabilization system

Phenol-free stabilization systems are capable of providing comparable melt flow stabilization when compared with traditional stabilization systems, while also providing improved color performance resulting from both gas fading and processing. A multiple extrusion pass study was performed to compare the color and melt flow stability performance of traditional stabilization system and a phenol-free stabilization system. The P-1/AO-1 resin contains 500 ppm of P-1 and 500 ppm of AO-1 while the P-1/P-2 resin contains 750 ppm P-1 and 450 ppm P-2. Figures 9 and 10 reveal that a phenol-free stabilization system can provide processing color equivalent to that of an unstabilized resin while also providing melt flow stabilization equivalent to that of a traditional stabilization system.
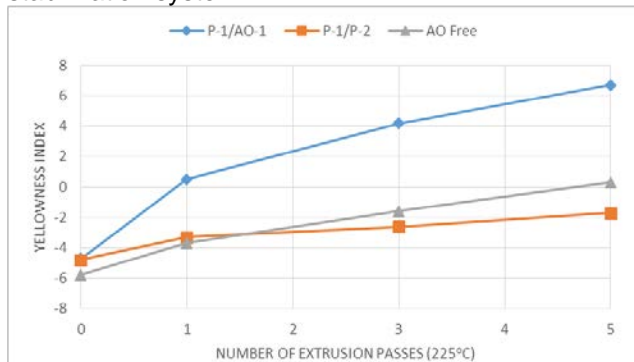
Figure 9 Color performance comparison of a traditional stabilization system (P-1/AO-1), a phenol-free stabilization system (P-1/P-2), and an unstabilized resin (AO Free) in a 1.0 MI LLDPE resin
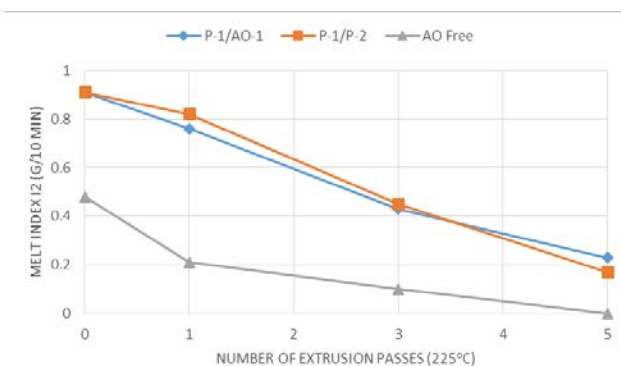

Figure 10 Melt flow stabilization performance comparison of a traditional stabilization system (P-1/AO-1), a phenol-free stabilization system (P-1/P-2), and an unstabilized resin (AO Free) in a 1.0 MI LLDPE resin

High performance secondary antioxidants, and in particular hindered aryl phosphites such as P-1 and P2, can often exhibit stabilization efficiency equivalent to or sometimes better than that of primary antioxidants. The justification for this is that at elevated temperatures (>180°C) hindered aryl phosphites become susceptible to hydrolysis type reactions which yield both a hydrogen phosphite as well as a phenol species, both of which are active antioxidants for the stabilization of polyethylene [3].

Conclusions

The rate, severity, and susceptibility of LLPDE resins to discolor as a result of a gas fading reaction was investigated. Discoloration was found to be directly correlated with the presence of primary antioxidants and their interactions with other additives in the polymer matrix. Antagonistic interactions with other additives such as HALS and TiO_2 were found to exacerbate the discoloration of the resin. Alternatively, secondary antioxidants can be used synergistically to suppress the effect of gas fading. The degree of oxidation of both the polymer and primary antioxidant have minimal significance on the rate and severity of discoloration. The gas fading reaction appears to be dependent upon the loading level of primary antioxidant and health of the secondary antioxidant. With that in mind, it is pertinent to select an appropriate stabilizer masterbatch for addition to heavily processed resin, or resin containing elevated levels or reprocessed material, in order to minimize the final materials susceptibility to discoloration.

While it is possible to control and even reduce the amount of discoloration through the appropriate selection of co-stabilizers and fillers/pigments, it is also important to note that all primary antioxidants are prone to the formation of colored species either during

processing or through gas fading reactions. Ultimately, the most effective means of reducing or even eliminating discoloration associated with gas fading and processing is through the use of a phenol-free stabilization system.

Recommendations

Film converters who require the combination of primary antioxidants and HALS (i.e. outdoor applications such as shingle wrap, mulch, etc.) should consider the use of a low interaction HALS system (e.g. HALS-2). Considerations should also be made for using TiO_2 (as well as other fillers such as talc and SiO_2) which has an optimal surface coating for reducing the interaction with primary antioxidants.

If a supplementary stabilizer masterbatch is required for a given application, considerations should be made to use either an elevated ratio of secondary antioxidant, or even a masterbatch which contains only secondary antioxidant, in order to best minimize discoloration of the final resin.

Acknowledgements

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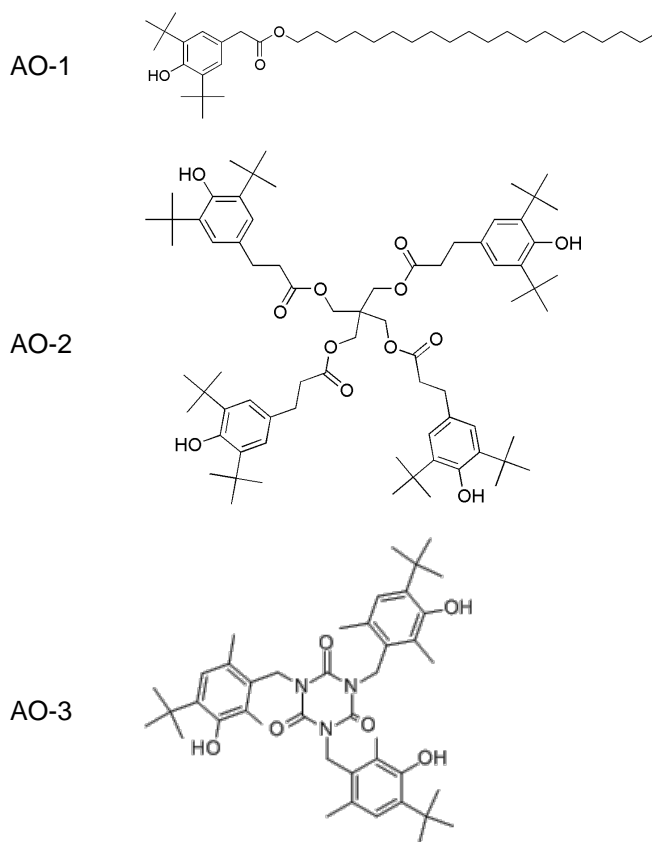BLUE M® is a registered trademark of TPS, LLC.
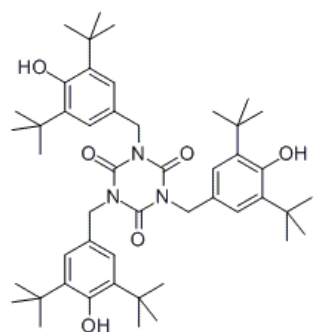
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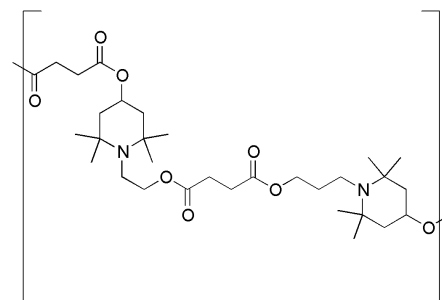
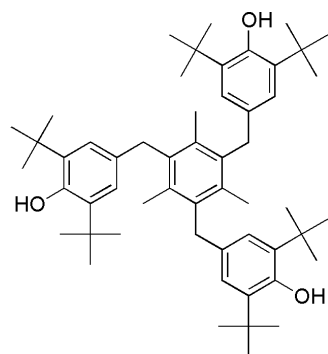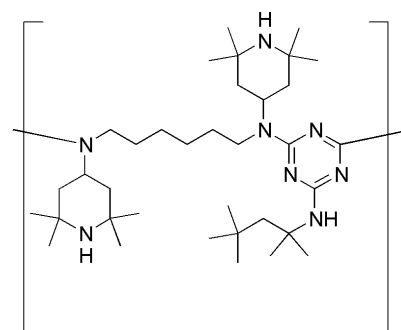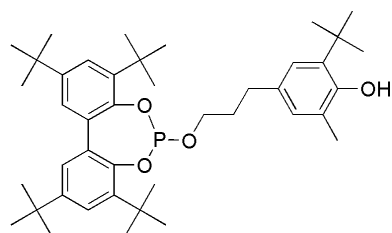## Appendix

Antioxidant Structures

AO-1

AO-2

AO-3

AO-4

HALS-1

AO-5

HALS-2

AO-6

AO-7

P-1

P-2