Title: The Influence of Polymer Process Additives (PPAs) and Hindered Amine Light Stabilizer (HALS) Combinations in LLDPE Blown Film Applications: Part IIB

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The Influence of Polymer Process Additives (PPAs) and Hindered Amine Light Stabilizer (HALS) Combinations in LLDPE Blown Film Applications: Part IIB

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ABSTRACT

Hindered Amine Light Stabilizers (HALS) are often used as the technology of choice to create polyolefin film products that can endure prolonged contact with the damaging effects of sunlight such as UV radiation. As such, industry segments such as heavy duty shipping sacks, silage, mulch, tunnel and greenhouse films are thriving. In these high value applications, it is important to reap the greatest benefit by maximizing the effect of the various additive chemistries, while minimizing the potential negative effects of additive interference. Since Polymer Processing Additives (PPAs) are often used in the LLDPE film products that go into these type of applications, it is important to understand if the HALS/PPA additive chemistry is synergistic, neutral or negative. To date, there has been no documentation of a negative effect regarding the impact of PPA on the effectiveness of HALS This study confirms, in detail, that there is no negative interaction (by examining combinations of three different PPA and five different HALS). In fact, there appears to be a boost in the performance of one of the HALS when used in combination with a PPA.

INTRODUCTION

The objective of this work was to elucidate the impact of polymer processing additives on the performance of hindered amines as light stabilizers during Xenon weathering. The work to date suggests that there is none; however, five different hindered amines were examined in this study in order to generate a data set that will validate that polymer processing additives do not negatively impact the performance of hindered amines in outdoor film applications. Accordingly, if it can be shown that PPAs and hindered amines can be used together without significant interference, it will hopefully lead to more cost-effective z/n-LLDPE and m-LLDPE films for outdoor applications.

BACKGROUND

Polymer Processing Additives (PPAs), which can be used as reagents for eliminating melt fracture in LLDPE blown films, are typically based on fluoropolymers, or proprietary blends of fluoropolymers in combination with other substituents. The PPA works by forming a boundary layer between the metal of the processing equipment and the molten polymer that is flowing through the equipment. In blown film applications, the most important region for the PPA to work is in the land region of the die, where shear rates and shear stresses are extremely high as the molten polymer is squeezed through a narrow die orifice. If the shear rates and shear stresses are not alleviated via the use of a processing additive, the flow of the molten polymer becomes turbulent, and the result is a marred film surface as it shimmies and shakes against the die lips. The resulting films are "melt fractured" due to this flow instability. If processing additive is used, the flow instability is alleviated and the film surface is smooth and clear. [1]

Work has been carried out over the years to try and quantify the impact of various co-additives on the performance of polymer processing additives[2]. As a result of this work, various types of co-additives have been classified as having a positive, neutral or negative impact on the performance of the polymer processing additive. For example, it has been shown that antioxidant and melt processing stabilizers can contribute to improved efficiencies regarding use levels of PPA necessary to eliminate melt fracture.[3] On the other hand, negative interactions have been documented as well. Recent work made a further attempt at quantifying the potential to observe this negative impact using two measures: 1) the time it takes to eliminate melt fracture during blown film experiments, 2) the amount of additional PPA that is necessary to eliminate melt fracture within a given period of time[4]. One type of co-additive that was shown to have a negative impact on the performance of the PPA was a hindered amine light stabilizer (HALS) such as HALS 3. (See Appendix 1).

The mechanism of the impact of HALS 3 on PPAs is not known, however there are two ongoing hypotheses. One hypothesis is based on the potential for a competition of the HALS and the PPA for the surface of the processing equipment. If the hindered amine can compete for the open coordination sites (partially hydrated metal oxide) of the processing equipment, then the mechanism by which the PPA works (forming a layer on the surface of the processing equipment) is impaired. Another hypothesis is based on the potential reactivity of relatively alkaline sites on the hindered amine and relatively acidic sites on the fluoropolymer. If a hindered amine can promote the dehydrofluorination of the fluoropolymer, then double bonds could be formed within the fluoropolymer. These double bonds are then susceptible to molecular weight enlargement, or crosslinking, reactions. If the unsaturated fluoropolymer does start to crosslink, it is hypothesized that the resultant higher molecular weight fluoropolymer may not function as effectively as a PPA to eliminate melt fracture during blown film operations.

Technical Challenge

While these initial range-finding studies have clearly elucidated the potential negative impact of a hindered amine, such as HALS 3, the effect of other types of hindered amines, such as HALS 1, was shown to have less of negative impact. Since the initiation of this rangefinding work in 1986, a variety of new PPA and hindered amines have been developed to solve ongoing challenges in the plastics industry. The point of this mutual study is to examine new hindered amines and PPA in regard to this interference; both in the elimination of melt fracture as well as the potential impact of the PPA on the effectiveness of HALS as light stabilizers. (See also the preceding paper, "The Influence of Polymer Process Additive (PPA) and Hindered Amine Light Stabilizer (HALS) Combinations in LLDPE Blown Film Applications: Part IIA[5]. In Part 2A of this study, we examined the impact of various HALS on rate of elimination of melt fracture, focusing on PPA-1. In Part IIB of this study, we are focusing on the UV stability of those films in order to determine the impact, if any, of different PPAs on the effectiveness of the HALS. Those in the field who are already using PPA-1 in blown film applications requiring outdoor stability are put in a position of whether or not they can effectively and/or efficiently use a proven light stabilizer, such as HALS 3, or need to formulate around it with another HALS and/or PPA. This work should address those concerns.

Experimental Design

Blown films were produced on a Kiefel blown film line, consisting of a 40 mm grooved feed extruder, 24/1 L/D, 18/35/60 mesh screen pack, using a 2 mm die gap and a single lip air ring. The output was ~14 kg/hr, running at 232°C (450°F). To determine the impact of the hindered amines on the effectiveness of the various PPAs a narrow die gap was used (1.14 mm). A set of film samples were also prepared for weathering studies in a Xenon Weatherometer using a wider die gap (2 mm) in order to avoid gross melt fracture. The base polymer for this work was an ethylene/octene solution phase zn-LLDPE copolymer (1 MI, 0.92 density). All PPA levels were held constant at 1000 ppm; all UV stabilizers at 1500 ppm. Three different PPAs and five hindered amines were examined. See Appendix 1 for the structure/attributes of the various HALS.

NOTE: PPA-1 = Dynamar™ FX 9613
PPA-2 = Dynamar™ FX 5920A
PPA-3 = Dynamar™ FX 5911

The conditions for the Xenon Weatherometer were as follows: Cycle = 108 minutes of light and 12 minutes of light and spray; Irradiance = 0.35 watts/m^2; Black Panel Temperature = 63°C, modeling ASTM G26-95. Retention of physical properties were measured on an Instron 1130 Tensile Tester using a modification of ASTM D882-91; 50 cm/min draw rate; 5 cm gauge length, using a Type V tensile bar die cutter that was used to cut test specimens from the exposed film sample (~90 microns, 3.5 mils). Note: The die cutter must have sharp clean edges.

Results

As can be seen in the Graphs 1A-6A for *% Retention of Elongation* and Graphs 1B - 6B for % *Retention of Tensile Strength*, each of the various HALS affords good light stability to the LLDPE film samples. Although all of the film samples have not reached the arbitrary failure point of 50% retained physical properties, the ranking of the HALS in regard to their ability to provide UV stability is as follows (at the 7000 hour Xenon WOM interval):

Good	Better	Better	Best	Best
HALS 1≤	**HALS 2≤**	**HALS 3≤**	**HALS 4≤**	**HALS 5**
(N-R)	(N-CH_3)	(N-H)	(N-H)	(N-OR)

As can also be seen from the various graphs, there is very little effect of the various polymer processing additives on the performance of the hindered amines as light stabilizers. In fact, if there is an effect, it is positive. This was not expected, but seems to be clear improvement, especially for HALS 1 and the PPA. Additional work is currently underway to determine if this effect can be reproduced as well as examining the generality of the apparent trend.

Discussion

As seen in Graphs 1A and 1B, the LLDPE films without any type of UV stabilization (control experiments) fail dramatically (as measured by time to 50% Retained Elongation or Tensile Strength) in less than 1000 hours. If one uses a rough conversion factor of 2000 - 2500 hours of time in the Xenon Weatherometer being equivalent to one year exposure in Florida, then these control experiments would fail in less than 3 - 6 months in the field. Accordingly, one can see the importance of including some type of UV stabilizer system.

In Graphs 2A and 2B, the addition of 1500 ppm of HALS 1 provides a significant improvement to UV stability compared to the control, which is to be expected. What was unexpected was the impact of the various polymer processing additives (PPAs) on apparently enhancing the UV stability afforded by HALS 1. At this time there are no obvious attributes of the fluoropolymer that should lead to an enhancement of UV stability, and the control experiments (with no HALS) bear this out. However, there still seems to be a recognizable impact. For example, the control formulation with 1500 ppm HALS 1 and no PPA affords roughly 4000 hours before dropping below 50% retained elongation. The addition of 1000 ppm of PPA-1, PPA-2 or PPA-3 increases the time to failure to roughly 4500, 5000 and 5500 hours, respectively. This effect of enhancing the performance of HALS 1 via the addition of a PPA was unexpected and further work is underway to better understand this effect.

In Graphs 3A and 3B, it can be seen that the addition of 1500 ppm of HALS 2 provides improved weatherability in comparison to HALS 1. By the 7000 hour interval, three (no PPA, PPA-1, PPA-2) out of the four formulations had almost failed or failed (using the criterion of 50% retained physical properties). By the next interval (9000 or 10000 hours) it is assumed that the formulations with PPA-3 will have failed, but it appears as if this particular formulation (with PPA-3) is the most durable among the four.

In Graphs 4A and 4B, the addition of 1500 ppm of HALS 3 provides a significant improvement in comparison to the performance of HALS 1, and recognizably better than HALS 3, since most of the samples are far from reaching the failure point of < 50% retention of physical properties. However, it can be seen from the graphs that the results at the 7000 hour interval are decreasing as they go down. In regard to the potential impact of the various PPAs on the performance of the HALS, there is no substantial evidence that there is any positive or negative effect, since the film samples have not reached the point of failure.

In Graphs 5A - 6A and 5B - 6B, the addition of 1500 ppm of HALS 4 or HALS 5 affords the greatest UV stability to the LLDPE film samples. At the 7000 hour interval, it can be seen that all of the formulations still retain > 75% retained physical properties. Taking from the discussion above, this correlates (roughly) to 3 - 4 years of outdoor weatherability. Again, in regard to the potential impact of the various PPA on the performance of the HALS, it is difficult to determine if there is any positive or negative effect, since the film samples are still far from failing.

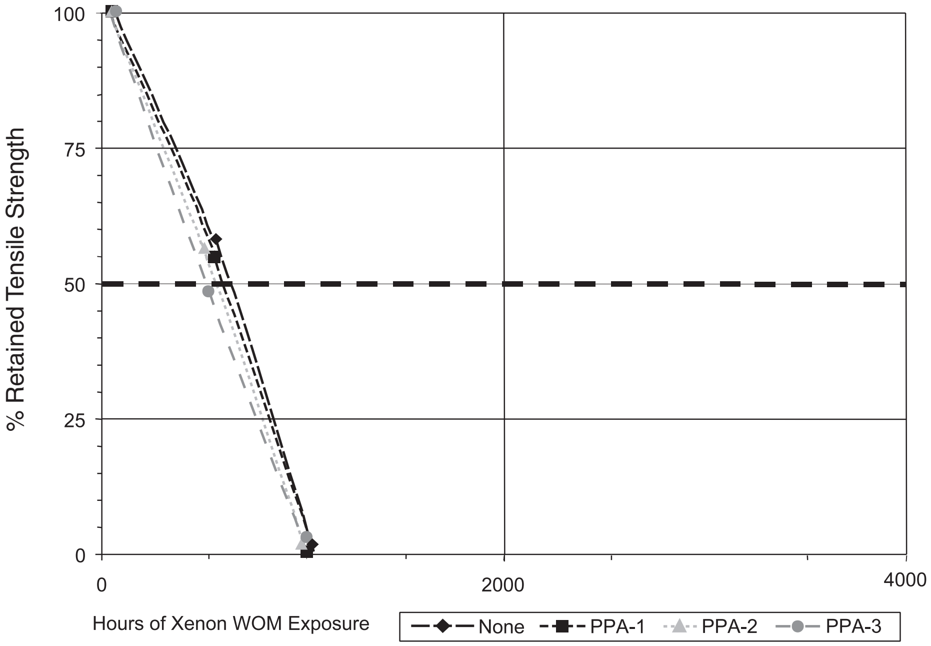
Observations

Many of the film samples lost around 10%-20% of their (% Retained Elongation) during the first 2000 hour interval of Xenon exposure. It is proposed at this time that this loss is not exactly a loss in physical properties, but rather may be due to a re-orientation of the crystalline lamella under the prolonged warmth (63°C) of Xenon exposure. The annealing of the film samples is most likely a reflection of the blown film conditions, and may not be observed in another set of film samples that were prepared differently. It is also interesting to note that there was an increase in % Retained Elongation between 4000-6000 hours of Xenon exposure for HALS 3, HALS 4 and HALS 5. It is not known what may be causing this, but since the samples were randomized during exposure and testing, it appears noteworthy. Additional work is necessary to better understand on a more fundamental level.

Performance of Various Hindered Amines in Xenon Weathering of LLPDE

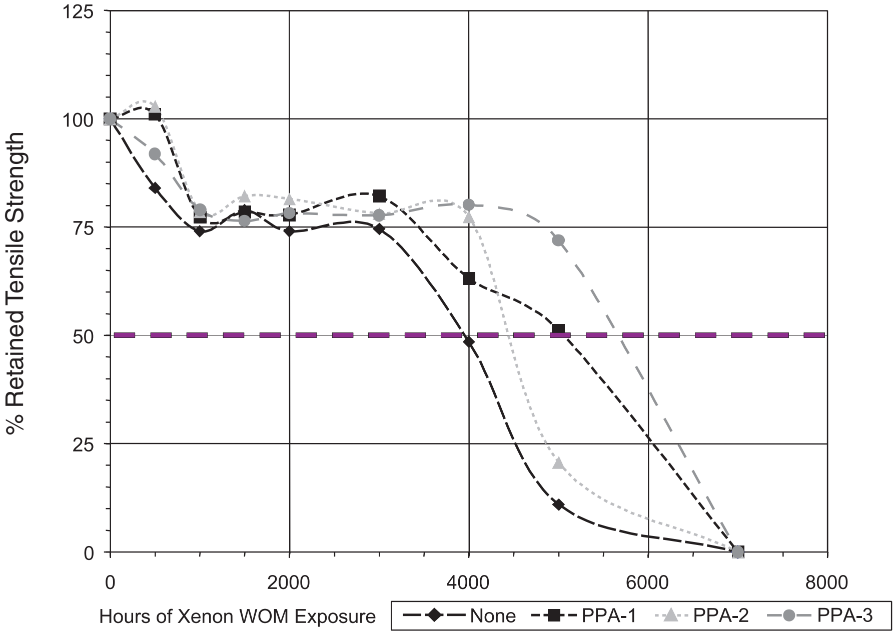
% Retained Elongation Data

Graph 1A: % Retained Elongation with no HALS



Impact of PPAs (1000 ppm) on
UV Stability of LLDPE–**Absence of HALS**

Graph 2A: % Retained Elongation with HALS 1

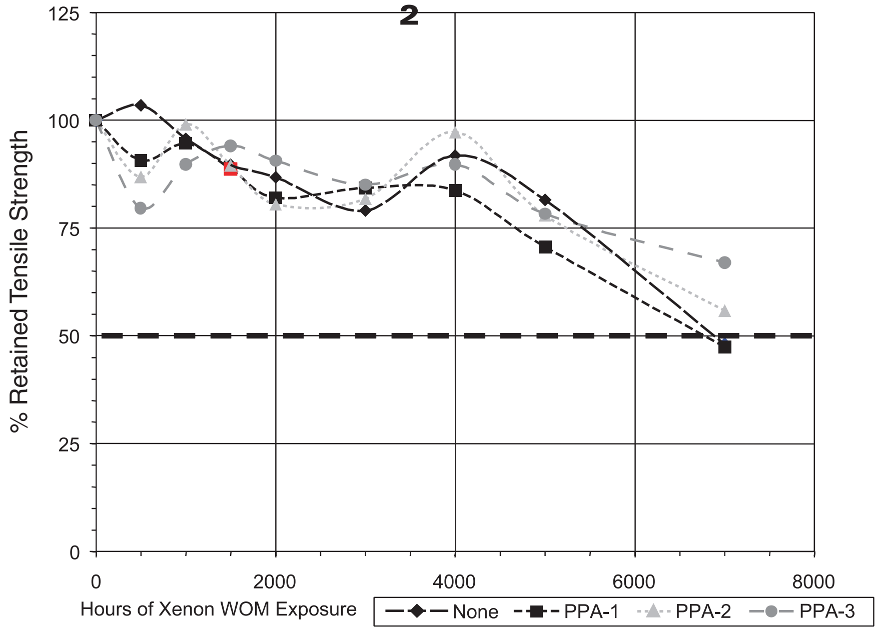


Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-1** (1500 ppm)

Performance of Various Hindered Amines in Xenon Weathering of LLPDE

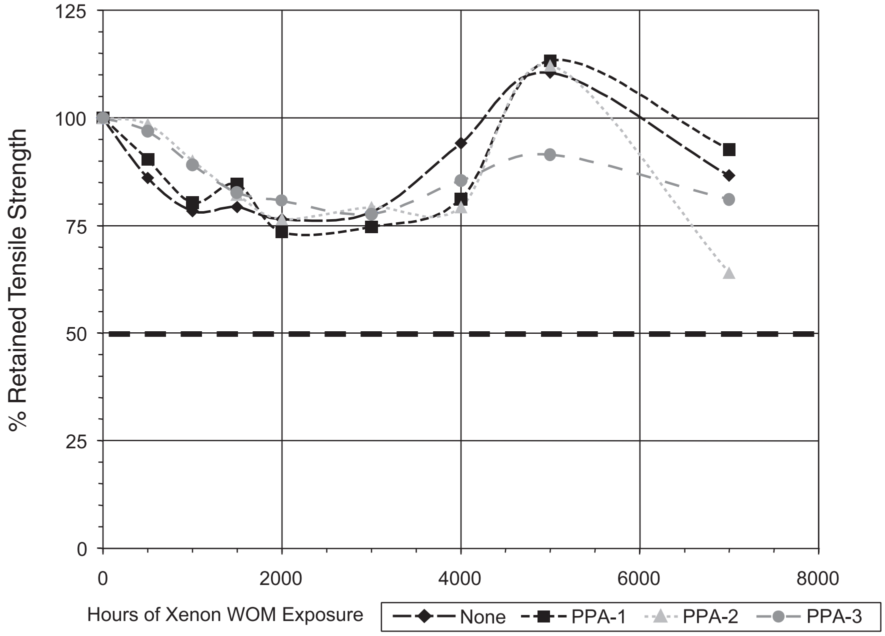
% Retained Elongation Data

Graph 3A: % Retained Elongation with HALS 2



Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-2** (1500 ppm)

Graph 4A: % Retained Elongation with HALS 3

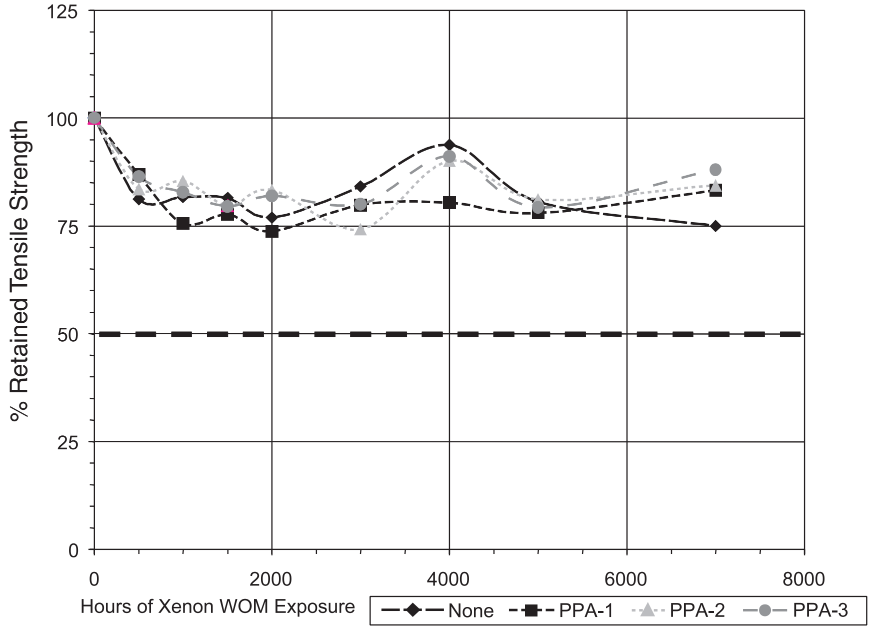


Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-3** (1500 ppm)

Performance of Various Hindered Amines in Xenon Weathering of LLPDE

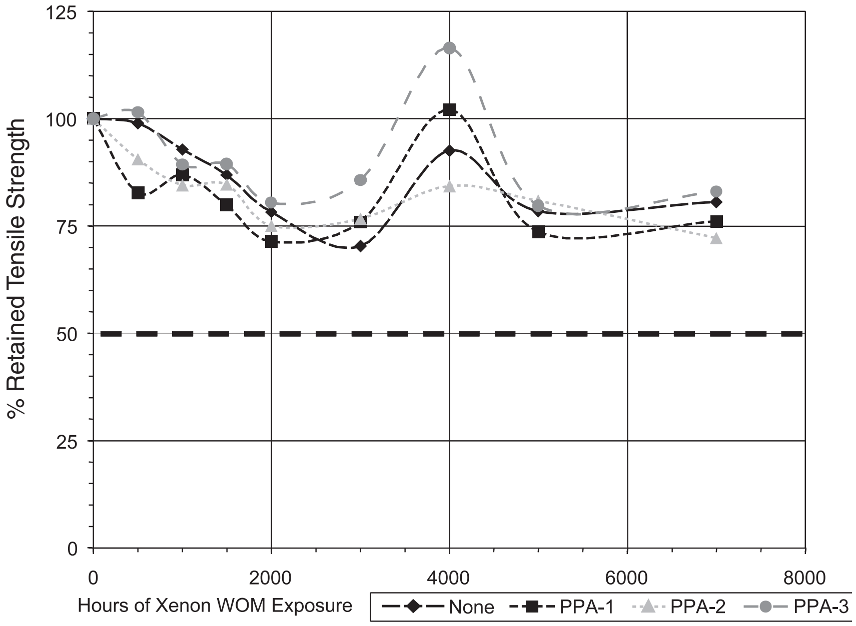
% Retained Elongation Data

Graph 5A: % Retained Elongation with HALS 4



Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-4** (1500 ppm)

Graph 6A: % Retained Elongation with HALS 5

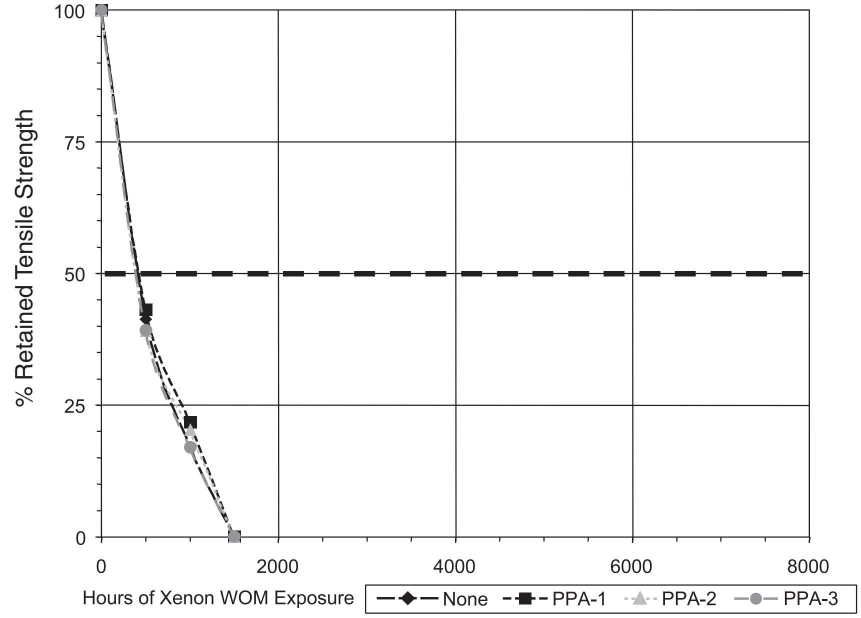


Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-5** (1500 ppm)

Performance of Various Hindered Amines in Xenon Weathering of LLPDE

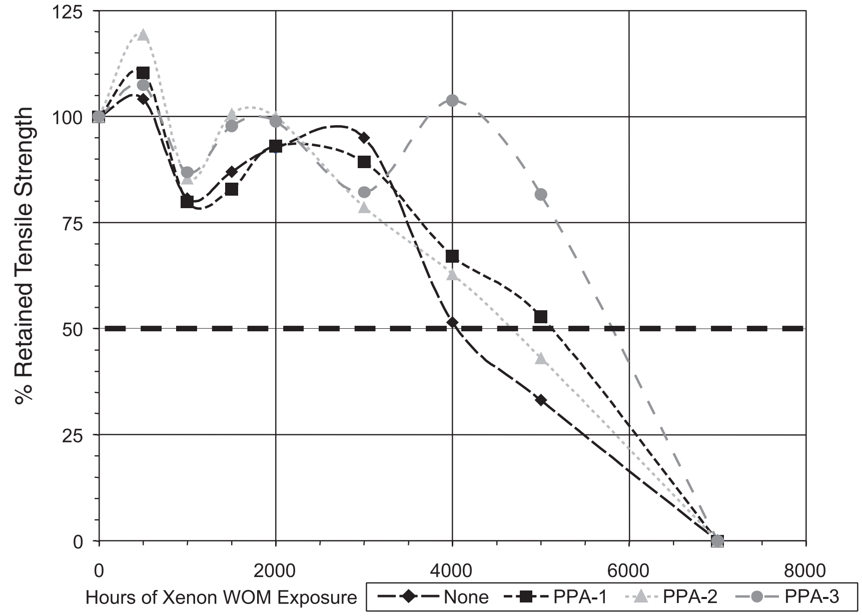
% Retained Elongation Data

Graph 1B: Retained Elongation with no HALS



Impact of PPAs (1000 ppm) on
UV Stability of LLDPE–**Absence of HALS**

Graph2B: Retained Elongation with HALS-1

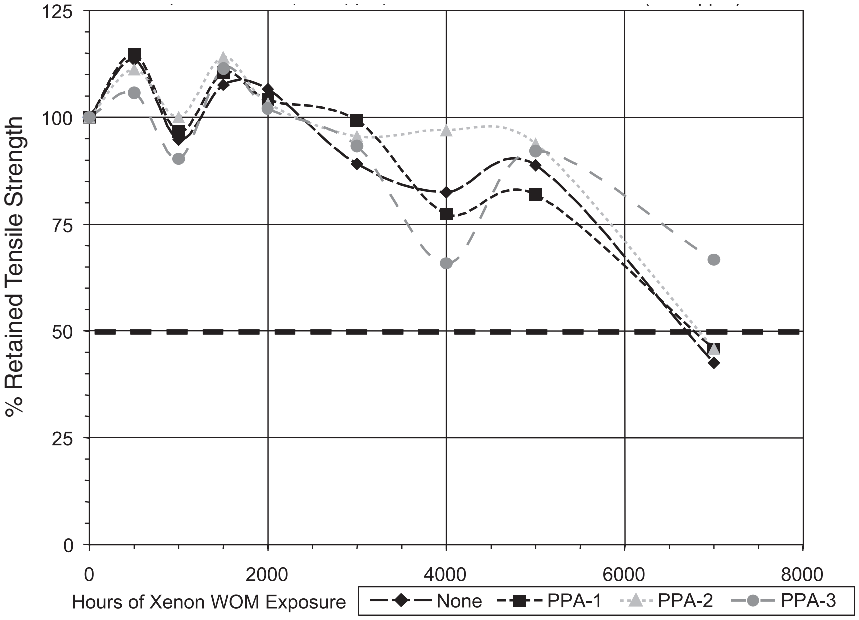


Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-1** (1500 ppm)

Performance of Various Hindered Amines in Xenon Weathering of LLPDE

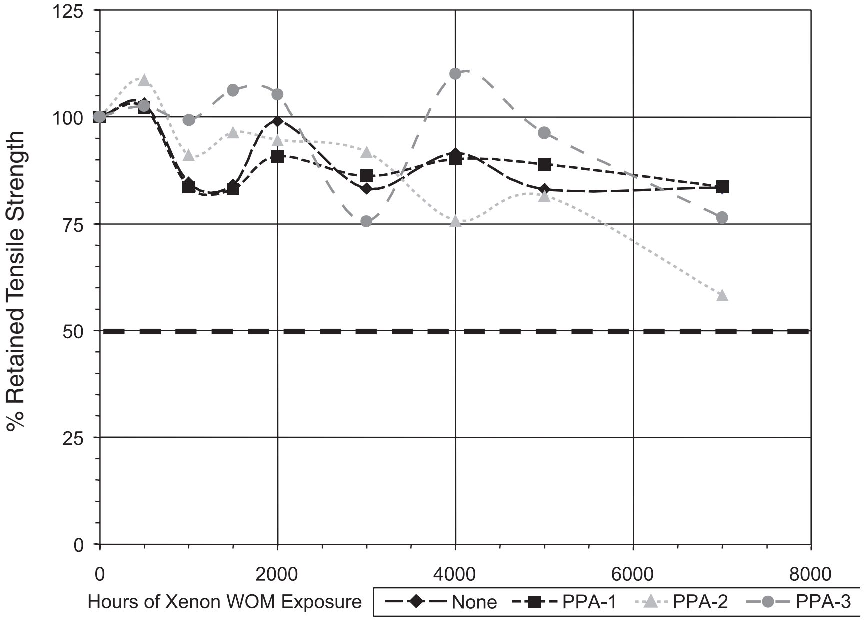
% Retained Elongation Data

Graph 3B: % Retained Elongation with HALS-2



Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-2** (1500 ppm)

Graph 4B: % Retained Tensile Strength with HALS-3

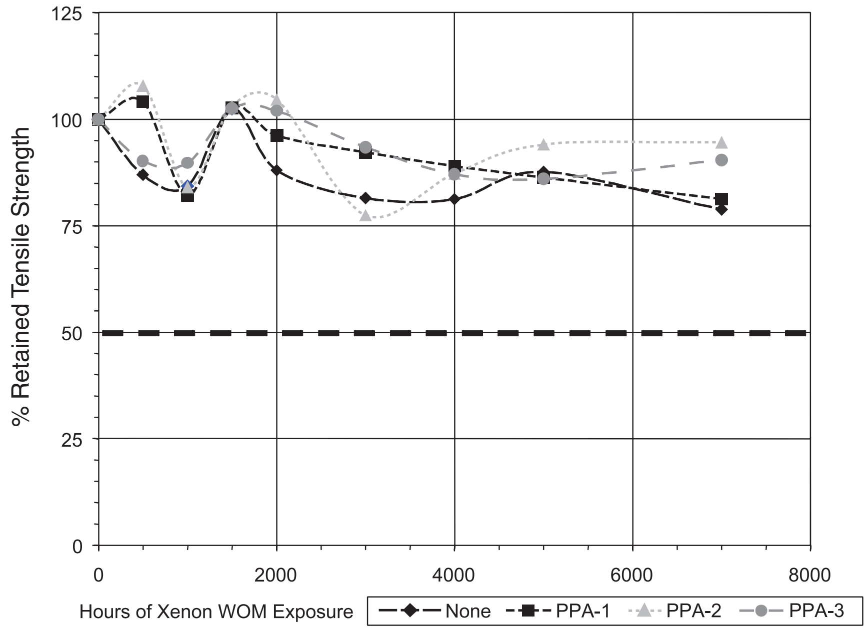


Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-3** (1500 ppm)

Performance of Various Hindered Amines in Xenon Weathering of LLPDE

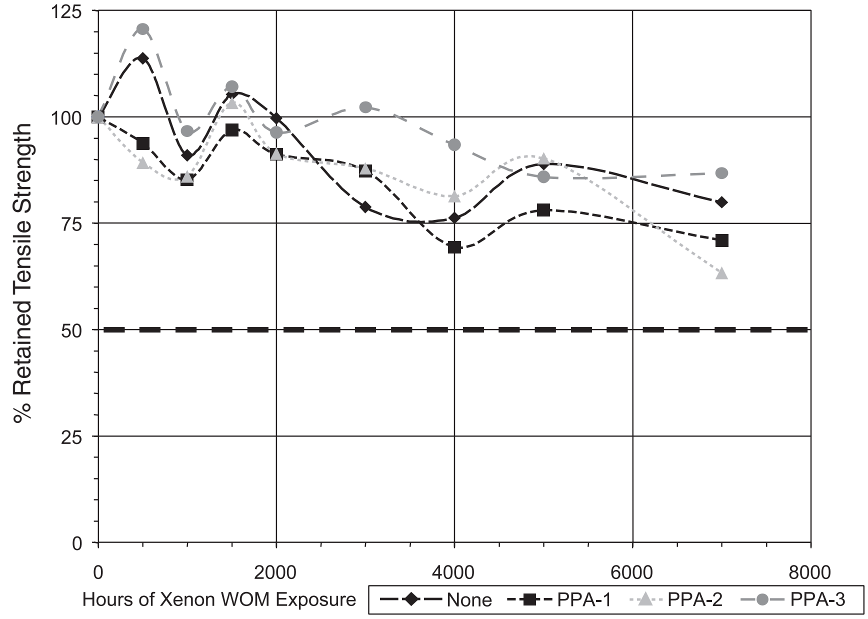
% Retained Elongation Data

Graph 5B: % Retained Tensile Strength with HALS-4



Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-4** (1500 ppm)

Graph 6A: % Retained Tensile Strength with HALS-5



Impact of PPAs (1000 ppm) on
Effectiveness of **HALS-5** (1500 ppm)

Comment on Correlating Xenon Weathering

Over the years there has been a significant amount of discussion regarding "How many hours in the Xenon equals how many hours in the field ?" This paper will not pursue this challenging subject since there are many factors that go into determining if there is "an exact" correlation between Xenon Weathering and outdoor weathering. Based on earlier work, there appears to be a good correlation[6], however, many variables need to be considered.

For example, it is important to realize that substrate selection has an effect on weatherability; e.g., LLDE (typically less than 20 tertiary carbon centers per 1000 carbon atoms) is intrinsically more stable than polypropylene (500 tertiary carbon centers per 1000 carbon atoms) to UV radiation. The base stabilization of the polymer can also have an effect; i.e., a poorly stabilized polymer may be significantly degraded during melt processing. The condition (old, new, dead spots) and operation (temperature, shear rates) of the processing equipment also has an impact on the weatherability of the film. The testing specimen to be weathered (dimensions, thickness, edge roughness, etc.) can also have an effect. In addition, the specific Xenon exposure conditions must be taken into account, i.e., the settings can be changed to meet certain specifications or guidelines. As such, it is the responsibility of the experimentalist to keep track of all these details in order to understand on a fundamental basis what might have affected the results of the weathering study. This does not even draw into discussion the proper deactivation of the polymerization catalyst residues, which can also have a detrimental effect on the weatherability.

Conclusions

To begin with, it should be re-stated that these results are a reflection of the combinations and concentration of the additives in this polymer under these experimental conditions (i.e., using an accelerated weathering device vs. outdoor weathering). While the results fall in alignment with other film studies that we have conducted, they cannot be taken as the definitive results that would be seen in all LLDPE blown films in all types of outdoor weathering. This disclaimer is necessary since there are many variables including polymer quality, processing condition, base stabilization, co-additives, film thickness, exposure conditions, pesticide by-products, etc. that can affect long term UV durability. Accordingly, testing under field conditions is the best indicator of long term UV durability.

On the other hand, these results demonstrate, nevertheless, that these films are very well stabilized for simple types of outdoor weathering and that there is a relatively clear ranking in the performance of the hindered amines. These results also clearly demonstrate that the addition of up to 1000 ppm of the various PPAs does not detract from the durability of the film samples. In selected formulations, the performance is significantly enhanced; most notably with HALS 1 and PPA-3. Further work is underway to determine the reproducibility and the generality of this observation. The remaining two intervals (8500 and 10000 hours), which will be taken later this year, will determine the final results for the remainder of the HALS/ PPA combinations.

Recommendations

It is clear from this work that, as expected, Hindered Amines as a general class of stabilizers are excellent for providing UV stability to LLDPE films. Accordingly, it is recommended that where UV stability is required for a particular outdoor film application, such as agricultural film (silage, mulch, greenhouse, etc.) or heavy duty shipping sacks, that HALS be the UV stabilizer of choice for providing good weatherability.[7] Based on other ongoing studies, this work should be applicable to both zn-LLDPE as well as m-LLDPE.

In regard to the Polymer Processing Additive (PPA), it is also clear from this study that the various PPA that were examined do not have a negative impact on the performance of the Hindered Amines as light stabilizers. As such, they can be used in both zn-LLDPE and m-LLDPE containing film systems to eliminate melt fracture without compromising the performance needed for outdoor applications.

A mentioned earlier, in our previous work, we demonstrated that HALS 3 had the most negative effect on the performance of polymer processing additives as measured by time to eliminate melt fracture, whereas HALS 1, HAL-2, HALS 4 and HALS 5 all have less of a negative impact.[4] In the parallel paper that was presented before this paper, "The Influence of Polymer Process Additive (PPA) and Hindered Amine Light Stabilizer (HALS) Combinations in LLDPE Blown Film Applications: **Part IIA**", the authors presented an update on the blown film application side of the story. In this paper, the potential for an interaction between the HALS and the PPA further updated and discussed. It is shown that HALS 3, once again, has a measurable impact on the time to complete elimination of melt fracture. There is be an examination of HALS blends, as well as a new high molecular weight NOR HALS, which represent the state of the art in UV stabilization. It is clearly shown that HALS 1 or HALS 2, as single components, or as binary blends, do not afford the same degree of interaction as HALS-3. Blends of HALS 1 with HALS 3 alleviate the interaction as well a new High Molecular Weight NOR Hindered Amine (specifically designed for outdoor applications where acidic by-products from pesticides may be an issue) also shows less interaction that HALS 3.

Accordingly, it is recommended that zn-LLDPE and m-LLDPE film products that may require both HALS and PPA be considered as excellent substrate opportunities for outdoor weathering applications. If there was a perception that, in general, HALS and PPA could not be used together due to a potential for a negative interaction, this paper (and the preceding paper) offers evidence to the contrary. It should be clear that this interaction could be easily avoided, or at least minimized, by choosing the appropriate PPA and HALS combinations. As such, we hope that both zn-LLDPE and m-LLDPE find a growing market share in films for outdoor applications.

Future Work

The measurement of a potential interaction between HALS and PPA during blown film experiments is complete. The ranking of the HALS and the PPA is clear. All that remains at this point in time is to finish the Xenon weathering for the first and the second set of film samples that were prepared during Part 1 and Part 2 of this study. When those results become available, the work will be published, or made available by an alternative method.

Acknowledgments

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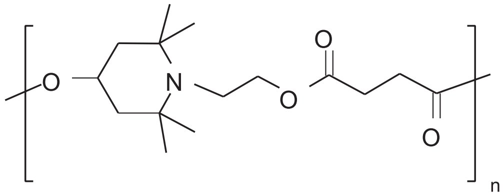
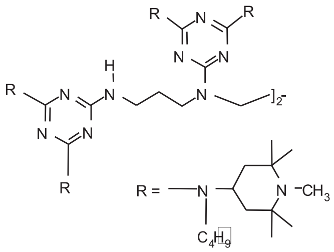
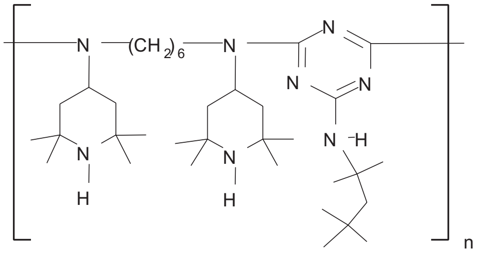
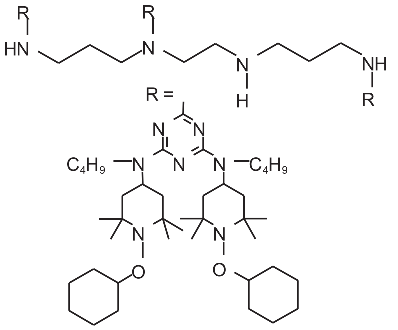
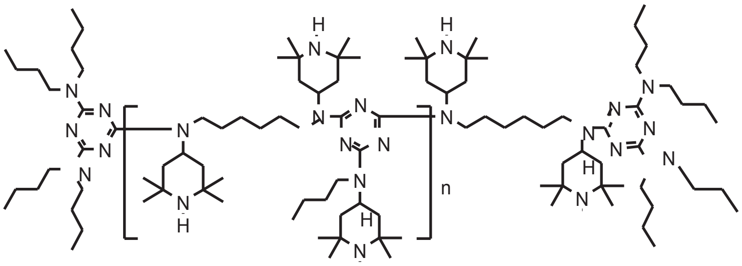
Appendix 1. Description of UV Stabilizers.

Code Class Tradename	Molecular Structure	Stabilizer Function
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)
HA-4 High Molecular Weight Aminoether (N-OR) Hindered Amine CGL-116		UV Stability Long Term Thermal Stability (<135°C)
HA-5 High Molecular Weight Secondary (N-H) Hindered Amine Chimassorb® 2020		UV Stability; Long Term Thermal Stability (<135°C)

See Chart 2C Below: HALS 2B = Cyasorb UV-3529, HMW / Tertiary (N-CH^3) Hindered Amine; HALS 3B = Cyasorb UV-3346, HMW / Secondary (N-H) Hindered Amine; HALS 8 = HMW NOR HALS (Ciba SC).

Appendix 2. Review of UV Stabilization and Issues

A more complete review of UV stabilizers can be found in the open literature. [8a] However, for this paper it may be helpful to cover some of the fundamentals of UV stabilization. The ultraviolet component of sunlight is known to contain the energy necessary to break covalent bonds that comprise organic polymers; see **Scheme 1C**. 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. (You could have any color, as long as it was black, white or shades of gray.) 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. [8b] 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:

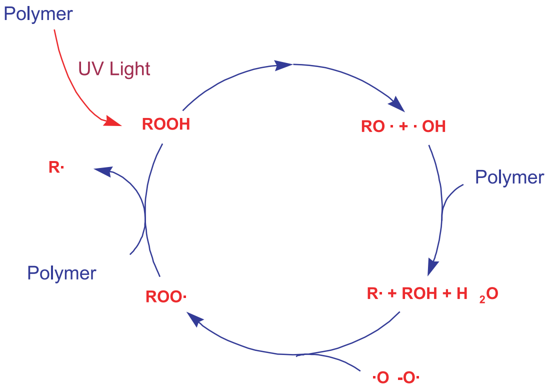
1) UV Absorbing (e.g., hydroxyphenylbenzotriazoles, hydroxyphenyltriazines, or hydroxybenzophenones)

2) Excited State Quenching (primarily based on nickel chelates)

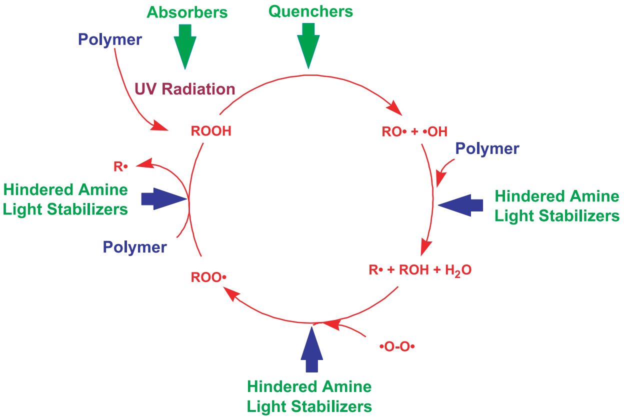
3) Free Radical Scavengers (hindered amine light stabilizers, HALS)

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. [9] "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 Scheme 2C, 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.



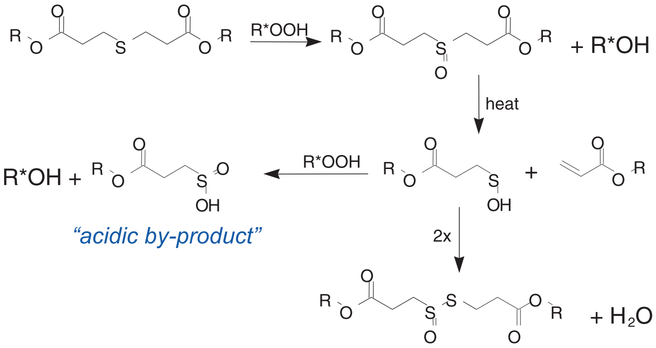
Scheme 1C: Uninhibited photo-oxidation cycle



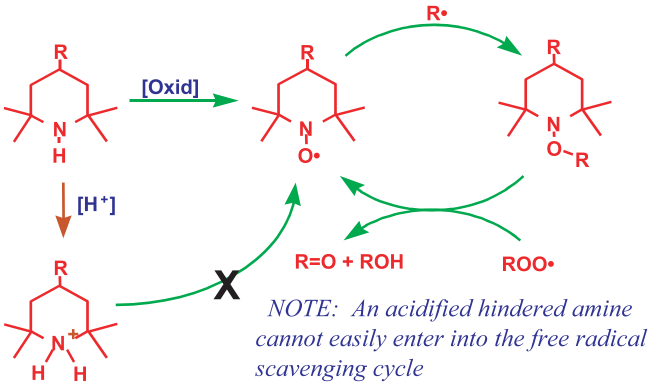
Scheme 2C: Inhibited photo-oxidation cycle

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. [10] The antagonistic relationship is due to the fact that an over-oxidized thiosynergist can lead to sulfenic and sulfonic type acids, see **Scheme 3C**, which can partially deactivate the hindered amine as shown in **Scheme 4C** 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 1C**.



Scheme 3C. Generation of Acidic by-Products via Overoxidation of Thiosynergists.

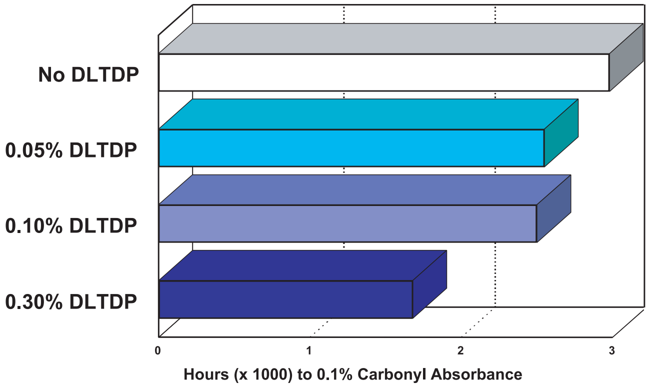


NOTE: An acidified hindered amine cannot easily enter into the free radical scavenging cycle

Scheme 4C. 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 effect 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 (such as HALS X), piperidine esters (such as HALS X), and amino ethers (such as HALS X) as well as piperizinones or piperizinediones.

The "alkalinity" of various hindered amines is illustrated in Chart 2C, where measuring the pKa of the hindered amine is a 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. [11] 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. [NOTE: The alkalinity of the HALS does not have an impact on the potency as a UV stabilizer; it is just an attribute that may potentially contribute to interactions with acidic additives or acidic by-products.] 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.



Polyethylene Containing 0.15% HALS in Xenon Weatherometer Exposure

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

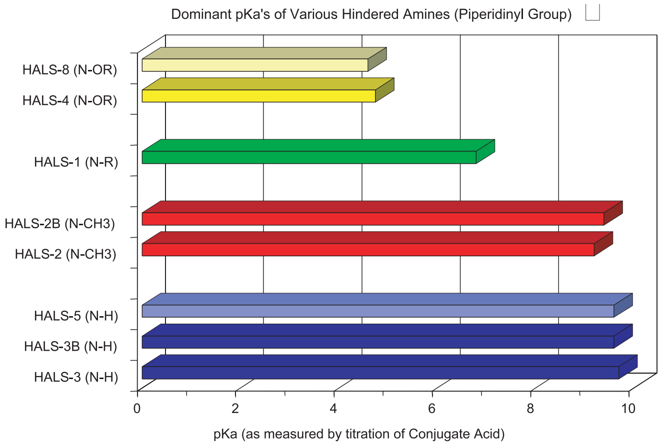


Chart 2C:
Dominant pKa's of the Piperinyl Group of Various Hindered Amines

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