

LIGHT STABILIZATION OF POLYPROPYLENE: AN INDEPENDENT PERSPECTIVE

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Abstract

The photodegradation and light stabilization of polypropylene are reviewed with an emphasis on thick-section applications. Specific topics covered include the chemical mechanism of degradation, undesired morphological changes resulting from the degradation process, chemistry and structure-activity relationships in hindered amine light stabilizers (HALS), and the utilization of synergism between HALS and other types of stabilizers to further improve the weatherability of polypropylene.

Introduction

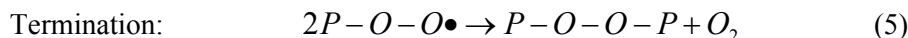
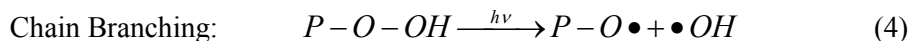
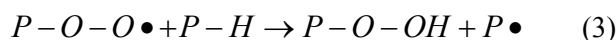
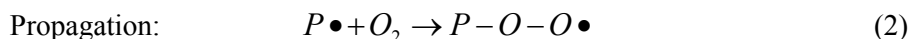
One of the principal engines for market growth of polypropylene and TPO's has become their use in the replacement of other materials for weatherable applications. In many instances molded-in-color polypropylene and TPO are replacing painted materials. Elimination of paint provides an opportunity for significant cost savings, but can place severe demands on the weatherability of the uncoated substrate. As a result, maximization of the light stability of the polymer in these applications is critical to prevent field failure.

The need for improved weatherability has spurred a great deal of investigation of the photodegradation chemistry of polypropylene as well as the development of a number of effective light stabilizer systems. These systems typically contain components that act by decomposing intermediates in the degradation process or by shielding the polymer from harmful ultraviolet radiation.

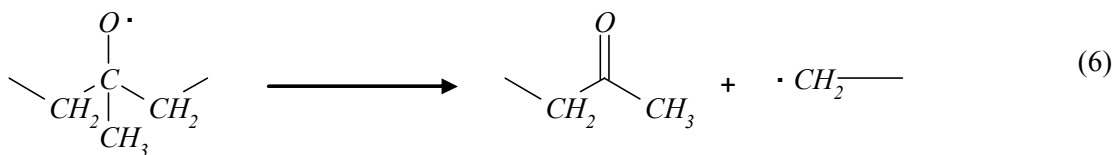
The following sections review the photodegradation chemistry of polypropylene, physical changes resulting from degradation, and light stabilizer systems that can be used to slow the onset of degradation.

Photodegradation Chemistry of Polypropylene

When organic materials such as polypropylene are exposed to ultraviolet light, free radicals are formed which initiate a photooxidation process. The basic oxidation chemistry has been known for over sixty years.[1] The oxidation process is characterized by initiation (equation 1), propagation (equations 2 & 3), chain branching (equation 4), and termination (equation 5) steps:[2]



The alkoxy radical derived from photolysis of the polypropylene hydroperoxide (in equation 4) readily undergoes fragmentation to give chain scission (equation 6). This is consistent with studies showing chain scission dominates over crosslinking in the photooxidation of polypropylene.[3]



Photooxidation takes place predominately in the amorphous phase of the polymer due to the higher solubility of oxygen vs. in the crystalline phase. Degradation as a function of depth has been studied.[3] In unstabilized polypropylene, oxidation takes place most rapidly at the surface of the part. In polymer stabilized with hindered amine light stabilizers, the extent of oxidation is much reduced but is still observed even deep within the part (> 1 mm below the surface).

Changes Resulting from Photodegradation

In polypropylene and other semicrystalline polymers, photooxidation is accompanied by an increase in crystallinity due to a process known as chemi crystallization.[4] When chain scission takes place during photooxidation, polymer chains in the amorphous phase are freed from some of their entanglements and can achieve sufficient mobility to crystallize. It is not clear whether crystallization takes place by formation of new crystals or by addition to existing ones. In any case, chemi crystallization results in the formation of voids which manifest as surface microcracks. These eventually grow large enough to be seen with the naked eye. Formation of surface cracks is a key factor in the embrittlement of semicrystalline polymers such as polypropylene. The increased roughness of the cracked surface scatters light, which in turn results in a loss of gloss (and subsequently chalking) and changes in the perceived color of the part, particularly in pigmented substrates.

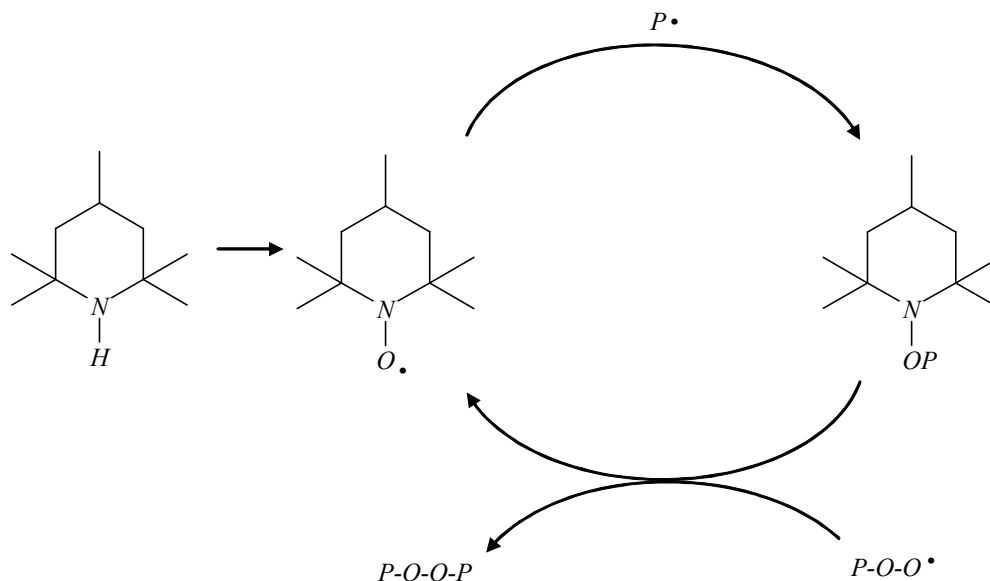
Photostabilization: Hindered Amine Light Stabilizers

The development of hindered amine light stabilizers (HALS) by Sankyo[5] in the 1970's and subsequent commercialization by Ciba-Geigy and other suppliers revolutionized the light stabilization of polyolefins. The development of these highly effective light stabilizers has been critical to the successful use of polyolefins in weatherable applications. Almost all of the commercial HALS are 4-substituted 2,2,6,6-tetramethylpiperidine derivatives ultimately derived from acetone and ammonia.[6]

A selection of commercial hindered amines is given in the Appendix. HALS-1 was one of the first products of this family to be developed, and continues to be widely used in polypropylene thick section applications. The 1980's saw the development of the first high molecular weight, polymeric HALS such as HALS-7 through HALS-9. These products have largely replaced the low molecular weight HALS in applications where migration can be an issue, such as in polyethylene and in thin-section polypropylene applications like fibers and films. More advanced oligomeric HALS such as HALS-10 through HALS-12, medium molecular weight HALS (HALS-4, HALS-5), HALS blends, and nonbasic "NOR HALS" were commercialized in the 1990's.

Chemistry of Hindered Amines

It has been long recognized that hindered amines and their transformation products (*i.e.* nitroxyl radicals and NOR derivatives) are capable of stabilizing polyolefins through multiple mechanisms involving the scavenging of radical and peroxide intermediates in the oxidation process.[7,8] An important feature differentiating hindered amines from other classes of stabilizers is their ability to act by a regenerative mechanism, which was first proposed by Denisov and coworkers (Scheme 1).[9] Through this regenerative mechanism a single hindered amine has been shown to be capable of deactivating multiple oxidation chains.[8]



Scheme 1. The “Denisov Cycle” Mechanism Proposed for Hindered Amine Light Stabilizers.

Important stabilizing reactions that have been proposed for hindered amines include:

1. Scavenging of alkyl radicals by the nitroxyl radicals derived from HALS;[7-9]
2. Decomposition of alkylhydroperoxides and peracids to nonradical products;[7]
3. Scavenging of alkylperoxy radicals and acylperoxy radicals by hindered amines and their NOR derivatives;[7] and
4. Deactivation of polymer-oxygen charge transfer complexes.[10]

Structure-Activity Relationships in Hindered Amine Light Stabilizers

A wide variety of hindered amines are commercially available. By varying factors such as the molecular weight, linking groups between the active piperidine moieties, and substitution on the piperidine nitrogen atom, products with a range of light stabilization activities and secondary properties (physical form, basicity, volatility, solubility, etc.) are obtained. HALS are conveniently classified as low- to medium-molecular weight (HALS-1 through HALS-6) or high molecular weight types (HALS-7 through HALS-12).

The effects of molecular weight on HALS diffusion in polyolefin matrices are well documented, as well as the importance of diffusion in the stabilization of polypropylene.[11-13] While hindered amines act by a regenerative mechanism, over the lifetime of a polyolefin article loss of the stabilizer can still occur, especially near the surface. In thick section parts containing low- to medium-molecular weight HALS (HALS-1 through HALS-6), the stabilizer content at or near the surface can be replenished by diffusion from the deeper layers of the part. For high molecular weight polymeric HALS diffusion is usually negligible and there is no replenishment mechanism. Thus the low- to medium-molecular weight HALS tend to give better protection in thick section polypropylene applications than high molecular weight HALS. However, for thin-section applications like fibers and films the replenishment mechanism is less important and high molecular weight HALS (HALS-7 through HALS-12) are favored due to their resistance to migration and loss by volatilization.

The solubility of HALS in the polyolefin matrix has also been reported to be an important factor influencing stabilization performance.[11] This has been used to explain the superior performance of HALS-2 over HALS-1 for the light stabilization of polypropylene (Figure 1),[11, 14] despite the lower active hindered piperidine content of the former. One explanation which has been suggested to explain this proposed relationship between solubility and performance is that the less soluble HALS-1 is lost from the surface layers of the article by exudation while the more soluble HALS-2 remains in the polymer matrix.[15] This is consistent with data showing an even larger performance advantage for HALS-2 over HALS-1 for test specimens washed with detergent and hot water prior to exposure (Figure 1).[14]

Exceptions do exist to the hypothesis that high solubility in the polymer is necessary for high performance with low molecular weight HALS. For example, HALS-3 has also been shown to provide better surface protection than HALS-1 in polypropylene (Figure 2), despite being even more polar and presumably even less soluble in the polyolefin matrix than HALS-1.

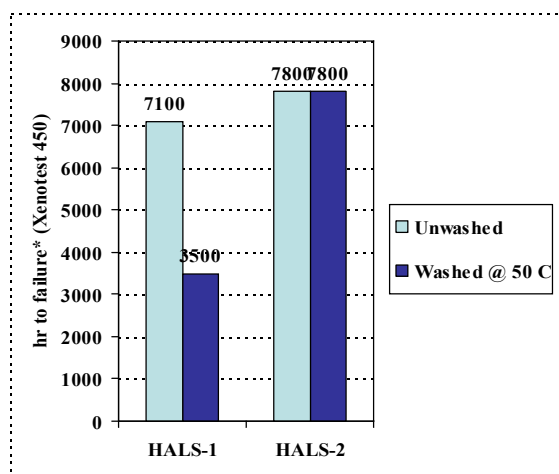


Figure 1. Performance Comparison of HALS-1 and HALS-2 (0.3%) in Polypropylene Homopolymer during Accelerated Weathering.

Data from Reference 14.

Test specimens: Films, thickness 0.5 mm

* Failure defined as carbonyl absorbance > 0.3.

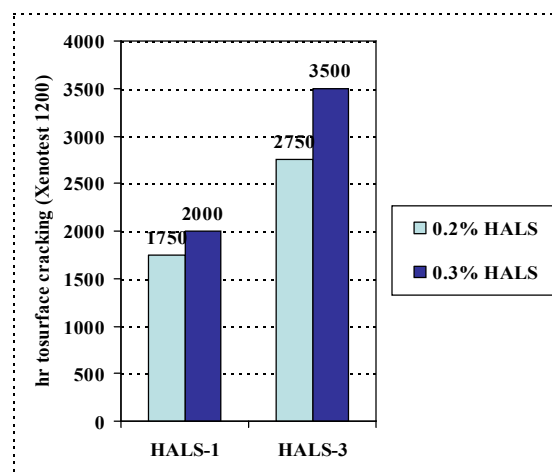


Figure 2. Performance Comparison of HALS-1 and HALS-3 in Polypropylene Homopolymer during Accelerated Weathering.

Test specimens: Injection moldings, 2 mm thickness
Data courtesy of BASF Corporation. Used with permission.

As photooxidation is expected to be a heterogeneous process, the affinity of some HALS to domains in the polymer in which oxidation is taking place has also been proposed to be an important factor in performance.[16] Migration of HALS to these domains is hypothesized to be driven by attractions between polar functional groups of the oxidizing polymer (*i.e.* hydroperoxides) and polar functionality of the HALS.

Nitroxyl radicals are formed from hindered amines by oxidation and play a key role in the stabilization mechanism. Thus it is to be expected that hindered amines resistant to oxidation to the nitroxyl will provide less effective light stabilization than those which are more easily oxidized. As a general rule, secondary amine HALS (*e.g.* HALS-1, HALS-2, HALS-3, HALS-4, HALS-7, HALS-9, HALS-11) and tertiary amine HALS bearing a methyl substituent (*e.g.* HALS-5, HALS-10, HALS-12) are rapidly oxidized to the nitroxyl radical during weathering. The reduced performance of N-acyl substituted HALS and polymeric HALS linked through the piperidine nitrogen (*i.e.* HALS-8) vs. other HALS in coatings has been explained by the slower conversion of the former to the nitroxyl radical.[17] Note that NOR HALS (*e.g.* HALS-6) are already in an oxidized form that can participate directly in the stabilization of the polymer. This has been proposed to explain their high performance vs. conventional HALS in some polyolefin substrates.[18]

Other Selection Criteria

Like other amines, many HALS are strongly basic, and this basicity can lead to undesired interactions with other formulation components. For example, the interaction between basic HALS and acid-cured automotive coatings used on TPO exterior parts is well known.[19] Interactions of basic HALS with brominated flame retardants and certain pesticides are also known.[20] For these applications, nonbasic conventional HALS (*e.g.* HALS-8,[2] HALS-11[21, 22]) or NOR HALS (*e.g.* HALS-6) can be used in place of more basic HALS. If the interaction is serious enough, hindered amine-free stabilizer mixtures are sometimes employed. For example, combinations of UVA-1, AO-2, and a phosphite have been used successfully in certain flame retardant polypropylene applications.[23]

HALS can also interact with the thiosynergists (*e.g.* DSTDP) which are used to enhance the long term thermal stability of polyolefins. This effect appears to result primarily from an interaction between the basic HALS and acidic transformation products of the thiosynergist.[24] There is evidence in the patent literature suggesting that this interaction may be overcome through proper selection of the acid neutralizer in the formulation.[25] Alternative technical approaches to developing formulations with both good weatherability and long term thermal stability exist. For example, the beneficial effect of some high molecular weight HALS on thermal oxidative stability[2] can be exploited to develop effective formulations without resorting to the use of thiosynergists.[26] The performance of the tertiary HALS-12 to enhance long term thermal stability in such systems is particularly noteworthy.

Food contact compliance is required for polypropylene applications such as food packaging. In other cases polymer producers and compounders may prefer to use food contact compliant additives to prevent cross-contamination issues between grades. A wide range of high molecular weight HALS are commercially available that have been designated as food contact compliant in polypropylene by the US FDA.[27, 28] Among the low- to medium-molecular weight HALS, only HALS-3 is food contact compliant for use in polypropylene.[29] In the European Union the selection of food contact compliant HALS for use in polypropylene is more limited and includes only HALS-7 and HALS-8.[30]

Synergists for Hindered Amine Light Stabilizers

The use of hindered amines by themselves is often sufficient to provide acceptable weatherability to polyolefins. However, for some applications such as automotive exterior parts and architectural applications further improvements in weatherability may be required. In these cases the performance of HALS can be enhanced by using them in combination with other additives.

HALS Combinations

Synergistic combinations of hindered amines are well known in the art,[31] and recent years have witnessed a surge of patent activity in this area.[32-44]

In thick-section polypropylene applications, combinations of the low-molecular weight HALS-1 and the high-molecular weight HALS-7 have been shown to provide somewhat better performance than would be expected based on the performance of the individual components (Figure 3). However, in this case the light stabilization performance of the HALS mixture is often found to be not significantly better than that of the low-molecular weight HALS used alone. The high molecular weight HALS may provide other benefits in the formulation such as improved thermal oxidative stability at moderate temperatures. The use of such combinations is most appropriate when the benefits provided by both components are required in the final application.

The mechanisms of synergistic interactions between HALS are not completely clear, but may involve different migratory characteristics of the components and/or differences in the rates of nitroxyl radical formation.

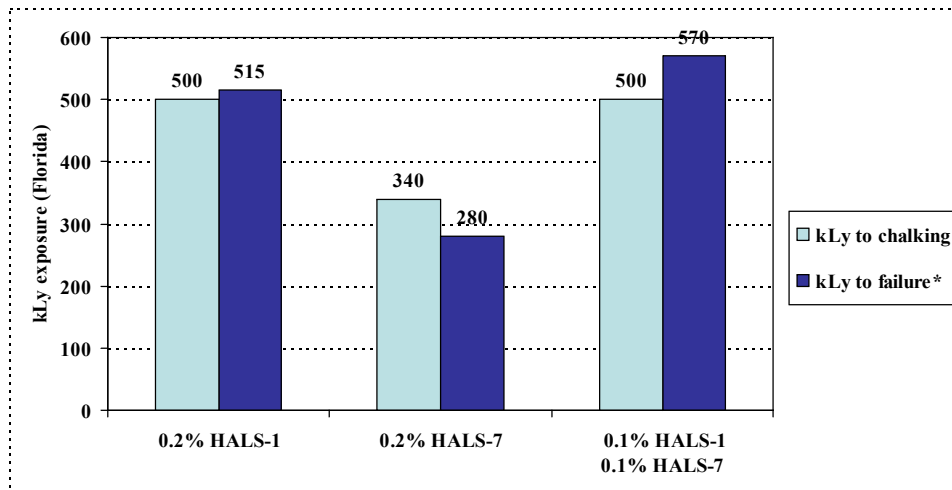


Figure 3. Performance of Low Molecular Weight HALS-1, High Molecular Weight HALS-7, and their Combination in Polypropylene Homopolymer During Natural Weathering in Florida.

Data from Reference 31.

Test specimens: Injection moldings, 2 mm thickness.

* Failure defined as $\leq 50\%$ retention of impact strength.

Ultraviolet Absorbers

Ultraviolet (UV) absorbers act largely by shielding the interior of the part from damaging UV radiation. Before the advent of hindered amines, light stabilization was accomplished with systems based on UV absorbers in combination with other additives. Today UV absorbers are often used in combination with HALS and sometimes other additives for the stabilization of polypropylene. They are also used in plastic packaging applications to provide content protection.

All of the compounds of this class share several general characteristics:

1. Strong UV absorption, especially in the 290 nm to 350 nm range which is very damaging to organic materials, and
2. Excited states formed upon UV absorption relax to the ground state extremely rapidly (picosecond time frame) and efficiently via radiation-less processes, which imparts high efficiency and excellent photostability.

Chemical classes of UV absorbers suitable for use in polyolefins include 2-hydroxybenzophenones (*e.g.* UVA-1), 2-(2-hydroxyphenyl)-2H-benzotriazoles (*e.g.* UVA-2, UVA-3), tris-aryl-o-hydroxyphenyl-s-triazines (*e.g.* UVA-4), and cyanoacrylate derivatives (*e.g.* UVA-5, UVA-6). Chemical structures of representative UV absorbers are given in the Appendix. For food contact applications, products that have been designated as food contact compliant in polypropylene by the US FDA include UVA-1, UVA-3, UVA-4, and UVA-6.[27, 45]

Absorption of UV radiation is governed by the Beer-Lambert Law:

$$A = \epsilon bc$$

where A is the absorbance, ϵ is the molar absorptivity of the UV absorber, b is the path length, and c is the concentration. Because the absorbance is directly dependent on the path length, UV absorbers provide little or no protection at the surface of a part where the path length is very short. In thin-section parts such as films, UV absorbers provide little protective benefit.[2] However, for the deeper layers (≥ 1 mm below the surface) of thick section parts, all of the UV radiation can be blocked with incorporation of

~ 0.1% UV absorber and photodegradation in these deeper layers is effectively prevented. This serves to improve retention of mechanical properties after exposure. As illustrated in Figure 4, the combinations of HALS and UV absorbers provide some improvement in physical property retention after exposure but no improvement in surface protection (exposure time to cracking) vs. the HALS alone.

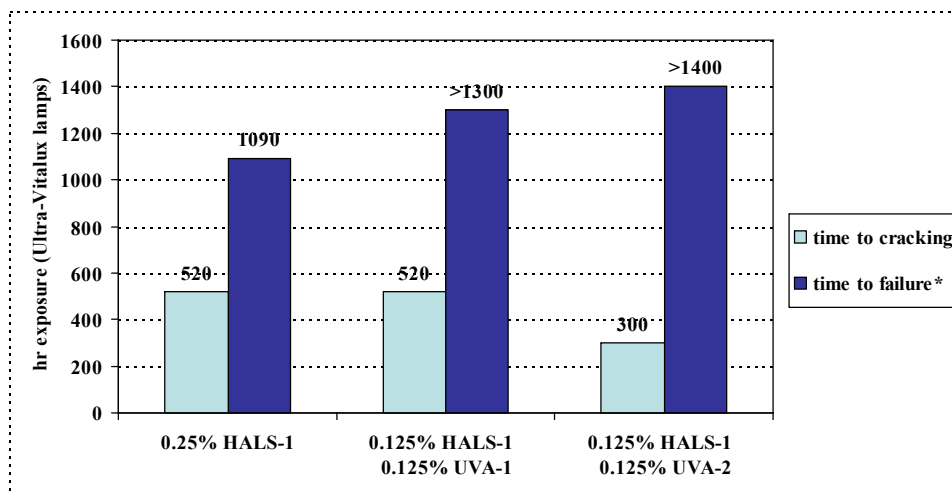


Figure 4. Performance of Combinations of HALS-1 with UV Absorbers vs. HALS-1 Alone in PP Homopolymer. Data from Reference 46.

Test specimens: Injection moldings, 1 mm thickness.

* Failure defined as < 50% retention of tensile strength.

UV absorbers can also improve surface protection indirectly if other stabilizers are able to migrate from the protected deeper layers to the layers closer to the surface in which photodegradation is taking place.[47] This can be a powerful effect and will be examined in greater detail in the next section when the effects of benzoates and other hindered phenols on light stability are addressed.

Other formulation components such as pigments can also perform the function of blocking the penetration of UV radiation. In this situation the UV absorbers would not be expected to be effective as light stabilizer synergists. Generally the benefits of using a UV absorber are most prominent in natural and lightly pigmented parts. However, in the case of some organic pigments with limited lightfastness the use of UV absorbers as part of the formulation can be highly beneficial, even in thin-section applications such as fibers[48] and films.[49] Here the UV absorber may be acting to improve the lightfastness of the organic pigments by quenching of their excited states or by another unknown mechanism.

Benzoates and Other Hindered Phenols

The use of derivatives of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (AO-1, AO-2) as light stabilizers for polyolefins predates that of hindered amines. Like other hindered phenols, the benzoates inhibit the oxidative degradation process by scavenging free radicals.[50] The downside of this mechanism is that it is sacrificial in nature and the benzoates are consumed, unlike the hindered amines which act by a regenerative mechanism. When compared directly, the hindered amines provide superior weatherability vs. benzoates. Benzoates are sometimes erroneously referred to as “UV absorbers”.

The synergy between benzoates and hindered amines in the stabilization of polypropylene has been known for some time.[51, 52] As shown in Figure 5, the combination of HALS-1 and AO-1 clearly gives better light stability than either component alone. Synergistic behavior was also reported at this conference last year for the combination of HALS-2 and AO-2.[53] This synergy suggests that the benzoates are more effective scavengers of certain types of free radicals involved in the degradation process than are the hindered amines.

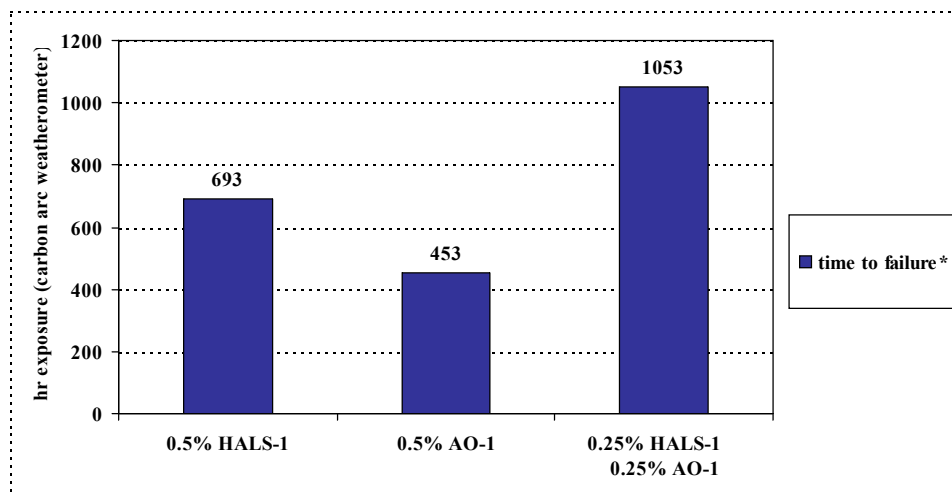


Figure 5. Performance of HALS-1, AO-1, and their Combination in PP Homopolymer Films (Thickness 0.005"). Data from Reference 51.

* Failure determined in 180° bending test.

It has also been reported that like benzoates, the conventional hindered phenol AO-3 exhibits a strong synergy with hindered amines,[54, 55] unlike the more widely used antioxidant AO-4 (Figures 6 & 7). This effect is not surprising given that an early mechanistic study found AO-3 to provide performance comparable to the benzoate AO-2 for the stabilization of PP films.[50] The positive effect for AO-3 vs. AO-4 appears to be linked to the ability of the lower molecular weight AO-3 to migrate to layers near the surface where photodegradation is occurring.[47, 54, 55]

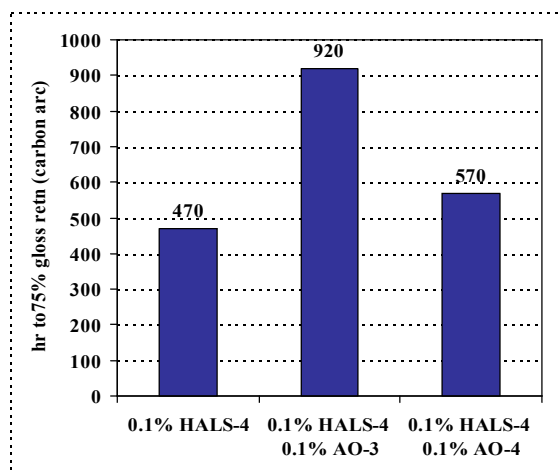


Figure 6. Effect of Primary Antioxidant on the Light Stability of Polypropylene Homopolymer Sheets Stabilized with HALS-4. Data from Reference 54.

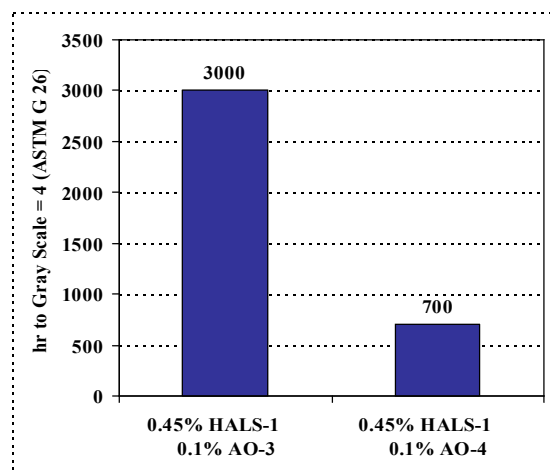


Figure 7. Effect of Primary Antioxidant on the Light Stability of Pigmented (Dark-Gray) High Impact Propylene/Ethylene Copolymer (14% Ethylene) Stabilized with HALS-1. Data from Reference 55. Test specimens: Injection moldings, 3.2 mm thickness.

Synergistic combinations of HALS, benzoates, and UV absorbers have also been reported.[56, 57] To understand the reason for this three component synergy, one has to consider that benzoates (unlike HALS) do absorb short-wavelength UV radiation ($\lambda < 300$ nm) and are vulnerable to photodegradation themselves. As we have already seen, incorporation of a UV absorber into the formulation prevents

photodegradation at the deeper levels of the part. Low molecular weight additives such as AO-1, AO-2, and AO-3 are then able to migrate from these protected deeper layers to layers closer to the surface in which photodegradation is taking place.[47] As shown in Figure 8, the use of the three component formulation containing HALS, benzoate, and UV absorber gives better performance than the two component formulations based on the HALS and benzoate or HALS and UV absorber.

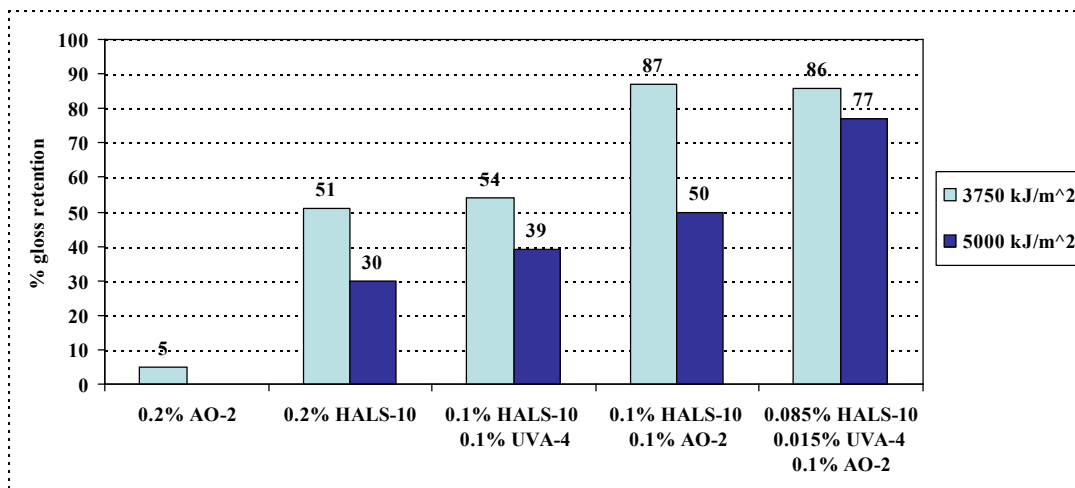
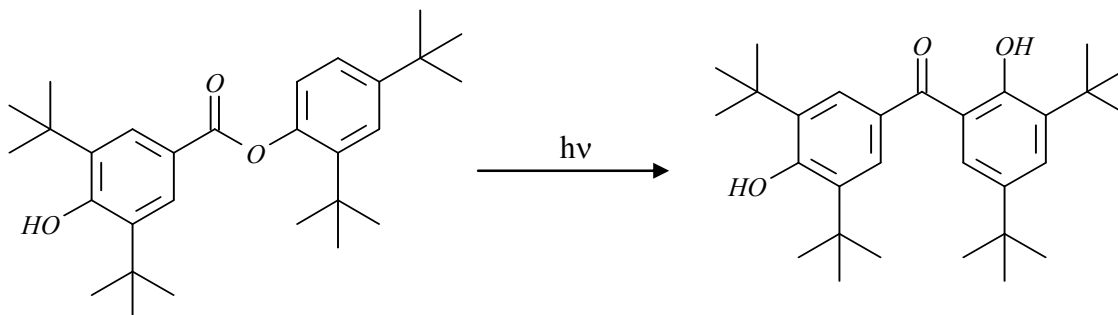


Figure 8. Performance of Light Stabilizer Systems Based on HALS-10, UVA-4, and AO-2 in a Gray Pigmented Reactor Grade TPO During Exposure per SAE J 1885 (Interior Auto Xenon). Data from Reference 57. Test specimens: Injection moldings, 0.125" thickness.

The photochemistry of benzoates and hindered phenols needs to be considered when selecting the most appropriate product for use in a particular application. AO-1 is well known to undergo a Photo-Fries rearrangement on exposure to light (Scheme 2),[50] giving a 2-hydroxybenzophenone derivative which is an effective UV absorber but also absorbs visible light and is discoloring to the substrate. The rearrangement can be inhibited to some degree and the amount of discoloration reduced by using AO-1 in combination with a UV absorber.



Scheme 2. Photo-Fries Rearrangement of AO-1.

The tendency of the oxidation products of AO-3 to give discoloration is also well known.[58] The discoloration imparted by the transformation products of AO-1 or AO-3 can be an issue in natural or lightly pigmented parts, where the use of the inherently less discoloring AO-2 presents a better alternative. In black or highly pigmented substrates the discoloration imparted by AO-1 or AO-3 may be masked by the pigment, in which case any of the products may be used.

For food contact applications, AO-1, AO-2, and AO-3 are all designated as food contact compliant in polypropylene by the US FDA.[27]

Other Possible Synergists

Shlyapintokh proposed that peroxide decomposers should also assist with the light stabilization of polyolefins if they are mobile and shielded in the bulk of the polymer by a UV absorber.[47] There is some evidence for this in the patent literature, where certain phosphites have been observed to give synergistic interactions with other light stabilizers.[52, 59, 60]. However, in these cases it is not clear whether the phosphites are acting as true light stabilizers or by an indirect mechanism involving the decomposition of hydroperoxides during processing which would otherwise initiate oxidation of the polymer on weathering.

Dialkylhydroxylamines have also been reported to be effective scavengers of peroxy radicals and hydroperoxides.[18] Thus it is possible that migratory dialkylhydroxylamines could also serve as synergists for hindered amines. There is some precedence for this in the patent literature.[61]

More recently, certain bridged amines have been shown to give synergism with hindered amines in the light stabilization of polypropylene.[62, 63] These compounds are proposed to act by quenching of polymer-oxygen charge transfer complexes which are thought to be involved in the initiation of photooxidation.

Conclusions

Polypropylene degrades when exposed to light by an oxidative mechanism in which chain scission predominates over crosslinking. Through the process of chemi crystallization, chain scission leads to an increase in crystallinity which in turn results in surface cracking. The formation of cracks leads to changes in appearance (color and gloss) as well as mechanical failure of parts.

Hindered amine light stabilizers (HALS) are very effective for improving the light stability of polypropylene. These compounds act by scavenging the radical intermediates in the oxidation process. Unlike other stabilizers, they appear to act by a regenerative mechanism. The performance of HALS in polypropylene thick section applications has been proposed to be related to factors such as diffusion, solubility in the matrix, affinity to oxidized domains of the polymer, and ease of oxidation to the active nitroxyl radical. Other factors to be taken into account when selecting a HALS for an application include potential for interaction with other formulation components and food contact requirements.

When higher performance is desired, improvements can often be achieved by using synergistic combinations of additives. Examples of synergists for HALS include other hindered amines, ultraviolet absorbers, benzoates, and some phenolic antioxidants. Combinations of low and high molecular weight hindered amines (*e.g.* HALS-1 and HALS-7) provide good light stability like low molecular weight HALS as well as improved heat aging performance. UV absorbers used in combination with HALS help improve physical property retention during weathering and may also improve weatherability in formulations containing organic pigments. Benzoates and select hindered phenolic antioxidants (*i.e.* AO-3) give the most powerful synergy with HALS, which can be further improved upon by addition of a UV absorber.

Final Words

The author is an independent contractor. Nothing in this paper should be construed as an endorsement of any particular supplier of additives or their products.

When developing new formulations, testing must be conducted to ensure that the formulation meets the requirements of the intended conditions of use. Furthermore, the formulator must make his own determination and satisfy himself that the formulations are in compliance with environmental, health, and safety regulations. Please note that food contact clearances may be subject to restrictions as to the

polymer substrate, food type, and conditions of use. When formulating for food-contact applications the applicable regulation should be consulted to ensure that the formulation is compliant.

The patent status of particular additives, combinations of additives, and their use in specific polymers, formulations, and applications can be very complex. When developing new formulations, it is recommended to conduct a thorough search of the literature to avoid infringement of any valid patents. When in doubt seek legal counsel.

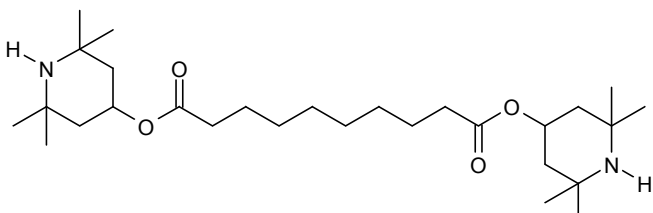
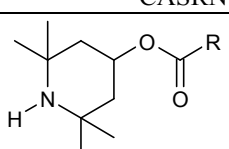
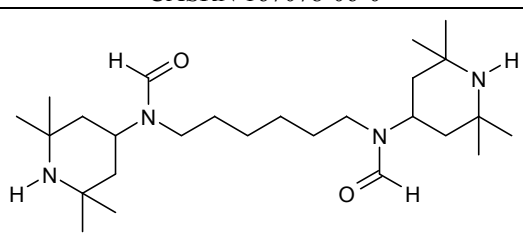
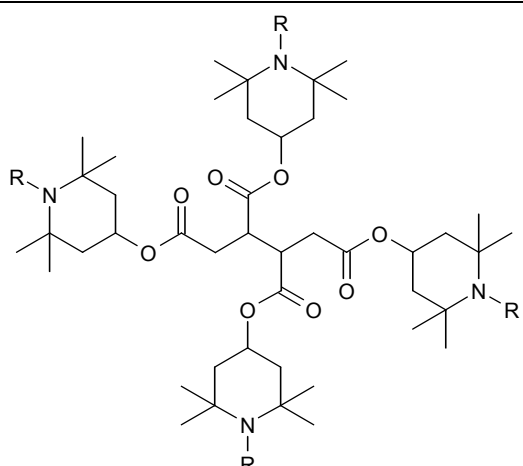
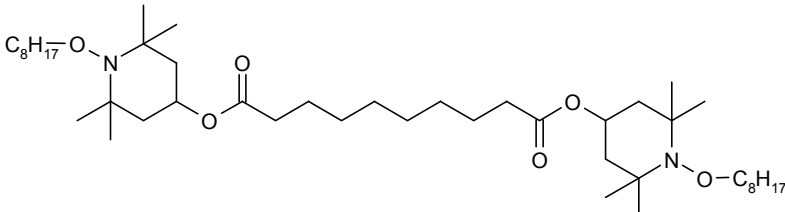
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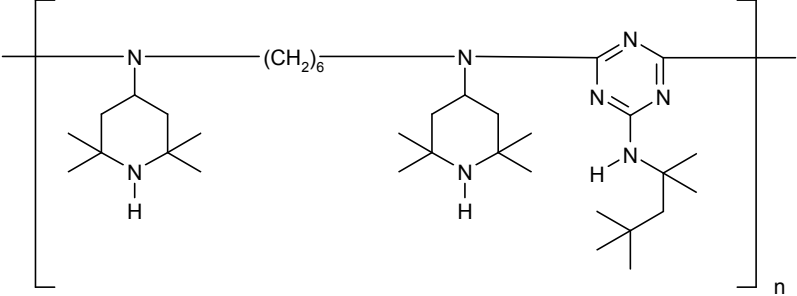
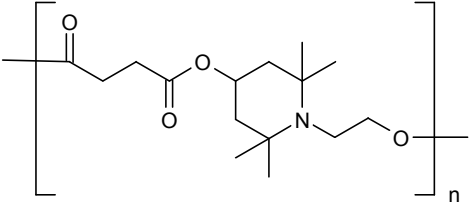
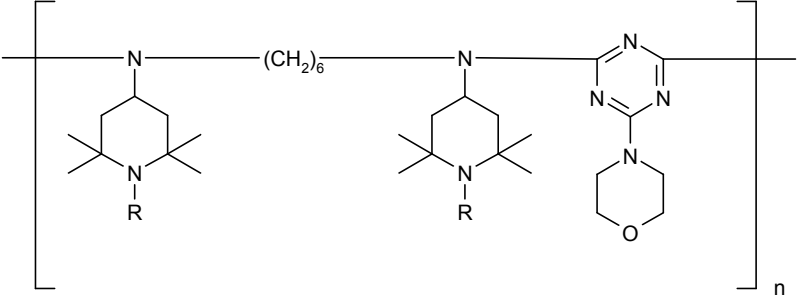
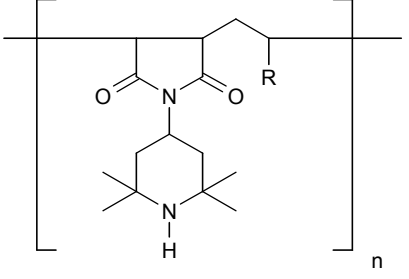
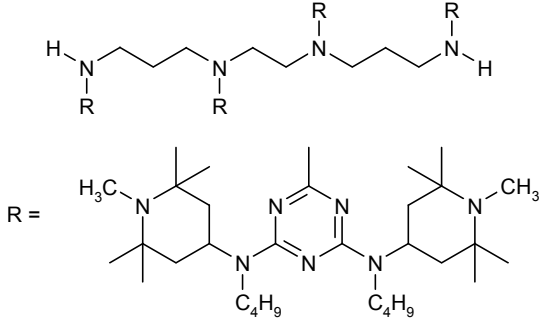
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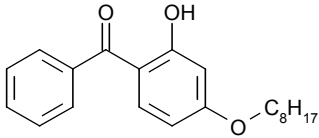
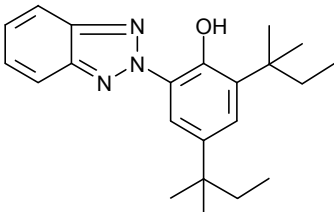
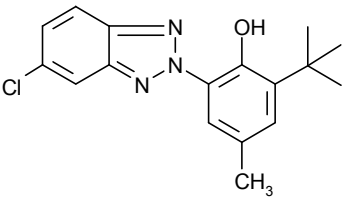
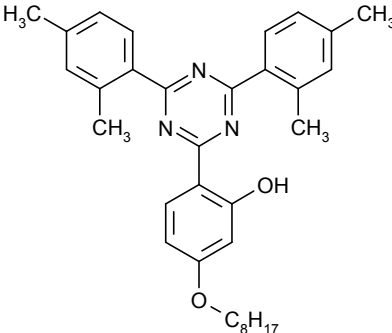
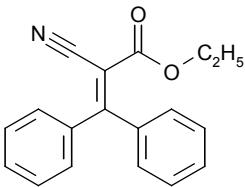
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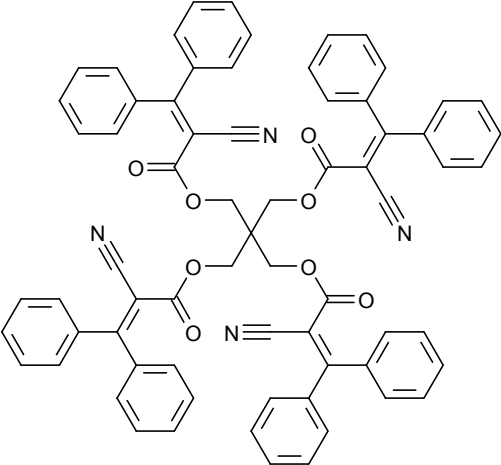
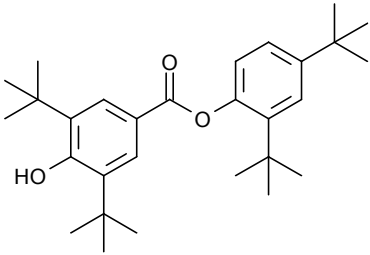
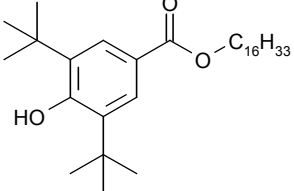
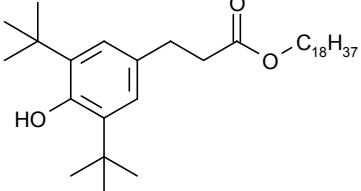
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Appendix: Some Commercially Available Hindered Amine Light Stabilizers, Ultraviolet Absorbers, Benzoates, and Phenolic Antioxidants

	Structure/CASRN
HALS-1	 <p>CASRN 52829-07-9</p>
HALS-2	 <p>R = C₁₁₋₂₀ predominantly C₁₆₋₁₈</p> <p>CASRN 167078-06-0</p>
HALS-3	 <p>CASRN 124172-53-8</p>
HALS-4	 <p>HALS-4: R = H, CASRN 64022-61-3 HALS-5: R = CH₃, CASRN 91788-83-9</p>
HALS-5	
HALS-6	 <p>CASRN 129757-67-1</p>

<p>HALS-7</p>	 <p>CASRN 71878-19-8, 70624-18-9</p>
<p>HALS-8</p>	 <p>CASRN 65447-77-0</p>
<p>HALS-9</p>	 <p>HALS-9: R = H, CASRN 82451-48-7 HALS-10: R = CH₃, CASRN 193098-40-7</p>
<p>HALS-11</p>	 <p>R = C₁₈₋₂₂H₃₇₋₄₅</p> <p>CASRN 152261-33-1</p>
<p>HALS-12</p>	 <p>CASRN 106990-43-6</p>

UVA-1	 <p>CASRN 1843-05-6</p>
UVA-2	 <p>CASRN 25973-55-1</p>
UVA-3	 <p>CASRN 3896-11-5</p>
UVA-4	 <p>CASRN 2725-22-6</p>
UVA-5	 <p>CASRN 5232-99-5</p>

<p>UVA-6</p>	 <p>CASRN 178671-58-4</p>
<p>AO-1</p>	 <p>CASRN 4221-80-1</p>
<p>AO-2</p>	 <p>CASRN 67845-93-6</p>
<p>AO-3</p>	 <p>CASRN 2082-79-3</p>

