Macromol. Symp. ***176****, 1–15 (2001)*

Structure-Property Relationships: Phenolic Antioxidants with High Efficacy and Low Color Contribution

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Summary: Antioxidants can be divided into two broad classes, primary and secondary, depending upon their mode of action. The most broadly used primary antioxidants are hindered phenols. Phenolic antioxidants have traditionally been based on 2,6-di-*t*-butyl-4-methylphenol (BHT). This functional moiety has been incorporated into larger molecules affording products with lower volatility or greater polymer compatibility. More recently, molecules have been introduced which vary in steric hindrance about the phenol and also the way in which multiple phenol functional groups are linked to form larger molecules. This has led to structures which have lower color contribution. Surprisingly, in some cases these molecules have shown higher levels of efficacy relative to other antioxidants with similar phenol/molecular weight ratios. This has included enhanced levels of synergism with secondary antioxidants. An attempt is made to correlate structural features of these molecules to the enhanced performance and/or lower color.

Introduction

The past decades have seen a rapid expansion in the use of polymers. Traditional materials such as wood and metals have been displaced in favor of lighter and stronger synthetic materials. The ability to melt process and mold polymers into intricately shaped parts, combined with the afore mentioned physical properties, ensure that plastics will continue to grow in use and application. Unfortunately, most polymers are not inherently stable to light or extremes of temperature. For example, the need to stabilize polyolefins against thermal degradation has been well documented.[1] During all phases of the polymer's life thermal and light induced degradation cause loss of both physical and aesthetic properties. Although often overlooked, the light stability of a polymer is strongly influenced by the thermal history during processing. In the absence of an effective process stabilization system, peroxides formed during melt processing will initiate multiple degradation reactions and thus reduce the long term heat aging and light stability of a polymer.

CCC 1022-1360/00/$ 17.50+.50/0

For these reasons it has become standard practice in the polymer industry to add various thermal stabilizers to plastics depending on the anticipated processing and end use.

Review and Discussion

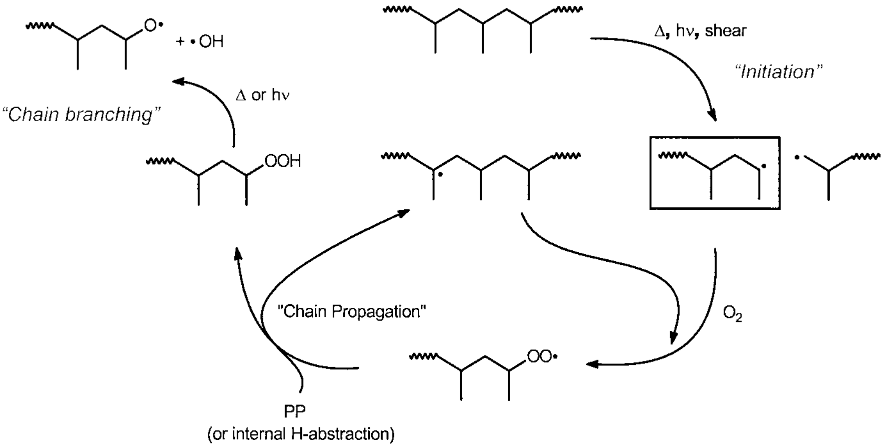
Antioxidants can be divided into two broad classes, primary and secondary, depending on their mode of operation. The degradation pathway of polyolefins, see Scheme 1, is dominated by free radical chain reactions. During the service lifetime of a polymer, thermoxidative degradation occurs during polymerization, storage, compounding, molding of plastic articles and in end use. Light energy, heat or shear lead to polymer chain breakage and the concomitant formation of two free radicals. These free radicals will usually react first with oxygen to form peroxyl radicals and these in turn abstract a hydrogen atom from a second polymer chain. As shown in Scheme 1, one initiation event leads to the formation of a highly reactive peroxide group and regeneration of a free radical. The peroxide can then cleave to yield two new oxygen based radicals that can both abstract hydrogens from the polymer chain and cause further degradation. Left unchecked, these chain reactions will lead to polymer oxidation and loss of polymer molecular weight. Degradation is observed as changes in color and surface appearance and simultaneous loss of physical properties.

The degradation cycle can be broken by two pathways; an H-atom source other than the polymer chain can be found, or the hydroperoxide can be decomposed into non-reactive products. In general, primary antioxidants break the degradation chain by donating H-atoms to free radicals, thus preventing those radicals from propagating the chain reaction. Secondary antioxidants act as hydroperoxide decomposers. Primary and secondary antioxidants are often used in combination to take advantage of the observed synergy. Several excellent reviews of degradation and stabilization of polyolefins are available [1,2,4].

The hindered phenol and aromatic amine classes of compounds best represent primary antioxidants. One of the earliest and simplest hindered phenols is, 2,6-di-t-butyl-4-methylphenol or BHT (AO-1). This compound is inexpensive and an effective radical scavenger. Unfortunately AO-1 does have several deficiencies.

First, it is a volatile molecule. As measured by weight loss in a dynamic TGA, 10% of the initial sample mass has volatilized by 157 °C. This low T-10 value means that a significant amount of AO-1 is lost during processing and subsequent heat cycles before it can take part in the stabilization cycle. Secondly, under thermo-oxidatative conditions it readily forms highly colored by-products as shown in Scheme 2.[3] While both the quinonemethide and the stilbenebisquinone by-products can act as stabilizers,[4] this advantage is strongly outweighed by the color they introduce to the plastic part. Another major deficiency of AO-1 is its tendency to discolor in the presence of gaseous byproducts formed during the combustion of fossil fuels.[5] These are commonly oxides of nitrogen formed during the burning of natural gas in heating systems or by gas powered forklift engines. Early work, with AO-1, has shown the mechanism for this discoloration (Scheme 3).[6]

Scheme 1



In spite of BHT's many limitations, the 2,6-di-*t*-butyl phenol moiety has been chemically modified and remains the functional group of choice for primary antioxidants. AO-2 is an example of a second generation of phenolic antioxidant. Increasing the molecular weight of the molecule by incorporating the C-18 alkyl chain affords the molecule improved compatibility with polyolefins and reduced volatility (T-10 of 287 °C). In addition, AO-2 has lower color contribution due to a unique side reaction of the oxidized intermediate (Scheme 4).[7,8] The resulting cinnamate has very low initial color contribution. Further reaction of the cinnamate leads to highly colored products, thus this second generation is still very susceptible to NOx gas fade discoloration. As shown in Figure 1, this discoloration can be significant, particularly in formulations that contain a hindered amine light stabilizer. Here the basicity of the amine exacerbates the problem.

Scheme 2

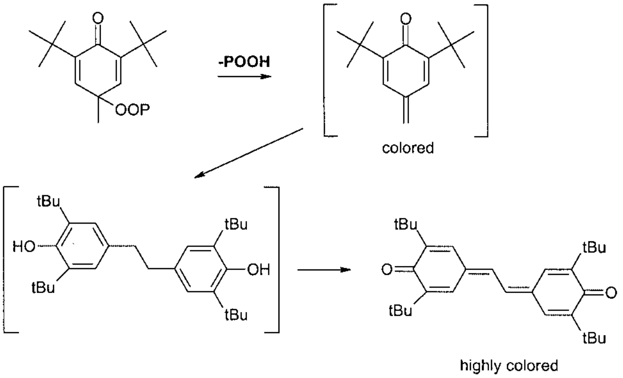
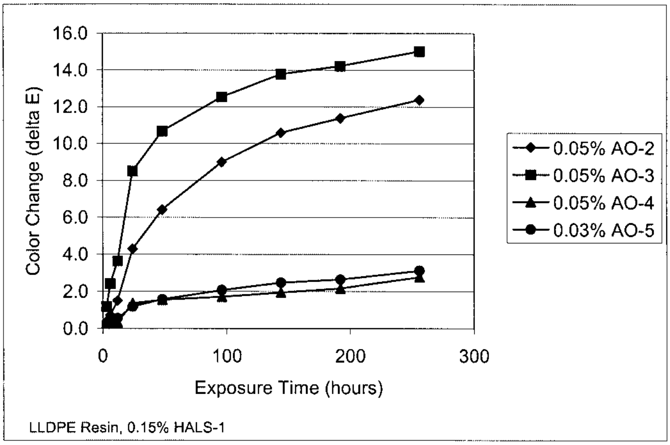
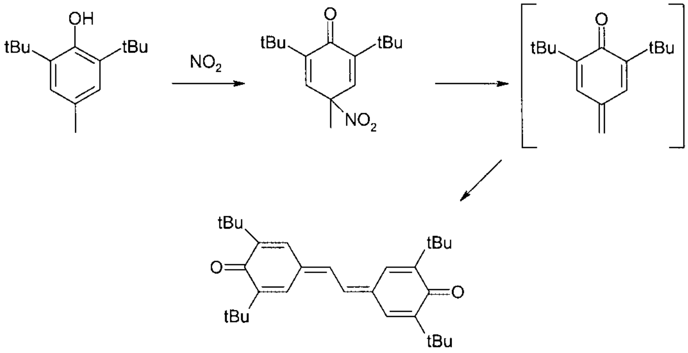


Figure 1. Gas Fade discoloration of phenolic antioxidants in LLDPE.

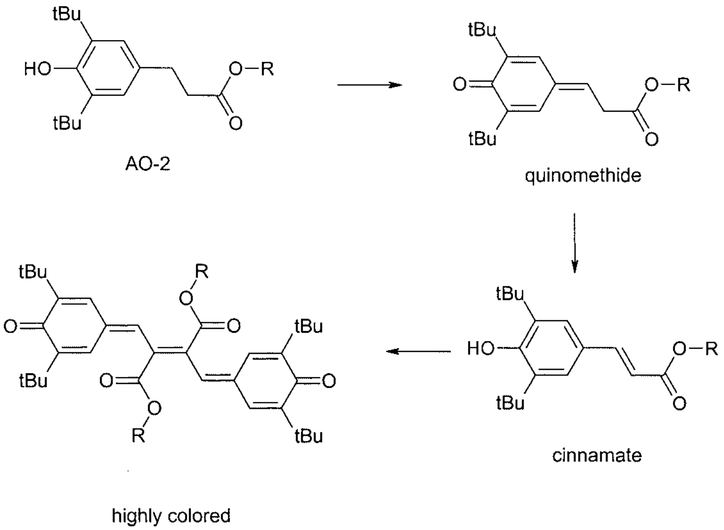


Scheme 3

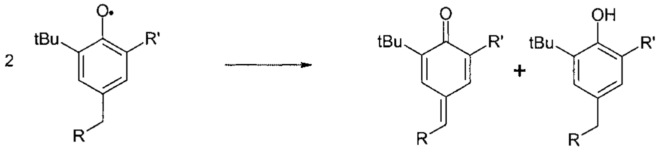


The third generation hindered phenols are multifunctional with an aliphatic center, such as AO-3. By tethering multiple hindered phenols together on the same molecule the volatility is effectively reduced while the equivalent weight of the molecule remains relatively low. Thus, multifunctional compounds allow high specific phenol concentrations without sacrificing the molecular weight (i.e. increased volatility), see Table 1. Not surprisingly, the effectiveness of an antioxidant is more closely related to the hindered phenol group concentration than the stabilizer concentration. The greater activity allows the use of lower stabilizer concentrations without sacrificing performance. A lower stabilizer concentration also reduces the amount of unwanted inter-stabilizer reactions such as aryl-aryl peroxide and stilbenequinone formation. These reactions are unlikely to happen intramolecularly because of steric considerations. With some multifunctional phenols the efficiency of stabilization is also due to intramolecular disproportionation to give a quinonemethide and starting hindered phenol (Scheme 5)[9]. Although these third generation phenolics have improved activity over the first and second generation phenols, AO-3 still shares the poor gas fade discoloration tendencies of AO-2 and AO-1 (Figure 1).

Scheme 4



Scheme 5



While keeping with the same strategy of a multifunctional hindered phenol, use of an isocyanurate center as a linking center was another breakthrough in antioxidant technology. Antioxidant-4 and AO-5 represent the fourth generation of hindered phenol antioxidants. As shown in Table 1, these compounds have a specific phenol concentration even higher than AO-3 and very low volatility. A further distinctive feature of isocyanurate based AO's is their resistance to reactions with nitrogenous gasses or "gas fade."

Table 1. Specific Phenol Concentrations and Volatility for Various Antioxidants.

Hindered Phenol	Specific Phenol Conc. (mole/kg)	Volatility (T-10)*
AO-1	4.5	157
AO-2	1.9	287
AO-3	3.6	344
AO-4	3.8	337
AO-5	4.3	360

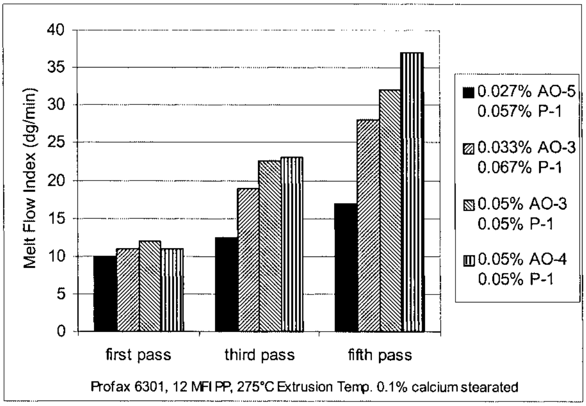
* the temperature at which 10% weight loss is seen in the TGA

Gas fade measurements are commonly done by exposing compounded samples of the stabilized resin to the combustion products of natural gas in a controlled environment.[10] Injection molded LLDPE plaques containing equal amounts of AO-2, AO-3, AO-4, and AO-5 were exposed in an United States Testing Co. Atmospheric Fume Chamber (Model 8727). The chamber was maintained between 57-60 °C. The excellent gas fade resistance of AO-4 and AO-5 is illustrated in Figure 1.

The structural feature common to both gas fade resistant phenols, AO-4 and AO-5, is the isocyanurate ring which may offer an explanation of the observed performance. The attachment of the phenolic groups to the isocyanurate ring, which is quite chemically inert and stable, hinders movement of the phenolic substructure. This would pre-empt formation of the highly conjugated stilbenequinone structure.

Using multiple extrusion passes as a measure of antioxidant performance, Figure 2 compares the melt stabilizing abilities of the 2nd, 3rd, and 4th generation phenolic antioxidants in combination with a phosphite secondary antioxidant in polypropylene. In this comparison, the best process stabilization, as evidenced by retention of initial melt flow, is afforded using AO-5 at 20-50% lower additive loading levels. In LLDPE, where degradation manifests itself through cross-linking and reduced melt flow, AO-5 again gives protection similar to AO-2 and AO-3, but again, at a much lower additive loading (Figure 3). A comparison of color development in AO-3 and AO-5 during multipass extrusion is shown in Figure 4. At typical use levels all of the compounds show equivalent color development.

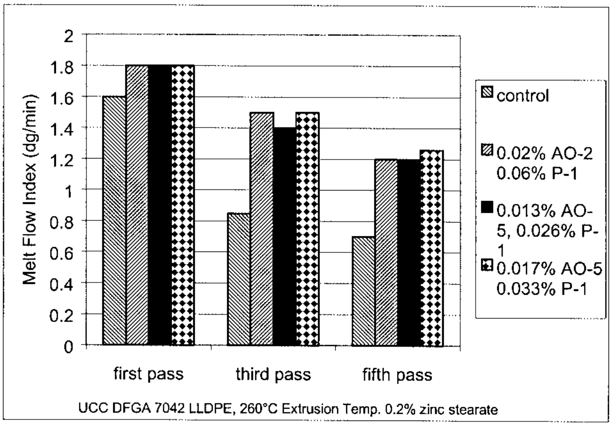
Figure 2. Multipass extrusion evaluation of phenolic antioxidants in combination with phosphite P-1 in polypropylene.



As mentioned earlier, primary and secondary antioxidants often perform synergistically when used in combination. Careful selection of a phosphite can enhance the performance of the phenolic. Figure 5 shows multiple pass extrusion results for a series of phosphites in combination with AO-5. The two high performance phosphites, P-2 and P-3, show higher activity than P-1. The primary structural difference between these compounds is that P-2 and P-3 contain aliphatic phosphite linkages, which are more reactive. These reactive bonds are also, however, more susceptible to hydrolysis. It has been reported that P-3 shows a good balance between hydrolysis resistance and stabilizer activity.[11]

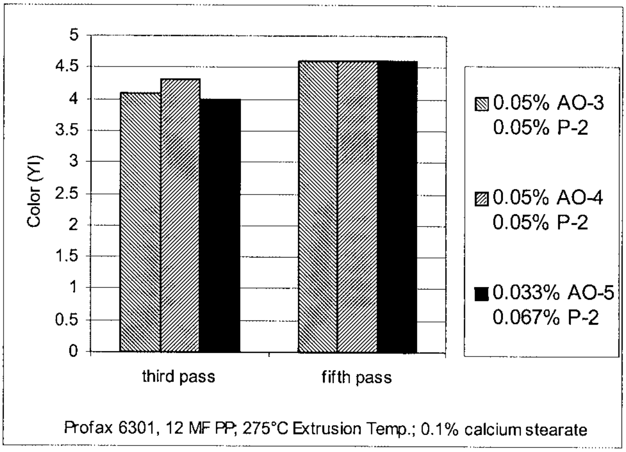
While the above experiments were all conducted on blends of the various phenolic AO's with a phosphite secondary antioxidant, it is important to note that similar synergism has been observed between phenolic AO's and thiodiesters such as distearyl dithiopropionate (DSTDP). Binary systems of this nature provide good process stabilization, low initial color, and excellent long-term heat aging stabilization. Figure 6 shows the process stabilization performance of phenolic antioxidants with DSTDP. While the melt flow retention using thiodiester secondary AO's does not approach that of blends using phosphites, advantages in long term heat aging performance are often observed.

Figure 3. Multipass extrusion results in LLDPE.



UCC DFGA 7042 LLDPE, 260°C Extrusion Temp. 0.2% zinc stearate

Figure 4. Color development in polypropylene samples versus extrusion pass.



Profax 6301, 12 MF PP; 275°C Extrusion Temp.; 0.1% calcium stearate

Figure 5. Multipass extrusion of polypropylene containing AO-5 and various phosphite secondary antioxidants.

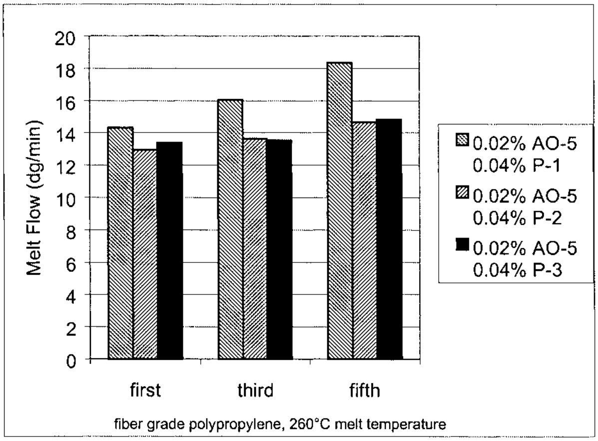
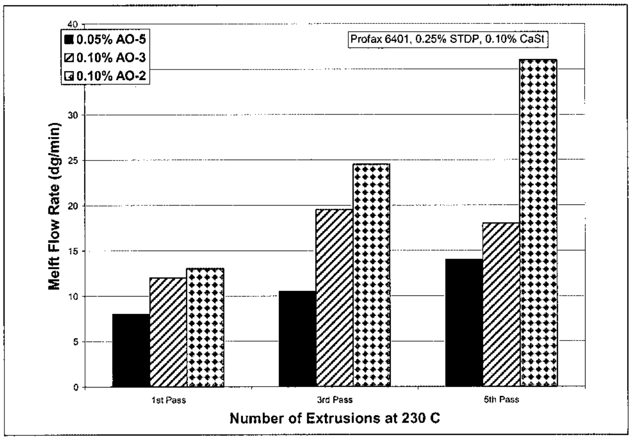


Figure 6. Multipass extrusion of polypropylene samples containing a phenolic AO in combination with DSTDP.



The increased efficacy of AO-5 compared to the other phenols discussed here can be rationalized on the basis of two unique structural features. The linkage from the phenol moiety to the isocyanurate nucleus is meta to the phenol and there are mixed alkyl groups adjacent to the phenol. The 2-t-butyl-6-methylphenol moiety has lower steric hindrance than a 2,6-di-t-butylphenol. It is likely that this would increase the rate of reaction with polymer centered radicals. It also gives another site for the second reaction, the CB-A step of the mechanism (Scheme 6[12]). The combination of these two effects dramatically increases this compounds ability to stabilize polyolefins. The relative contribution of these two factors to the enhanced performance of AO-5 in process stabilization conditions has been investigated further. In multipass experiments, AO-5 was evaluated along side AO-6, a phenolic with the same amount of steric hindrance, in polypropylene. The results of this study are shown in Figure 7 and demonstrate that even at reduced concentration, AO-5 still outperforms AO-6. This suggests that the dual sites for peroxyl radical trapping (Scheme 6) afforded by the meta-linkage to the isocyanurate center are critically important to the enhanced process stabilization. The fact that the compound has a meta linkage to the isocyanurate nucleus also precludes the formation of highly conjugated systems that would lead to colored products since this linkage is more chemically stable than a para linkage.

Scheme 6

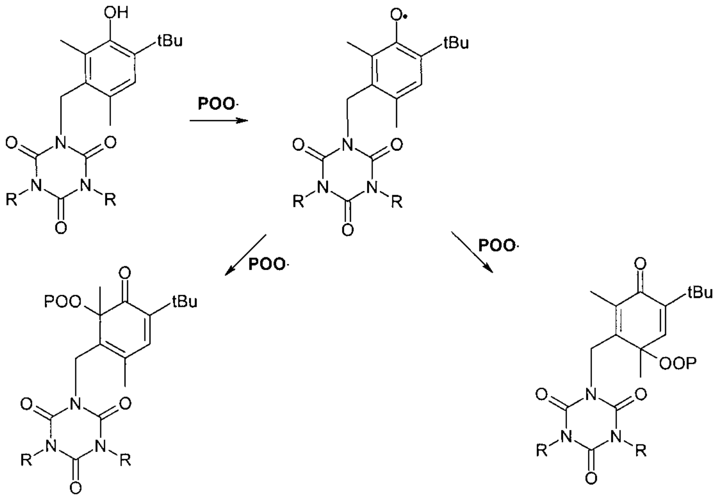
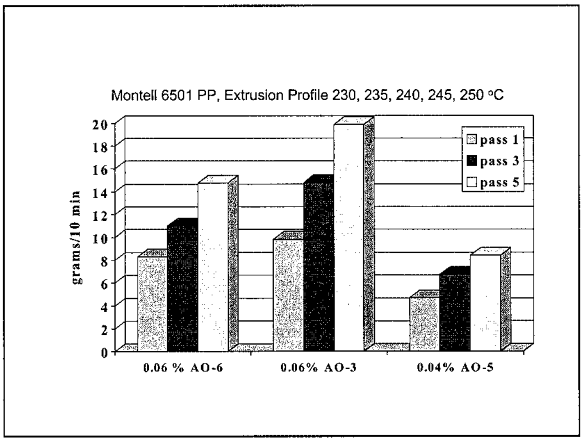
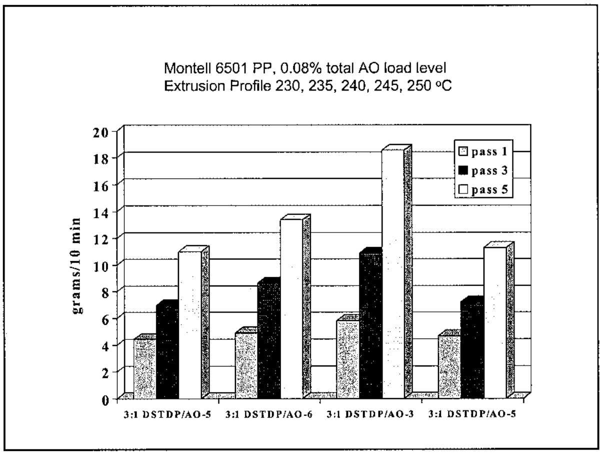


Figure 7. Multipass evaluation of "half hindered" phenolic antioxidants in comparison to a fully hindered phenol.



It has been reported in the literature that phenolic AO's with reduced steric hindrance about the phenol moiety, give enhanced synergism with thiodiesters. It has been hypothesized that the lower steric hindrance about the phenol allows hydrogen bonding between the phenol moiety and the thiodiester.[13] This close association presumably facilitates synergism especially during long term heat aging. In a multipass extrusion comparison of the process stabilizing efficacy of "half hindered" phenolic antioxidants in combination with DSTDP, AO-5 again performed better than AO-6 (Figure 8). Long term heat aging studies are underway to further investigate the extent of this synergism and these results will be reported in due course.

Figure 8. Evaluation of "half hindered" phenolics in combination with DSTDP (DSTDP + AO5 run in duplicate).



Conclusion

Phenolic antioxidants have undergone significant structural modification since their inception with BHT (AO-1). Modifications of this base structure have created molecules (AO-2) which are low in volatility, lower in color contribution and have excellent compatibility with polyolefins. Unfortunately, these molecules have low relative phenol content and are thus lower in activity on a per gram basis. This second generation (AO-2) exhibits better permanence and improved color but still suffers from a strong tendency to gas fade. The multifunctional phenolic antioxidant AO-3 overcomes the lower activity of AO-2, but this molecule still undergoes gas fade discoloration, particularly when used in combination with hindered amine light stabilizers. The fourth generation phenolics (AO-4 and AO-5) are also low in volatility but also exhibit exceptional gas fade resistance. Within the fourth generation, the unique 2-*t*-butyl-6-methyl hindered phenol of AO-5 results in an antioxidant with superior melt stabilizing abilities and superior gas fade resistance. Dependant upon the plastic application, a secondary antioxidant can be selected for use with AO-5 to design a system having improved melt process stability, lower color or enhanced long term heat aging. The relatively higher activity of AO-5 makes possible the use of lower concentrations of phenolic antioxidant while achieving excellent melt flow stabilization.

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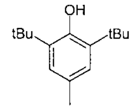
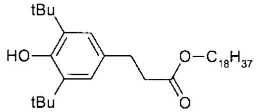
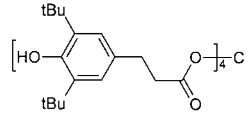
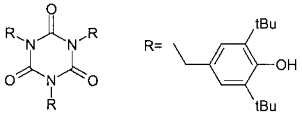
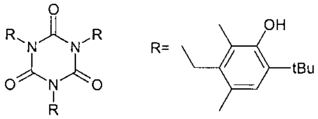
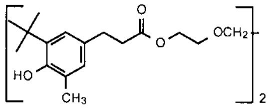
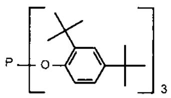
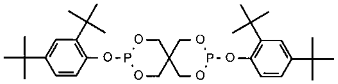
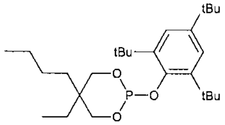
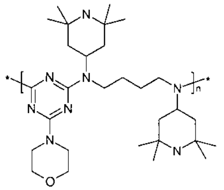
Appendix 1. Antioxidant Structures.

AO-1		BHT
AO-2		Irganox 1076
AO-3		Irganox 1010
AO-4		Cyanox® 1741 antioxidant
AO-5		Cyanox® 1790 antioxidant
AO-6		Irganox 245
P-1		Cyanox® 2704 antioxidant
P-2		Ultranox 626
P-3		Ultranox 641
HALS-1 **(see Figure 1)**		Cyasorb® 3346 light stabilizer