

Stabilization of High-Density Polyethylene*

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Synopsis

Several types of antioxidants are evaluated in high-density polyethylene for color and physical property stabilization during processing and thermal aging. A wide variety of evaluation tests are used and discussed. Heat- and light-induced oxidation mechanisms are reviewed. Antioxidants such as octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate and tetrakis[methylene 3-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl) propionate]methane were found to provide very high retention of physical properties, excellent initial color and color retention. Combinations of antioxidant- and ultraviolet light absorbers were evaluated for stabilizing high density polyethylene exposed to artificial light and outdoor weathering. The combination of octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate and 2-(2'-5'-di-*tert*-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole was found to be a very efficient stabilizer system. Polymer containing this stabilizer combination had excellent color stability and minimum crosslinking and embrittlement after Arizona weathering.

INTRODUCTION

High-density polyethylenes (HDPE) possess a combination of favorable physical properties, chemical resistance, and economic characteristics which render them extremely versatile and suitable in a wide variety of applications. Because of the high linearity and high degree of crystallinity of HDPE, both processing and service temperatures are considerably higher than for the lower-density, branched polyethylenes. Many molding and packaging film applications using high-density polyethylene must withstand boiling water as well as autoclave sterilization (250°F.) temperatures. High-density resins have also found widespread use in products designed for outdoor applications where degradation from sunlight and other weathering conditions becomes an important factor in the utility of the polymer. For the polymer successfully to withstand degradative oxidation accelerated by high processing and service temperatures as well as outdoor weathering conditions, a stabilizer or combination of stabilizers must be incorporated. The type and concentration of additives required to stabilize the polymer adequately will depend on the severity of the processing conditions and service environment, the thickness of the fabri-

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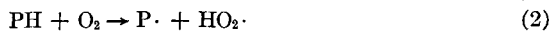
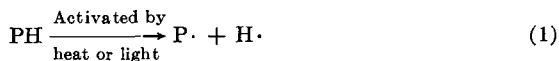
cated piece, mechanical strain, chemical environment (chlorine, hot water, etc.), and the duration of useful life desired.

DEGRADATIVE OXIDATION MECHANISMS

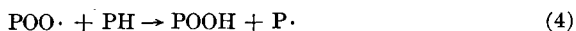
Unlike polypropylene and highly branched low-density polyethylene, high-density linear polyethylene possesses very few tertiary hydrogen atoms which are one of the primary sites for initiation of oxidative degradation. However HDPE does have a small amount of branching and greater ethylenic unsaturation than low-density polymer.¹ Unstabilized HDPE is more oxidatively stable than polypropylene but less stable than low-density polyethylene. This is due in part to (1) the higher processing temperatures which HDPE is subjected to which results in the formation of initiating sites for oxidation and (2) the high ratio of crystalline to amorphous content. Throughout the polymer there are large numbers of microscopic, highly crystalline regions or "spherulites," linked together by loosely arranged molecular chains. The spherulites are denser than the amorphous regions and therefore less readily penetrated by oxygen. The amorphous regions in a sense protect the polymer against rapid degradation by preferentially absorbing oxygen. The more crystalline polyethylenes are more vulnerable to degradation because although their greater density decreases the overall oxygen absorption, the penetration that does occur results in greater damage. Bobalek et al.² have shown experimentally that physical degradation of linear polyethylene was greater, although the oxygen absorbed in a given time was less than for branched polyethylene. Other investigators³ have obtained similar results studying ultraviolet light-initiated oxidation of linear polyethylene.

A number of authors have dealt with autocatalytic oxidation mechanisms in hydrocarbons and polyethylenes in particular.⁴⁻⁷ A general kinetic mechanism for the oxidation of polypropylene summarizing many of the above papers was recently presented⁸ as shown in eqs. (1)–(16) and is applicable to high-density polyethylene.

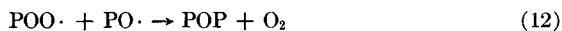
Initiation:



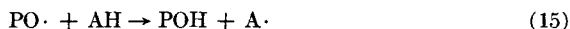
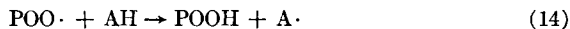
Propagation:



Termination by recombination:



Termination by antioxidant stabilization:



Degradation of physical properties is caused by both chain scission and crosslinking which occur simultaneously but to different degrees at any one time. The polymer properties after exposure depend on whether scission or crosslinking is predominant. In the case of HDPE properties such as melt index, tensile strength, per cent elongation, and folding endurance decrease with oxidation. In addition, the polymer becomes brittle, and surface cracking may occur. The rapid decrease in melt index generally indicates that crosslinking is the predominant reaction.

EXPERIMENTAL PROCEDURE

For high-density polyethylene some of the measurements which define polymer degradation are embrittlement, folding endurance, color, melt flow stability, and retention of tensile properties. Test conditions used to evaluate each of these properties are detailed below.

Process Stability

This property was evaluated by following change in melt index (g./10 min. at 190°C.) as the polymer was successively reextruded through a 24:1 *L/D* 1-in. extruder at an extrusion temperature of 550°F. Hunter ($L + 3a - 3b$) color was also measured after each extrusion where *L* is the total white color reflectance, *a* is the red-green reflectance, and *b* is the yellow-blue reflectance as measured with a Hunter color and color difference meter. In addition, process stability was evaluated by measuring the change in melt index as a function of residence time in a Tinius Olsen Extrusion Plastometer at 300°C.

High-Temperature Stability

Hunter *L-b* color (ASTM D1365-60T), hand-stressed (sample bent 180° after aging) embrittlement, and tensile properties were used to evaluate the stability of 40-mil high-density polyethylene plaques placed in a forced draft oven at 120°C. The plaques were attached to revolving

shelves within the oven. Tensile properties were determined on an Instron testing machine at a crosshead speed of 10 in./min. as described in ASTM D638-60T; 20-mil plaques were evaluated for folding endurance after oven aging at 100°C. Measurements were made on a MIT Plastic Folding Endurance Machine in accordance with ASTM D2176-63T. All the plaques were compression-molded at a platen pressure of 2000 psi and temperature at 350°F.

Accelerated Artificial Light Stability

The stability of 60-mil plaques was determined after exposure to an XW-type Atlas Weather-O-meter and a fluorescent sunlamp-black light

TABLE I

Polymer	Melt index, g./10 min. at 190°C.	Density, g./cc.
A	3.0	0.957
B	0.9	0.960
C	1.5	0.955
D	4.5	0.955

TABLE II
Identification of Stabilizers

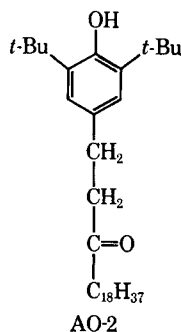
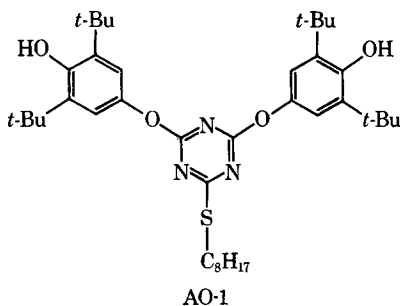
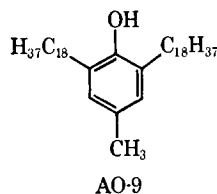
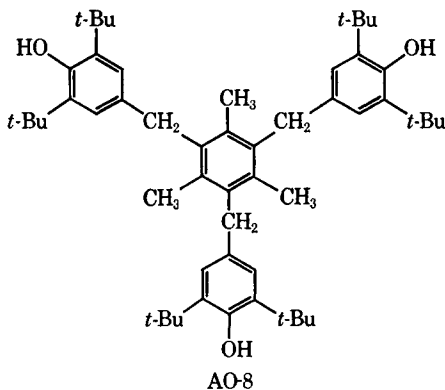
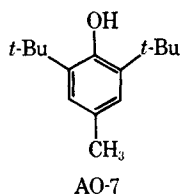
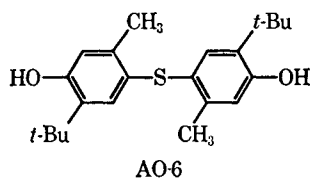
Class	Code	Chemical name
Antioxidants	AO-1	2,4-Bis(4-hydroxy-3,5-di- <i>tert</i> -butylphenoxy)-6-(<i>n</i> -octylthio)-1,3,5-triazine
	AO-2	Octadecyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate
	AO-3	Tetrakis[methylene 3-(3',5'-di- <i>tert</i> -butyl-4'-hydroxyphenyl)-propionate]methane
	AO-4	1,1,3-Tris(5- <i>tert</i> -butyl-4-hydroxy-2-methylphenyl)butane
	AO-5	4,4'-Butylidenebis(6- <i>tert</i> -butyl- <i>m</i> -cresol)
	AO-6	4,4'-Thiobis(6- <i>tert</i> -butyl- <i>m</i> -cresol)
	AO-7	2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol
	AO-8	1,3,5-Trimethyl-2,4,6-tris(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl)benzene
	AO-9	2,6-Di-octadecyl- <i>p</i> -cresol
UV Absorbers	UV-1	2-(3'- <i>Tert</i> -butyl-2'-hydroxy-5-methylphenyl)-5-chlorobenzotriazole
	UV-2	2-(3',5'-Di- <i>tert</i> -butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole
	UV-3	2-(3',5'-Di- <i>tert</i> -butyl-2'-hydroxyphenyl)-benzotriazole
	UV-4	2'-Hydroxy-4- <i>n</i> -octyloxybenzophenone

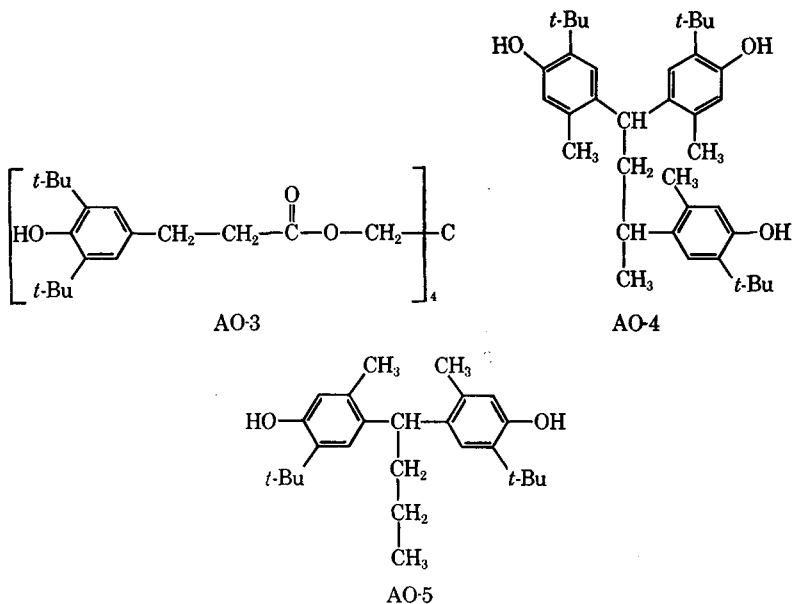
device (FS/BL) by measuring Hunter *L-b* color, hand-stressed embrittlement, and melt index (at 190°C.). The fluorescent sunlamp-black light device consisted of a vertical, circular array of 18 alternating 40-w. fluorescent sunlamps and black lights. Samples are arranged on the periphery of circular rotating shelves within the circle of lamps, 2 in. from the surface of the lamps. The plaques were molded under the same conditions as those above.

Outdoor Weathering

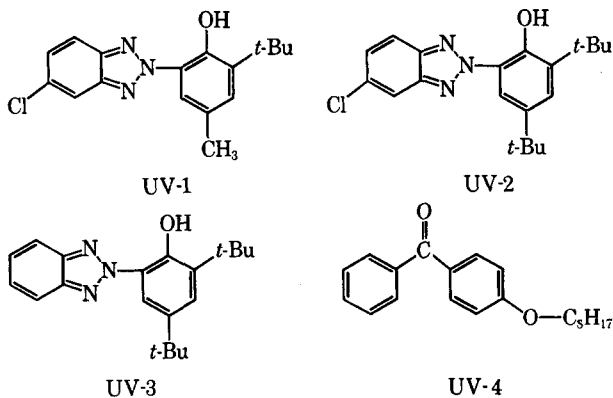
The stability of 60-mil plaques was evaluated after exposure to Arizona sunlight at 45°, south, direct and unbacked by determining hand-stressed embrittlement and melt index at 190°C.

Four unstabilized high-density polyethylene resins were used in this study; their properties are summarized in Table I.





Nine hindered polyphenol antioxidants (Table II), three substituted hydroxyphenylbenzotriazole ultraviolet absorbers, and one hydroxybenzophenone ultraviolet absorber (Table II) were evaluated in this study. Combinations of antioxidant and ultraviolet light absorber were evaluated in 60-mil plaques exposed to accelerated artificial light and to outdoor weathering.



RESULTS AND DISCUSSION

Process Stability

An essential factor in the manufacture of a useful high-density polyethylene polymer is the preservation of its inherent properties during various manufacturing processes such as drying and extrusion. These operations are conducted at temperatures which could rapidly degrade an unstabilized

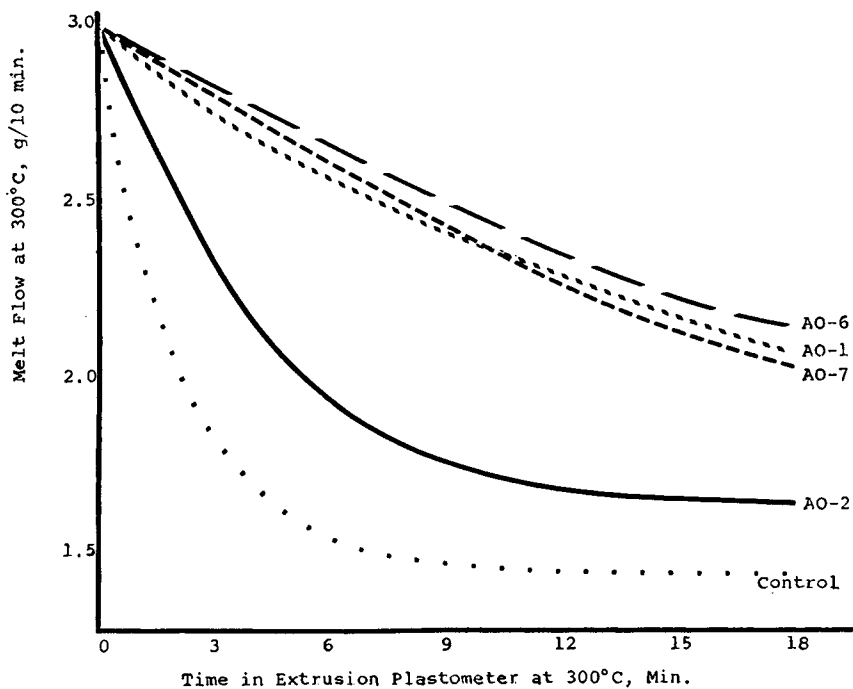


Fig. 1. Process stability of HDPE. Initial melt index, 0.9; density, 0.960 g./cc.; 0.05% antioxidant.

polymer. Antioxidants are also needed to prevent additional degradation which can occur during end-use fabrication operations.

A comparison of four different antioxidants at 0.05% in stabilizing HDPE at 300°C. is shown in Figure 1. Degradation is measured by a change in melt flow after various periods of time in an extrusion plastometer under a constant load (2.16 kg.). The rapid degradation of the unstabilized control clearly indicates the need for an antioxidant. AO-6, AO-1, and AO-7 appear to be equally effective.

Another method of evaluating process stability is measuring the change in melt flow (at 190°C.) after each of five successive extrusions at 550°F. Six antioxidants are evaluated at 0.02% as shown in Figure 2. AO-6, a thiobisphenol, appears to be the most effective antioxidant according to this test. Although the maximum shear rates in the plastometer are lower than those found in the extruder at normal operating screw speeds, the temperature in the plastometer is slightly higher (300°C. versus 288°C.).

An important aspect of process stability is the ability of an antioxidant to provide continued thermal stability after the polymer has been extruded more than once. This would simulate the use of scrap regrind which is dictated by the economics of many molding operations. A comparison of antioxidants to provide thermal stability at 100°C. after one and five successive extrusions at 550°F. is shown in Table III. AO-7, being a low

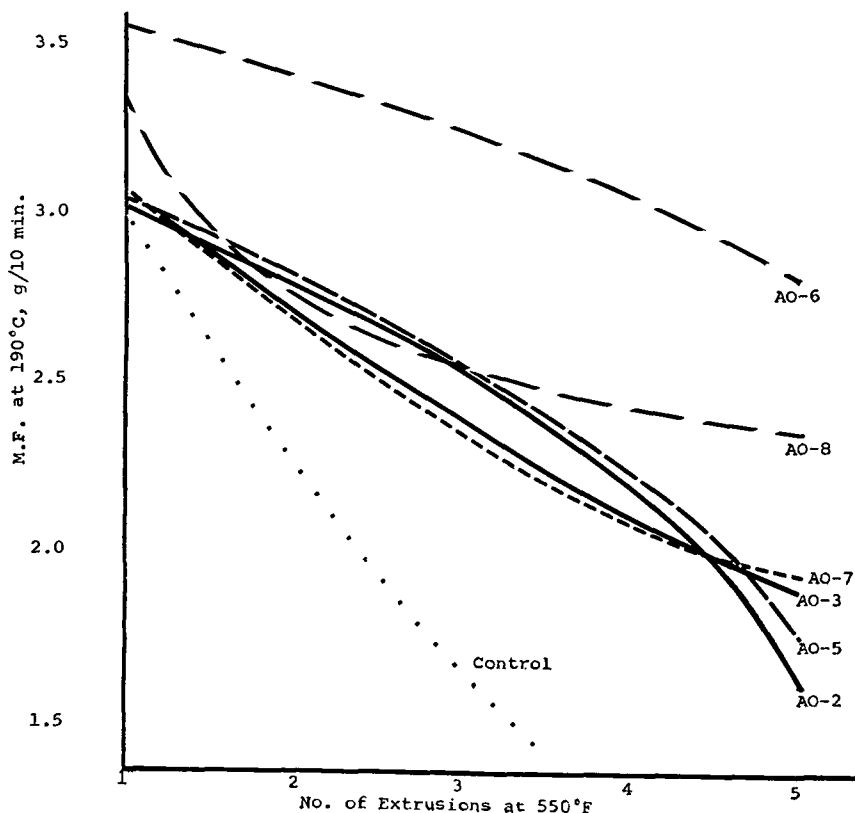


Fig. 2. Process stability of HDPE. Initial melt index, 4.5; density, 0.955 g./cc.; 0.02% antioxidant.

molecular weight phenol, is readily lost during repeated extrusions and becomes ineffective as a thermal stabilizer. AO-2, AO-3, and AO-8 are high molecular weight phenols and are only slightly affected by successive extrusion of the polymer.

TABLE III
Thermal Stability of HDPE Multiple Extrusions*

Antioxidant	Time to failure at 100°C., hr.		
	After 1 extrusion	After 5 extrusions	Retention, %
Control	230	160	70
AO-2	3720	3420	92
AO-3	4440	3720	84
AO-5	2315	1320	57
AO-6	2315	1835	79
AO-7	1130	475	42
AO-8	4355	3970	91

* 30-mil plaques; initial melt index, 4.5; density, 0.955 g./cc.; 0.02% antioxidant.

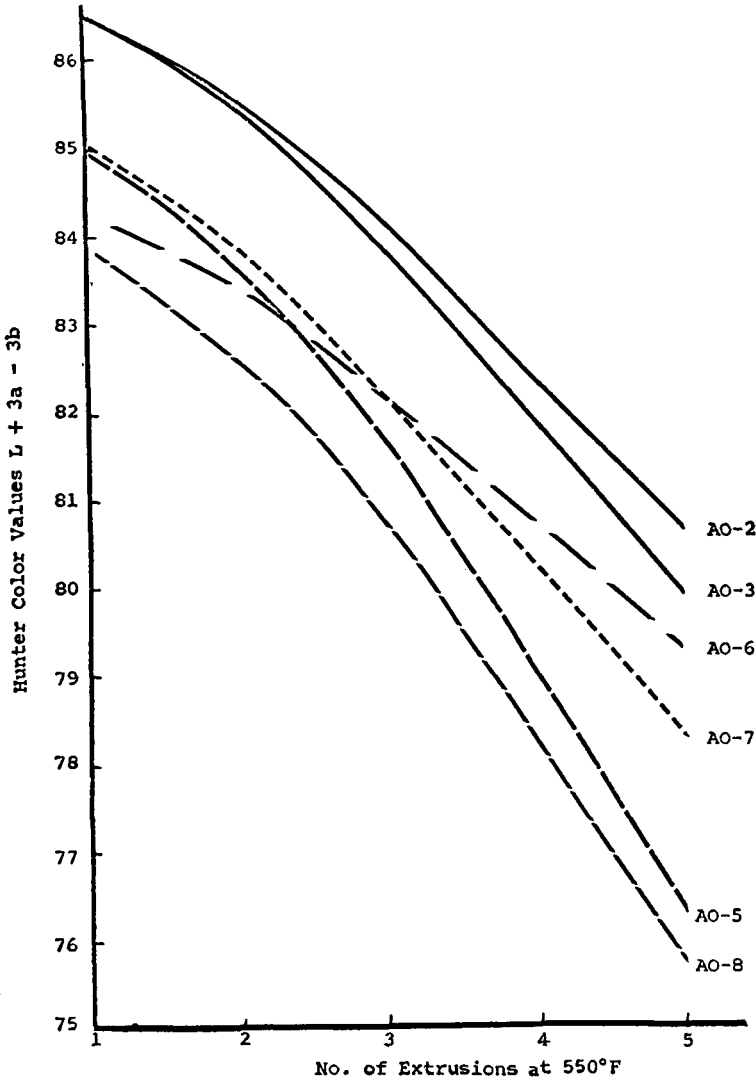


Fig. 3. Color of HDPE after multiple extrusions. Initial melt index, 4.5; density, 0.955 g./cc.; 0.02% antioxidant.

Besides providing viscosity stability to the polymer melt during processing, antioxidants should not discolor the polymer and should protect against color change at processing temperature. This is particularly important in packaging, closure, and container applications. Color measurements during the repeated extrusions above as shown in Figure 3 indicate that AO-2 and AO-3, hindered phenols, not only provide the best color retention but by adding the least amount of color to the polymer also provide the best initial color. Although AO-6 provides good viscosity stability it is not a very effective color stabilizer. A comparison of the

curves in Figure 3 indicate that most of the differences in color stability occur during initial processing (i.e., after first extrusion). These differences appear to remain the same for subsequent extrusions. AO-2 and AO-3 stabilize the polymer in a somewhat different manner than AO-6; the latter, a thiobisphenol, stabilizes by trapping free radicals with the labile hydrogen on the phenol and also possibly by a peroxide decomposition mechanism, reduction carried out with the two pairs of unshared electrons on the sulfide linkage. AO-2 and AO-3 stabilize only by the free radical-trapping mechanism. However, the degree of stabilization will vary greatly for a given polymer at a given set of conditions depending on antioxidant properties such as volatility, polymer compatibility, number of labile hydrogen atoms available, location of substituent groups, and the stability of the antioxidant free radical after removal of the labile hydrogen.

Extended Stability at High Temperatures

As mentioned earlier, HDPE lends itself to such applications as sterilizable containers, kitchenware which can be cleaned in dishwashers, and boilable food packages. For these types of high-temperature applications a stabilizer must be able to provide an extended useful life to the fabricated product. Two types of accelerated tests are used in this study to measure polymer degradation. These are (1) retention of physical properties after oven aging at 100°C. and at 120°C. and (2) retention of color after oven aging at 120°C.

Six antioxidants at two concentrations are compared for efficiency in retaining tensile properties of HDPE after oven aging at 120°C. as shown in Figures 4 and 5. AO-1 and AO-2 appear to provide the best stability to the polymer. At an increase in concentration from 0.015% to 0.03% AO-8

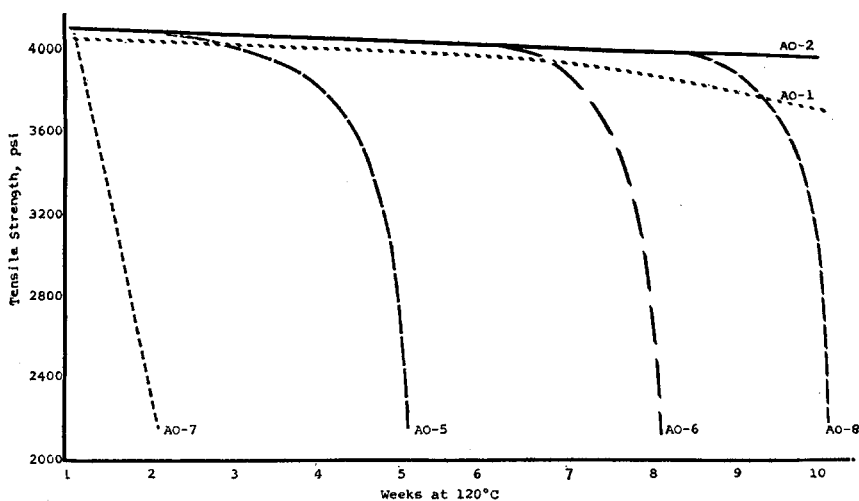


Fig. 4. Tensile retention of HDPE at 120°C. Initial melt index, 1.5; density, 0.955 g./cc.; 0.015% antioxidant.

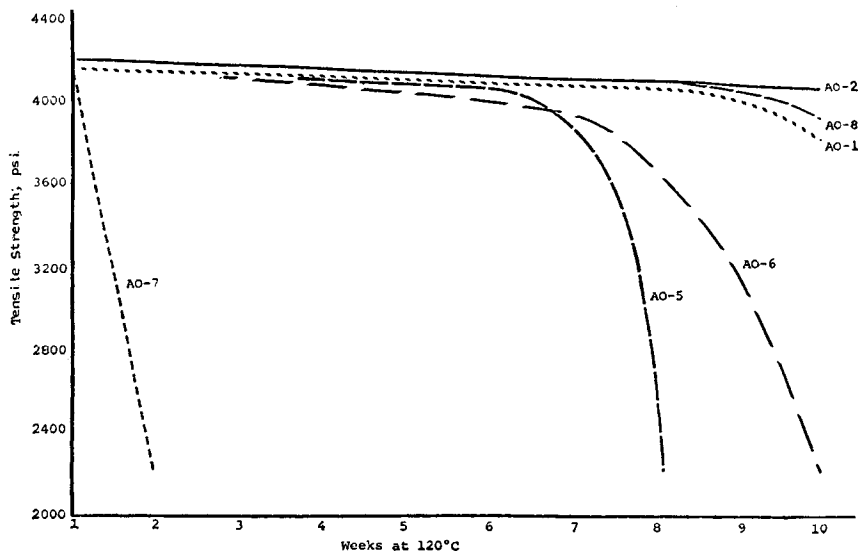


Fig. 5. Tensile retention of HDPE at 120°C. Initial melt index, 1.5; density, 0.955 g./cc.; 0.03% antioxidant.

approaches the stability of AO-1, while AO-2 at either concentration does not show any sudden decrease in tensile strength throughout the duration of the test. AO-7, which appeared to be a fairly effective processing stabilizer, has very poor high-temperature long-term stabilizing properties. This is probably due to the relatively high volatility of AO-7 compared to many of the other antioxidants in this study. Other investigators⁹ have found that antioxidants having the same number of OH groups per unit weight of antioxidant (equal free radical-terminating potential) and similar oxygen absorption induction periods had very different oven-aging lifetimes. This was due primarily to differences in the volatilization of the antioxidant and the polymer oxidation products while in the oven.

Folding endurance after oven aging at 100°C. is another means of evaluating antioxidant efficiency as shown in Figure 6 for nine antioxidants at three different concentrations. Again, AO-2 and AO-3 have superior stabilizing properties, no failure being observed after 20 weeks of oven aging. It is interesting to note that AO-1, AO-2, and AO-3 show the strongest response to increasing concentration. Here again AO-7 appears to have negligible stabilizing efficiency. AO-9, the octadecyl analog of AO-7, shows a marked increase in stabilizer efficiency which may reflect a lower volatility.

The same nine antioxidants are compared for stabilization against hand-stressed embrittlement after oven aging at 120°C. as shown in Figure 7. At this higher temperature AO-3 provides the most effective stabilization. Less effective are AO-2, AO-8, and AO-1 in the same relative order as in the folding endurance test above. The greater efficiency of AO-3 to

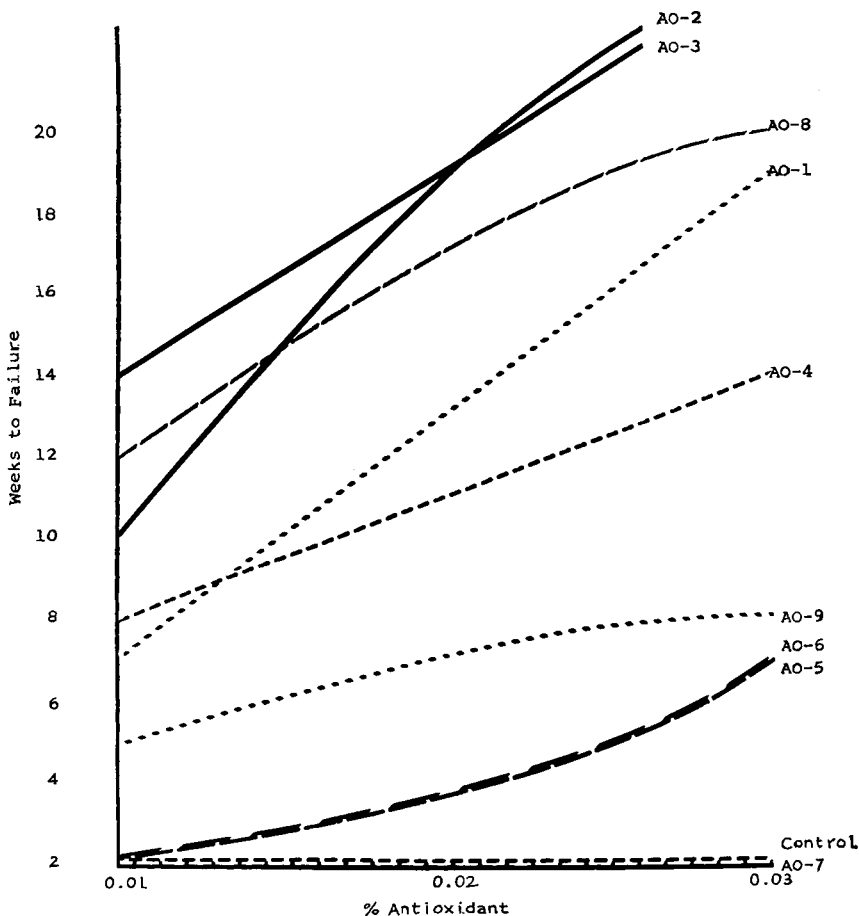


Fig. 6. Folding endurance of HDPE at 100°C. Initial melt index, 3.0; density, 0.957 g./cc.; 20-mil plaques.

AO-2 at this temperature may be due to the lower volatility of AO-3 as a result of its higher molecular weight.

Retention of color is another important stabilizer requirement during high temperature oven aging. A comparison of antioxidant efficiency at two concentrations at 120°C. is shown in Figures 8 and 9. The comparative rating of antioxidants is similar to the tensile retention evaluation shown in Figures 4 and 5. At a level of 0.03% AO-1 and AO-2 there is very little change in color after 12 weeks at 120°C.

Light Stability

To stabilize HDPE for both indoor and outdoor use where photodegradation as well as thermal degradation can occur, a combination of antioxidant and ultraviolet absorber is used. The antioxidant component is needed because polymer degradation is not only caused by initial photo-

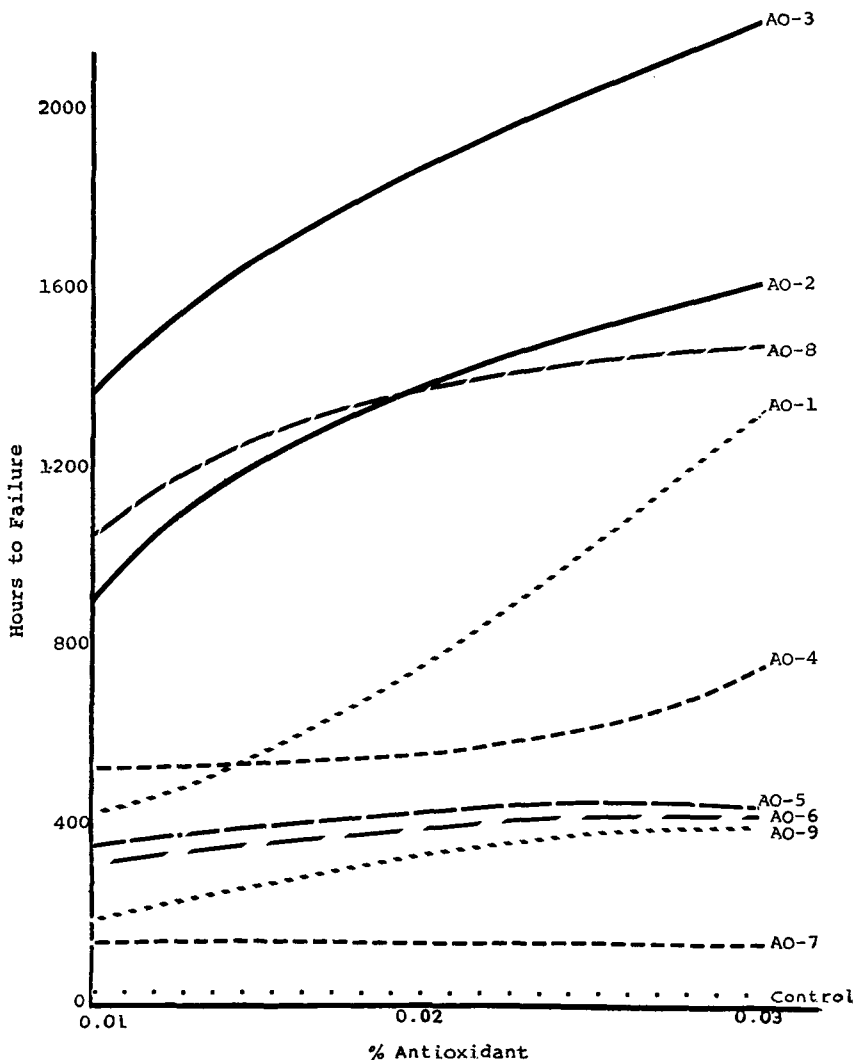


Fig. 7. Embrittlement of HDPE at 120°C. Initial melt index, 3.0; density, 0.957 g./cc.; 40-mil plaques.

chemical reactions but also by post-irradiation chain reactions. This combination is synergistic in the sense that the ultraviolet absorber reduces the rate of free-radical formation and thus prolongs the life of the chain-terminating antioxidant.

Accelerated Artificial Light. Time to embrittlement (hand-stressed) was the criterion for evaluating the effectiveness of: (a) six antioxidants at 0.05% in combination with 0.3% UV-2 and (b) four ultraviolet absorbers at 0.3% in combination with 0.05% AO-2 after exposure to a fluorescent sunlamp-black light (FS/BL) device and an Atlas Weather-O-meter respec-

tively, as shown in Table IV. Antioxidants, AO-2, AO-3, and AO-7 appear to be equivalent and more effective than either UV-2 or AO-2 alone. Among the four ultraviolet absorbers, there does not appear to be much difference in stability.

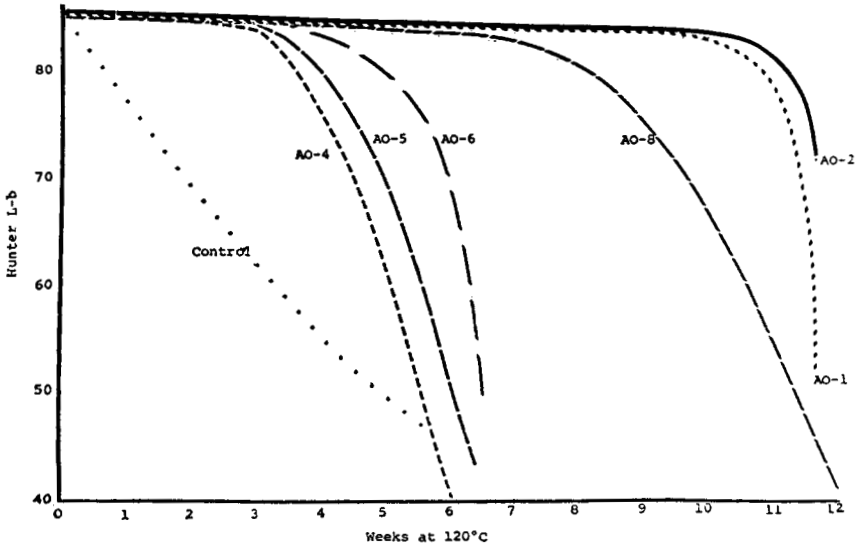


Fig. 8. Color retention of HDPE at 120°C. Initial melt index, 1.5; density, 0.955 g./cc.; 0.015% antioxidant.

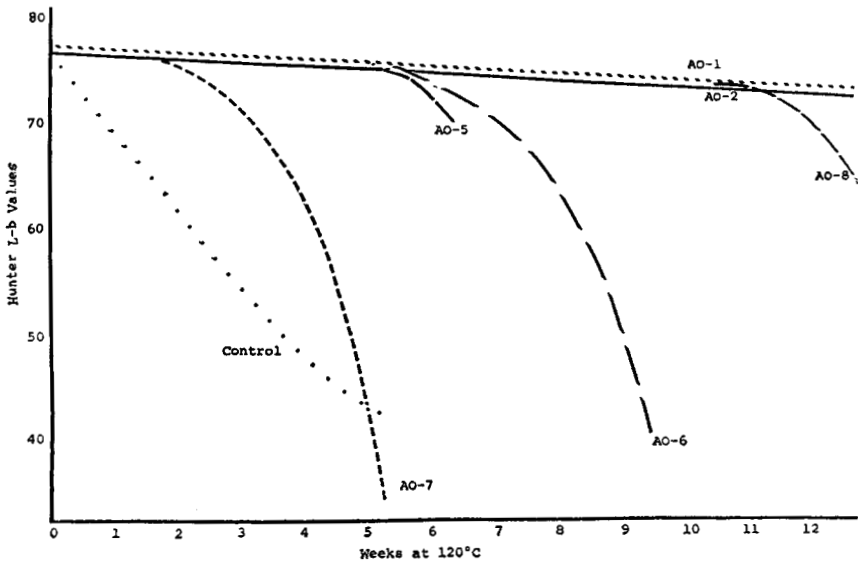


Fig. 9. Color retention of HDPE at 120°C. Initial melt index, 1.5; density, 0.955 g./cc.; 0.03% antioxidant.

TABLE IV
Brittleness of High-Density Polyethylene
After Various Light Exposures*

Stabilizer level	Stabilizer	Kilolangleys to embrittlement Arizona, 45° S	Time to embrittlement, hr.	
			FS/BL	Weather-O-meter
0.05% AO + 0.3% UV-2	Control	< 25	450	150
	UV-2 alone	75	850	500
	AO-2	>125	>1500	800
	AO-3	100	>1500	800
	AO-4	75	1400	350
	AO-5	75	1450	400
	AO-7	>125	1500	800
	AO-8	75	>1500	700
0.05% AO-2 + 0.3% UVA	AO-2 alone	< 25	450	150
	UV-1	>125	>1500	800
	UV-2	>125	1500	800
	UV-3	125	1500	800
	UV-4	>125	>1500	800

* Melt index, 3.0; density, 0.957 g./cc.; 60-mil plaques.

TABLE V
Melt Index at 190°C. After Light Exposures*

Stabilizer level	Stabilizer	Unexposed	Melt index at 190°C. after exposure, g./10 min.	
			500 hr. Weather-O-meter	125 kangleys, Arizona, 45° S
0.5% Antioxidant + 0.3% UV-2	Control (no AO or UVA)	2.3	0.2	0.1
	UV-2 alone	2.2	1.4	2.3
	AO-2	2.9	2.3	2.5
	AO-3	2.7	2.1	2.2
	AO-4	2.7	2.1	2.5
	AO-5	2.6	2.1	2.4
	AO-7	2.8	2.4	2.4
	AO-8	2.7	2.2	2.5
0.05% AO-2 + 0.3% UVA	AO-2 alone	2.8	2.3	2.6
	UV-1	2.8	2.2	2.4
	UV-2	2.9	2.3	2.5
	UV-3	2.8	2.3	2.4
	UV-4	2.7	1.9	1.7

* Melt index, 3.0; density, 0.957 g./cc.

Since embrittlement may be due to greater oxidation on the surface of the plaque rather than through its cross-section melt indices of the exposed plaques were used as an additional test to determine any possible degradation in the bulk of the polymer. A comparison of the above six antioxidants and four ultraviolet absorbers after 500 hr. of Weather-O-meter exposure is shown in Table V. Unstabilized polymer (control) is highly cross-linked, as indicated by a decrease in melt index from 2.3 to 0.2. AO-2 and AO-7 are the most effective antioxidants, the former also providing the best initial stability. In contrast with the embrittlement data, none of the ultraviolet absorbers are more effective than AO-2 alone. Interestingly

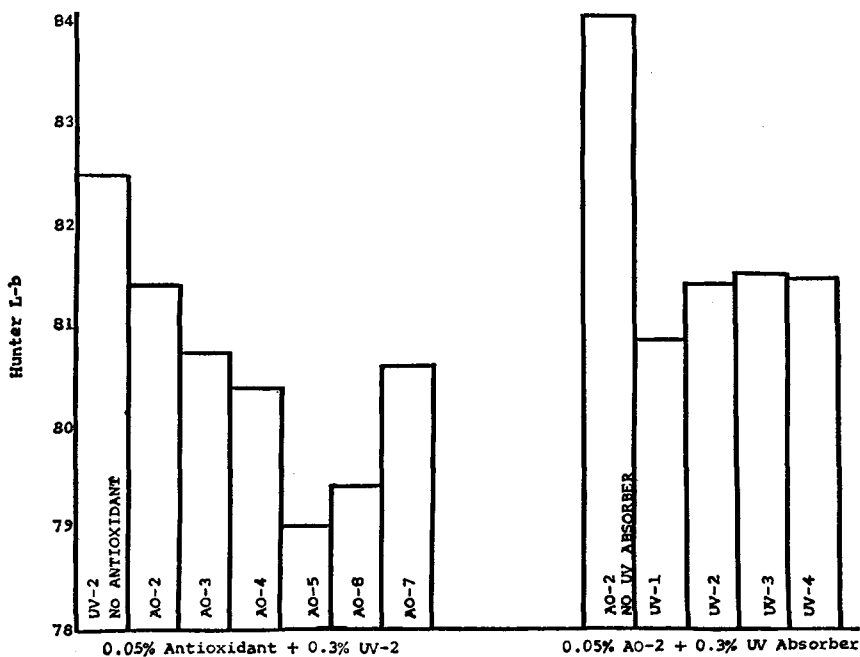


Fig. 10. Color of HDPE after 1500 hr. of FS/BL exposure. Initial melt index, 3.0; density, 0.957 g./cc.

UV-4 which appears quite effective in preventing embrittlement is the least effective ultraviolet absorber in providing stability against crosslinking degradation. Other investigators¹⁰ have measured tensile strength, elongation, and melt index of HDPE during exposure in a Weather-O-meter and have observed that surface cracking and embrittlement occur at about the same time as a significant decrease in the above physical properties.

In addition to retention of physical properties, color stability was evaluated for the two above stabilizer systems (0.05% AO + 0.3% UV-2 and 0.05% AO-2 + 0.3% UV) after 1500 hr. of FS/BL exposure as shown in Figure 10. The antioxidants all provide less stability than UV-2 (an hydroxyphenyl benzotriazole) alone, although AO-2 is the most effective

of the six antioxidants. AO-2 alone at 0.05% provides the best color stability of either stabilizer system.

Outdoor Weathering. The same two AO/UVA stabilizer systems as discussed above are evaluated for outdoor weathering stability by determining the number of klangleys to embrittlement after exposure to Arizona sunlight, 45° south, direct, unbacked as shown in Table III (A langley unit is defined as 1 g.-cal./cm.² or 3.69 Btu/ft.²). Polymer containing antioxidant (AO-2) alone have little light stability failing before 25 langleys are reached. This may be due to a "swamping" of the antioxidant with photoinitiated free radicals as well as possible degradation of antioxidants themselves when exposed to UV light. Polymer containing ultraviolet absorber (UV-2) alone is equivalent to several less effective antioxidants in combination with UV-2. This points out the importance of using a highly efficient antioxidant such as AO-2 in combination with the ultraviolet absorber. Of the antioxidants, AO-2 and AO-7 are the most effective stabilizers, while UV-1, UV-2, and UV-4 provide equivalent stability and are slightly more effective than UV-3.

Melt indices of the exposed plaques after 125 klangleys of Arizona, 45° south sunlight indicate little differences in stability among the antioxidants. Comparing the ultraviolet absorbers, the hydroxyphenyl benzotriazoles (UV-1, UV-2, and UV-3) are approximately equivalent in stability and are not quite as effective as AO-2 alone. Again as when exposed in a Weather-O-meter, the *o*-hydroxybenzophenone (UV-4) is less effective in providing stability against photoinitiated crosslinking degradation.

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References

1. M. N. Berger and T. H. Boulton, *J. Appl. Chem.*, **9**, 490 (1959).
2. E. G. Bobalek, J. N. Henderson, T. T. Serofini, and J. R. Shelton, *J. Appl. Polymer Sci.*, **2**, 210 (1959).
3. S. Ozawa and K. Maekawa, *Kobunshi Kagaku*, **20**, 357 (1963).
4. W. L. Hawkins, W. Matreyek, and F. H. Winslow, *J. Polymer Sci.*, **41**, 1 (1959).
5. W. L. Hawkins, *Polymer Eng. Sci.*, **5**, 196 (1965).
6. B. Baum, *J. Appl. Polymer Sci.*, **11**, 281 (1959).
7. B. Wright, *Brit. Plastics*, **36**, No. 9, 111 (1963).
8. D. A. Gordon and E. C. Rothstein, *Polymer Eng. Sci.*, **6**, 231 (1966).
9. M. Blumberg, C. R. Boss, and J. C. W. Chien, *J. Appl. Polymer Sci.*, **9**, 3837 (1965).
10. C. Gottfried and M. J. Dutzer, *J. Appl. Polymer Sci.*, **5**, 612 (1961).

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