The Effect of Hindered Phenol Stabilizers on Oxygen Induction Time (OIT) Measurements, and The Use of OIT Measurements to Predict Long Term Thermal Stability – Philip Jacoby, Vice President of Technology, Mayzo Inc., Norcross, GA

Introduction:

The Oxygen Induction Time (OIT) test is an accelerated aging test that is often used to predict the long term stability of hydrocarbon materials including plastics, rubbers, and adhesives. The OIT test can also be used to measure the level of effective antioxidant present or remaining in a polymeric material after some environmental exposure. Since thermal-oxidatative degradation requires the presence of oxygen at elevated temperatures, the OIT test is designed to accelerate this degradation in order to achieve meaningful comparisons in a short period of time. The standard OIT test is performed according to ASTM D3895, and uses a Differential Scanning Calorimeter (DSC). A few mg of the material to be tested are introduced into the DSC at room temperature, and the sample is heated to about 200 ^{o}C under a nitrogen atmosphere. When 200 ^{o}C is reached the cell is maintained in an isothermal condition, and the gas is changed from nitrogen to oxygen. The pressure and flow rate of the oxygen are maintained at 35 kPa and 50 cc/min, respectively. Under these conditions the stabilizer is consumed over time until it is totally depleted. At this point the polymer sample catastrophically degrades or oxidizes liberating additional heat (exotherm). The time it takes for this exotherm to appear from the time that the oxygen is introduced is reported as the OIT time, and is a measure of the thermal stability of the material. A typical OIT curve for polyethylene is illustrated in Figure 1.

A high pressure version of the OIT test can also be performed using a cell that can withstand a pressure of 5500 kPa, and this test follows ASTM D5885. The high pressure test is generally used when lower test temperatures are desired, such as 150 ^{o}C. Sometimes higher test temperatures will bias the test results for certain types of antioxidants, as discussed later in this paper. If the standard OIT test were used at these low temperatures the duration of the test would be very long. At high oxygen pressure the concentration gradient of oxygen atoms across the specimen's surface increases, and this accelerates the oxidation process and reduces the testing time.

The OIT value generally follows a linear relationship with antioxidant concentration, as illustrated in Figure 2. This behavior makes the OIT test a useful quality control procedure for tracking the concentration of the antioxidant.

Background of the OIT Test:

The OIT procedure was first developed at Bell Laboratories as a test method for screening polyethylene insulation used in telephone wire and cable for its oxidation resistance. The method first became available as a Western Electric specification[1] and later as an ASTM Standard[2]. It is well known that the effectiveness of antioxidants, as measured by the OIT test, is sensitive to the temperature range where the measurement is made[3]. A number of factors influence this sensitivity including changes in the degradation and stabilization mechanism, volatility of the antioxidant at high test temperatures, etc. These difficulties can be minimized by moving the test temperature closer to that of the end-use temperature, and then using a high pressure DSC to further accelerate the test.

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[1] Western Electric Manufacturing Standard 17000, Section 1230 (1971)

[2] ASTM D3895, "Test method for Oxidative Induction Time of Polyolefins by DSC".

[3] Howard, J.B., and Gilroy, H.M., Polym. Eng. Sci., 15, 268-271 (1975)

Introduction To Polymer Stabilization:

All organic polymers will degrade when exposed to certain environmental conditions such as high temperatures, mechanical shear, and high energy radiation (e.g. UV exposure). The presence of oxygen will often accelerate this degradation. The first step in the degradation process is usually the loss of a hydrogen atom from the polymer chain due to this energy input. This polymer "free radical", [R*], can then react with an oxygen (O_2) molecule to form a peroxy radical [ROO*] which will in turn abstract a hydrogen atom from another polymer chain to form a hydroperoxide [ROOH]. The hydroperoxide can split into two new free radicals, [RO*] + [*OH], which continue to propagate the reaction to other polymer molecules. For certain polymers, such as polypropylene, a polymer chain containing a free radical is likely to split into two smaller chains, while for polyethylene chains, the free radical often causes one chain to graft onto another chain leading to crosslinking.

One way to interrupt this process is to incorporate an antioxidant into the polymer. There are different types of antioxidants that interrupt the degradation cycle at different points, and these types are listed in Table 1. The primary antioxidants, such as hindered phenol compounds, are designed to react with the initial free radicals that are formed, as illustrated by the schematic in Figure 3. These hindered phenols are often referred to as radical scavengers, since they react rapidly with peroxy radicals thereby breaking the degradation cycle. The various hindered phenols can differ from one another in molecular weight, number of hindered phenol groups per molecule, volatility, and solubility in the polymer. Higher molecular weight compounds, such as BNX 1010, are less volatile and more effective at higher temperatures and at longer exposure times.

A secondary antioxidant such as a phosphite compound can interrupt the degradation cycle at another point by reacting with the hydroperoxides that are formed. A schematic of this function is illustrated in Figure 4. A combination of a primary and a secondary antioxidant is particularly effective in minimizing degradation, since the two act in a synergistic manner. The choice of the particular combination of stabilizers used and the stabilizer level required, is influenced by the severity of the thermal history experienced by the polymer, as well as the needed end-use lifetime.

Another class of stabilizers are the light or UV stabilizers, and the most common types are listed in Table 2. The Hindered Amine Light Stabilizers (HALS) react with the free radicals that are formed when a high energy UV photon causes a chemical bond in the polymer to break. The HALS molecule is actually regenerated as it "mops up" the free radicals, so that HALS are often very effective as long term stabilizers. HALS can also be used to provide thermal stability at the appropriate temperature range. The UV absorbers promote stability by absorbing harmful UV radiation before it leads to the production of free radicals.

In choosing the most appropriate stabilizer package, it is important to know what temperature range the polymer will be exposed to when stabilization is required. The best package should protect the polymer during both the processing stage, where high temperatures are used to melt and form the material, and the lower end-use temperatures that it will be exposed to during its useful lifetime. The effective temperature ranges for four different chemical types of stabilizers are illustrated in Figure 5. The hindered phenols and phosphates are very effective processing stabilizers due to their high temperature performance, while the hindered phenols, thiosynergists, and HALS (hindered amine light stabilizers) provide excellent long-term protections at lower temperatures. Although HALS are more commonly used to provide UV protection, they are excellent long term thermal stabilizers at use temperatures below about 125 °C. It should also be noted that HALS and thioesters are generally not used in the same formulation, since the acidic byproducts from the thioesters can react with the basic HALS rendering it ineffective as a stabilizer.

Accelerated Aging Tests:

In addition to stabilizing a polymer to minimize degradation during processing, it is also important to insure that the polymer does not degrade during its useful lifetime in the field. Post-processing degradation reactions can lead to a loss of physical properties resulting in premature part failure, or to unacceptable changes in appearance such as color changes and loss of surface gloss. Since this useful lifetime may extend to several months or years, it is necessary to use accelerated aging tests in order to gauge the effectiveness of a given stabilization package. Predicting service lifetimes has been a major challenge for the plastics industry.

The type of accelerated test used depends on the nature of the environment that the end-use part is exposed to. One of the most important environmental stresses seen by polymers is high temperature exposure in the presence of air, also known as thermal-oxidative (TO) degradation. The general method for accelerating the TO degradation is to expose the material to elevated temperatures in either an air or pure oxygen environment. Forced air ovens are often used for this purpose. The test specimens may consist of either molded bars, films, fibers, or pressure sensitive adhesive tapes. The extent of degradation can be assessed via changes in appearance (color, gloss, gross embrittlement), or a reduction in a physical property such as tensile strength, elongation, peel strength, or shear adhesion. If the part is exposed outdoors, and UV degradation is a concern, a UV weatherometer can be used for accelerated testing.

If oven aging is used, high temperatures are generally employed so that failures occur in a reasonable length of time. In order to predict performance at lower temperatures, the oven aging is done at several different elevated temperatures. An Arrhenius plot is then constructed where the time to embrittlement (on a log scale) is plotted vs the inverse of the absolute temperature. If a single chemical process controls the rate of degradation, this plot will often be linear, and the extrapolated degradation time at the temperature of interest can then be determined. A common problem with this technique, however, is that the degradation mechanism at elevated temperatures may be different from the mechanism at lower temperatures. This is particularly true if hindered amine light stabilizers (HALS) are being compared to thioesters such as DSTDP for their effectiveness as long term heat stabilizers. It is well known that HALS are generally superior relative to thioesters if the accelerated testing is done below 125 °C. Many oven aging tests are done at temperatures above 140 °C, in order to obtain results in a reasonable period of time. Although this is expedient, it can lead to erroneous predictions of lifetimes at lower temperatures. If a HALS-based formulation is tested at temperatures much above 125 °C, the Arrhenius extrapolation will predict a much shorter lifetime at the lower end-use temperatures then is actually the case.

An even more extreme example of test acceleration is the use of the Oxygen Induction Time (OIT) test to measure stability. Here a small sample (a few mg) is placed in a DSC (Differential Scanning Calorimeter) at a temperature of about 200 °C with pure oxygen, and the time to degradation, as measured by the evolution of heat due to sample oxidation, is measured. Typical OIT values range from a few minutes up to about 90 minutes. Since the OIT test is often performed on molten samples, its validity for predicting long term performance in the solid state is questionable, and it has been shown to give far different lifetime predictions compared to the oven aging of solid specimens as discussed above.

Examples of Accelerated Aging Studies in Polyolefin Systems:

In this section of the paper we will compare OIT results with oven aging data, and highlight some of the advantages and disadvantages of the OIT test.

1. OIT vs Oven Aging Data For Polyethylene Films

In Figure 6 oven aging stability data is plotted vs OIT data for a series of LDPE blown films containing different stabilizer packages. The oven aging test measured the time for the films to lose 50% of their breaking elongation at 120 ^{o}C in an air atmosphere, while the OIT data showed the time to catastrophic degradation under pure oxygen at 190 ^{o}C. The structures of the hindered phenol and HALS stabilizers are shown in Figures 7 and 8. The film samples containing the hindered phenol-based stabilizer packages showed dramatically better OIT values than the HALS-containing films, with the AO-3 sample having the longest OIT. In terms of oven aging stability, the HALS samples were clearly superior to most of the hindered phenol packages. Although the HALS-based stabilizer system may have offered the best long-term stability at actual end-use temperatures, the OIT test by itself would not have predicted this result, since the OIT test temperature was well above the range where HALS are effective.

2. OIT vs Oven Aging Data For HDPE Plaques

In Figure 9 oven data is plotted vs OIT data for a series of hindered phenol stabilized HDPE plaques. Two of these samples also contain a phosphite secondary stabilizer. We see here that the addition of the phosphite results in a significant improvement in OIT times, but not much of a change in oven stability at 125 ^{o}C. This result illustrates the fact that although phosphates are excellent co-stabilizers for providing stability in the melt, they are not very effective at improving long term thermal stability in the solid state.

3. OIT Study of Hindered Phenol Stabilizers in Natural Rubber and Hot Melt Adhesives

In this study four different hindered phenol stabilizers, at the same loading level, were used and the OIT results were compared. The structures are the four stabilizers are given in Figure 7. Certain other characteristics of these hindered phenols are listed in Table 3. These compounds differ from one another in terms of both their molecular weight and the number of hindered phenol groups per molecule. The last column in this Table 3 represents the number of moles of hindered phenol per kg of stabilizer, and is referred to here as the relative hindered phenol content. In Table 4 the OIT values are given for both natural rubber and a hot melt adhesive containing these stabilizers, and plots of OIT vs the relative hindered phenol content are illustrated in Figures 10 & 11.

Both plots illustrate the strong correlation between relative hindered phenol content and OIT stability, and show that the AO-5 gave the longest OIT times. This result is consistent with the earlier observation that the OIT value varies in a linear manner with the hindered phenol concentration. In this case AO-5 had the highest molar concentration of phenolic groups by virtue of having two groups per molecule and a relatively low molecular weight.

In light of the earlier discussions, however, one must exert some caution in relying on OIT data to predict long-term thermal stability under typical end-use conditions. In addition to the differences in stabilizer efficiency at different temperature ranges as seen in Figure 5, there are also issues of stabilizer compatibility in the polymer, as well as migration and volatility. For example, the hindered phenol BHT (butylated hydroxytoluene or 2,6 di-t-butyl para cresol) has a high relative hindered phenol content of 4.5 moles/kg, but it also has high volatility due to its low molecular weight (220). The high volatility of the BHT causes it to evaporate from the polymer surface at high temperatures, so that it is not available for long term stabilization.

3. OIT Study of Different Hindered Phenol Stabilizers in HDPE

In this study three different hindered phenols were used in HDPE at the 1000 ppm level, and the OIT data was obtained. Two of these were sulfur containing stabilizers (AO-2 and AO-6), and their structures are given in Figure 12. The relative hindered phenol contents of these stabilizers were 3.1 (AO-2) and 5.8 (AO-6). A plot of OIT vs relative hindered phenol content is illustrated in Figure 13, and again we see a very linear relationship.

Summary and Conclusions:

For hindered phenol stabilized systems, the OIT value is directly related to the concentration of hindered phenol, and can be a useful tool for monitoring hindered phenol content. If different hindered phenol stabilizers are being compared against one another at the same weight percent loading of stabilizer, the OIT value should be plotted vs the relative level of hindered phenol in terms of moles of hindered phenol per kg of stabilizer. One must very cautious in using the OIT test to compare systems containing different stabilizer types, due to variations in stabilizer efficiency at different temperature ranges. One must be especially cautious about using OIT data to predict the long term thermal stability of a polymer at end use temperatures that are very far below the OIT test temperature. Hindered amine light stabilizers (HALS) give excellent long term thermal stability at temperatures below 125 ^{o}C, but give very poor OIT results when tested at higher temperatures.

Acknowledgements

I would like to thank Mayzo Inc. for support of this work and the PSTC council for their invitation to present this paper.

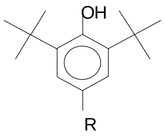
Tables

Table 1. Types of Antioxidant Compounds

Antioxidant Types

•**Primary Antioxidants**: **Scavenge free radicals.**

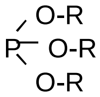
Hindered phenols and secondary amines



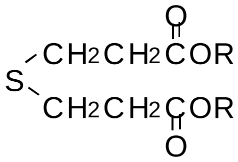
Phenolics
(Primary AO)

•**Secondary Antioxidants**: **Provide supplemental stability. React with hydroperoxides.**

Phosphites and Thioesters



Phosphites
(Secondary AO)

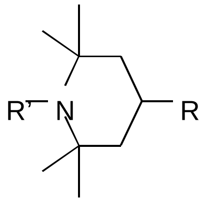


Thio-synergist (Secondary AO)

Table 2. Types of UV Stabilizer Compounds

UV Stabilizer Types

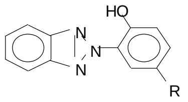
- **<u>Hindered Amine Light Stabilizers (HALS):</u> React with free radicals, and are regenerative.**



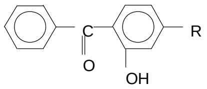
HALS- Hindered Amine Light Stabilizers
(Primary AO- Radical Trap)

- **<u>UV Absorbers:</u> Absorb harmful UV radiation before it can lead to free radical formation.**

Benzotriazoles **Benzophenones**



UVA- Benzotriazole



UVA--Benzophenone

Table 3. Melting Points and Hindered Phenol Content of Antioxidants

Phenolic Content of Antioxidants

Antioxidant	Mol. Wt.	M.P. (deg. C)	# of OH Groups	OH's/Mol. Wt. X 1000
AO-6	340.5	120-132	2	5.9
AO-1	531	49-54	1	1.9
AO-3	1178	115-118	4	3.4
AO-1/AO-3	-	-	2.5	2.7
AO-4	650-850	105-118	3-4	4.7

Note: AO-1/AO-3 is a 1:1 blend of AO-1 and AO-3

Table 4. OIT Values of Different Hindered Phenols in Natural Rubber and Hot Melt Adhesives

Antioxidant	# of OH's	Mol. Wt.	1000 x OH/Mol. Wt.	OIT in Natural Rubber (min.)	OIT in Hot Melt (min.)
None	0		0	2.28	1.28
AO-1	1	531	1.9	6.23	6.73
AO-4	3.5	750	4.7	14.7	11.28
AO-6	2	341	5.9	17.48	26.44

Figures

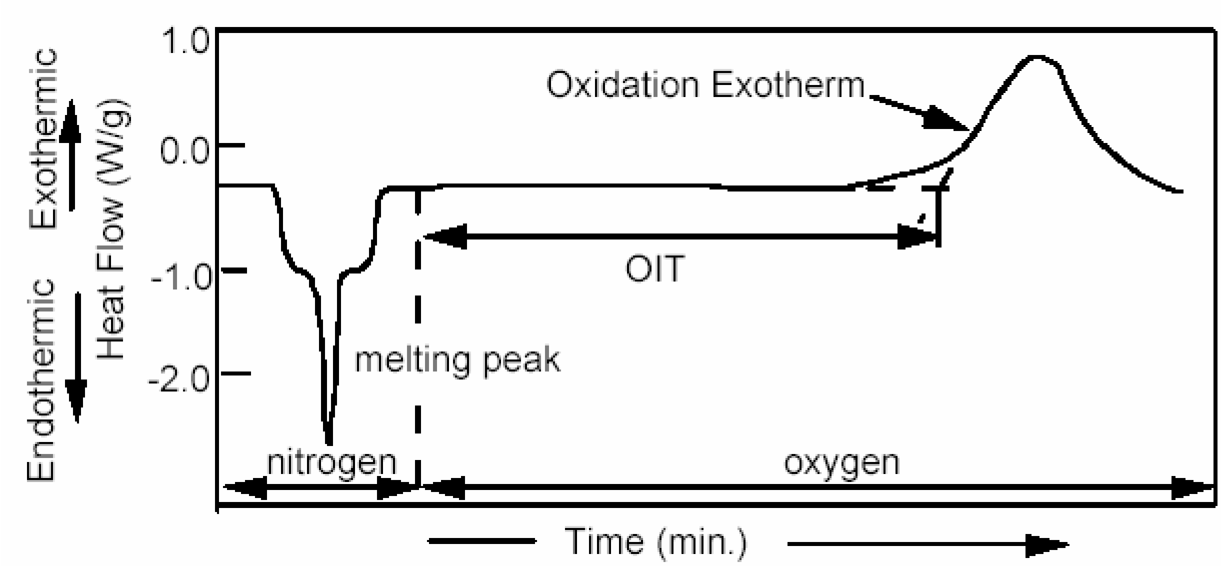


Figure 1. Thermal Curve of a Standard OIT Test

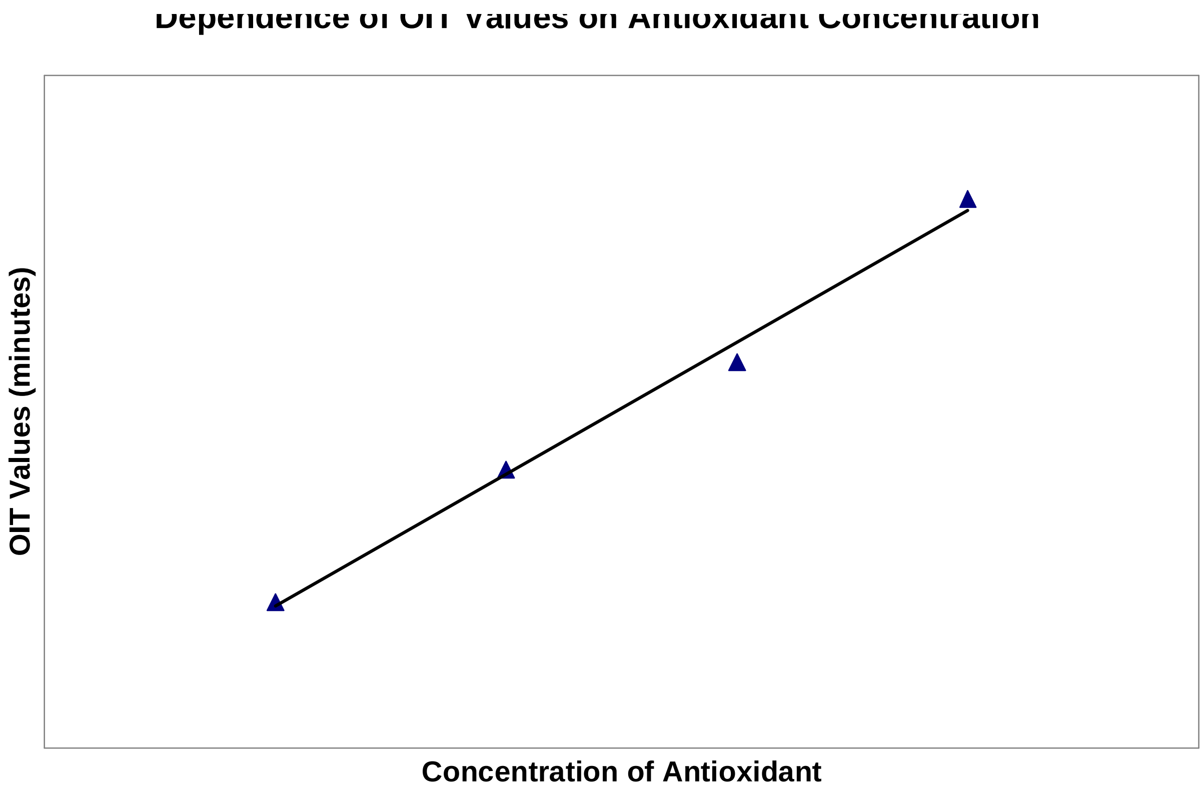


Figure 2. Dependence of OIT Times on The Concentration of Antioxidant

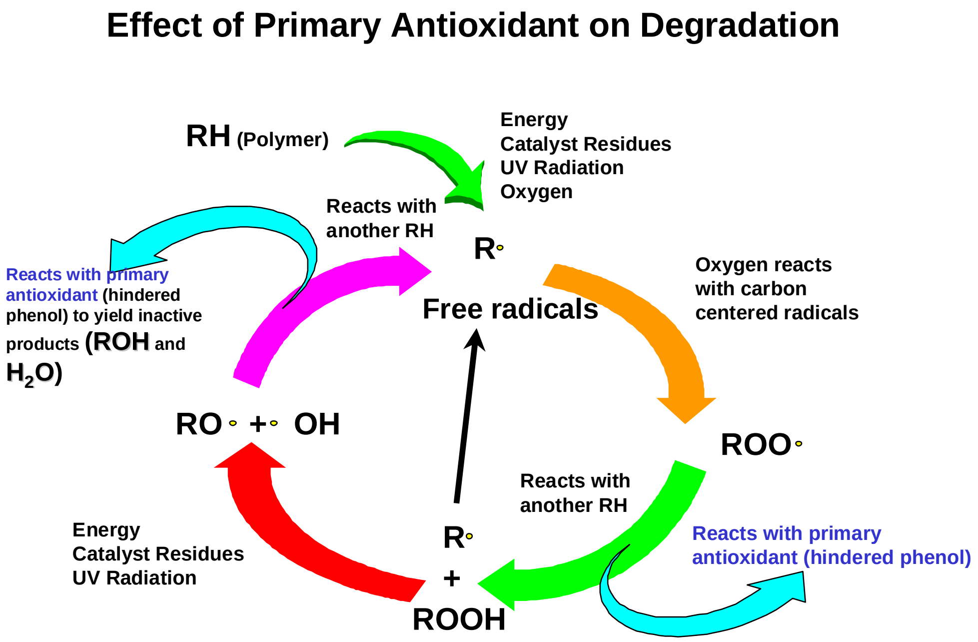


Figure 3. Effect of Primary Antioxidants on Degradation

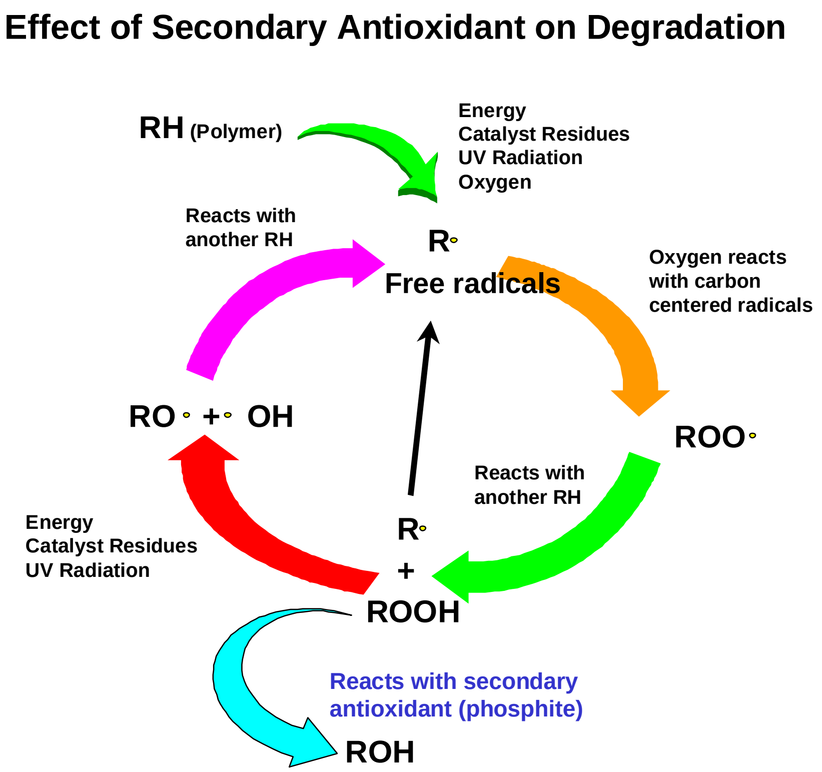


Figure 4. Effect of Secondary Antioxidants on Degradation

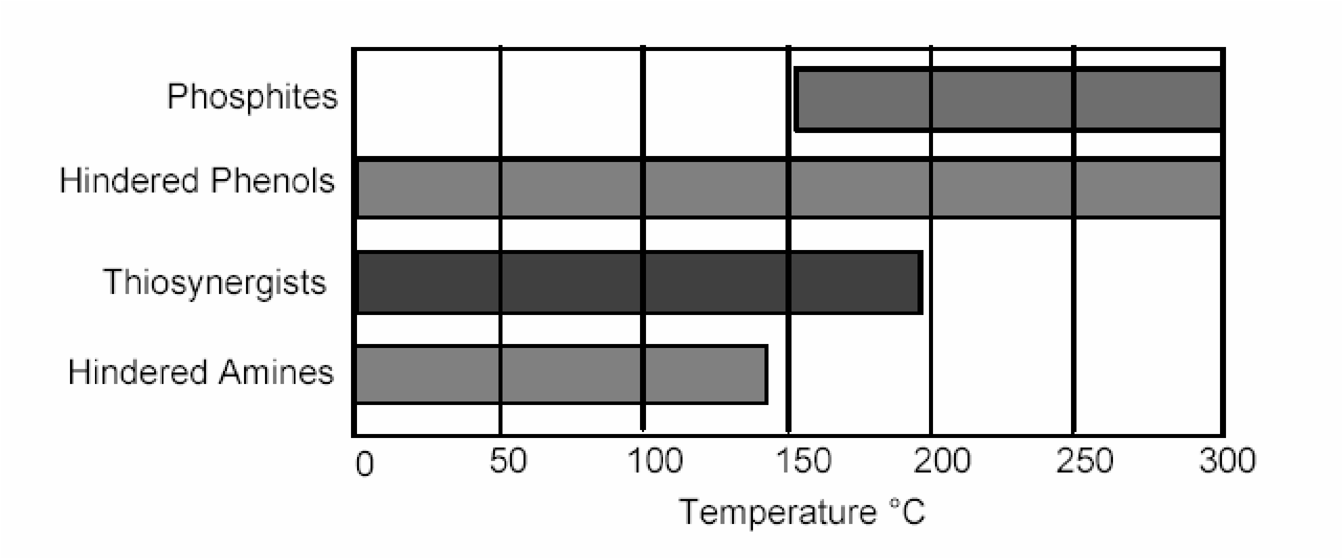


Figure 5. Effective Temperature Ranges of Four Different Types of Stabilizers

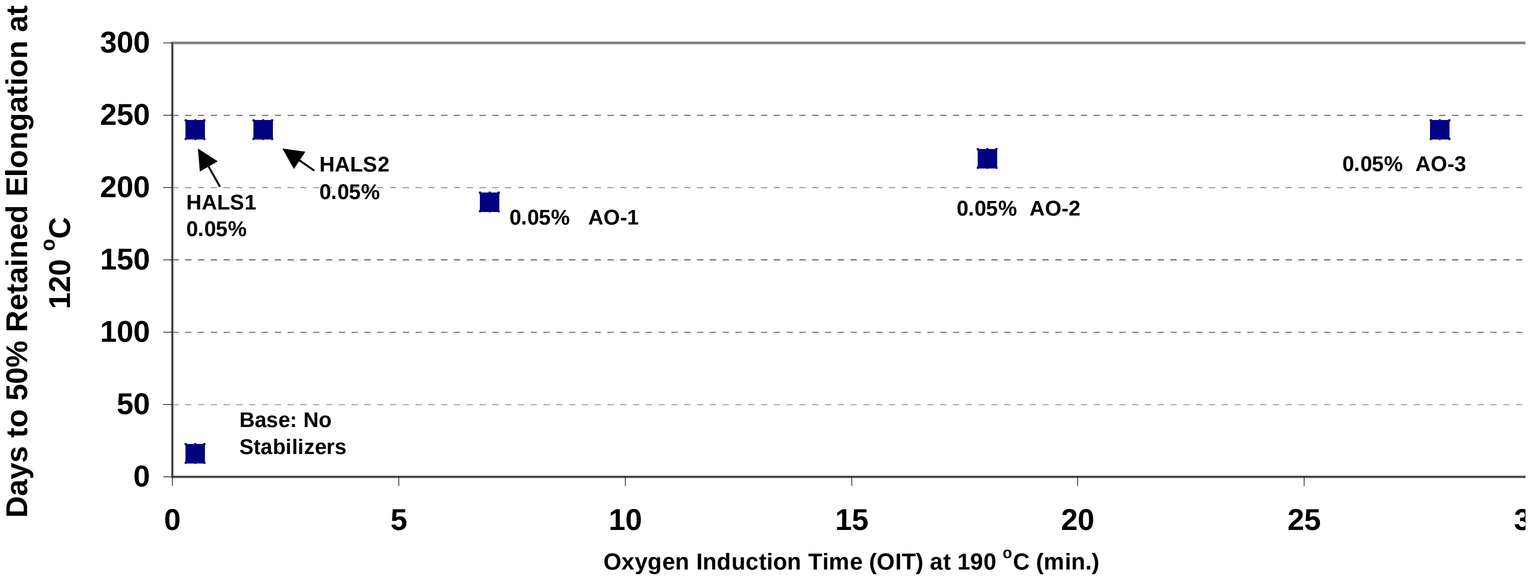
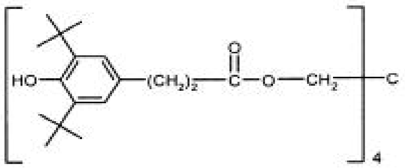


Figure 6. Oven Aging Stability vs OIT Values For LDPE Blown Film

Hindered Phenol Compounds

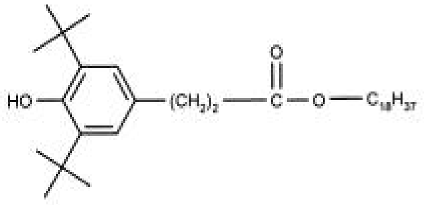
AO-3

Mol. Wt. = 1178



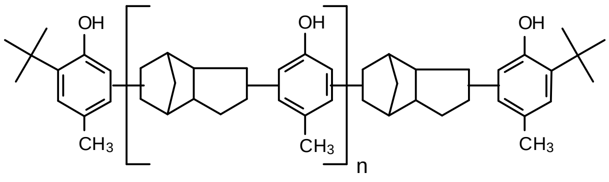
AO-1

Mol. Wt. = 531



AO-4

Mol. Wt. = 650-750



AO-5

Mol. Wt. = 341

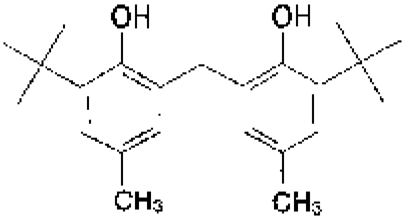
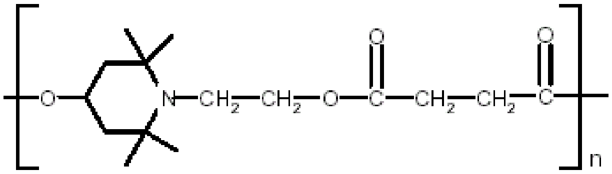


Figure 7. Structures of Hindered Phenol Stabilizers

HALS1



HALS2

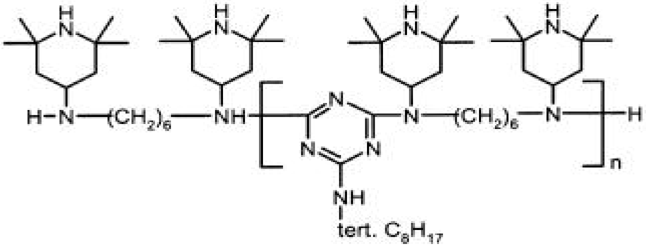


Figure 8. Structures of Hindered Amine Light Stabilizers

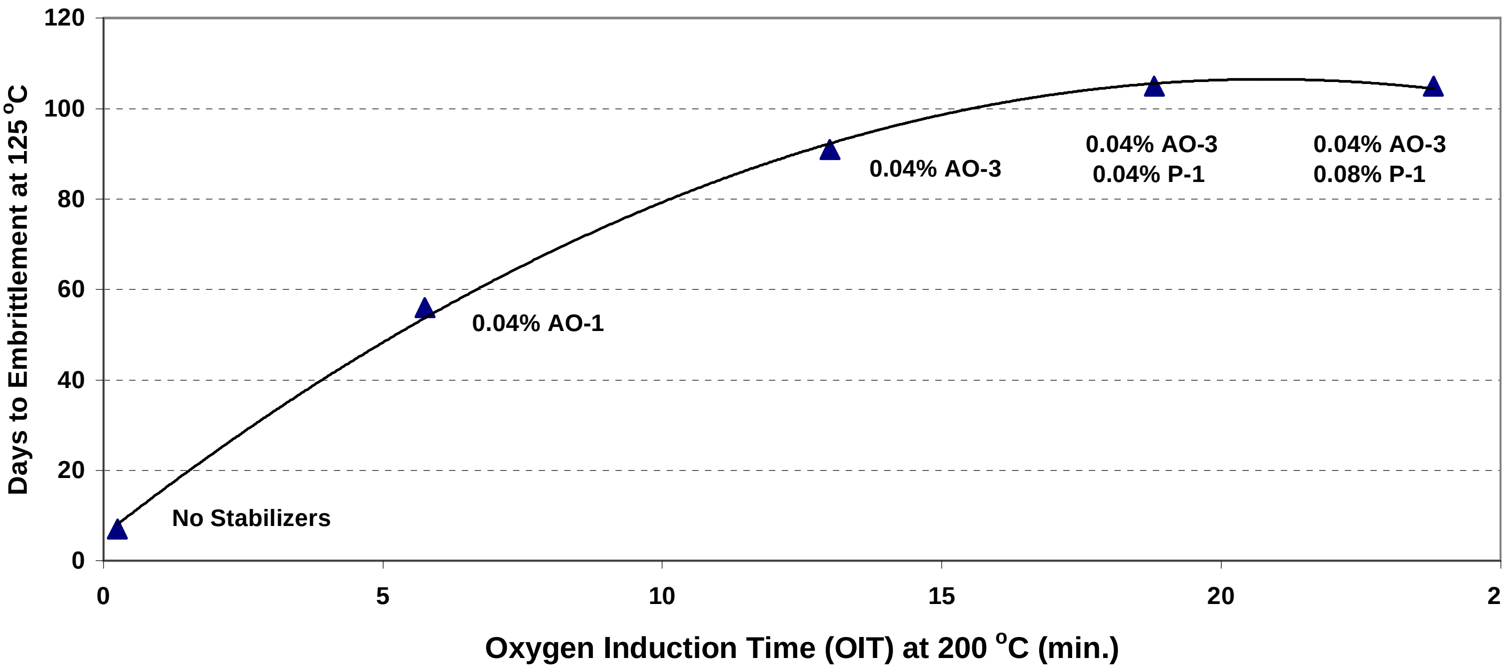


Figure 9. Oven Aging Stability vs OIT Values For HDPE Plaques

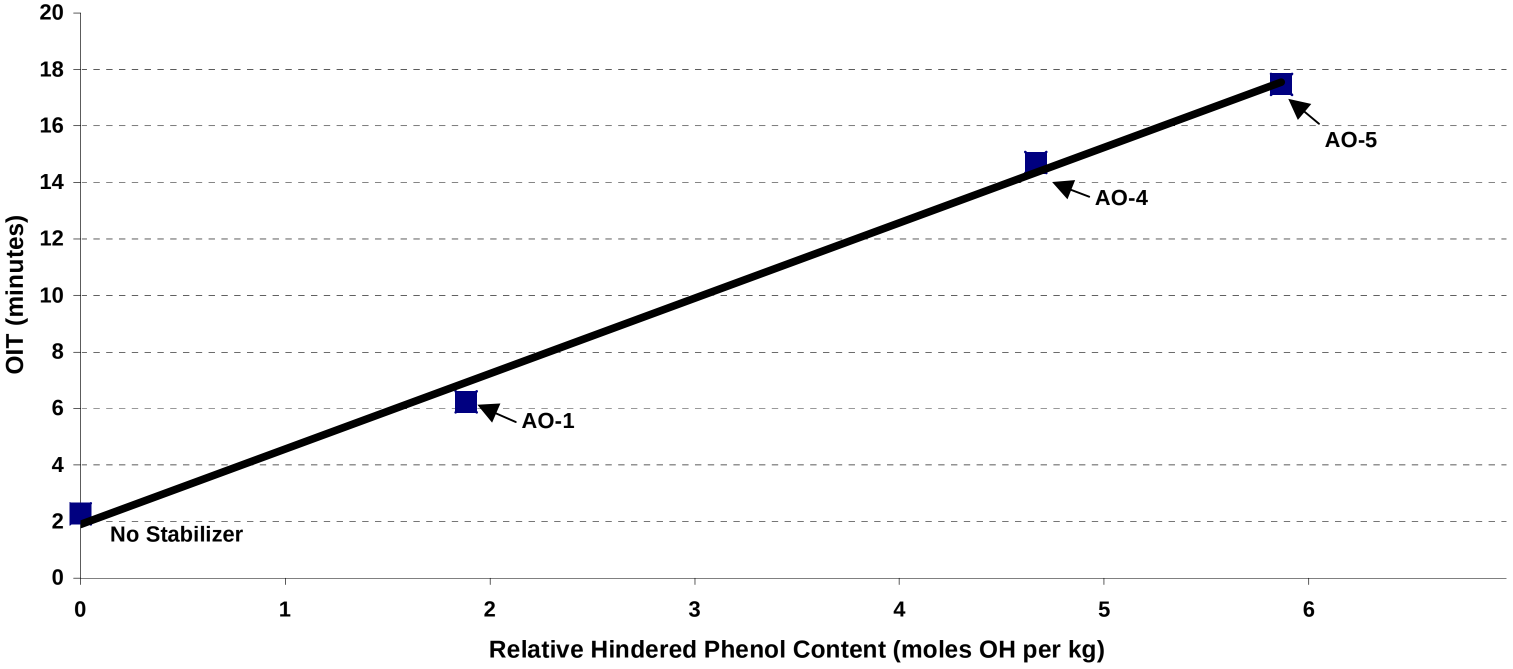


Figure 10. OIT vs Relative Hindered Phenol Content For Natural Rubber Samples

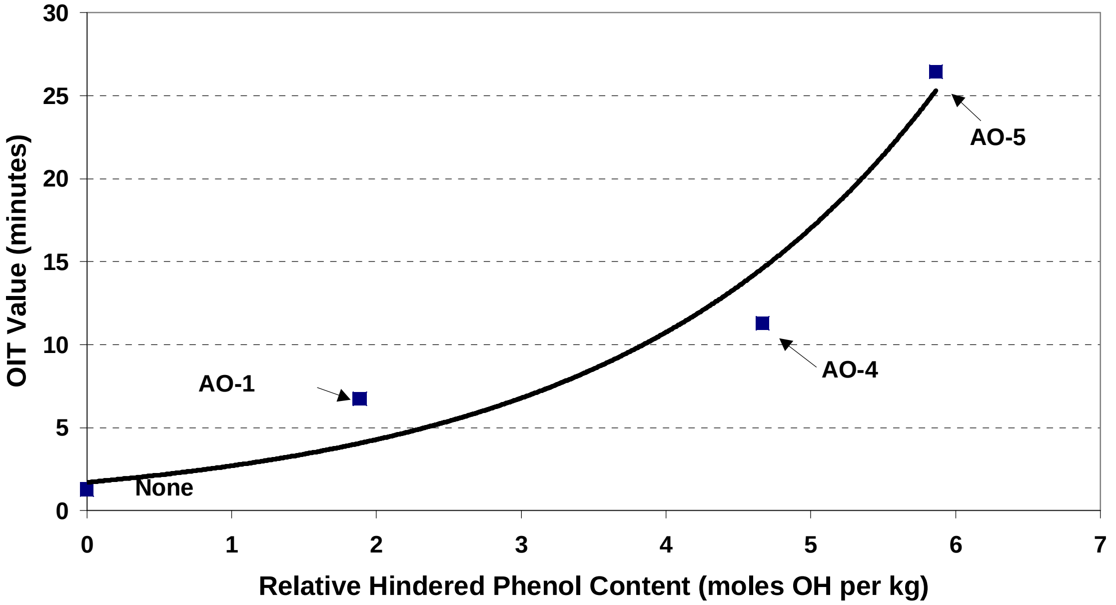
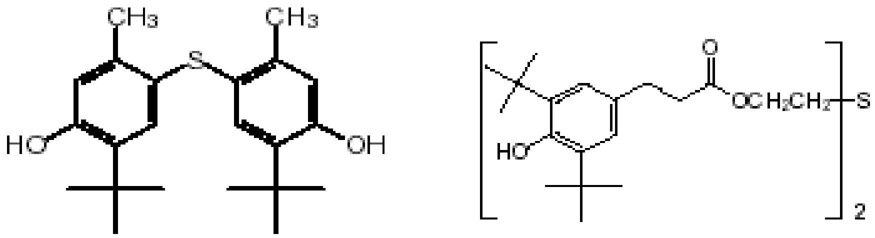


Figure 11. OIT vs Relative Hindered Phenol Content For Hot Melt Adhesive Samples

Sulfur Containing Antioxidants



AO-6

Mol. Wt. = 358

AO-2

Mol. Wt. = 642

Figure 12. Structures of Sulfur Containing Hindered Phenol Stabilizers

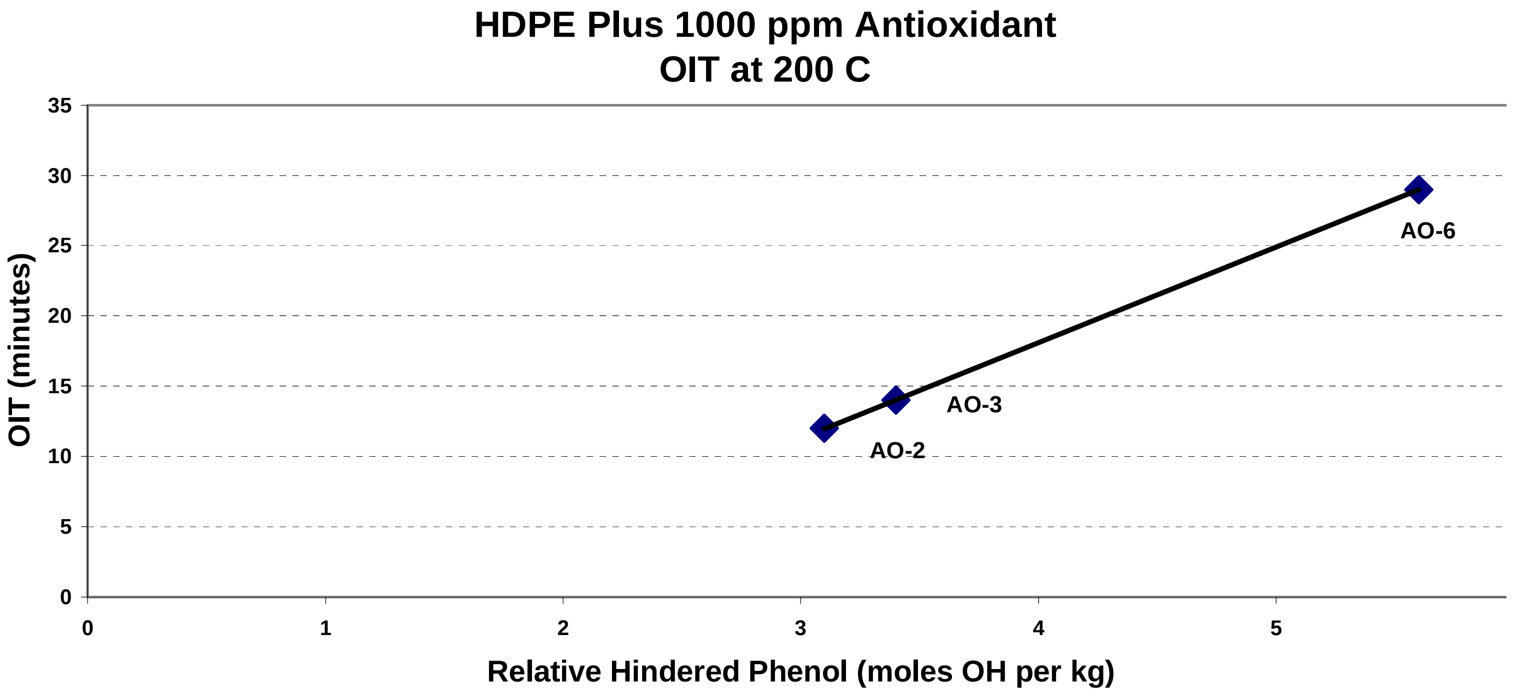


Figure 13. OIT Values For HDPE Containing Various Hindered Phenols

Philip Jacoby: Mayzo Corporation

Phil Jacoby received a B.S. degree in Chemistry from the City College of New York, and a Ph.D. in Physical Chemistry from the University of Wisconsin in Madison, Wisconsin. In 1975 he joined the Amoco Chemical Company where he held various positions in the Polymer Physics and Product Development groups. In early 2002 Dr. Jacoby retired from the Polypropylene Business unit of BP Amoco where he was a senior product development chemist. He holds 12 US patents covering such products as microporous polypropylene films, foamable polypropylene, and thermoformable polypropylene. Dr. Jacoby joined Mayzo Corporation in October 2002, as Vice President of Technology. Mayzo provides polymer additives and stabilizers to the plastics, rubber, and adhesives industries, and is headquartered in Norcross, Georgia. Dr. Jacoby also serves on the Board of Directors of the Southern Section of the Society of Plastics Engineers, where he is Vice President in charge of technical programs.