

Retention of Thermal Antioxidants in Polyethylene by Silane Coupling Agents. II. Concentration and Induction Time Studies

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Synopsis

Thermal antioxidants were incorporated into polyethylene as solutions in the silane coupling agent *N*- β -(aminoethyl)- γ -aminopropyltrimethoxysilane. Substantial improvements in retained concentration and induction time were observed for commercial phenolic and amine-type antioxidants on prolonged oven aging in thin polyethylene films. As an alternative to solution formation, a stabilizer was bonded directly to silicon as the organic functional group in a silane coupling agent, resulting in improved dispersion and induction time. Improvements in antioxidant retention and induction time appear to correlate with compatibility of the silane-polyethylene system.

INTRODUCTION

It has been demonstrated that some conventional thermal antioxidants, when incorporated into polyethylene, are lost by diffusion through the polymer matrix.¹ Absence of a suitable concentration of antioxidant results in oxidation of the polymer, with eventual loss of important bulk physical properties.²

A recent study was concerned with the effect of silane coupling agents on the migration of thermal antioxidants in polyethylene.³ It was found that reacting antioxidants with silanes resulted in new species with antioxidant capabilities which apparently were more compatible with polyethylene. Where no reaction between the silane and antioxidant could occur, forming a solution of the two materials was found to be effective in lowering the rate of diffusion of some antioxidants.³ The study also established the importance of correct surface washing procedures of aged films prior to spectral analysis, by comparing exudation rates of antioxidants in films exposed to different surface washing procedures.

To the techniques previously employed for measuring the concentration of residual antioxidant,³ the present study has added induction time and infrared measurements on aged films. The resulting data relate total antioxidant concentration, active antioxidant concentration, and silane concentration in thin polyethylene films as a function of aging time and temperature. Antioxidants with substantial activity in terms of initial induction

time were selected. They are *N,N'*-diphenyl-*p*-phenylenediamine (DP-PD), *p*-2-naphthylaminophenol (NAP), 4,4-thiobis(6-*t*-butyl-3-methylphenol) (TBBMP), *N*-(3-trimethoxysilylpropyl)-2,7-dioctylphenothiazine (TDP), and its control, *N*-ethyl-2,7-dioctylphenothiazine (EDP).

EXPERIMENTAL

Films for the study were prepared by compression molding milled low-density polyethylene (DYNK, Union Carbide Co.) Milling and molding conditions are listed in Table I. Film thicknesses are listed in the figure captions; control of film thickness was achieved by limiting the amount of

TABLE I
Polyethylene Compositions for Antioxidant Migration Studies

Additive ^a	Structure	Molecular weight	Source
(1) 0.105% DPPD ^b		260	Eastman
(2) 0.104% DPPD 1.01% Aminosilane			
(3) 0.104% TBBMP		359	Monsanto
(4) 0.103% TBBMP 1.02% Aminosilane			
(5) 0.102% NAP		235	K&K Labs
(6) 0.104% NAP 1.02% Aminosilane			
(7) 0.11% EDP 0.12% Aminosilane		451	°
(8) 0.11% TDP 0.12% Aminosilane		586	°
(9) 1.02% Aminosilane			
(10) DYNK Polyethylene	$(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\overset{\text{H}}{\text{N}}\text{CH}_2\text{CH}_2\text{NH}_2$	222	Union Carbide Union Carbide

^a Milling conditions: 3-6 minutes at 124-130°C; mill temperature, 10 passes high shear. Molding conditions: 0.8 g milled polyethylene molded against 5-mil polished aluminum sheet; heated rapidly to 144-152°C under pressure, cooled rapidly.

^b Recrystallized from ethanol.

° Synthesized by Dr. P. Adams, Millmaster—Onyx Corporation, Berkeley Heights, N.J.

material molded. Two sets of films were molded from the compounds listed in Table I. Ultraviolet measurements were taken exclusively from one set, while the other supplied infrared data and material for the induction time measurements. Films were aged at 60°C in air and at room temperature.

Antioxidant concentration was determined by use of ultraviolet spectroscopy as in the previous study.³ Films were rinsed with acetone prior to recording spectra, but the rinsing time was reduced to 30 sec. Criteria for selection of wavelengths used in the absorbance measurements were maximum antioxidant absorbance consistent with control baseline stability. All of the materials studied, with the exception of TBBMP, had one or more clearly defined peaks of maximum absorption which were selected as the wavelength of measurement. Baselines for spectra derived from films prepared from I-4,6 were referred to spectra of films prepared from I-9, while I-3,5,7,8 were referred to I-10. Baselines for I-1,2 were drawn using the baseline technique.

Concentrations of N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane were determined by infrared absorbance at $\sim 1100\text{ cm}^{-1}$, the stretching frequency of Si—O—, as compared to a polyethylene control. Hydrolysis of the silane is assumed to occur after molding of thin films but could not be confirmed by infrared measurements. After the silane-containing films were exposed to a humid environment, it became exceedingly more difficult to extract the silane. This material replaced the γ -aminopropyltriethoxysilane of the previous study.

Induction times in oxygen at 200°C were measured by means of a Perkin-Elmer differential scanning calorimeter (DSC) Model DSC-1B. As this instrument is less frequently employed for measuring induction times than differential thermal analysis (DTA),⁴ several experiments were devised to establish its reliability. Figure 1 gives representative curves for DYNK polyethylene (unstabilized) (0 min), DYNK + 0.1% Irganox 1010 (Geigy Chemical Co.) (31 min), and DYNK + 0.1% TBBMP (83 min). The induction times agree with DTA induction times for the same materials. All baselines were found to be extremely straight, with distinct breaks at the initiation of oxidation. Samples cut from the molded films (Table I and figure captions) were in the form of 1/4-in. discs weighing about 4 mg.

RESULTS

Infrared analysis established that the N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane (aminosilane) is compatible with polyethylene at 1% concentration. Recent evidence concerning the interfacial tensions of the silane-hydrocarbon system suggest similar results.⁵ An infrared spectrum of composite no. 4, Table I, compared to its control no. 3, is given in Figure 2. The broad absorption band at 8.6–10 microns is due to Si—O— and remained constant for 1194 hr at 60°C. A similar result was obtained for all samples containing this particular amino silane.

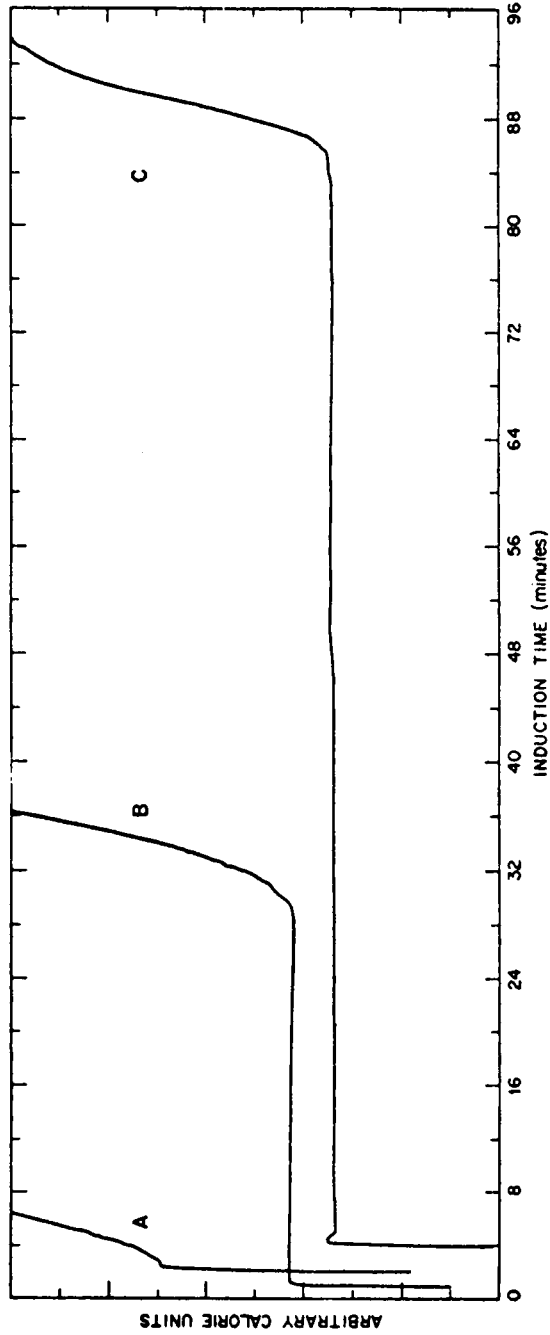


Fig. 1. Polymer induction times by differential scanning calorimetry in oxygen at 200°C: (A) DYNK polyethylene, 1 min; (B) DYNK polyethylene + 0.1% Irganox 1010, 32 min; (C) DYNK polyethylene + 0.10% TBBMP, 83 min.

Effects of the aminosilane on antioxidant concentration and induction time are given in Figure 3 through 10. Concentrations are directly proportional to spectral absorbance scales. Aging times for the room-temperature studies refer to the time of molding and, for the 60°C studies, to cumulative time at 60°C. Each silane-antioxidant pair is compared to a control containing only the antioxidant. For the most rapidly changing DSC (I-1,5,7,8) and UV (I-5) results, an effort was made to ensure a minimum delay between time of molding and the first measurement. Films of the remaining composites were allowed a prolonged period of hydrolysis prior to the first measurement.

Table II summarizes results in terms of per cent loss of concentration and induction time at arbitrarily selected aging times for TBBMP (Figs. 3 and 4) and NAP (Figs. 5 and 6). After 1300 hr of aging at room temperature, the TBBMP concentration in polyethylene as determined by UV has decreased by about 40% and induction time by 94%, while TBBMP in the

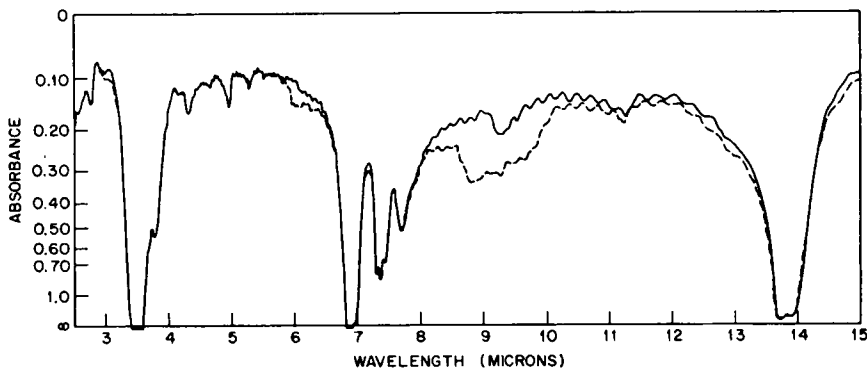


Fig. 2. Infrared analysis of an amino-functional silane in stabilized DYNK polyethylene: (—) 0.104% TBBMP, 6.1 mils, 1194 hr at 60°C; (- - -) 0.103% TBBMP + 1.02% aminosilane, 6.1 mils, 1194 hr at 60°C.

silane mixture in polyethylene has decreased by 3% with a 16% loss in induction time. After 2500 hr, the loss of induction time is 19%. Similarly, for 60°C aging at 1300 hr, TBBMP alone has declined by 52% and induction time by 100%, while the TBBMP-silane concentration has dropped by 7% with 25% loss of induction time. After 2300 hr at 60°C, induction time has decreased 43%. An estimate of the relative useful lifetime of the antioxidant may be obtained from the induction time graphs.

NAP results are best summarized by examination of Figures 5 and 6. The extreme incompatibility of NAP resulted in almost 100% loss of induction time at short times. Effects of the amino silane are notable. After 1600 hr of aging at 25°C, 21% of the compound is lost and 33% of the induction time. After 1600 hr at 60°C, the concentration in polyethylene has decreased by 40% and the induction time by 66%. The induction times are evidently unchanged at 2500 hr.

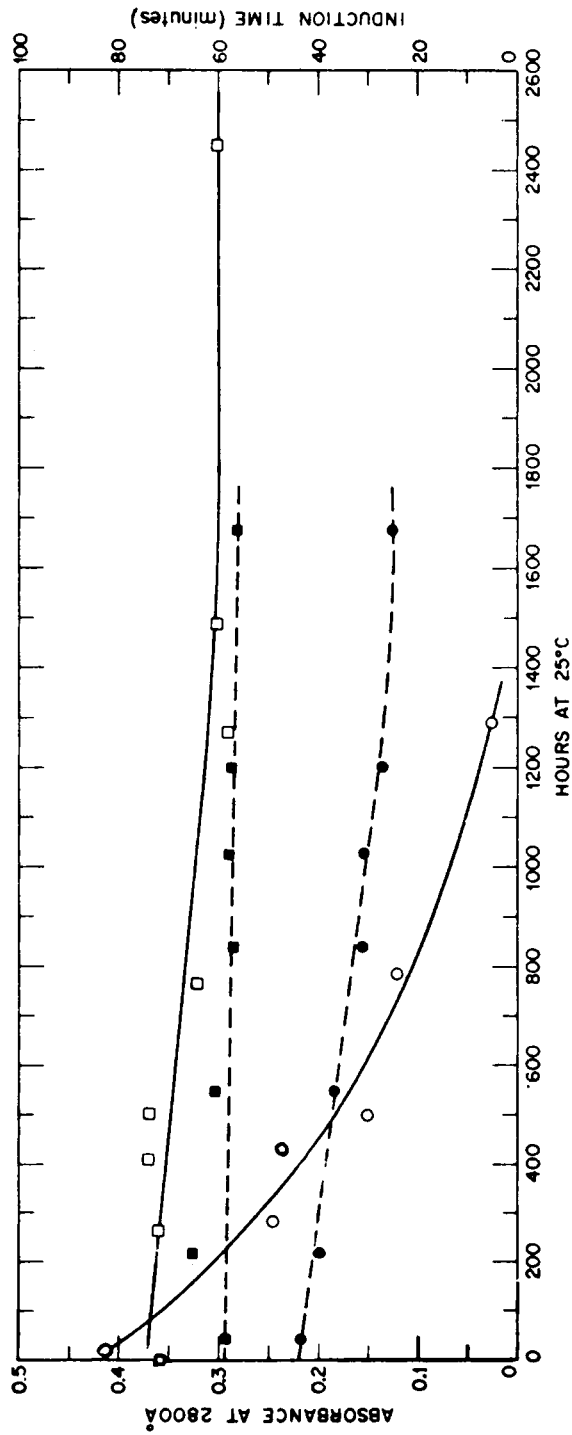


Fig. 3. TBBMP in DYNK polyethylene; 25°C aging temperature, UV absorbance at 2800 Å, DSC induction time in oxygen at 200°C: ●---0.104% TBBMP, absorbance, 5.8 mls; ○—0.104% TBBMP, induction time, 6.2 mls; ■---0.103% TBBMP + 1.02% aminosilane, absorbance, 6.3 mls; □—0.103% TBBMP + 1.02% aminosilane, induction time, 6.3 mls.

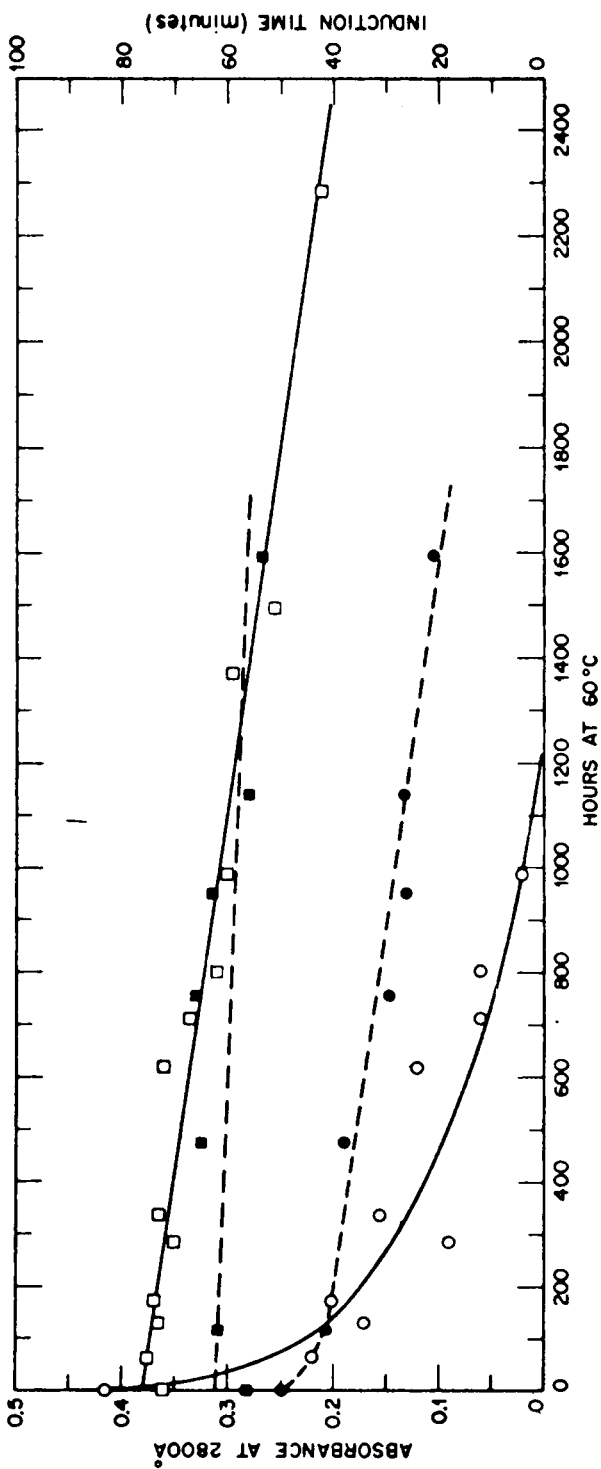


Fig. 4. TBBMP in DYNK polyethylene; 60°C aging temperature, UV absorbance at 2800 Å, DSC induction time in oxygen at 200°C: ●---0.104% TBBMP, absorbance, 6.1 mils; ○---0.104% TBBMP, induction time, 6.1 mils; ■---0.103% TBBMP + 1.02% aminosilane, absorbance, 6.1 mils; □---0.103% TBBMP + 1.02% aminosilane, induction time, 6.1 mils.

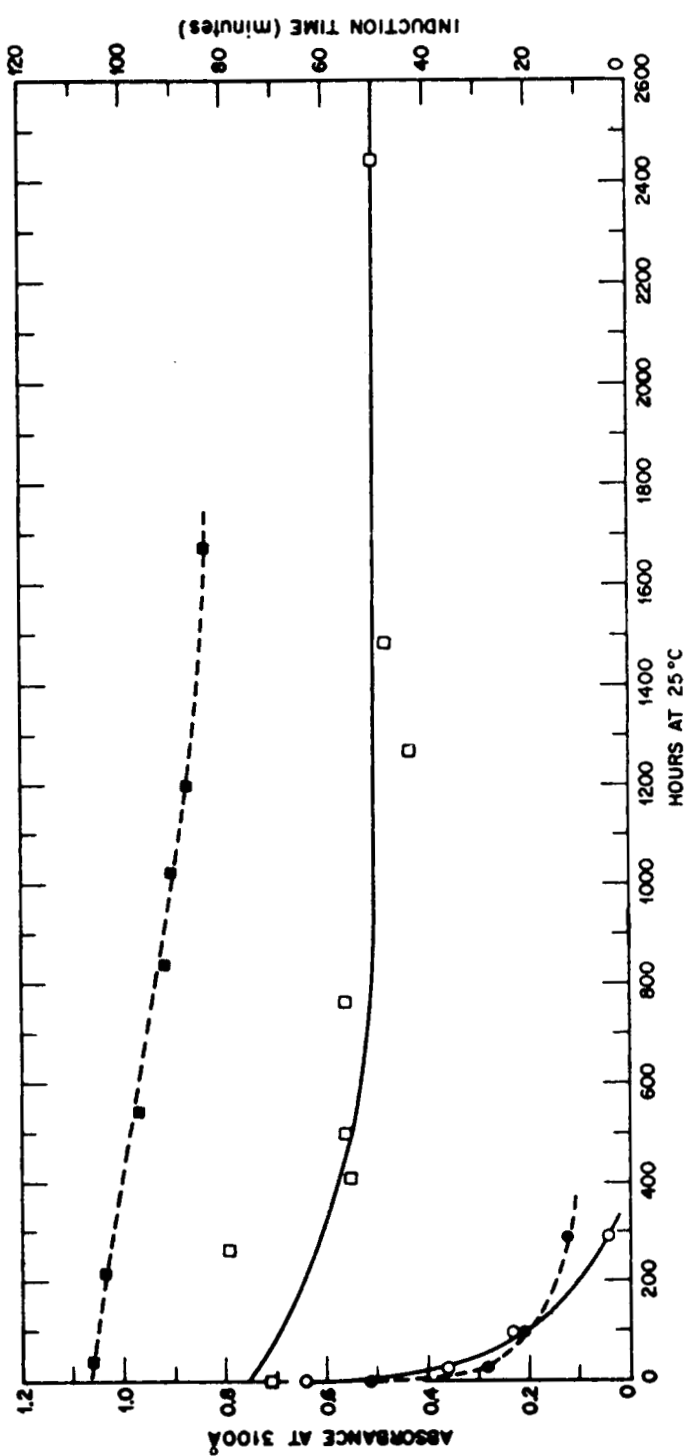


Fig. 5. NAP in DYNK polyethylene; 25°C aging temperature, UV absorbance at 3100 Å, DSC induction time in oxygen at 200°C: ●-----0.102% NAP, absorbance, 6.9 mils; ○-----0.102% NAP, induction time, 6.9 mils; ■-----0.104% NAP + 1.02% aminosilane, absorbance, 6.1 mils; □-----0.104% NAP + 1.02% aminosilane, induction time, 6.3 mils.

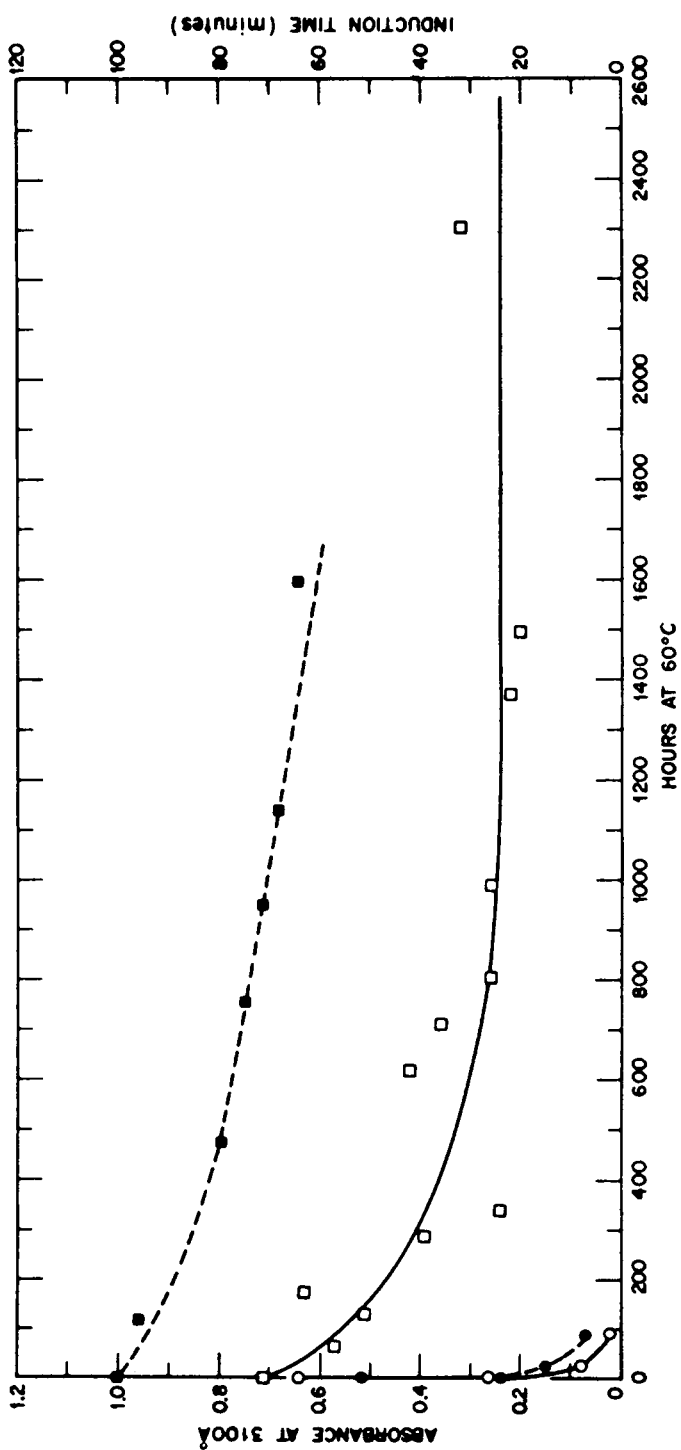


Fig. 6. NAP in DYNK polyethylene; 60°C aging temperature, UV absorbance at 3100 Å, DSC induction time in oxygen at 200°C; ●-----0.102% NAP, absorbance, 6.7 mils; ○-----0.102% NAP, induction time, 6.7 mils; ■-----0.104% NAP + 1.02% amminosilane, absorbance, 5.9 mils; □-----0.104% NAP + 1.02% amminosilane, induction time, 6.3 mils.

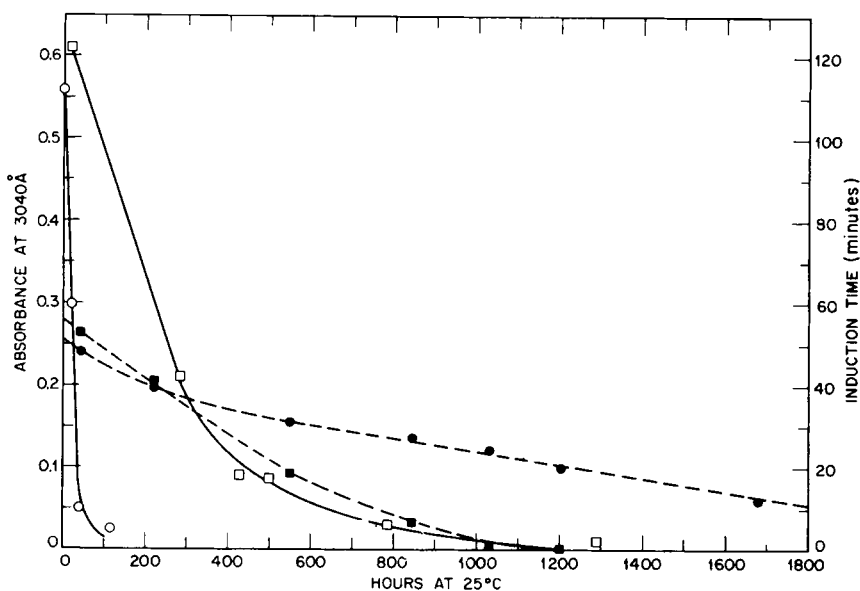


Fig. 7. DPPD in DYNK polyethylene, 25°C aging temperature, UV absorbance at 3040 Å, DSC induction time in oxygen at 200°C; ●--- 0.105% DPPD, absorbance, 5.9 mils; ○— 0.105% DPPD, induction time, 6.3 mils; ■--- 0.104% DPPD + 1.01% aminosilane, absorbance, 5.9 mils; □— 0.104% DPPD + 1.01% aminosilane, induction time, 6.5 mils.

TABLE II

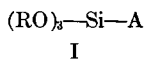
Effects of Amino-Functional Silane Coupling Agent on Concentration and Induction Time of TBBMP and NAP Antioxidants in Polyethylene

Polyethylene composition	Hours aging		Loss of concentration, %		Loss of induction time, %	
	at 25°C, hr	at 60°C, hr	25°C	60°C	25°C	60°C
0.104% TBBMP	1300		40		94	
		1300		52		100
0.103% TBBMP 1.02% Aminosilane	1300		3.4		16	
	2500				19	
		1300 2300		7.4		25 43
0.102% NAP	300		78		95	
		100		86		97
0.104% NAP 1.02% Aminosilane	300		4		19	
	1600		21		33	
	2500				33	
		100		6		23
		1600 2500		40		66 66

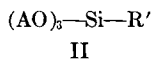
Analysis of DPPD concentration (Figs. 7 and 8) was unfortunately marred by loss of DPPD band shape in the ultraviolet and development of a UV-visible continuum. This may be due to derivatives of DPPD arising from chain termination or oxidation. The continuum was most severe in the DPPD-silane solutions at room temperature. Ultraviolet results support enhanced retention of solid DPPD and derivatives at room temperature and comparable retention at 60°C. Induction time measurements, however, clearly support greater retention of active stabilizers in the presence of the amino silane. Results for TDP and EDP will be discussed in the next section.

DISCUSSION

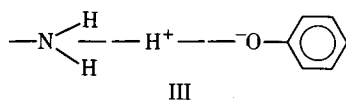
It was stated previously³ that silanes may be made to interact with antioxidants chemically, resulting in bond formation, and physically, by dissolving existing antioxidants. Of the former, we distinguished structures of the type



and



where structure I would presumably be most stable and II may undergo slow hydrolysis in the presence of water. Solutions may be subdivided into those which interact strongly, such as a phenol and amine, and those which



possess no special forces of interaction.

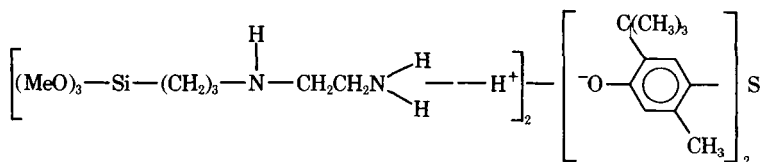
Results for TBBMP, NAP, and DPPD appear consistent with these states of interaction. Where strong antioxidant-silane interactions occur, such as complex formation or direct coupling, enhanced retention would be expected compared to the solid control. Where a weak interaction between antioxidant and silane exists, little or no enhancement of retention would be expected.

TBBMP was originally believed to interact strongly as the result of partial or complete neutralization of the basic aminosilane by the acidic phenol. An alternative to acid-base neutralization, that of coupling with elimination of methyl alcohol as in II, appeared less probable where the phenol is sterically hindered.

To determine the state of TBBMP in the amino silane, the infrared spectrum of the mixture was recorded and isolated from that of the pure silane. When compared to the spectrum of TBBMP in nujol mull, several

prominent changes were observed, most notable being loss of the sharp hindered phenolic —OH as in the previous case. An attempt was next made to separate TBBMP from the silane by precipitation. A solution of the two constituents in 1.0 to 16.2 molar ratio was made, warmed to about 120°C, diluted with methanol, and added to a large excess of water. A milky, white precipitate appeared at once on contact with water. The precipitate was aged, filtered, and washed with acetone, which was collected and evaporated. A yellow-white solid, >90% of the weight of the starting material, was collected. Infrared analysis in nujol mull identified the material as TBBMP when compared to the IR spectrum of another TBBMP sample evaporated from acetone.

From these results, it appears that TBBMP does not couple to the silane as in II. Although loss of the hindered phenolic —OH band is consistent with coupling or complexation, recovery of the TBBMP from aqueous media is consistent with the following complex:



While complex formation is sufficient to explain TBBMP-silane retention in polyethylene, strong antioxidant activity of this system was also observed. DSC measurements were generally made at 200°C, but activity was observed at 160°C, consistent with an activation energy of 35 kcal/mole. It is suggested that dissociation of the complex occurs at these temperatures, regenerating TBBMP and implying that the complex may not act as antioxidant at temperatures too low to bring about dissociation. Experiments are underway to measure the effectiveness of the TBBMP-silane system at lower temperatures.

Naphthylaminophenol results (Figs. 5 and 6) are in accord with enhanced retention due to strong interaction with the aminosilane. Complex formation is likely, but direct coupling to the unhindered phenol as in II is a stronger possibility than with TBBMP. It was not determined which of the two mechanisms are operative. It is noted that the percentage loss of the NAP-silane exceeds that of TBBMP, which may correlate with one available phenolic site on NAP compared to two on TBBMP. NAP antioxidant activity is observed and is attributed mainly to the aromatic amine functionality which is expected to be independent of the silane. This result suggests that other, less toxic compounds with similar functional groups and one or more unhindered phenolic groups could be effective practical antioxidants in solution with the amino silane.

Results for DPPD (Figs. 7 and 8) illustrate the case of a weakly interacting antioxidant-silane solution. The loss of solid DPPD bears little relationship to the extremely rapid decline in induction time, perhaps due to secondary crystallization within polyethylene. In solution, the amino-

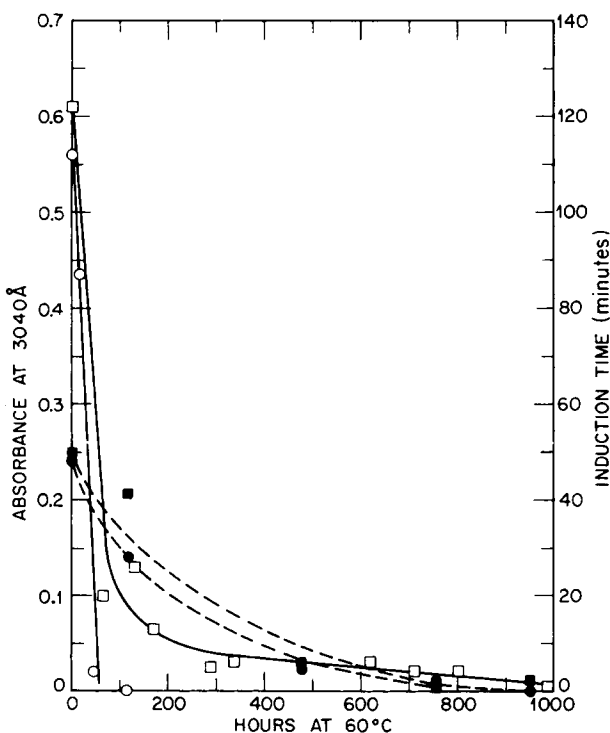


Fig. 8. DPPD in DYNK polyethylene, 60°C aging temperature, UV absorbance at 3040 Å, DSC induction time in oxygen at 200°C: ●--- 0.105% DPPD, absorbance, 6.0 mils; ○— 0.105% DPPD, induction time, 6.6 mils; ■--- 0.104% DPPD + 1.01% aminosilane, absorbance, 6.4 mils; □— 0.104% DPPD + 1.01% aminosilane, induction time, 6.3 mils.

silane had little effect on retention at 60°C, and a more rapid loss was observed at 25°C. As in all other films containing the aminosilane, IR analysis showed no loss of silane on prolonged aging. This suggests the necessity of phenolic or other interacting sites on the antioxidant molecule for improvements in retention. Assuming crystallization of DPPD explains the rapid loss of induction time for the solid, a solution of DPPD would not be expected to crystallize, and induction time should bear a closer relation to concentration, as may be observed in Figures 7 and 8.

In earlier studies concerned with retention of silanes in polyethylene, it was noted that the property of rapid hydrolysis in air correlated with retention in polyethylene, suggesting a mechanism of crosslinking in the amorphous region of the polymer. Of the silanes studied, the most rapidly curing was *N*- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, employed in the present study. It was further noted that hydrolysis of slowly curing silanes was greatly accelerated by the presence of this material. For this reason, the TDP compound was mixed with an equal weight of the aminosilane, as was the control, EDP.

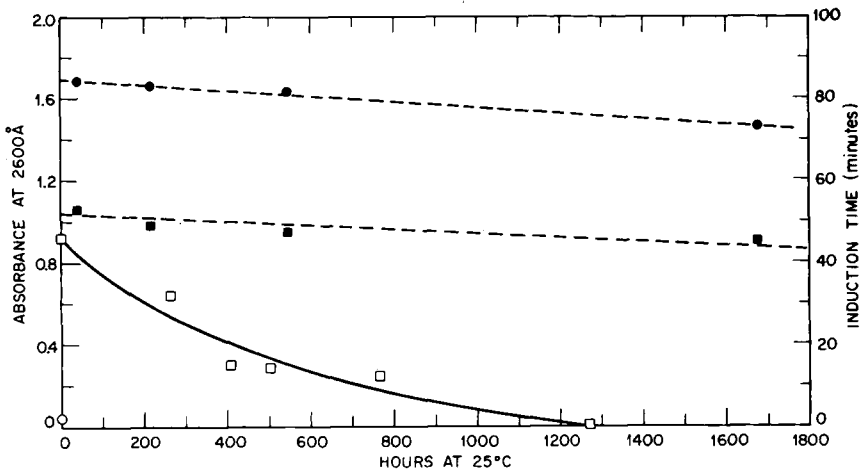


Fig. 9. TDP in DYNK polyethylene; 25°C aging temperature, UV absorbance at 2600 Å, DSC induction time in oxygen at 200°C; ●---0.107% EDP + 0.121% aminosilane, absorbance, 6.1 mils; ○—0.108% EDP + 0.126% aminosilane, induction time, 6.3 mils; ■---0.113% TDP + 0.115% aminosilane, absorbance, 6.3 mils; □—0.113% TDP + 0.115% aminosilane, induction time, 6.3 mils.

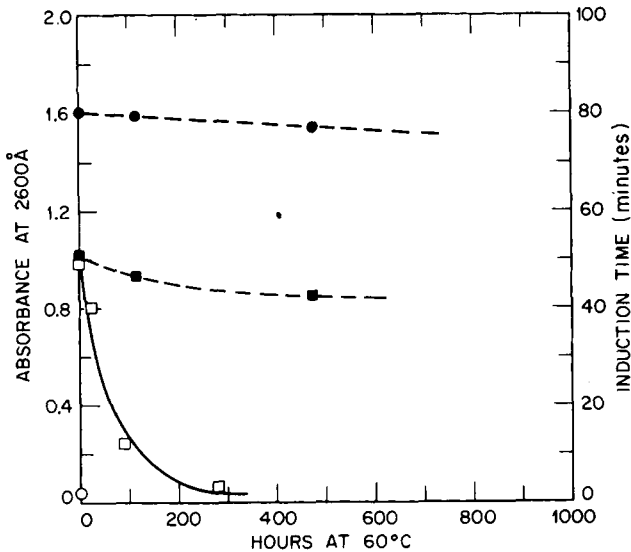


Fig. 10. TDP in DYNK polyethylene; 60°C aging temperature, UV absorbance at 2600 Å, DSC induction time in oxygen at 200°C; ●---0.107% EDP + 0.121% aminosilane, absorbance, 5.8 mils; ○—0.108% EDP + 0.126% aminosilane, induction time, 6.4 mils; ■---0.113% TDP + 0.115% aminosilane, absorbance, 6.1 mils; □—0.105% TDP + 0.116% aminosilane, induction time, 6.5 mils.

Figures 9 and 10 show EDP to be inactive while TDP exhibited considerable activity. The induction time of a material similar to TDP, N-(3-trimethoxysilylpropyl)phenothiazine in the absence of the aminosilane at 0.3% concentration was approximately 13 min, pointing to a

possible synergistic effect for the TDP-silane mixture. No such effect exists for the control, EDP, which may illustrate the importance of dispersion in the efficiency of a polymer stabilizer. Efforts are underway at present to prepare isomers of this material.

CONCLUSIONS

A number of thermal antioxidants have been shown to be incompatible with polyethylene. Physical loss is accompanied by rapid loss of induction time. Retention of thermal antioxidants with available phenolic groups may be significantly increased by use of the silane coupling agent N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane. Induction times correlate with the enhanced retention, corresponding to a greater projected lifetime of the polymer composite. Of particular importance is the enhanced retention and activity of the NAP-silane complex.

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