

Retention of Antioxidants in Polyethylene by Silane Coupling Agents

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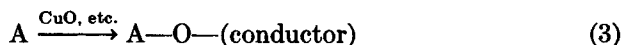
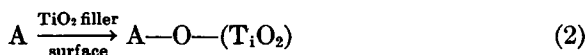
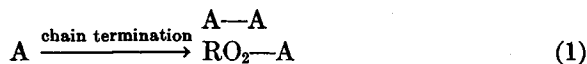
Synopsis

Antioxidant additives in polyethylene films have been shown to diffuse to the surface where they are subsequently lost, exposing the polymer to oxidation. Compatibility of antioxidants with polyethylene may be increased by use of silane coupling agents. In this study, three approaches to antioxidant modification are examined: (1) bonding antioxidant directly to silicon, (2) coupling the silane to an antioxidant hydroxyl function, and (3) dissolving antioxidants in silanes. All three approaches are shown to be effective in reducing antioxidant loss by diffusion.

INTRODUCTION

Polyethylene stabilized against thermal oxidation by conventional antioxidants is observed to undergo loss of oxidative stability with time.¹ Two possible mechanisms which could account for this are (1) depletion of active antioxidant by chemical reaction, and (2) physical loss of stabilizer through diffusion and subsequent volatilization or sublimation. Recently, attention has been focused on the latter mechanism.²

Loss of stabilizer activity through chemical reactions occurs as the stabilizer functions as a chain terminator or otherwise participates in the reactions of thermal oxidation. These reactions have been the subject of extensive study as has the uninhibited oxidation of olefins.³ However, in polyethylene composites containing oxide fillers and pigments, and in contact with an oxidized metal surface, further complexities arise. We summarize below several chemical reactions whereby an antioxidant of the chain-terminator type may lose activity in filled polyethylene systems:



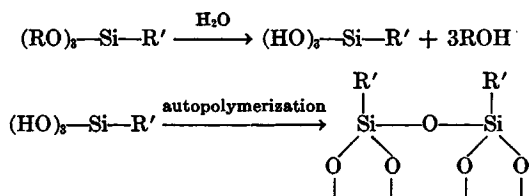
Possible stabilizer mobility in polyethylene² and reactions (2) and (3) may serve to remove active stabilizer. It is to be added that reaction of the

phenolic function of a conventional antioxidant at the oxide surface is not mandatory for loss of activity; simple adsorption onto the filler surface may suffice to eliminate the stabilizer as a chain terminator.

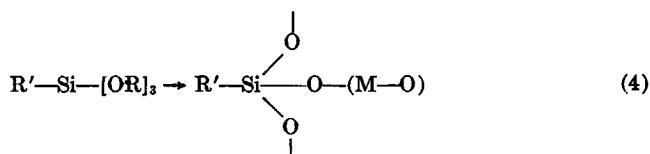
Stabilizer loss through diffusion is a simple phase separation of two incompatible materials, the nonpolar polymer and the polar antioxidant. Factors relating to the rate of diffusion include temperature, molecular weight, and polarity, among others, and hence the rate of diffusion is specific for a given additive. Diffusion presumably continues to the level of equilibrium solubility of the antioxidant which, for antioxidants such as tetrakis[methylene-(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane (Irganox 1010, Geigy Chemical Co.) and 4,4'-thiobis(6-*t*-butyl-3-methyl phenol) (Santnox R, Monsanto Company), may be below the nominal concentration of 0.1%.² It is noted that concentration and solubility are used here only in the macroscopic sense; only the amorphous phase of semicrystalline polymers is expected to be accessible to the additive,³ assuming complete expulsion from the crystalline regions on solidification. In the next section, we propose several methods for modification of antioxidants which simultaneously increase compatibility with polyethylene while eliminating adverse effects of adsorption reactions (2) and (3).

In a recent study,⁴ the effect of silane coupling agents on the resistance of polyethylene to environmental stress cracking was investigated. A necessary property of such additives is retention in polyethylene; in the course of the study many silane liquids were found to be compatible with polyethylene.

The general structure of a silane coupling agent is $[\text{RO}]_3\text{—Si—R}'$, where R is often methyl or ethyl and R' may be almost any organic functional group. In the presence of water, acids, bases, or certain metal ions, hydrolysis of the alkoxy function occurs as follows,

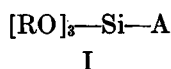


creating a network structure, often solid, with elimination of ROH. A typical application of silane coupling agents is the treatment of metal oxide surfaces, where chemical coupling to the surface is assumed to occur by the following mechanism,

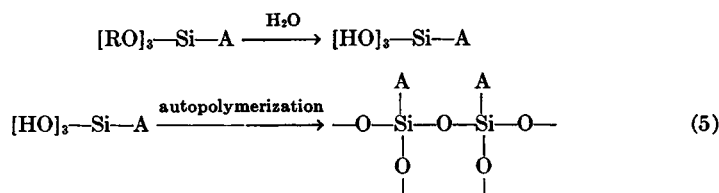


where R' is selected for the particular application.

These properties of compatibility, network formation, and surface reactivity present potential solutions to the specific problems associated with antioxidants discussed earlier. Consider a silane modified to include a polyethylene antioxidant A as the R' group:

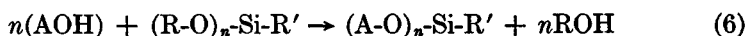


The (liquid) silane-antioxidant will generally be far more compatible with polyethylene than the antioxidant alone. On prolonged exposure to the atmosphere, hydrolysis and autopolymerization will occur:



yielding the network structure discussed earlier. Interwoven in the amorphous phase after polymerization, this structure should be considerably less mobile than A alone, thereby reducing physical loss of the stabilizer by diffusion.

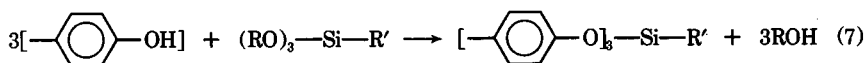
Alternatively, antioxidants may be coupled to the silane molecule by reaction of an antioxidant hydroxyl group with the silane alkoxy:



There may be as many as four antioxidant molecules for each silane molecule. However, this method is considered inferior to the first, as it interferes with the network formation, prevents surface coupling, and the

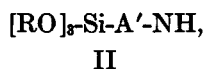
(A—O—)Si— bond may be subject to slow cleavage by hydrolysis.

For both types of structural modification of the silane molecule, the antioxidant may be limited to those not dependent upon —OH for activity since

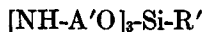


Clearly, antioxidant activity is lost by reaction with the silane. However, hindered phenols may not react in this manner. Likely candidates for this type of modification are the aryl amines: $\varphi\text{—NH—}\varphi$, $\varphi\text{—NH—R}$, etc., as well as sulfur and phosphorous compounds.

Stabilizers of type I, that is

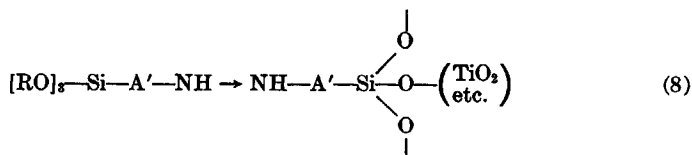


where $A = A'-NH$, but not those coupled to the OH functionality such as



III

may also be useful in dealing with loss of stabilizer activity through surface reactions. In the period between polymer compounding and hydrolysis, migration to the filler surfaces could occur:



thereby orienting the active center of the stabilizer away from the filler surface. However, the same effect could be accomplished by silane treatment of fillers prior to incorporating into polyethylene.

An entirely physical approach to retention of antioxidants is likewise based on the compatibility of high-boiling silane liquids with polyethylene. Phenolic-type antioxidants such as Irganox 1010 and Santonox R, and amine types such as 3-hydroxydiphenylamine (3HDA) and sym-dibetanaphthyl-*p*-phenylenediamine have been found to be soluble in such high-boiling silanes as gamma-aminopropyltriethoxysilane (APTS) and vinyltris(betamethoxyethoxy)silane. Incorporation of the antioxidant as solute in a silane solvent should result in a molecular dispersion of the antioxidant. In contrast to the previously discussed methods of chemically bonding antioxidant to silane, the molecular dispersion is a simple physical modification which may be applied to standard antioxidants and commercially available silanes.

EXPERIMENTAL

In this report we have employed ultraviolet spectroscopy to study the exudation of Irganox 1010, Santonox R, 3-hydroxydiphenylamine, and γ -N-phenylaminopropyltrimethoxysilane Y5669 (Union Carbide Corp.) from thin films of DYNK polyethylene. As this is a direct method of analysis, it yields total antioxidant content, active (with respect to polymer stabilization) as well as inactive, in contrast to the indirect methods such as DTA and TGA which indicate only active antioxidant concentration. This is because inactive molecules retain an ultraviolet spectrum similar to that of the active species provided no gross changes of molecular conjugation have occurred.

Stabilizers and silane additives were incorporated into polyethylene by milling, after which films were pressed. Details of compounding and molding are given in Tables I and II, along with composition, additive identity and structural formulas. Films were cut to fit a sample holder designed to expose the same portion during successive spectral analyses. Oven

TABLE I
Polyethylene Compositions for Stabilizer Migration Study (Detergent Wash)

Sample no.	Additive ^a	Structure	Origin
1	Control		
2	0.10% Irganox 1010		Geigy
3	0.10% I-1010 0.69% (APTS)		
4	0.10% Santonox R		Monsanto
5	0.11% Santonox R 0.71% (APTS)		
6	0.10% 3-hydroxy-diphenylamine		Aldrich
7	0.10% 3-hydroxy-diphenylamine 0.70% (APTS)		
8	0.27% Y5669 Silane 0.035% (APTS)		Union Carbide
9	0.70% A-1100 Silane (APTS)	$(C_2H_5O)_2-Si-(CH_2)_3NH_2$	Union Carbide

^a Milling conditions: 4-5 minutes at 127-129°C, 10 passes high shear, run off ~1/8 in. thick. Molding conditions: 0.7 g milled material molded against 5-mil polished aluminum sheet. Heated rapidly to 151-153°C platen temperature under pressure, cooled rapidly. Films stored in room temperature water for 64 hr following molding.

TABLE II
Polyethylene Compositions for Stabilizer Migration Study (Acetone Wash)

Sample no.	Identity	Additive ^a
1	DYNK control	—
2		0.10% Irganox 1010
3		0.11% Irganox 1010 0.71% (APTS)
4		0.10% Santonox R
5		0.10% Santonox R 0.73% (APTS)
6	Silane control	0.71% (APTS)

^a Milling conditions: 4-5 min at 127-132°C, 10 passes high shear, run off ~1/8 in. thick. Molding conditions: 0.6-0.7 g milled material molded against 5-mil polished aluminum sheet. Heated rapidly to 127-134°C platen temperature under pressure, cooled rapidly.

TABLE III
Change of Spectral Absorbance at 2800 Å for
Polyethylene Films After 40-Second Acetone Wash^a

Composition	Thickness, mils	Absorbance	
		Before acetone wash	After 40-sec acetone wash
0.1% I-1010	6.6	0.089 ± .005	0.091 ± .005
0.1% I-1010 + 0.7% (APTS)	6.5	0.083	0.081
0.1% Santonox R	6.4	0.249	0.238
0.1% Santonox R + 0.7% (APTS)	6.7	0.302	0.294

^a Films molded 5-7 hr prior to spectra. (Small spectral changes may represent extraction or room temperature loss of antioxidant.)

aging took place in forced-air ovens; aging time refers to cumulative time at oven temperature.

As the method of analysis of retained antioxidant was ultraviolet (transmission) spectroscopy, it was essential that all exuded antioxidant be removed from the surfaces. Two cleaning procedures were adopted. The first consisted of a detergent wash (2 g Alkanox plus 500 cc water) with mild rubbing by finger pressure, followed by a thorough water rinse, prior to recording spectra (Table I). A second method, suggested by Bair,⁵ consisted of a 40-sec acetone wash prior to analysis. This was applied only to the study of Santonox and Irganox 1010 (Table II). To test the ability of acetone to extract these antioxidants, films were molded several hours before initial spectral analysis. They were then given a 40-sec acetone wash and spectra were repeated. Results of this study (Table III) indicate little or no extraction by acetone in the 40 sec of contact.

Another critical factor relating to migration may be film thickness; most films used in the study fell in the range 5.5-6.5 mils. Control films were generally thicker than test films containing the silanes. (More rapid loss is noted from thinner films.) Film thicknesses are listed in the figure captions.

Determination of spectral baselines was specific for each stabilizer. For Irganox 1010, the baseline technique, which consists of extrapolating the baseline, appeared valid, as the peak is a clear departure from the control baseline. For Santonox R, 3HDA, and Y5669, a baseline technique was employed which eliminated the high levels of scattering associated with UV analysis of polyethylene. This consisted of recording the spectrum of the appropriate control film (Table I, 1 and 9; Table II, 1 and 6) of a given sample, tracing it onto the sample spectrum, and taking the difference of absorbance at a given wavelength as a measure of sample concentration. Figure 1 illustrates the procedure for Santonox R at 71°C. The wavelengths at which spectral measurements were taken were, for Santonox R and Irganox 1010, 2800 Å; for 3-hydroxydiphenylamine, 2900 Å; and for

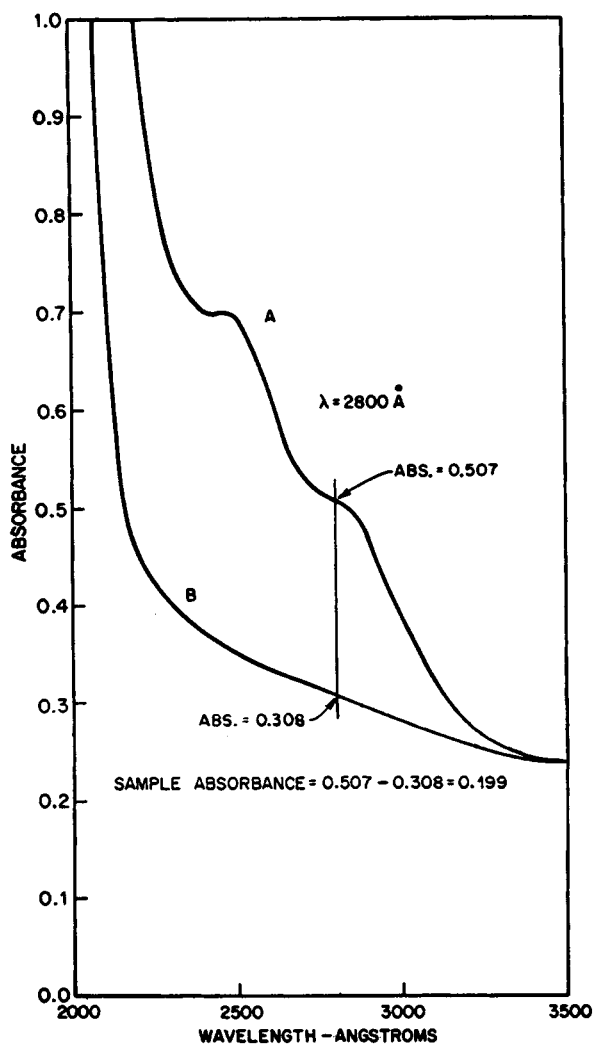
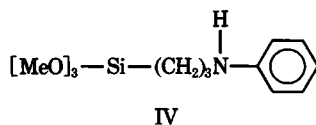


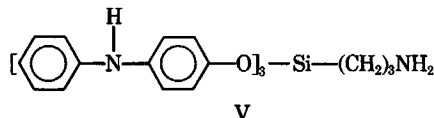
Fig. 1. Baseline technique for UV analysis: (A) Spectrum of 0.1% Santonox R (I-4) in polyethylene aged 134 hr at 71°C in air; (B) spectrum of unstabilized polyethylene (I-1) aged 134 hr at 71°C in air.

Y5669 silane, 2500 Å. These wavelengths were selected to give maximum intensity of absorption consistent with baseline stability.

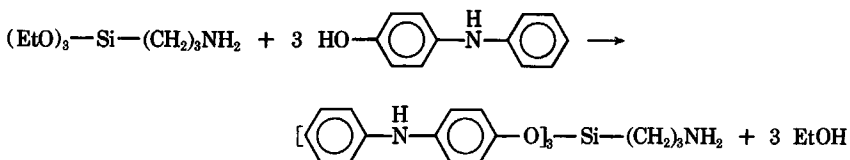
The antioxidant materials employed for this study represent the various stabilization approaches previously discussed. In Table I, compounds I-7 and I-8 are the two fundamental structural types, with antioxidant bonded directly to silicon (I-8):



and via substitution at the methoxy function (I-7),



where structure IV is disclosed by the manufacturer and structure V is assumed correct based on the known coupling of silanes to $-\text{OH}$ in acidic or basic media:



The reaction mixture gave an oil on addition of water, indicating coupling took precedence over complex formation.

Composites I-3, I-5, II-3, and II-5 are Irganox 1010 and Santonox R, respectively, dissolved in $(\text{C}_2\text{H}_5\text{O})_3\text{-Si}-(\text{CH}_2)_3\text{NH}_2$, a silane selected for its rapid hydrolysis in the presence of water as well as its ability to dissolve antioxidants. Melt index measurements at various concentrations of this material indicated no crosslinking of polyethylene.

On concluding the study of Table I (detergent wash), infrared spectra were recorded on all films. These results will be discussed along with the UV studies in the next section.

RESULTS AND DISCUSSION

Figures 2-7 are graphs of antioxidant concentration versus time as derived from ultraviolet spectra for 60° and 71°C aging temperatures. The ordinate for all but Irganox 1010 is A/A_0 , representing a fraction of the initial concentration remaining. Irganox 1010 concentrations have been plotted as absorbance versus log time. Pertaining only to Santonox R and Irganox 1010, Figures 2-5, each graph includes four curves representing the two different approaches to surface washing: 0.1% antioxidant versus 0.1% antioxidant plus 0.7% silane with a detergent wash and with a 40-sec acetone wash.

Santonox R and Irganox 1010 results may be summarized for both temperatures as follows: For Santonox (Figs. 2 and 3), the greatest rate of loss was exhibited for those films subjected to the acetone wash (B and B'); Santonox incorporated into polyethylene as a solid (A and B) always exuded significantly faster than Santonox incorporated as a solution (A' and B').

Irganox 1010 (Figs. 4 and 5) appeared less sensitive to the mode of washing. At 60°C, the rate of loss for (solid) Irganox was somewhat greater for the acetone-washed films; at 71°C, the curves were nearly parallel. The effect of molecular dispersion was less evident than in the case of Santonox;

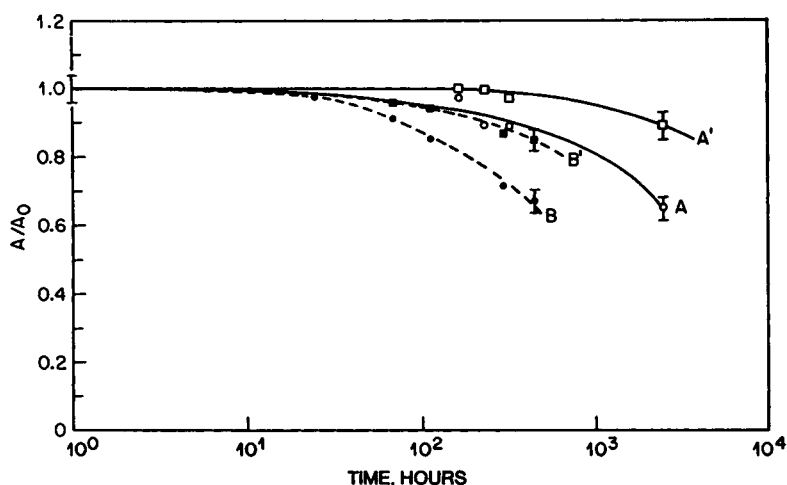


Fig. 2. Concentration of Santonox R in DYNK polyethylene at 60°C vs. time: (A) 0.10% Santonox, 6.0 mils; (A') 0.11% Santonox + 0.71% (APTS), 5.1 mils; (B) 0.10% Santonox, 6.4 mils; (B') 0.10% Santonox + 0.73% (APTS), 6.7 mils; (—) detergent wash; (---) acetone wash.

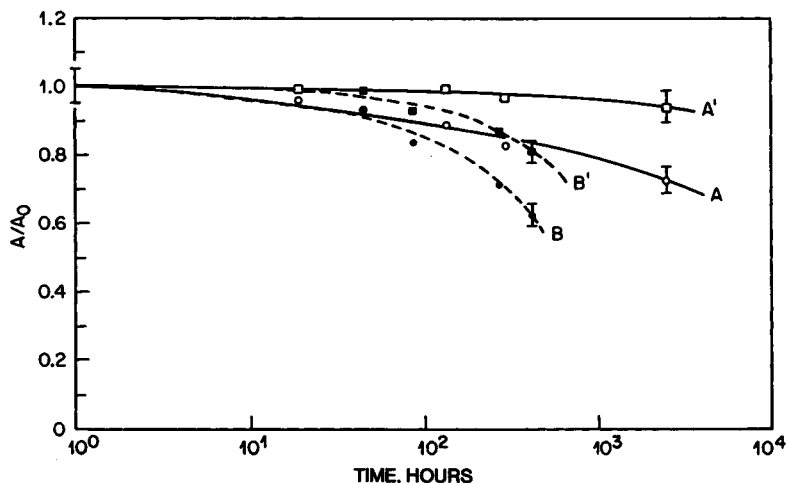


Fig. 3. Concentration of Santonox R in DYNK polyethylene at 71°C vs. time: (A) 0.10% Santonox, 6.0 mils; (A') 0.11% Santonox + 0.71% (APTS), 5.2 mils; (B) 0.10% Santonox, 6.4 mils; (B') 0.10% Santonox + 0.73% (APTS), 6.4 mils; (—) detergent wash; (---) acetone wash.

long-term rates were slower for 60°, acetone wash (Fig. 4, B,B') and 71°, detergent wash (Fig. 5, A,A'). These results are summarized in Table IV for 400 hr.

In general, a decreased rate of loss is evident for Santonox incorporated into polyethylene as a molecular dispersion. The moderate loss of the silane-antioxidant complex is probably associated with a delay in hydrolysis as there is likely to be a competition between migration of the complex and

TABLE IV
 Fraction of Initial Santonox R Concentration Remaining in
 Polyethylene after 400 Hours at 60° and 71°C

Polyethylene composition	60°C		71°C	
	Acetone wash	Detergent wash	Acetone wash	Detergent wash
0.1% Santonox R	0.670	0.887	0.635	0.838
0.1% Santonox R 0.7% (APTS)	0.859	0.980	0.818	0.974

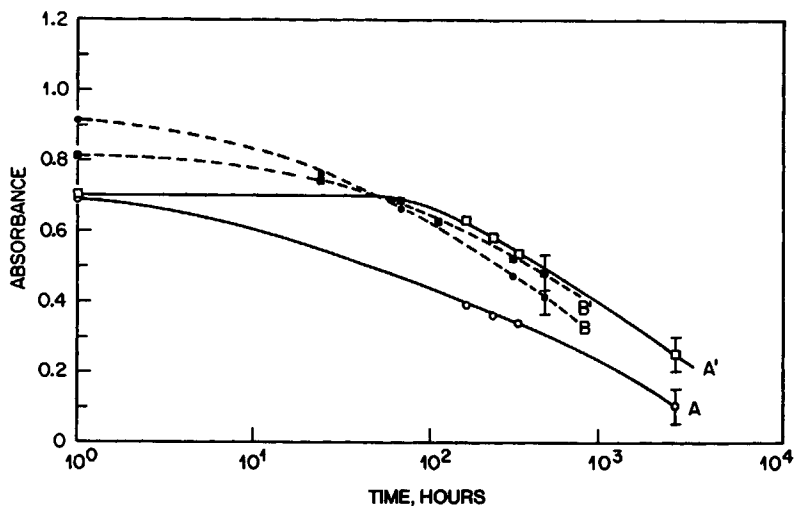


Fig. 4. Concentration of Irganox 1010 in DYNK polyethylene at 60°C vs. time: (A) 0.10% Irganox 1010, 5.4 mils; (A') 0.10% I-1010 + 0.69% (APTS), 5.8 mils; (B) 0.10% I-1010, 6.6 mils; (B') 0.11% I-1010 + 0.71% (APTS), 6.5 mils; (—) detergent wash; (---) acetone wash.

crosslinking of the silane. This would account for the gradual loss of Santonox and Irganox 1010 incorporated as solutions. Clearly, antioxidant loss in such dispersions will follow silane loss, therefore high compatibility prior to hydrolysis, as well as ability to dissolve the antioxidant are necessary qualifications for any silane.

Silane antioxidants I-7 and I-8 are represented by Figures 6 and 7. The control for I-7, 3-hydroxydiphenylamine (I-6), exuded so rapidly that virtually 100% was lost before the initial spectra were recorded; the same molecule coupled to a silane (I-7) exhibited superior retention for the 60°C as well as the 71°C experiments. A similar situation exists with I-8. The proper control for this would have been phenylpropylamine. However, it was assumed that the material would be lost rapidly, similar to 3-hydroxydiphenylamine, hence a control was not employed. These results indicate the effect of bonding an otherwise incompatible antioxidant molecule to a silane. The tests also indicate stability of both types of bonding, directly to Si and through oxygen, in air at elevated temperatures.

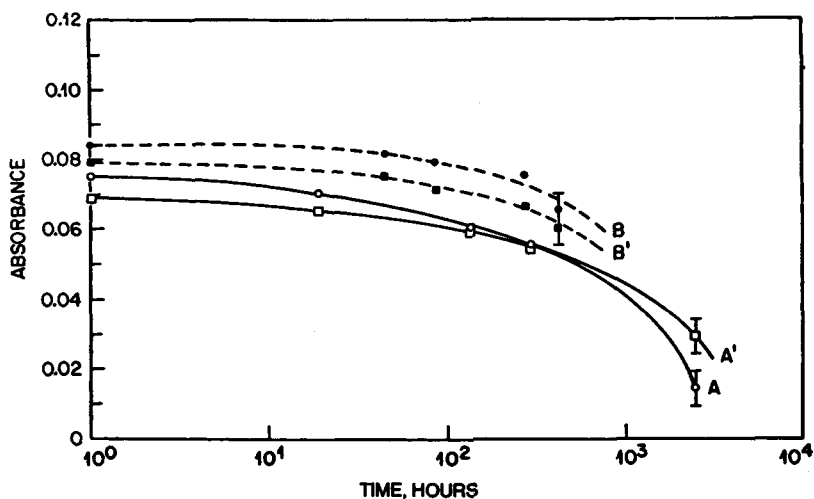


Fig. 5. Concentration of Irganox 1010 in DYNK polyethylene at 71°C vs. time (A) 0.10% I-1010, 5.6 mils; (A') 0.10% I-1010 + 0.69% (APTS); 5.6 mils; (B) 0.10% I-1010, 6.3 mils; (B') 0.11% I-1010 + 0.71% (APTS), 6.4 mils; (—) detergent wash; (---) acetone wash.

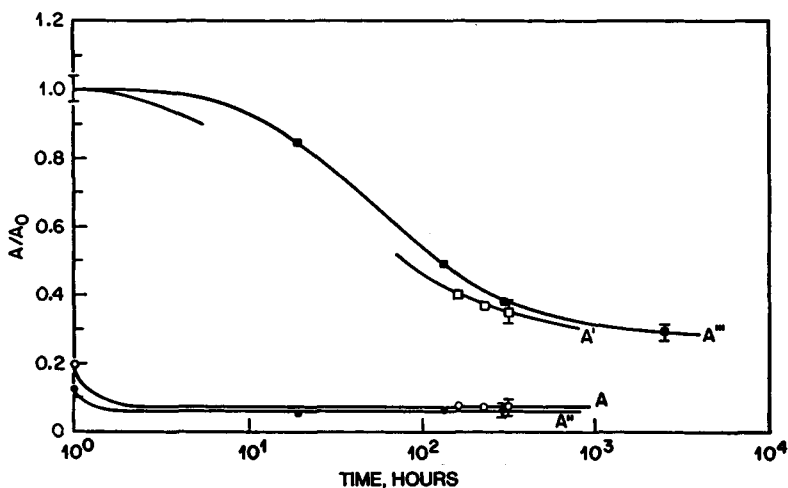


Fig. 6. Concentration of 3-hydroxydiphenylamine in DYNK polyethylene at 60° and 71°C vs. time: (A) 0.10% 3-hydroxydiphenylamine, 60°C, 6.0 mils; (A') 0.10% 3-HDA + 0.70% (APTS), 60°C, 5.5 mils; (A'') 0.10% 3-HDA, 71°C, 6.0 mils; (A''') 0.10% 3-HDA + 0.70% (APTS), 71°C, 5.6 mils.

In summary, it is noted that all three approaches to silane modification—in the dissolved state, bonded via an oxygen linkage, and bonded directly to silicon—are effective in lowering the rate of loss of antioxidants from polyethylene.

On terminating the detergent wash study (Table I), infrared and DTA measurements were taken on the aged samples. These were in accord with

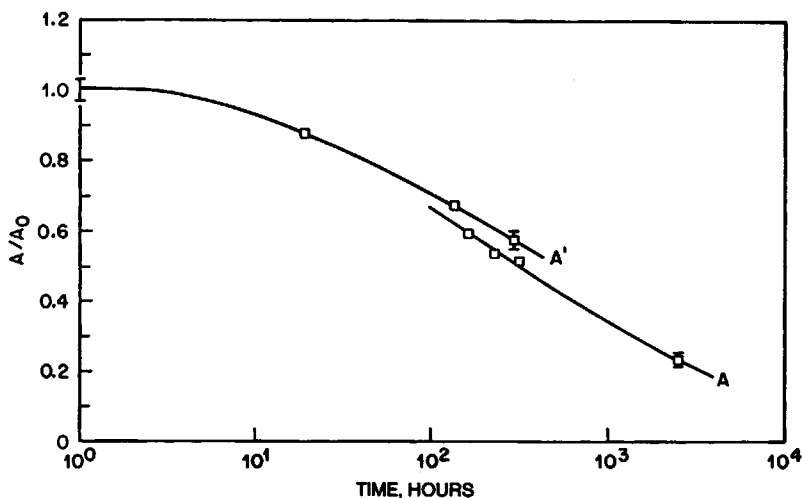


Fig. 7. Concentration of γ -*N*-phenylaminopropyltrimethoxysilane in DYNK polyethylene at 60°C and 71°C vs. time: (A) 0.27% silane + 0.035% (APTS), 60°, 5.8 mils; (A') 0.27% silane + 0.035% (APTS), 71°, 6.0 mils.

the ultraviolet results. Where a finite concentration of antioxidant was indicated by ultraviolet, no carbonyl was observed by infrared (I-2 to 5, 60° and 71°C). Oxidation was observed for I-6, 60° and 71°C (very substantial at the latter temperature). Films I-7 and I-8, 60° and 71°C, all revealed minor oxidation, probably consistent with their limited effectiveness as antioxidants. Although present, they were inactive as antioxidants. All controls were severely oxidized. Curiously, the silane control I-9 consistently oxidized far less than the DYNK controls I-1a and b.

Apart from the migration studies, another observation of value concerns the information derived from our approaches to surface washing (Table III). Clearly, Santonox R and Irganox 1010 exude rapidly to the surface but are not totally removed in the environment of the forced-air oven. More surprising, they are not totally removed by strong detergent wash in lukewarm water. Acetone, which is shown to be incapable of stabilizer extraction from the bulk in the brief time of 40 sec, removes these accumulated surface deposits.

CONCLUSIONS

These results support the prediction made earlier that the superior compatibility of silanes with polyethylene may be used to advantage in arresting the migration of antioxidants. Work is underway to prepare type I antioxidants which appear most generally useful. Further study will be made of the concept of molecular dispersions of standard antioxidants.

The authors thank E. A. Chandross for helpful discussions.

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