

## Retention of Thermal Antioxidants in Polyethylene by Silane Coupling Agents. III. Copper Deactivators

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### Synopsis

Stabilizer activity has been correlated with physical retention and state of dispersion in aged polyethylene films. Incompatibility and poor state of dispersion were found to limit long-term performance of otherwise chemically efficient stabilizers. A practical method to improve compatibility and state of dispersion of stabilizers involves complexation of nonfunctional stabilizer phenolic groups with *N*- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane. Substantial improvement in retention and state of dispersion may be realized with antioxidant-silane weight ratios of 1:1.

### INTRODUCTION

Polyethylene, in certain applications such as wire insulation, contains copper deactivators, antioxidants and pigments. Deactivators, which function as copper-chelating agents are intended to counteract the enhanced oxidation of polyethylene in the presence of copper. Long-term protection of the polymer requires efficient chemical functioning of deactivators and antioxidants (stabilizers) initially as well as physical compatibility and chemical stability comparable to the intended lifetime. Many stabilizers show considerable initial chemical effectiveness but are subject to long-term depletion arising from incompatibility.<sup>1,2</sup>

Loss by diffusion of the antioxidant 4,4'-thiobis(6-*t*-butyl-3-methylphenol) (TBBMP) was first observed by spectroscopic measurements on aged polyethylene standards.<sup>3</sup> Our initial studies were confined to measurements of concentration versus time of standard thermal antioxidants on oven aging, as well as methods to reduce loss. The approach to retention was based on observations of the apparent compatibility of several organofunctional silane coupling agents with polyethylene,<sup>4</sup> and the expectation that strong interactions between silane and stabilizer would improve retention of the latter in polyethylene. Loss by diffusion was confirmed for a variety of antioxidants and the effects of silanes on retention were measured.<sup>1,2</sup>

With continued observations of the physical behavior of stabilizers, the phenomena of crystallization and agglomeration within the polymer have assumed greater importance. Crystallization appears to be one of two major responses of an incompatible additive to the polymer, the other being exudation. Aggregation of an additive in microscopic domains greatly reduces intimate contact with the polymer, regardless of the degree of order within the

domains. Unless the additive is sufficiently volatile to evaporate from these regions and thereby permeate the polymer medium, the polymer is essentially unexposed to the additive, and therefore unprotected. Recent experimentation indicates that crystallization and agglomeration are important for some thermal antioxidants and for most copper deactivators belonging to derivatives of *N,N'*-dibenzal oxalyldihydrazide (OABH).

In this study, we extend the application of silanes to dispersion of copper deactivators. In addition, an antioxidant migration study is presented in which silane concentration is considerably reduced, and the mechanism of the aminosilane-phenol activity is further considered. Derived from these results, a study of stabilized polymer in the presence of copper is presented. Finally, an approach to copper passivation is suggested based on the standard use of coupling agents as treatments for oxidized metal surfaces.

### EXPERIMENTAL

A spectral method devised for measurement of stabilizer loss in polyethylene is reported elsewhere.<sup>1</sup> In general, the spectral method is valid only where gross chemical changes of stabilizer do not occur on aging. Such changes would alter the stabilizer spectra and invalidate the analytical procedure. Except where noted to the contrary in Table III, spectral contours remained stable over the aging intervals, hence the absorbance changes are attributed to physical migration.

The antioxidant study presents simultaneous concentration and induction time measurements on antioxidants. Use of the differential scanning calorimeter for induction times was discussed previously.<sup>2</sup> Material for these measurements was removed from the upper portion of the same film used for UV measurements. A secondary study of that section employs initial induction time measurements to provide mechanistic data on the antioxidant-silane mixtures.

The section on copper deactivators is concerned with concentration-versus-time measurements of copper deactivators, from which information as to state of dispersion has been derived. Studies of stabilized polyethylene in the presence of copper and on silane treatment of copper conclude this report. The strongly overlapping ultraviolet spectra of antioxidants and deactivators here precludes use of UV spectroscopy for concentration, hence the effectiveness of these mixtures has been determined by the traditional measurement of induction time. However, stabilizer concentrations in these two sections may be inferred from results of the first two sections.

From the combined graphs of antioxidant concentration and induction time versus time of the antioxidant study, unique information as to antioxidant efficiency may be obtained. Two classes of behavior are distinguished. Simultaneous loss of antioxidant concentration and induction time is indicative of polymer destabilization resulting from expulsion of the antioxidant. Loss of induction time with retention of antioxidant concentration may be interpreted in either of two ways. Where the antioxidant is functioning as intended, loss of induction time is characteristic, the spectrum being that of retained inactive antioxidant. However, where gradual crystallization of antioxidant occurs, leading to a poor state of dispersion, the same type of behav-

ior would be observed, provided the stabilizer domains do not diffuse back into the bulk polymer during induction time measurements.

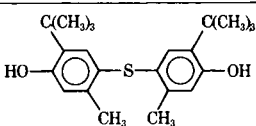
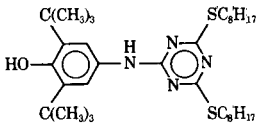
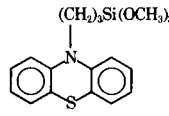
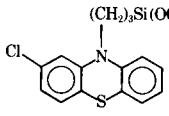

## RESULTS AND DISCUSSION

### Antioxidant Study

Efficient retention of antioxidants complexed with the amino functional silane was demonstrated with silane concentrations about ten times higher than the antioxidant.<sup>2</sup> Practical considerations suggested a reduction in silane concentration. The studies presented here were undertaken to establish lower limits to the silane concentration necessary for retention of stabilizers by the mechanism of complexation.

Table I lists polymer compositions, conditions of film preparation, film thicknesses, and wavelengths of measurement. Antioxidant concentration

TABLE I  
Polyethylene Compositions for Antioxidant Migration Studies

Additive <sup>a</sup>	Structure	Film thickness, mils		Wave-length, Å
		60°C	25°C	
1. 0.201% TBBMP		6.4	6.3	2800
2. 0.199% TBBMP +0.447% Aminosilane		6.8	6.5	2800
3. 0.103% TBBMP		6.8	6.5	2800
4. 0.100% TBBMP +0.420% Aminosilane		6.7	6.2	2800
5. 0.155% Irganox-565		6.7	6.4	~2550
6. 0.150% Irganox-565 +0.429% aminosilane		6.5	6.3	~2550
7. 0.257% PFSS <sup>b</sup> +0.064% aminosilane		6.8	6.4	3100
8. 0.260% CPFS <sup>b</sup> +0.059% aminosilane		6.5	6.4	~3150
9. None <sup>c</sup>		6.5	6.8	
10. 0.428% Aminosilane <sup>d</sup>		6.5	6.8	

<sup>a</sup> Milling conditions: 3–6 min milling at mill temperature of 127–132°C, 15 passes high shear. DYNK polyethylene. Molding conditions: 0.9 g milled polyethylene molded against 5-mil polished aluminum sheet; heated to 149–151°C under pressure, cooled rapidly.

<sup>b</sup> Synthesized by Dr. P. Adams, Millmaster-Onyx Corp., Berkeley Heights, New Jersey.

<sup>c</sup> Spectral baseline for #1, 3, 5, 7 and 8.

<sup>d</sup> Spectral baseline for #2, 4 and 6.

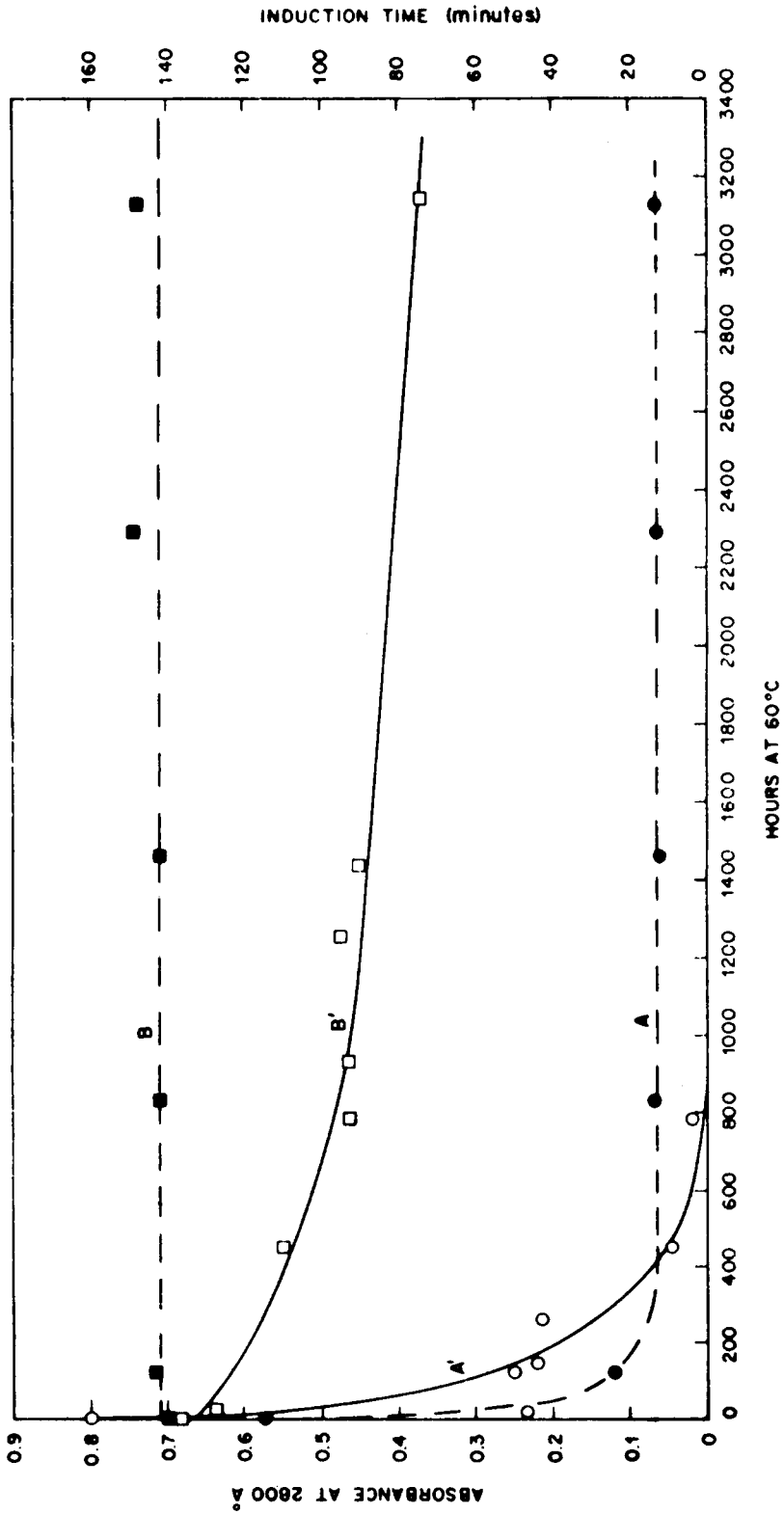


Fig. 1. TBBMP in DYNK polyethylene, 60°C aging: (A) UV; (A') DSC Table I-1; (B) UV; (B') DSC Table I-2,

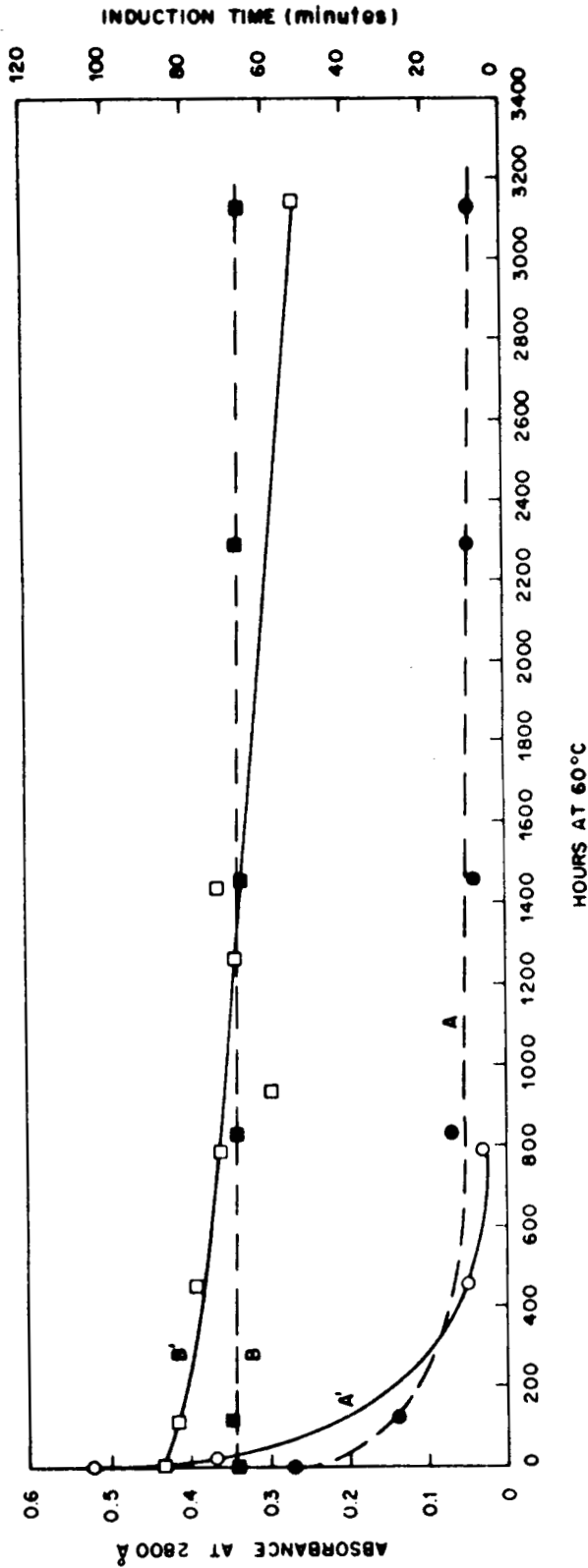


Fig. 2. TBBMP in DYNK polyethylene, 60°C aging: (A) UV; (A') DSC Table I-3; (B) UV; (B') DSC Table I-4.

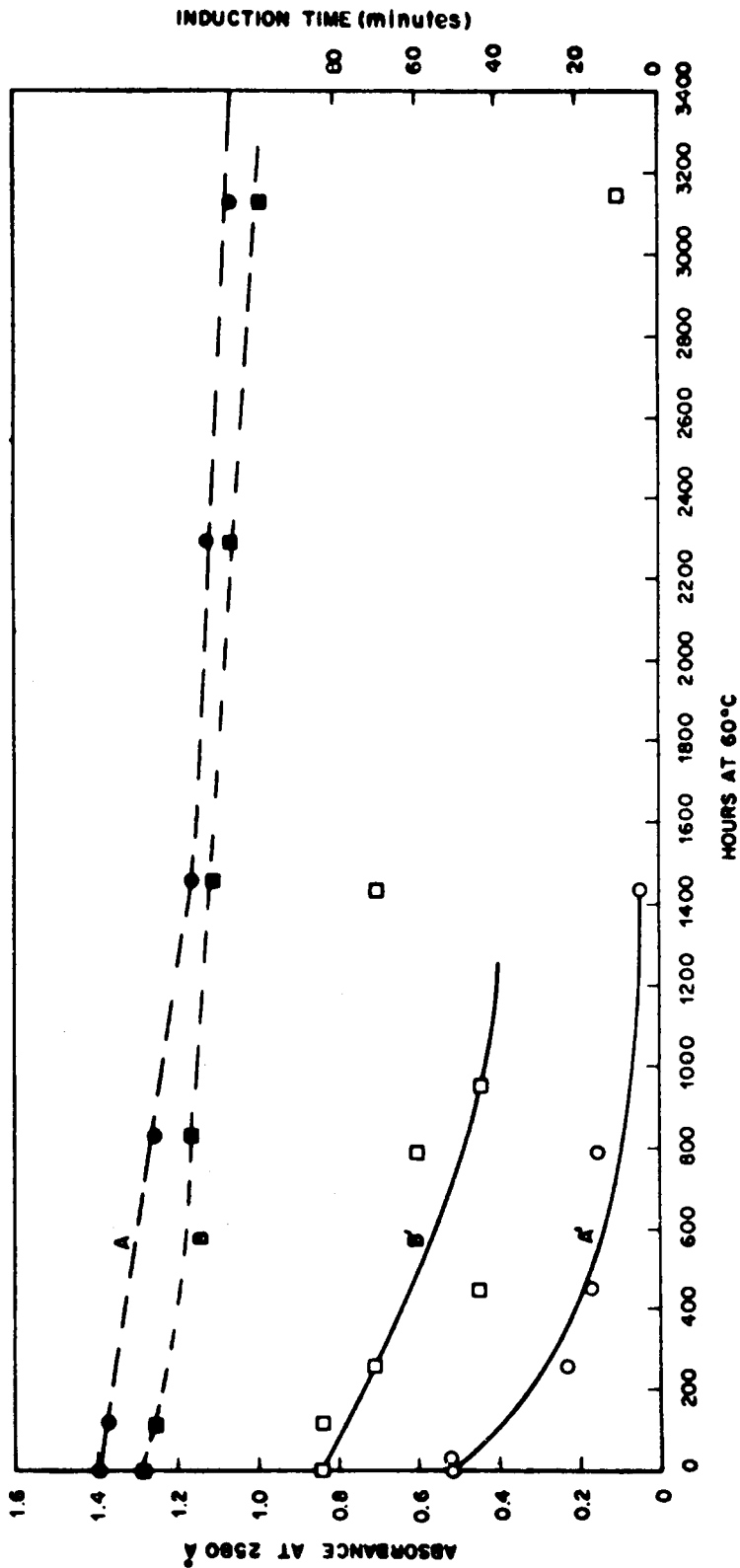


Fig. 3. Irganox 565 in DYNK polyethylene, 60°C aging: (A) UV; (A') DSC Table I-5; (B) UV; (B') DSC Table I-6.

was monitored by UV analysis and activity by DSC induction times. Each polymer composition was subjected to 25°C aging in air and 60°C aging in forced-air ovens. Spectral baselines for I-1, -3, -5, -7 and -8 were derived from spectra of I-9, while I-2, -4, -6 were referred to I-10.

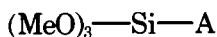
Inspection of Figures 1-3, representing compounds I-(1-6), indicates much lower amino silane concentrations are effective for retention and dispersion. TBBMP has been effectively retained with weight ratios of 1:2 TBBMP-silane (Fig. 1B, B') and 1:4 (Fig. 2B, B'). Especially noteworthy is the accelerated loss of solid TBBMP at 0.2% (Fig. 1A, A'), as compared to 0.1% (Fig. 2A, A'). No such effect of concentration exists for the 1:2 TBBMP-silane mixture (Fig. 1B, B'), as compared to the 1:4 TBBMP-silane mixture (Fig. 2B, B'), despite the twofold increase in TBBMP concentration. This suggested the possibility of further reductions in silane concentration. In an experiment involving only induction time measurements on a variety of compositions, 0.2% TBBMP was compared to 0.2% TBBMP + 0.2% amino silane. Solid TBBMP lost 75% of initial induction time in 280 hr at 60°C, compared to 24% for TBBMP in silane solution. Hence TBBMP-silane weight ratios of between 1:1 and 1:2 may be optimum.

In contrast to solid TBBMP, which is clearly a case of parallel loss of antioxidant concentration and stability, Irganox 565 (Fig. 3) is well retained in the solid state on prolonged aging at 60°C but declines in activity. Complexation with the aminosilane in a ratio of 0.15:4 has had no effect on retention but results in a considerable increase in activity which declines at approximately the same rate as the solid, retaining about 8 min at 3200 hr. The spectrum of Irganox 565 was constant over the aging interval. This suggests agglomeration of the solid, resulting in less antioxidant activity than the well-dispersed liquid. In the 280-hr study at 60°C, 0.2% Irganox 565 and 0.2% Irganox 565 + 0.2% amino silane both showed no loss of induction time. It appears that weight ratios of 1:1-1:2 are sufficient for dispersion.

Results of the 25°C aging studies for I-(1-6) were consistent with the 60°C studies. A more gradual decline in concentration and induction time was observed, particularly for solid TBBMP, I-(1, 3), and Irganox 565, I-5, all of which retained activity at 3200 hr.

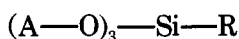
Stabilizers I-7 and -8 are true stabilizer-functional silane coupling agents. Removal of the octyl groups and increasing concentration over the previous study<sup>2</sup> resulted in good long-term aging and retention at 60°C and 25°C. PFS was considerably more active than CPFS.

In formalizing the approach to retention of stabilizers,<sup>1,2</sup> three methods of exploiting the compatibility of certain coupling agents with polyethylene were suggested. Two of these entailed synthesis of molecules of the type



I

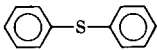
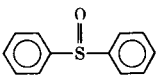
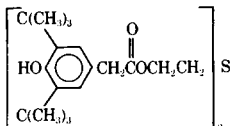
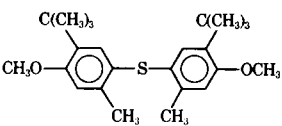
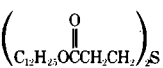
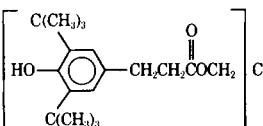
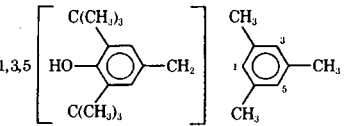
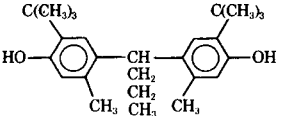
and



II

where A is a stabilizer group. Compounds of structure II were dismissed due to the likely disruption of autopolymerization. While materials of type I

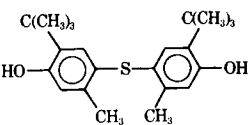
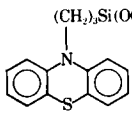
TABLE II  
Polyethylene Compositions for Antioxidant Activity Study

Antioxidant structure	Nominal concn.	Analysis UV	IR	Induction time at 200°C, <sup>b</sup> min
1. 	0.213%	+		0
2. #1 + aminosilane	0.206%	+		2
3. 	0.214%	+		0
4. #3 + aminosilane	0.205%	+		2
5. 	0.207%	+		123
6. #5 + aminosilane	0.199%	+		33
7. 	0.149%	+		0
8. #7 + aminosilane	0.102%	+		3
9. 	0.202%			4
10. #9 + aminosilane	0.203%			7
11. 	0.154%	+		80
12. #11 + aminosilane	0.148%	+		33
13. #11 + NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (diethylenetriamine) (DETA) <sup>c</sup>	0.592%		+	
	0.158%	+		47
	0.655%			
14. 1,3,5- 	0.150%	+		46
15. #14 + aminosilane	0.154%	+		76
16. #14 + DETA	0.631%		+	
	0.151%	+		62
	0.635%			
17. 	0.151%	+		68

(continued)



TABLE II (continued)  
 Polyethylene Compositions for Antioxidant Activity Study

Antioxidant structure	Nominal concn.	Analysis		Induction time at 200°C, <sup>b</sup> min
		UV	IR	
18. #17 + aminosilane	0.149%	+		61
	0.630%		+	
19. #17 + DETA	0.151%	+		68
	0.637%			
20. TBBMP				
	0.153%	+		116
	0.668%			
+ DETA <sup>c</sup>				
21. 	0.312%	+		13
22. Aminosilane control	0.807%		+	1
23. Aminosilane control	0.596%		+	2
24. Aminosilane control	1.95%		+	2
25. DETA	0.657%			1

<sup>a</sup> Milling conditions: 4-7 min milling at mill temperatures of 127-132°C, 15 passes high shear. DYNK polyethylene. Molding conditions: milled compound molded against 5-mil polished aluminum sheet. Heated to 150-152°C under pressure, cooled rapidly.

<sup>b</sup> Film thicknesses 6-8 mils.

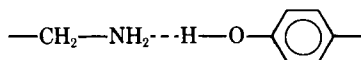
<sup>c</sup> DETA dried over KOH, distilled.

were considered attractive for several reasons, it now appears that the preparation and development of such materials are tasks of considerable magnitude, comparable to the development of existing stabilizers.

A third approach, dissolving existing antioxidants in compatible silanes, has been studied at length. It has been established that silane and stabilizer must interact strongly, as in the case of a phenol and amine. Where weak interactions exist (*N,N'*-diphenyl-*p*-phenylenediamine),<sup>2</sup> no enhancement of retention is likely to occur.

For the purpose of examining the utility of the phenol-amine complex, we consider separately nonphenolic- and phenolic-type thermal antioxidants. Clearly, nonphenolic antioxidants with one or more available but nonfunctional phenol groups (*p*-2-naphthylaminophenol, 3-hydroxydiphenylamine)<sup>1,2</sup> and Irganox 565 should remain active at all temperatures when complexed. No deleterious interaction with the active center —NH— is expected, and complexation is a viable approach to retention and dispersion of such stabilizers.

In the large and important class of phenolic thermal antioxidants, the serious question arises as to activity of the complexed phenolic site at ambient temperatures:



Logically, an exchanged proton may not be available for chain termination. As all induction time measurements are made at 200°C, where activity is observed, it is suggested that the complex dissociates, regenerating the active phenol. Evidence in support of activity at lower temperatures includes the negative slope of the TBBMP-amine induction time curves (Figs. 1B' and 2B'), compared to the constant concentration (Figs. 1B and 2B), consistent with a gradual consumption of active TBBMP at 60°C. NMR studies also indicated a strong interaction between hindered phenols, the aminosilane, and *t*-butylamine, but the data were insufficient to establish the nature of the coordination.

Table II lists 25 compounds prepared from DYNK polyethylene to obtain additional information concerning the phenol-amine interaction. Each experiment consisted of film preparation and UV or IR analysis to confirm additive presence, and induction time measurements at 200°C in oxygen. Compositions II-(1-4) and -(7-10) rule out sulfur as the active center in the TBBMP-amine results. Experiments II-(5, 6, 11-20) indicate activity in a wide variety of phenol-amine complexes, while II-(13, 16, 19, 20) demonstrate the complexes are not specific to the aminosilane molecule. Physically, the DETA-phenol complexes behaved in a manner similar to the silane-phenol complexes, forming viscous solutions miscible in all proportions on warming. Composition II-21 indicates little activity for an N-substituted phenothiazine (13 min). The result suggests a synergistic effect for the PFS-amine mixture (Table I-7), which exhibited greater activity (40 min) at a slightly lower concentration of 0.26%. Control compounds II-(22-25) exclude activity of the amines. The sharp decreases in II-6 and II-12 over their controls, II-5 and II-11, suggests a chemical modification of the antioxidant species, possibly a fragmentation.

In conclusion, phenol-aminosilane complexes function as antioxidants at 200°C, and available evidence suggests activity at lower temperatures. Non-phenolic thermal antioxidants with nonfunctional phenol groups should be active at all temperatures with retention and dispersion superior to the solid.

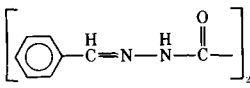
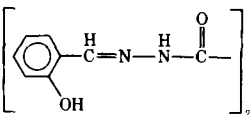
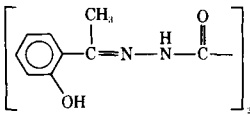
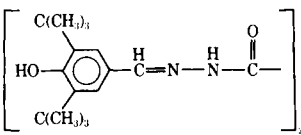
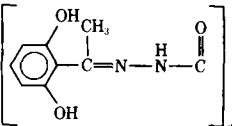
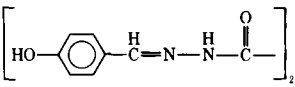
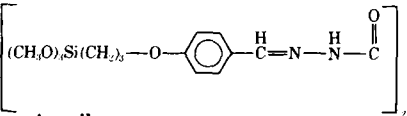
## COPPER DEACTIVATORS

Copper deactivators have been studied for retention and state of dispersion in polyethylene. Similar considerations with regard to loss by diffusion and agglomeration, both processes exposing the material to the deleterious effects of copper. State of dispersion is considered important for deactivators in view of their function as copper complexing agents on a molecular level.

Table III lists seven deactivators<sup>6</sup> III-(1, 3, 5, 7, 9, 11, 13) selected for study together with the corresponding materials in the aminosilane solution III-(2, 4, 6, 8, 10, 12) and the appropriate controls III-(14-17). Films containing these stabilizers were aged at 60°C and 25°C and analyzed periodically by UV spectroscopy. Conditions of film preparation, thickness, and results of the migration studies are given in Table III.

Results for deactivators in solution are consistent with the previously established conditions of interaction. Where no available —OH is present, enhanced retention is not observed. Deactivators III-2, -4, and -6 are rapidly lost at 60°C and gradually at 25°C. It is noted that the orthophenolic groups

TABLE III  
Polyethylene<sup>a</sup> Compositions for Copper Deactivator Studies

Structure	Nominal Concn <sup>b</sup>	Hours at 60°C	Per cent loss	Hours at 25°C	Per cent loss
1. 	0.100%	800	0	800	0
2. #1 + aminosilane	0.100% 1.03%	800	92	800	26
3. 	0.103%	800	0	800	0
4. #3 + aminosilane	0.100% 0.995%	800	71	800	29
5. 	0.101%	800	0	800	0
6. #5 + aminosilane	0.100% 1.01%	800	86	800	19
7. 	0.100%	800	60	800	0
8. #7 + aminosilane	0.102% 0.431%	800	83	800	10
9. 	0.101%	2000	6	2000	0
10. #9 + aminosilane	0.102% 0.423%	2000	15	2000	0
11. 	0.100%	1000	0	1000	0
12. #11 + aminosilane	0.100% 0.625%	1000	c	1000	0
13. 	0.153%	1000	c	1000	0
+ aminosilane	0.416%				
14. No additive	0.417%				
15. Aminosilane	0.395%				
16. Aminosilane	1.03%				
17. Aminosilane	0.596%				

<sup>a</sup> DYNK polyethylene.

<sup>b</sup> Milling conditions: 4-7 min milling at mill temperatures of 121-132°C, 15 passes high shear. Molding conditions: 0.8-0.9 g milled compound molded against 5-mil polished aluminum sheet; heated to 148-151°C under pressure, cooled rapidly.

<sup>c</sup> Analysis not possible due to spectral changes. High retention likely.

<sup>d</sup> Film thickness at 60°C: 6.3-7.6 mils; at 25°C: 6.3-7.3 mils.

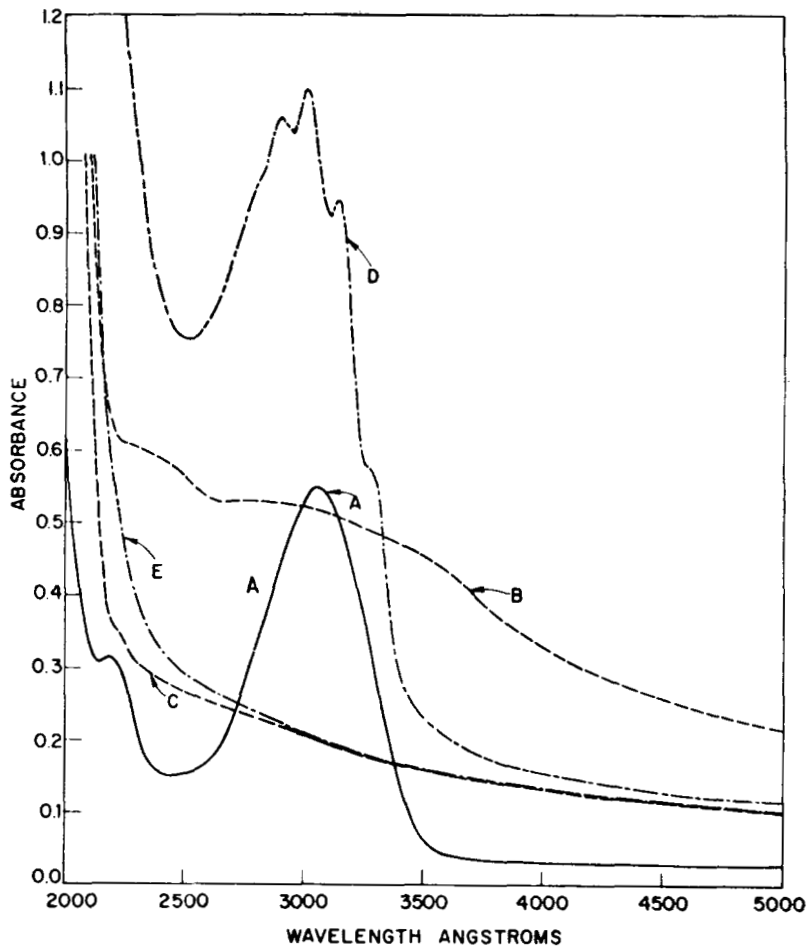


Fig. 4. (A) OABH in ethanol; (B) OABH in DYNK polyethylene, 0.100%, 7.3 mils; (C) DYNK polyethylene, 6.7 mils; (D) 0.100% OABH + 1.03% aminosilane in DYNK, 7.0 mils; (E) 1.03% aminosilane in DYNK polyethylene, 6.4 mils.

of III-4 and -6 are internally hydrogen bonded, reflected in low solubility in the aminosilane; concentrations higher than the 1:10 ratio resulted in precipitation. III-10 and -12 are better retained at 60°C and 25°C and III-8 at 25°C; higher solubility in the aminosilane was observed. As solubility is an important criterion of complexation, it appears that these constituents form a weak complex, reflected in enhanced retention. In apparent contradiction to the results for dissolved deactivators, the solids III-1, -3, -5, -9, and -11 are retained and III-7 is retained at 25°C.

Figure 4A is the UV spectrum of OABH in saturated ethanol solution. Figure 4B is the same material in DYNK polyethylene at 0.1%, and Figure 4C is unstabilized DYNK. Figure 4D represents 0.1% OABH + 1% aminosilane in polyethylene. An explanation of the great increase in scattering (Fig. 4B) is a high degree of crystallization of OABH in polyethylene, resulting in additional scattering centers. Microscopic analysis confirmed the presence of bi-

refrangent crystalline needles measuring 1-3 microns. Crystallinity was also observed for III-11 and agglomerates for III-3, -5, -7, and -9.

These results suggest severe incompatibility of OABH and derivatives with polyethylene, leading to crystallization or agglomeration of the solids and mechanical entrapment within the polymer. In weakly bound solution, crystallization is impossible and rapid expulsion occurs. Where complexation may occur, better retention is observed. Mechanical trapping of the solids raises the question of effectiveness as copper complexing agents at ambient temperatures. Molecular dispersions such as III-10 and -12 should function more efficiently.

### STUDIES OF STABILIZED POLYETHYLENE IN THE PRESENCE OF COPPER

Table IV lists polymer compositions which were molded on 100 mesh copper gauze, aged at 60°C, and tested periodically for induction time at 180°C in oxygen. Composites containing antioxidant and copper deactivator (odd numbered) were compared to the same in solution (even numbered). A slight excess of aminosilane was used. The ratio (copper area)/(PE weight) was found to be proportional to induction time, imposing control of composite thickness. Thicknesses of 14 mils gave ratios of about 130 cm<sup>2</sup> copper/g

TABLE IV  
Polymer Induction Times at 180°C in the Presence of Copper

Polyethylene composition <sup>a</sup>	Composite thickness, <sup>b</sup> mils	60°C Oven aging, hr			
		0 min <sup>c</sup>	404 min	1001 min	1988 min
1. 0.102% TBBMP 0.102% III-11	13.4	23	7	5	6
2. 0.102% TBBMP 0.103% III-11 0.638% Aminosilane	13.3	17	16	14	12
3. 0.101% TBBMP 0.112% III-13	13.3	18	9	6	8
4. 0.101% TBBMP 0.107% III-13 0.639% Aminosilane	13.5	23	22	20	16
5. 0.150% Irganox-565 0.100% III-11	13.3	9	0	0	0
6. 0.153% Irganox-565 0.103% III-11 0.632% Aminosilane	13.5	9	9	8	7
7. 0.153% Irganox-565 0.111% III-13	13.5	5	0	0	0
8. 0.154% Irganox-565 0.107% III-13 0.610% Aminosilane	13.6	9	9	9	7

<sup>a</sup> DYNK polyethylene.

<sup>b</sup> Milling conditions: 4-6 min milling at mill temperatures of 129°C, 15 passes high shear. Molding conditions: milled compound molded into 6-7 mil films at 150-151°C. Films molded into 100 mesh copper gauze, 150-151°C.

<sup>c</sup> Induction time at 180°C.

PE, compared to about 50 cm<sup>2</sup>/g for 14 mil copper wire with 6-mil insulation. Gauzes were solvent cleaned in hexane before use.

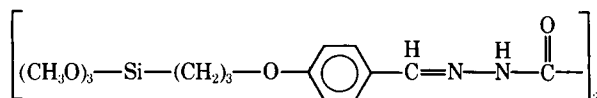
In practice, a wide variety of deactivator-antioxidant combinations must be tested as their functions appear to influence each other. For the purposes of this study, TBBMP and Irganox 565 were combined with III-11 and -13 without regard for synergism.

Results of the study (Table IV) are expressed in terms of induction time at 180°C versus hours of 60°C oven aging. Complexed stabilizers, Table IV-2, -4, -6, -8 retain activity in every case as compared to controls, IV-1, -3, -5, -7. Among the controls, TBBMP performs better than Irganox 565. As complexes the composites stabilized with Irganox 565 lose a smaller percentage of their original induction times. All complexed stabilizer composites confirm expectations as to the effects of dispersion and retention, despite the limited selection.

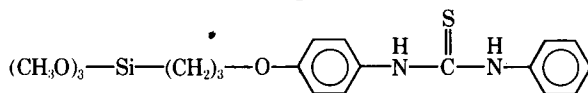
### SILANE TREATMENT OF COPPER

A study has examined the passivation of copper surfaces with silane coupling agents possessing deactivator-functional groups. Two effects of such treatment may be formation of a barrier preventing physical migration of copper, and complexation of copper at the metal oxide surfaces. Such treatments are presently used for metal oxide surfaces and reflect the intended use of silane coupling agents. In addition, a commercial silane (Owens Illinois Type 650 glass resin) has been applied, forming a physical barrier without complexing ability. The organic portion of this silane is a methyl functionality.

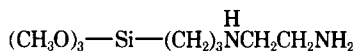
Silanes I-IV below were applied to solvent-cleaned copper gauze (100 mesh):



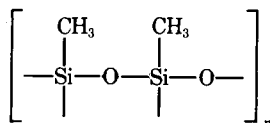
I



II



III



IV

Compounds I and II were applied by boiling the gauze for 10 min in approximately 0.4% methanolic solution. A small weight gain of the gauze was ob-

served. Compound III was applied by boiling for 5 min in 0.4% methanolic solution, which assumed a deep blue color. A weight loss for the gauze was observed, consistent with amine complexation of copper and removal from the substrate. A thin film of the material is believed likely to remain. Compound IV was applied by a momentary dip in 0.4% methanol followed by a 3-min cure at 110°C. A weight increase was observed.

Compounds consisting of TBBMP (0.1%) and TBBMP (0.1%) + amino silane (0.4%) were prepared without deactivators and molded onto the treated gauzes. Controls consisted of similar compositions molded onto untreated gauze. Initial induction times for the treated copper gauzes were greater than for untreated. All composites show a sizable fraction of their initial induction times at 1340 hr of aging at 60°C.

### CONCLUSIONS

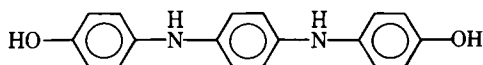
Stabilizer activity has been correlated with physical retention and state of dispersion in aged polyethylene films. Incompatibility and poor state of dispersion have been found to limit long-term performance of otherwise chemically efficient stabilizers.

A practical method has been devised to improve compatibility and state of dispersion of stabilizers by association with certain silane coupling agents which are themselves compatible. Of several possible approaches, one for which synthesis of new materials is not mandatory involves complexation of non-functional stabilizer phenolic groups with N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane.

Results of these studies indicate substantial improvement in retention and state of dispersion may be realized with antioxidant-silane weight ratios of 1:1. Stabilizers are first dissolved in the silane by warming after which the viscous mixture is incorporated into the hot polymer melt.

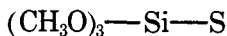
Important criteria for selection of polymer stabilizers include the presence of available phenol groups for complexation with the aminosilane and the absence of other deleterious reactions which may destroy stabilizer activity. From the deactivator study of this report, it appears that internally hydrogen bonded phenolic groups may not be available for complexation. Suitable antioxidants are aromatic amines with unhindered phenol sites. The toxicity of such materials has not been determined.

Resolution of the question of activity of the complexes formed by hindered phenolic type antioxidants with the aminosilane at temperatures lower than 160°C is necessary before complexed hindered phenolics may be employed as antioxidants at ambient temperatures. A practical stabilizer may consist of 0.08% antioxidant such as



with 0.02% metal deactivator, such as III-11, dissolved in 0.1% aminosilane. A considerable reduction in deactivator concentration is believed possible in view of its increased state of dispersion in the liquid state.

Further improvements in compatible stabilizers await the development of coupling agents of structure



where S denotes an antioxidant, deactivator, or UV absorber. Such materials should be especially suited to filled polymer systems, where coordination with filler surfaces will place the stabilizer in the important interfacial region. In unfilled polymer systems, the stabilizers may be used alone or, if necessary, with a small percentage of the basic amino silane to promote autopolymerization.

Extention of these results to a wide variety of polymers is believed possible. Applications of special importance include thin polymer coatings on metal surfaces and sheets requiring long-term stability.

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### References

1. R. V. Albarino and H. Schonhorn, *J. Appl. Polym. Sci.*, **17**, 3323 (1973).
2. R. V. Albarino and H. Schonhorn, *J. Appl. Polym. Sci.*, **18**, 635 (1974).
3. J. P. Luongo and G. A. Pasteur, unpublished data, 1971.
4. H. Schonhorn, H. L. Frisch, and R. V. Albarino, *J. Polym. Sci.*, **11**, 1013 (1973).
5. R. Kroker and K. Hamann, *Angew. Makromol. Chem.*, **13**, (1970); N. Fery, R. Laible, and K. Hamann, *Angew. Makromol. Chem.*, **34**, 81 (1973); E. Dietz, N. Fery, and K. Hamann, *Angew. Makromol. Chem.*, **35**, 115 (1974).
6. R. L. Hartless and A. M. Trozzolo, *ACS Preprints, Div. Organ. Coatings and Plastics Chem.*, **34**, 177 (1974).

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