

## New Thermal Antioxidants for Polyethylene Containing Carbon Black

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Carbon black in 2 or 3% concentration, which is often added to protect polyethylene against photo-oxidation, has an adverse effect on conventional antioxidants such as substituted phenols or secondary aromatic amines.<sup>1</sup> The protection which these antioxidants impart to clear polyethylene is considerably reduced when carbon black is added to the polymer. In contrast, certain organo-sulfur compounds have now been shown to be outstanding antioxidants in carbon-containing polymers, losing none of their effectiveness, but rather exhibiting a synergistic effect with carbon black. Furthermore, several organo-sulfur compounds which show no appreciable antioxidant activity in the clear polymer become excellent antioxidants in the presence of carbon black.

The relative effectiveness of the various antioxidants has been determined by direct measurement of the rate of oxygen absorption at 140°C. Similar measurements over a temperature range are now in progress and will be reported at a later date.

### EXPERIMENTAL METHODS

The procedure for preparing samples and for measuring their oxidation rates was identical with that described in the preceding paper. Antioxidants were obtained from commercial sources or, when not available, were synthesized by conventional methods. In all instances where the melting point of the antioxidant under study was above 124°C., a master batch of antioxidant in polyethylene was first prepared. The master batch was then cut back to the desired antioxidant concentration. Carbon containing formulations were prepared from a 25% master batch of a typical channel black having a particle size of 180 A. and pH of 4 to 5.

### RESULTS AND DISCUSSION

Phenolic antioxidants, which have received considerable attention recently due to their non-

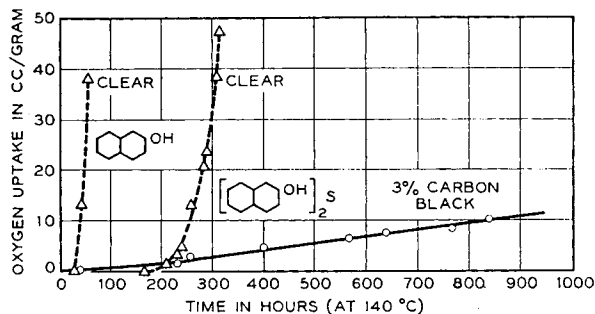


Fig. 1. Relative effect of 2-naphthol and thiobis-(2-naphthol) in 0.1% concentrations on the thermal oxidation rate of polyethylene.

staining characteristics, are usually less effective inhibitors for polyethylene oxidation than are the amines. Indeed, many of the common phenols in 0.1% concentration are no more effective than carbon black alone in 3% concentration. Even those which show moderate protection against oxidation lose most of their effectiveness in the presence of carbon black. Addition of long alkyl chains to the aromatic nuclei of many phenols improves their antioxidant activity,<sup>2</sup> presumably through increased compatibility, but these modified phenols are no better in the presence of carbon black than the simple phenols from which they are derived.

2-Naphthol (0.1%), which has been used extensively as a stabilizer in simple hydrocarbon systems, inhibits oxidation of polyethylene to about the same extent as 3% carbon black. However, when 2-naphthol is condensed with sulfur dichloride, the resulting thioether is not only more effective in the clear polymer, but is also a much better antioxidant in the presence of carbon black (Fig. 1). In fact, the mixture of carbon black and thiobis-(2-naphthol) appears to be synergistic. The linear rate curve, showing no evidence of autocatalysis throughout the reaction, resembles that obtained with retarders rather than antioxidants.<sup>3</sup> Absence of autocatalysis may indicate that this carbon black-antioxidant combination prevents

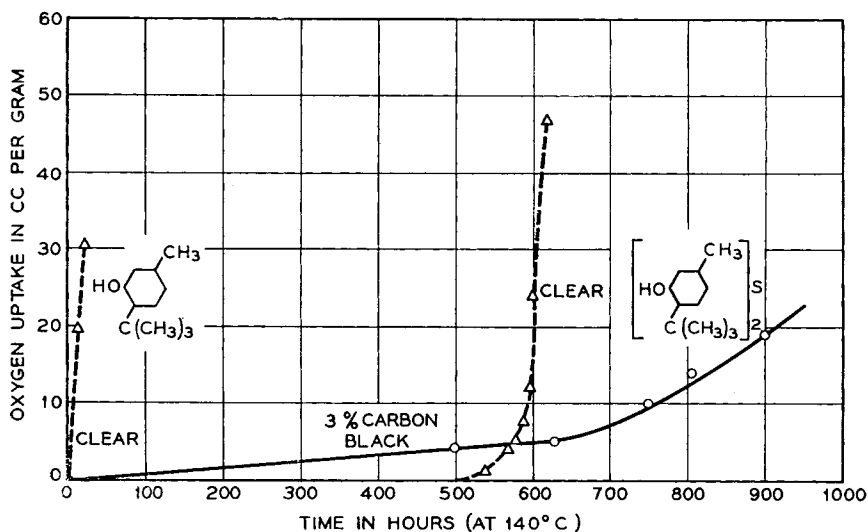


Fig. 2. Thermal oxidation rate of polyethylene containing 0.1% 4,4'-thiobis-(3-methyl-6-*tert*-butyl phenol) in polyethylene.

radical formation from reaction products like hydroperoxides. Either hydroperoxides are not formed in the presence of the sulfur compounds or, if formed, they do not decompose by a radical mechanism.

The unusual effect of carbon black on thiobis-(2-naphthol) has been observed with many thioethers derived from moderate or weak antioxidants. For example, 3-methyl-6-*tert*-butylphenol is a poor antioxidant for polyethylene but its corresponding thioether, 4,4'-thiobis-(3-methyl-6-*tert*-butylphenol), is a very good antioxidant in clear polyethylene and exhibits a synergistic effect with carbon black (Fig. 2). In this instance the rate curve in the presence of carbon black shows some evidence of autocatalysis, but the steady state rate is much lower than that observed with this compound in clear polyethylene. 5-Pentadecyl-1,3-benzenediol, in contrast, is a good antioxidant in

clear polyethylene and little improvement results from condensation to a thioether. The condensation product does, however, show the synergism typical of thioethers when carbon black is present. Similarly *N*-phenyl-2-naphthylamine, a good amine antioxidant for polyethylene, is not substantially improved by conversion to a thioether except in the presence of carbon black. Phenothiazine, however, is only about half as effective in the presence of carbon black as in the clear polymer. In this instance, where the sulfur atom is part of the ring system, the compound does not show the synergism with carbon black characteristic of the substituted thioethers.

Results obtained with two commercial antioxidants having the following chemical structures indicate that the effect of carbon black can be attributed to the thioether bond.

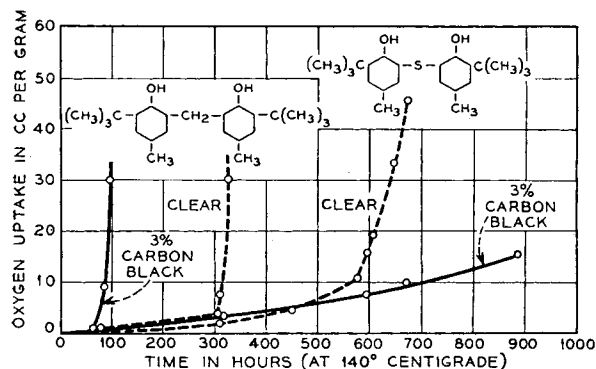
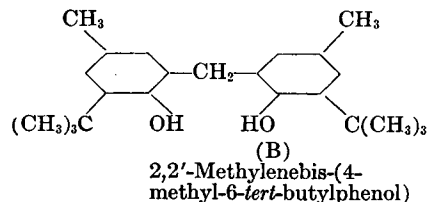
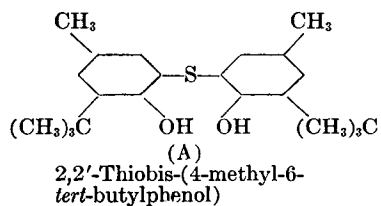


Fig. 3. Comparison of 0.1% 2,2'-thiobis-(4-methyl-6-*tert*-butyl phenol) with 0.1% 2,2'-methylenebis-(4-methyl-6-*tert*-butyl phenol) as an antioxidant for polyethylene.



These compounds differ only in the nature of the bridge between the aromatic rings. Whereas the methylenebis compound (B) loses most of its

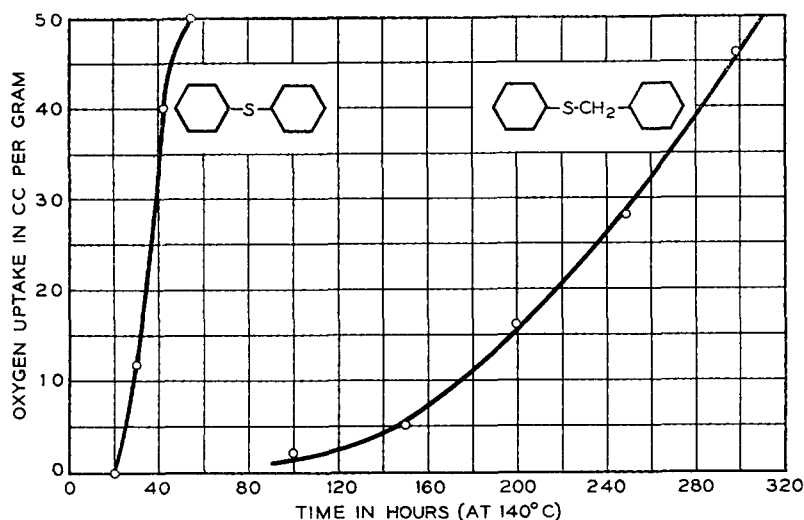


Fig. 4. Relative effectiveness of phenyl sulfide and phenyl benzyl sulfide in 0.1% concentrations on the thermal oxidation rate of polyethylene containing 3% carbon black.

antioxidant activity when carbon black is present (Fig. 3), the degree of protection derived from the combination of carbon black with the corresponding thioether (A) is greater than would be anticipated from the activity of each component. Thus a variety of relatively inferior inhibitors may be modified by coupling with sulfur dichloride. Antioxidant activity is thereby increased in clear polyethylene to varying degrees and generally is further improved in the presence of carbon black. The improvement is not due to greater retention of the sulfur compound resulting from a gain in molecular weight, because many of the thioethers have vapor pressures as high as some of the less effective antioxidants. The presence of active hydrogen in hydroxyl or amine groups is essential, however, since on methylation these substituted

thioethers are no longer effective as antioxidants either in clear or carbon black formulations. In this respect the thioethers resemble conventional antioxidants. However, the difference in behavior in the presence of carbon black between thioethers which contain active hydrogen and conventional antioxidants seems enough to indicate that two different mechanisms are involved.

Perhaps the most direct evidence supporting this suggestion has been found in the remarkable antioxidant properties of compositions containing carbon black and sulfur compounds lacking amino and phenolic groups and having no other active hydrogens. Such compounds would not be expected to function as conventional antioxidants, and consequently any protective action must result from reactions involving the sulfur bond. For

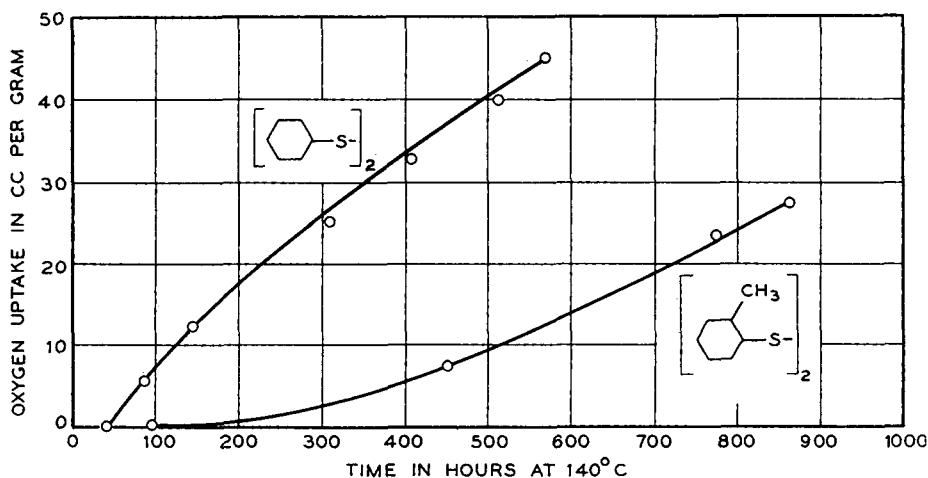


Fig. 5. Relative effectiveness of phenyl disulfide and 2-tolyl disulfide in combination with 3% carbon black as thermal antioxidants for polyethylene.

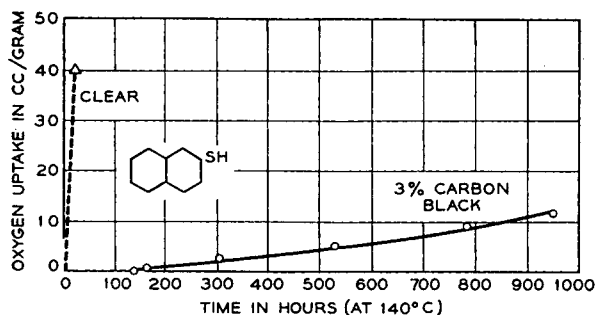


Fig. 6. 2-Naphthalenethiol in 0.1% concentration as an antioxidant for polyethylene in the presence of 3% carbon black.

example, benzylthiobenzene, though it does not inhibit the oxidation of clear polyethylene, becomes a good antioxidant in the presence of carbon black (Fig. 4). Benzyl sulfide and 2-(2-propenylthio)naphthalene are also effective, but only in combination with carbon black. Each of these thioethers has a relatively weak bond between sulfur and the carbon of a methylene group. In contrast, phenylsulfide, with a much stronger carbon-sulfur bond, does not have antioxidant activity either in clear polyethylene or in the presence of carbon black.

The behavior of phenyl disulfide in polyethylene containing carbon black, as shown in Figure 5, is further evidence for a relationship between bond strength and antioxidant activity. In this instance the weaker bond would presumably be between the two sulfur atoms. Disulfides in general give good protection against polyethylene oxidation but only in carbon black compositions. Alkylation of the aromatic nuclei, exemplified by 2-tolyl disulfide in Figure 5, increases antioxidant efficiency. Similarly 2-naphthyl disulfide is much more effective than phenyl disulfide. Heterocyclic

disulfides, such as 2-benzothiazyl disulfide, are also effective antioxidants with carbon black. These data indicate a relationship between bond strength and the ability of these compounds to function as antioxidants in the presence of carbon black.

Results obtained with disulfides containing no active hydrogen indicate that the corresponding thiols should also be considered as potential antioxidants. 2-Naphthalenethiol provides very little protection for clear polyethylene but becomes an excellent antioxidant in the presence of carbon black. This thiol-carbon black composition, as shown in Figure 6, exhibits a gradual, linear oxygen uptake over a period of 2000 hours without reaching an accelerating stage. The degree of protection imparted to polyethylene under accelerated test conditions by the combination of carbon black and 2-naphthalenethiol exceeds that obtained with previous antioxidants except for the thioether derived from 2-naphthol.

At lower temperature, 2-naphthalenethiol does inhibit oxidation of clear polyethylene to a very slight extent. The low level of activity, however, is much less than that observed with 2-naphthol. This may be interpreted as an indication that the active hydrogen in thiols is not primarily a terminator of the oxidative chain, or, as suggested by Hammond and co-workers,<sup>4</sup> that hydrogen abstraction is not the rate-controlling step in antioxidant reactions. Wide variations have been noted in antioxidant behavior of other thiol-carbon black compositions. The toluene thiols, for example, present an interesting trend from the para isomer which follows the ordinary rate curve for conventional antioxidants to the ortho isomer which behaves more like a retarder.

Nearly all commercial organic antioxidants con-

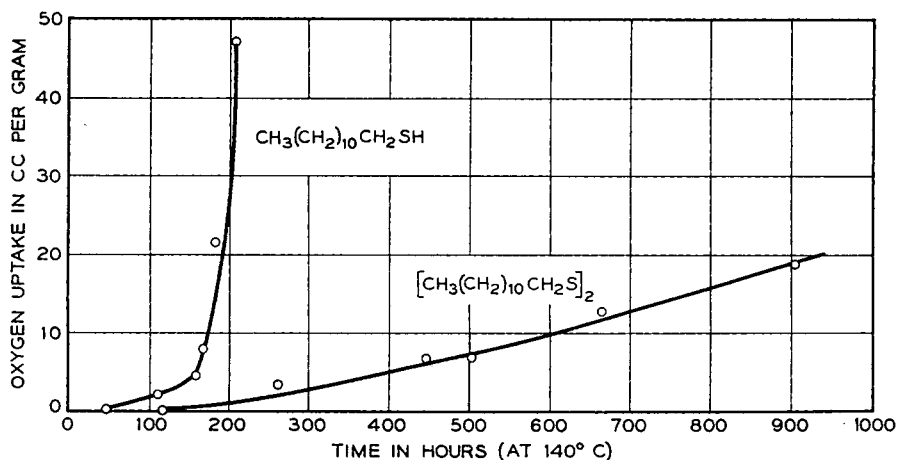


Fig. 7. Effect of 1-dodecanethiol and 1-dodecyl disulfide in 0.1% concentrations on the thermal oxidation rate of polyethylene containing 3% carbon black.

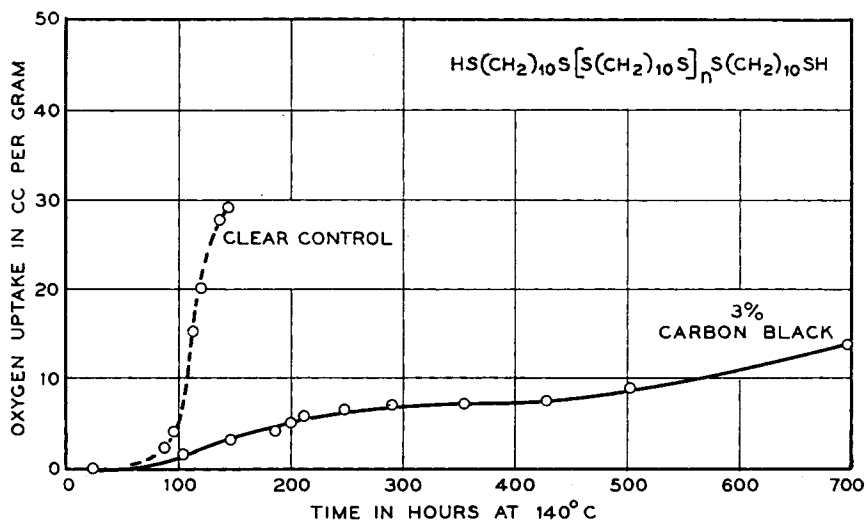


Fig. 8. Thermal oxidation rate of polyethylene containing 0.1% of a polymer derived from 1,10-decamedylenedithiol.

tain aromatic groupings such as those in the thioether, thiol, and disulfide compounds discussed thus far. Few aliphatic substances have approached the activities attained with even mediocre aromatic antioxidants. However, in conjunction with carbon black, alkyl disulfides, such as 1-dodecyl disulfide, or thiols, such as 1-dodecanethiol and 1, 10-decanedithiol (Fig. 7), and also polymers of alkyl dithiols (Fig. 8) have been found to be good antioxidants for polyethylene. Polymeric antioxidants have the added advantage of providing variations in concentrations of active sulfur groupings over a wide range of molecular weight, allowing better retention of the sulfur compound by the polymer substrate. The various groups of sulfur antioxidants are summarized in Table I with typical examples of each group and references to the synthetic method used.

Certain thiols and disulfides provide slight protection for clear polyethylene. The active hydrogens in thiols might function to some extent as chain terminators since methylation of 2-naphthalenethiol to methylthionaphthalene nullifies the antioxidant effectiveness both in the clear polymer and in the presence of carbon black. However, another mechanism is required to adequately explain the behavior of disulfides. Inhibition by disulfides in clear polymer resembles reactions proposed for compounds such as 10,10'-diphenothiazine,<sup>13</sup> tetraphenylhydrazine,<sup>14</sup> and tetramethyl-1,4-benzenediamine.<sup>15</sup> Furthermore, the thermal initiation of styrene polymerization by certain disulfides<sup>16</sup> indicates the formation of radicals by sulfur-sulfur bond cleavage. Carbon black may tend to promote rupture of  $-\text{S}-\text{X}$  bonds where X

is S, H,  $-\text{CH}_2\text{AR}$ ,  $\text{CAr}$ , etc. The resulting product,



$\text{RS}\cdot$ , in a free state or combined with carbon black may then trap radical intermediates in polymer oxidation. Conversely, the sulfur compounds may merely prolong and accentuate the antioxidant properties of the carbon surface. In that event the sulfur compound would not function as an antioxidant at all, but would promote or possibly regenerate the inhibiting effect of the carbon.

### CONCLUSION

Antioxidants which contain a thioether bond are usually more effective than the simple compounds from which they are derived. More significant is the effect of carbon black on these improved antioxidants, generally resulting in even greater protection than in the clear polymer. This is in contrast to the behavior of conventional antioxidants which do not contain a thio-bond. In all cases examined, these conventional antioxidants lose a large proportion of their effectiveness in the presence of carbon black. Recent studies concerned with the chemical nature of the carbon black surface strongly suggest the presence of reactive chemical groupings which may account for the weak antioxidant activity of some carbon blacks. Apparently the carbon black surface interacts with organo-sulfur antioxidants since this unique behavior has not been observed in other materials of comparable particle size, such as alumina, titania, or silica, nor do these materials themselves inhibit polyethylene oxidation.

TABLE I

Summary of the Effect of Organo-Sulfur Compounds in 0.1% Concentration on the Oxidation of Polyethylene with and without Carbon Black

Compound	Reference to method of synthesis	M.p., °C.	Hours to absorb 10 cc. O <sub>2</sub> /g.	
			Clear	3% carbon black
Polyethylene controls	Commercial		6	35
Elemental sulfur (1%)	Commercial		—	120
<b>Thioethers</b>				
4,4'-Thiobis-(3-methyl-6- <i>tert</i> -butylphenol)	5	160	600	750
Thiobis-(2-naphthol)	5	214	240	730
Thiobis-( <i>N</i> -phenyl-2-naphthylamine)	5	184	190	260
Benzylthiobenzene	7	41-42	6	180
Methylthio-2-naphthalene	8	64-65	6	55
2-Naphthyl thiobenzoate	6	107	6	70
4-Aminophenyl sulfide	10	110-111	15	35
<b>Disulfides</b>				
Phenyl disulfide	Commercial		6	120
2-Tolyl disulfide	Commercial		6	520
2-Acetamidophenyl disulfide	12	155-156	6	480
1-Dodecyl disulfide	9	34	20	520
2-Benzylthiazyl disulfide	Commercial		8	350
4,4'-Dithiodimorpholine	Commercial		120	600
Polymeric 1,10-decanedithiol	9	64-65	110	540
<b>Thiols</b>				
2-Toluenethiol	Commercial		6	200
2-Naphthalenethiol	Commercial		6	900
2-Mercaptobenzothiazole	Commercial		35	380
1-Dodecanethiol	Commercial		6	160
1,10-Decanedithiol	Commercial		16	200
<b>Miscellaneous</b>				
Thianthrene	Commercial		20	230
Phenothiazine	Commercial		430	250
2-Naphthyl diselenide	11	129-130	19	200

Thioethers and disulfides which contain no amine or phenol groups and hence no active hydrogen constitute another class of antioxidants which are unusual in that they attain a significant degree of activity only in the presence of carbon black. Although the mechanism through which these simple compounds function as antioxidants has not been established, there is considerable evidence that a relationship exists between antioxidant activity and bond dissociation energy. Some thiols may act to a slight extent as conventional antioxidants in clear polyethylene, but when carbon black is present, they appear to function through the same mechanism as do the simple organo-sulfur compounds which contain no active hydrogen. It is significant that within the general class of organo-sulfur antioxidants, alkyl compounds exhibit strong antioxidant activity in the presence of carbon black, and are often comparable with their aromatic counterparts.

The authors wish to thank Dr. B. S. Biggs for stimulating discussions during the course of these studies.

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### Synopsis

Common secondary aromatic amine and alkylated phenolic antioxidants lose much of their activity in polyethylene containing carbon black. In contrast their thioether derivatives provide more protection against oxidation than the sum of the separate contributions of carbon black and the sulfur compounds. Organic disulfides and some thio-ethers without amino or phenolic hydrogen also safeguard polyethylene from oxidation but only in the presence of carbon black. Likewise thiols are excellent protectants in combination with carbon black but not in clear polymer. Aliphatic thiols, disulfides, and their polymeric derivatives and related selenium compounds exhibit similar activity.

### Résumé

Une amine aromatique secondaire ordinaire et des antioxydants phénoliques alcoylés perdent beaucoup de leur activité dans du polyéthylène contenant du noir de carbone. Au contraire leurs dérivés thioéthers protègent mieux contre l'oxydation que la somme de leurs contributions individuelles et du noir de carbone. Les disulfures organiques et cer-

tains thioéthers sans hydrogène aminé ou phénolique préservent également le polyéthylène de l'oxydation, mais nullement en présence de noir de carbone. De même, les thiols sont d'excellents agents protecteurs en combinaison avec le noir de carbone mais pas si le polymère est pur. Les thiols aliphatiques, les disulfures et leurs dérivés polymériques ainsi que les composés du sélénium correspondants témoignent une activité similaire.

### Zusammenfassung

Die gewöhnlichen Antioxydantien, wie sekundäre aromatische Amine und alkylierte Phenole, verlieren in russhaltigen Polyäthylenen viel von ihrer Wirksamkeit. Im Gegensatz dazu liefern ihre Thioätherderivate einen grösseren Schutz gegen Oxydation, als der Summe der einzelnen Beiträge von Russ und den Schwefelverbindungen entspricht. Auch organische Disulfide und manche Thioäther ohne Amin- oder Phenolwasserstoff schützen Polyäthylen gegen Oxydation, allerdings nur in Gegenwart von Russ. In gleicher Weise sind Thiole in Kombination mit Russ ausgezeichnete Schutzmittel, nicht aber in klaren Polymeren. Aliphatische Thiole, Disulfide und ihre polymeren Derivate und verwandte Selenverbindungen weisen eine ähnliche Wirksamkeit auf.

Received May 29, 1958