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Loss of Antioxidants from Polyethylene by Evaporation and Aqueous Extraction

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INTRODUCTION

Antioxidants which inhibit the thermal oxidation of polyethylene eventually fail to give adequate protection, and rapid degradation of the polymer occurs. Ideally, an antioxidant would be lost only through direct reaction with propagating radicals. There are, however, several other factors which may contribute to antioxidant failure. The direct reaction of antioxidants with oxygen could reduce their effectiveness, and it has been reported[1] that carbon black, which is often added as a light screen, has an adverse effect on many antioxidants. Evaporation of the antioxidant during compounding and its loss during weathering, either by evaporation or aqueous extraction, may also be partly responsible for antioxidant failure.

MacLeod[2] measured the oxidation rate of stabilized polyethylene under conditions where either extraction or evaporation could have occurred simultaneously with normal antioxidant exhaustion. Although the proportional effect of the various factors was not determined, MacLeod concluded that in general the less volatile antioxidants were more effective, and that antioxidant leaching could be partly responsible for antioxidant failure in polyethylene pipe conveying hot water.

In this investigation the relative rate at which different types of antioxidants are removed from polyethylene as a result of evaporation or extraction was observed, independent of the normal antioxidant reaction. These antioxidant types varied from simple molecules to polymers and included activated carbon black.[3]

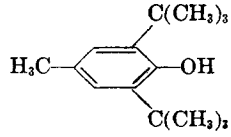
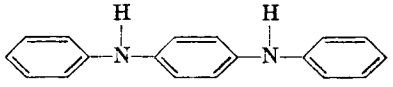
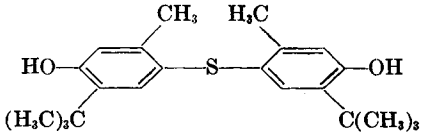
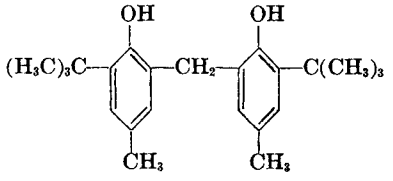
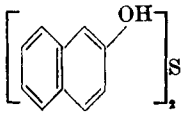
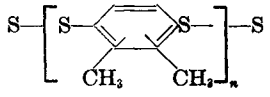
EXPERIMENTAL

Antioxidants used in evaporation and extraction are listed in Table I. The polyethylene was a branched, low-density resin designated DYNK by its supplier, the Bakelite Company. All organic antioxidants were introduced by milling 0.1 g. into 100 g. polyethylene, and the carbon blacks were added in the same way as 3% by weight. (The only exception was one formulation containing 0.07% DPPD plus 3% Kosmos BB.) Samples were cut from 10 mil sheets which had been molded from the milled material.

The apparatus used to study the evaporation of antioxidants from polyethylene appears in Figure 1. A 0.2-g. strip of polymer was inserted into the evaporation sample holder made from 10 mm. o.d. Pyrex tubing. Seven of these holders were connected with butyl tubing to a manifold through which nitrogen flowed. The other end of each holder was connected by Tygon tubing to a bubbling tube. After being flushed with nitrogen, all seven holders were placed in a bath maintained at 105 ± 1°C. The flow rate of the nitrogen was regulated to 1.05 l./min. as indicated by a flowmeter immediately preceding the manifold. The rate of flow to each sample was equalized by adjusting each stopcock in the manifold so the rate of bubbling was approximately the same for all. To assure an average flow of 150 cc./min. to all tubes, their positions in the manifold were rotated every other day. After two weeks the samples were removed, cut into two 0.1-g. strips, and oxidized at 140°C. by a procedure described previously.[1]

For extraction, 0.1-g. strips about $^3/_{16}$ in. wide were cut from the molded film. The weighted sample strips were dropped into the extraction vessel which contained distilled water. (No significant difference was found between distilled water and filtered sea water for DPPD and Santonox at room temperature.) A nitrogen atmosphere was maintained at all times. For room temperature the extraction vessel was a 500-ml. brown bottle which was placed in a constant temperature room. Since the volume was large in these experiments, the water was not changed. Other

TABLE I
Antioxidants Studied in Evaporation and Extraction

Commercial Name	Supplier	Chemical name	Structure
Ionol	Shell	2,6-Di-*tert*-butyl-4-methylphenol	
JZF (DPPD)	Naugatuck	*N*,*N*′-Diphenyl-*p*-phenylenediamine	
Santonox	Monsanto	4,4′-Thiobis(3-methyl-6-*tert*-butylphenol)	
CAO-5[a]	Catalin	2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	
Thiobis-2-naphthol[a]	Synthesized in these laboratories	Thiobis-2-naphthol	
Thiokol C13338ER	Thiokol Corporation	Polymeric xylene disulfide	
CK3/S	Degussa	Sulfur-activated carbon black	8.7% chemically combined sulfur
Kosmos BB	United Carbon Company	Normal channel carbon black	6.5% oxygen

[a] Used only in evaporation.

samples were placed in 125-ml. Erlenmeyer flasks equipped with water-cooled condensers. The flasks were placed in a 60°C. constant-temperature bath, and the water changed each week. A Soxhlet extractor (68°C., exchange every hour) was also used. The samples of each different antioxidant were placed in separate extractors to avoid contamination. At various intervals the strips were removed, dried in a vacuum desiccator, and oxidized at 140°C.

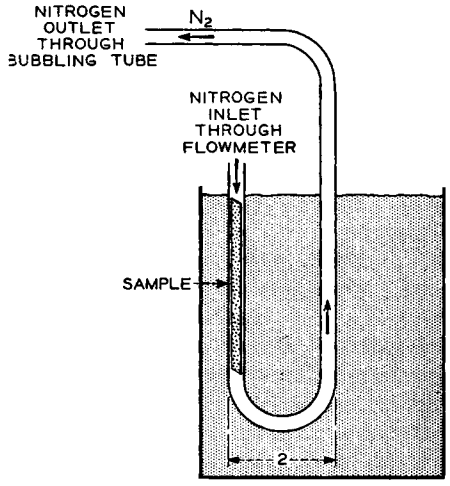


Fig. 1. Apparatus used to study the evaporation of antioxidants from polyethylene.

DISCUSSION

By carrying out the processes of evaporation and extraction in a nitrogen atmosphere and then oxidizing the sample in a closed system, it was possible to separate the effects of antioxidant loss from those of oxidation. The accelerated oxidation tests then provided an accurate way for determining directly the extent to which the previous treatment had impaired the effectiveness of each antioxidant in polyethylene, either by its direct removal or modification.

In evaluating the oxidation data, the volume of oxygen absorbed per gram polymer was plotted against time. For those reactions which became autocatalytic, the induction period was determined by extrapolating the rapid steady-state rate curve to the time axis. This was compared with the induction period of control samples which had not been subjected to evaporation or extraction. In certain instances the rate curves never became autocatalytic, and these were interpreted individually.

Evaporation

The per cent effectiveness retained E for each antioxidant studied in evaporation is summarized in Table II. This quantity is defined as

$$E = 100\ (I - C)/(I_0 - C)$$

where I_0 and I are the induction periods before and after evaporation, respectively, and the constant C is the induction period of uninhibited polyethylene, which is approximately 4 hr. at 140°C.

TABLE II
Evaporation of Antioxidants from Polyethylene

Antioxidant	Induction period, hr. Before evap.	Induction period, hr. After evap.	Effectiveness retained, %
Normal channel black	31	49	100
Sulfur-activated carbon black	—	—	100
Thiokol polymer	151	170	100
Ionol	70	15	17
DPPD	470	70	14
Santonox	440	40	8
CAO-5	340	14	3
Thiobis-2-naphthol	140	19	11

The conditions of evaporation were sufficient to indicate the great difference between monomolecular antioxidants and those of very high molecular weight, such as carbon black and polymeric protectants. Whereas the latter were completely unaffected, the effectiveness retained by the simpler antioxidants was reduced to between 3 and 17% (Table II). Since the results of this accelerated test show that large molecules are not lost at 105°C., it is most unlikely that they would be removed at lower temperatures. Typical organic antioxidants, on the other hand, are susceptible to evaporative loss on exposure and are certainly lost to some extent during milling.

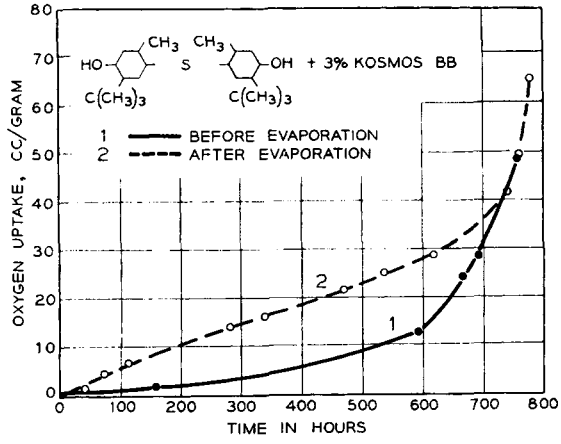


Fig. 2. Retention after evaporation of 4,4′-thiobis(3-methyl-6-*tert*-butylphenol) by polyethylene which contains 3% carbon black.

The possibility that carbon black might alter the retention of antioxidants was explored by incorporating them into polyethylene containing 3% Kosmos BB. In no instance did carbon black accelerate the rate of removal, which is consistent with the adsorbing ability of carbon black. On the other hand, carbon black failed to retain Ionol, thiobis-2-naphthol, or DPPD as completely as it held Santonox. After two weeks evaporation, traces of these four antioxidants were all that remained, in contrast to Santonox which lost only a slight amount of its original effectiveness (Fig. 2).

Extraction

Interpretation of extraction data was facilitated by plotting the induction period against extraction time for each set of conditions. The results (Figs. 3–5) showed a rapid initial loss of antioxidant effectiveness, followed by gradual tapering off. Soxhlet extraction, because it employed the highest temperature and most frequent exchange of water, affected the antioxidants more severely than the other conditions.

Monomolecular compounds* were more rapidly removed than the Thiokol polymer in all three instances. This confirms the results of evaporation studies and proves that simple organic antioxidants are removed by both evaporation and extraction at a faster rate than polymeric protectants.

Another additive included in the extraction experiments was sulfur-activated channel black (De-

* The induction period for 0.1% Ionol before extraction was higher than that normally observed. This was probably due to uneven dispersion.

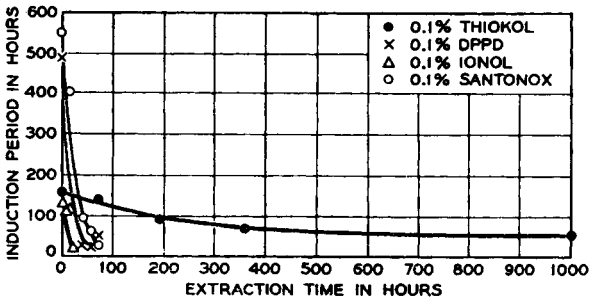


Fig. 3. Soxhlet extraction of Ionol, DPPD, Santonox, and Thiokol polymer.

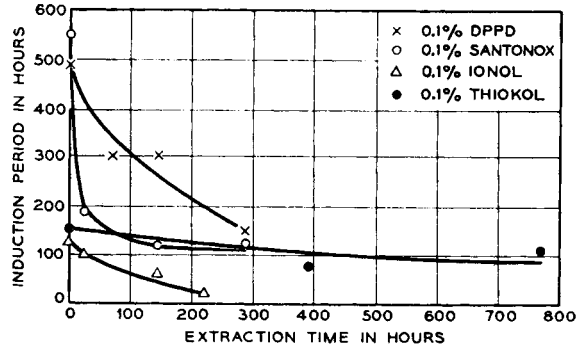


Fig. 4. Extraction at 60°C.

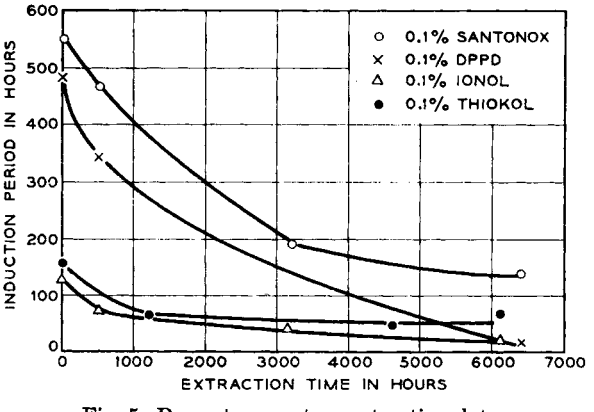


Fig. 5. Room temperature extraction data.

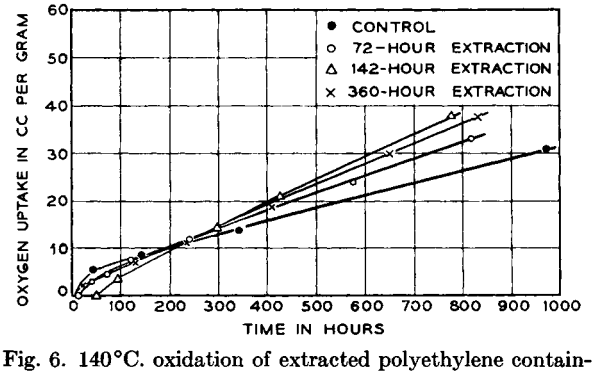


Fig. 6. 140°C. oxidation of extracted polyethylene containing 3% sulfur-activated channel black.

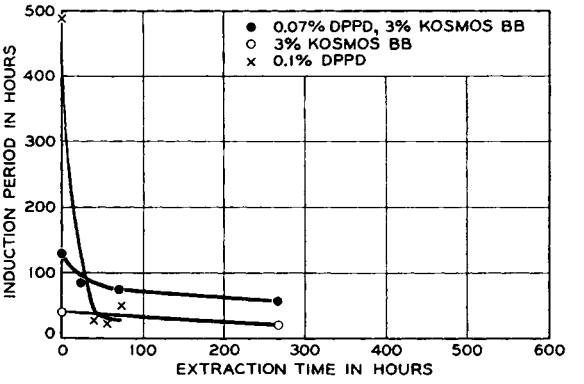


Fig. 7. Effect of extraction on polyethylene protected with 0.07% DPPD and 3% Kosmos BB.

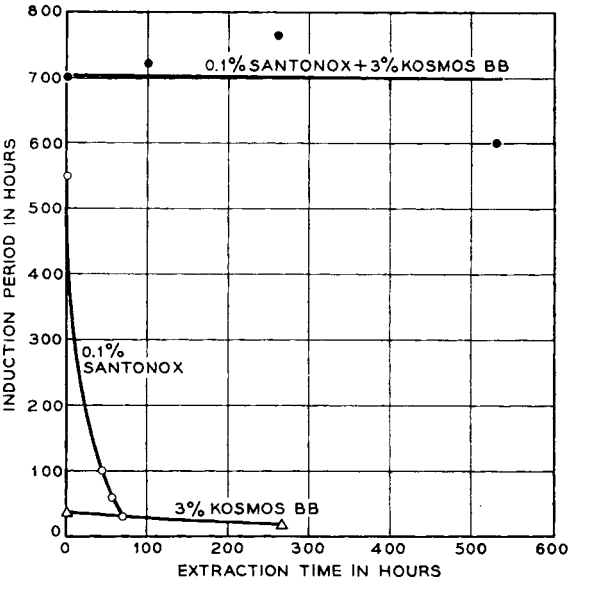


Fig. 8. Retention after extraction of 0.1% Santonox in polyethylene containing 3% Kosmos BB.

gussa CK3/S) in 3% concentration. It is an excellent antioxidant, restricting the oxidation of polyethylene to a slow, steady rate with no evidence of autocatalysis for over 1000 hr.[3] After 72 hr. of Soxhlet extraction the effectiveness of this antioxidant was reduced slightly (Fig. 6), with very little subsequent change. The same small initial loss was observed at 60°C. and at room temperature. Some decrease was also observed in the ability of 3% Kosmos BB to protect polyethylene after 267 hr. of Soxhlet extraction. This probably is not due to the extraction of the carbon black, but perhaps to the effect of adsorbed water at reactive centers on the carbon.

Soxhlet extraction of a DPPD-Kosmos BB formulation resulted in a slower initial loss than

was observed for DPPD alone (Fig. 7). The extent of protection was never reduced to that obtained with Kosmos BB alone, indicating that the carbon may have retained a small amount of the antioxidant. The same effect was observed for Ionol. As in evaporation, neither of these was as completely retained by carbon black as Santonox (Fig. 8).

CONCLUSION

Ultimate failure of stabilized polyethylene on exposure is probably hastened in many instances by the removal of the antioxidant by aqueous extraction and/or evaporation. This loss can be overcome by using those compounds which are most resistant to these influences, such as polymeric-type antioxidants and carbon blacks. Although the retention of the few monomolecular compounds studied here was not appreciably improved by carbon black, a notable exception was Santonox. Before considering a new antioxidant for outdoor applications, it should be evaluated in terms of its resistance to evaporation and extraction by approximating conditions of actual use.

References

1. Hawkins, W. L., R. H. Hansen, W. Matreyek, and F. H. Winslow, *J. Appl. Polymer Sci.*, **1**, 37 (1959).

2. MacLeod, N. D., "The Ageing of Polythene Compositions," presented at Third Annual Symposium, Wires and Cables, Signal Corps Engineering Laboratories, New Jersey, December 1954.

3. Hawkins, W. L., Mrs. M. A. Worthington, and F. H. Winslow, in *"Proceedings of the Fourth Biennial Conference on Carbon,"* to be published.

Synopsis

Polyethylene containing various types of antioxidants was either heated in a stream of nitrogen or placed in water maintained at several different temperatures under nitrogen. The polymer was then oxidized to determine how greatly the evaporation or extraction treatment had reduced the antioxidant effectiveness as compared with a control. Polymeric materials and carbon blacks were more completely retained than monomolecular organic compounds. The presence of carbon black did not greatly alter the rate of loss for any of these substances except Santonox, which was almost completely retained.

Résumé

Un polyéthylène contenant différents types d'antioxydants a été chauffé dans un courant d'azote ou placé dans de l'eau maintenus à plusieurs températures différentes sous azote. Le polymère a été alors oxydé pour déterminer l'étendue de la diminution de l'efficacité antioxydante provoquée par évaporation ou extraction par comparaison à un témoin. Le polymère et le noir ont été plus complètement retenus que les composés organiques monomoléculaires. La présence de noir animal ne change pas beaucoup la vitesse de déperdition pour aucune de ces substances excepté pour la Santonox, qui a été beaucoup plus complètement retenu.

Zusammenfassung

Polyäthylen mit einem Gehalt an verschiedenen Typen von Antioxydantien wurde entweder in einem Stickstoffstrom erhitzt oder in Wasser gebracht, das unter Stickstoff bei mehreren verschiedenen Temperaturen gehalten wurde. Das Polymere wurde dann oxydiert, um festzustellen, wie stark die Verdampfungs- oder Extraktionsbehandlung die Wirksamkeit des Antioxydans im Vergleich zu einem Kontrollversuch beeinflusst hatte. Polymere Stoffe und Russ wurden vollständiger zurückgehalten als monomolekulare, organische Verbindungen. Die Gegenwart von Russ hatte bei keiner dieser Substanzen einen grossen Einfluss auf die Geschwindigkeit, mit der sie abgegeben wurde, mit Ausnahme von Santonox, bei dem fast vollständige Festhaltung auftrat.

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