

The Effect of Carbon Black on Thermal Antioxidants for Polyethylene

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INTRODUCTION

Oxidation of polyethylene, which results eventually in physical and dielectric failure of the polymer, is caused by heat and ultraviolet radiation. Photo-oxidation is practically stopped by the addition of 3% by weight of fine particle size carbon blacks¹ which also act under accelerated test conditions as mild thermal antioxidants. Small amounts of organic inhibitors, which are stronger high temperature antioxidants than carbon black, are customarily added to polyethylene to provide additional thermal protection during processing and subsequent exposure. In many instances carbon black and a conventional amine or phenol antioxidant are added together to protect polyethylene against both thermal and photo-oxidation. Though it effectively protects against photo-oxidation, carbon black reduces the activity of many thermal antioxidants, rendering several completely ineffective.

EXPERIMENTAL METHODS

The polyethylene used for all oxidation tests was taken from a single batch of high pressure, high molecular weight polymer of 0.92 density. The carbon black was an acidic channel black having an average particle diameter of 120-180 Å. The antioxidants used were commercial samples.

Mixtures of polyethylene with carbon black and/or antioxidant were prepared by mill massing on a 6-inch by 12-inch, 2-roll mill having roll speeds of approximately 25 to 35 rpm with the rolls at a temperature of 120°C. (250 ± 5°F.). A master batch of antioxidant in polyethylene was prepared and then cut back to the desired antioxidant concentration. Mixtures containing carbon black were prepared from a 25% master batch of carbon black in the polyethylene described above. This procedure insured optimum dispersion of the carbon black.

Oxidation rates were determined by an accelerated test in which the amount of oxygen reacting with the sample was measured volu-

metrically. All data reported herein are the result of measurements made at 140°C. in the apparatus shown in Figure 1. A detailed study of these reactions over a temperature range extending down to 80°C. is in progress and will be reported later.

Reaction vessels consisted of 14-inch lengths of 8-mm. o.d. Pyrex tubing sealed at one end. Enough Type 4A Linde Molecular Sieve, a synthetic zeolite, to fill 1 to 1½ inches of the tube was used as an adsorbent for water and carbon dioxide. The adsorbent was held in place by a small plug of glass wool, and 0.1 g. of the milled polyethylene sample approximately 50 mils thick was then inserted. A second plug of glass wool was placed about 1½ to 2 inches from the open end of the tube, at about the point where the tube was to pass through a hole in the side of the oven. The purpose of this plug was to prevent heat loss and to catch any condensing materials which might otherwise contaminate the gas buret. The air in the reaction tube was replaced with oxygen by alternate evacuation and refilling with oxygen.

The reaction tubes were placed in an air-circulating oven maintained at 140 ± 0.5°C. and immediately connected to gas burets filled with oxygen. After temperature equilibrium was reached, the system was adjusted to atmospheric pressure and an initial reading was made. Oxygen uptake was measured by subsequent readings at atmospheric pressure. Similar tubes containing no polyethylene samples were placed in the oven as blanks to provide a correction for changes due to fluctuating room and oven temperature and atmospheric pressure. All materials were run at least in duplicate, and reaction tubes were discarded at the end of each run.

RESULTS AND DISCUSSION

Carbon black, in addition to being a light screen for ultraviolet radiation, also functions as a mild thermal antioxidant at 140°C. In concentrations of 2 or 3%, customarily used in polyethylene, a

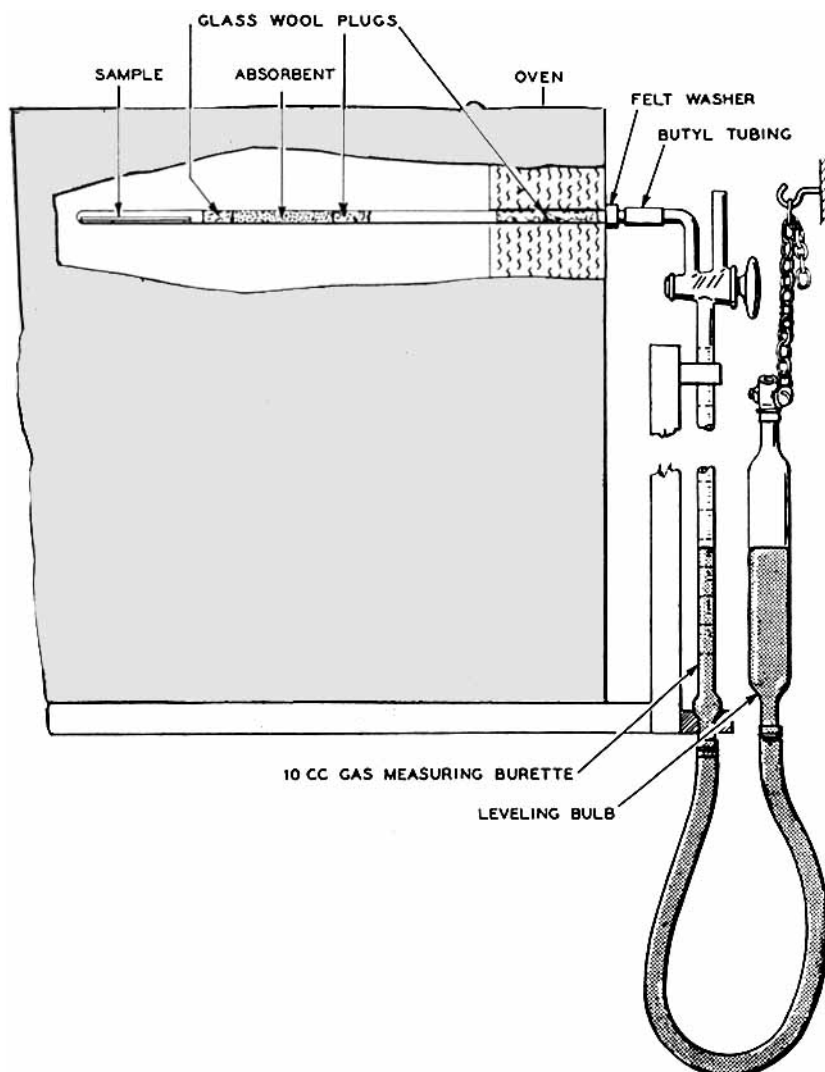


Fig. 1. Schematic diagram of oxygen uptake apparatus.

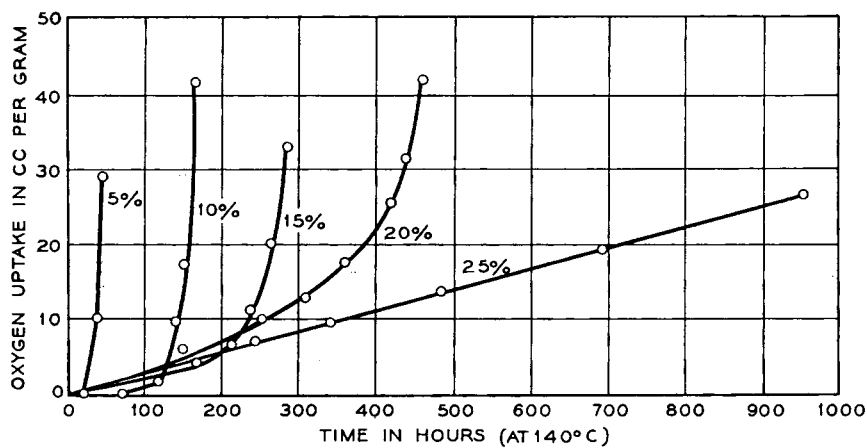


Fig. 2. Relationship between increasing carbon black concentration and the thermal oxidation rate of polyethylene.

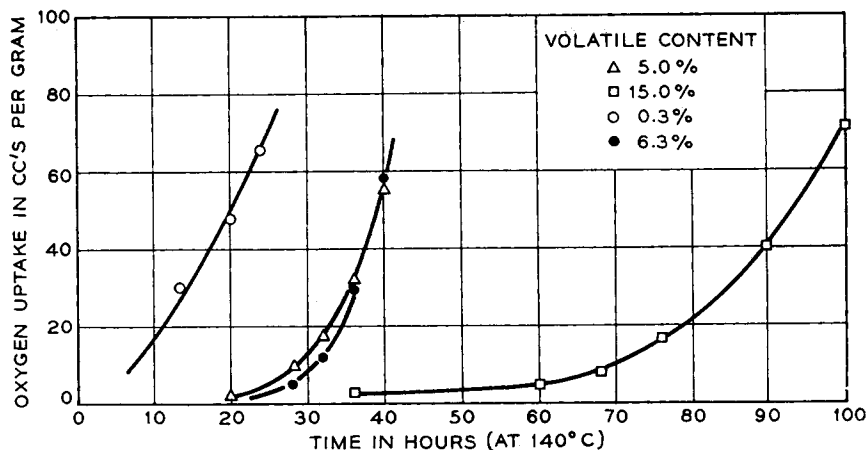


Fig. 3. Dependence of the thermal oxidation rate of polyethylene containing 3% carbon black on the volatile content of the carbon black.

well dispersed carbon black in the size range of 500 A. or less compares favorably with some of the less effective thermal antioxidants. The amount of protection derived from carbon black increases in proportion to its concentration in the polymer (Fig. 2). At the lower concentrations the rate curves are typical of an autocatalytic reaction, but autocatalysis becomes less evident with increasing concentration until at 25% carbon black, oxidation proceeds at a slow, steady rate for a period of 1000 hours. Higher concentrations of carbon black seemingly remove peroxides so effectively that their homolytic cleavage into new, chain-initiating radicals becomes negligible. However, for many polyethylene applications concentrations of carbon black above 5% are believed to have a deleterious effect on physical and dielectric properties.

Carbon black may function as a trap for propagating radicals, or its role as an antioxidant could be due to the presence of a low molecular weight fraction capable of migrating into the polymer. The latter possibility seems unlikely since exhaustive evacuation of carbon black at 200°C. does not decrease antioxidant effectiveness. However, reactions which are believed to modify chemical groups on the carbon surface do influence antioxidant behavior.² A typical channel black (Fig. 3) with 5% "volatile" content* at 3% concentration gives about 30 hours of protection to polyethylene at 140°C. When this carbon black is activated by heating in air until the volatile content reaches 15.0%, it becomes a much more

* The "volatile" content of carbon black is measured by ASTM Method D 271-48 which removes essentially all of the oxygen containing groups from the carbon surface by pyrolysis.

effective antioxidant. The process may be reversed by deactivation at high temperature in the absence of oxygen, converting the carbon black to a form (0.3% volatile) which gives no thermal protection. The deactivated form may be partially reactivated to a volatile content of 6.3% by reheating in oxygen. The exact nature of the chemical reactions which occur during these treatments is not known, but the volatile content, as measured by standard techniques, increases as the carbon black is activated and decreases with deactivation. Polarographic and infrared data indicate the presence of a variety of oxygen groupings on the surface of carbon black.^{3,4} Presumably the content or nature of such groupings is modified in the cycle of heat treatments. The effect of a wide variety of reactions on the chemical composition of carbon black and the behavior of

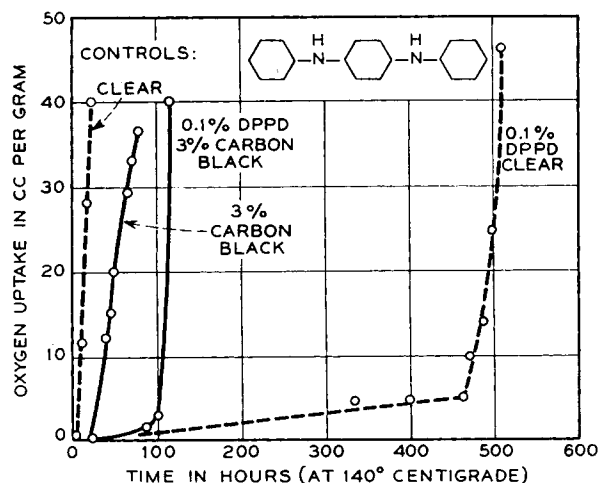


Fig. 4. Effect of carbon black on the behavior of *N,N'*-diphenyl-*p*-phenylenediamine as an antioxidant in polyethylene.

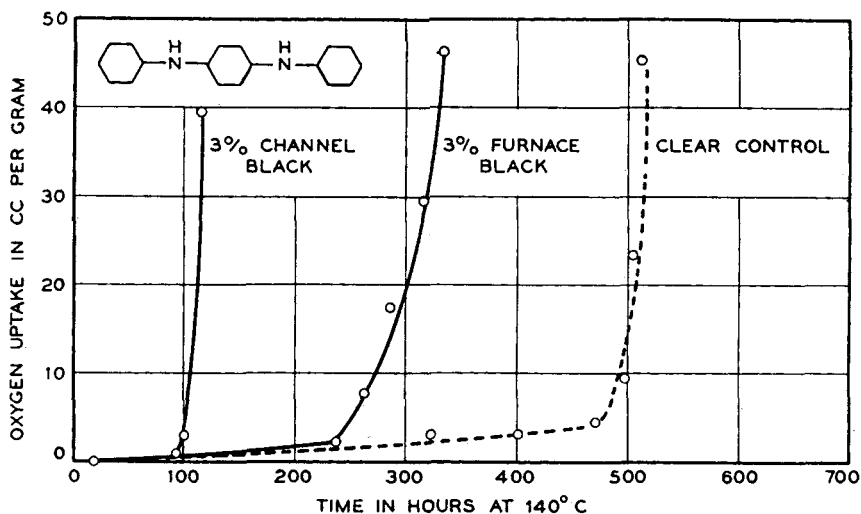


Fig. 5. Thermal oxidation rate of polyethylene containing 0.1% *N,N'*-diphenyl-*p*-phenylenediamine in the presence of various carbon blacks.

these modified carbons with various antioxidants is now under way.

Antioxidants which had been developed for the protection of natural rubber were the first to be used as inhibitors for the thermal oxidation of polyethylene. These antioxidants were characteristically amines or phenols containing one or more active hydrogen atoms. Diphenyl-*p*-phenylenediamine, a typical amine antioxidant, when present in only 0.1% concentration extends the initiation of oxidation from less than an hour for uninhibited polyethylene to approximately 500 hours at 140°C. (Fig. 4). Under these same conditions, 3% carbon black affords about 40 hours of protection. However, when both the antioxidant and carbon black are added to

polyethylene, the effectiveness of the antioxidant is considerably reduced and protection against oxidation is less than 150 hours. This adverse effect has been observed generally with conventional amine or phenol antioxidants. The effect of two carbon blacks of comparable particle size, one an acidic carbon black of pH 4.5 and the other a basic furnace black of pH 7.5, on diphenyl-*p*-phenylenediamine is shown in Figure 5. The acidic carbon has a greater adverse effect than the basic carbon, but both reduce the effectiveness of this amine antioxidant. These data indicate that the adverse effect may be due to adsorption and/or decomposition of the antioxidant by carbon black, the amine being more strongly adsorbed by the acidic carbon. Di- β -naphthyl-*p*-phenylenedi-

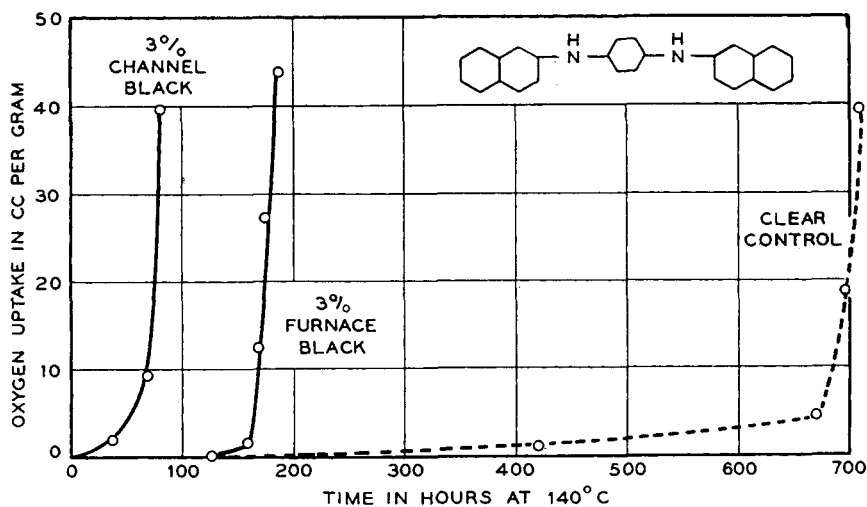


Fig. 6. Influence of various carbon blacks on the antioxidant behavior of 0.1% *N,N'*-Di- β -naphthyl-*p*-phenylenediamine in polyethylene.

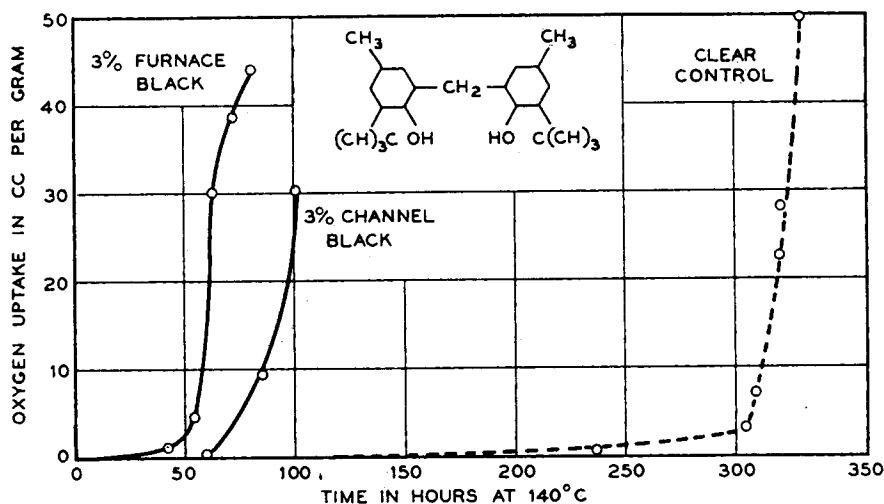


Fig. 7. Loss of antioxidant effectiveness of 0.1% 2,2'-methylenebis-(4-methyl-6-tert-butyl phenol) in the presence of various carbon blacks.

amine is a somewhat better antioxidant for clear polyethylene than diphenyl-*p*-phenylenediamine. This antioxidant (Fig. 6) is also affected to a greater extent by the acidic carbon. Both carbon blacks have a greater adverse effect on the larger dinaphthyl compound.

Phenol antioxidants have received considerable attention recently because they do not stain polyethylene as do the amines. Although most phenols are not good antioxidants for polyethylene, complex compounds such as 2,2'-methylenebis-(4-methyl-6-tert-butyl phenol) do give good protection to the clear polymer (Fig. 7). In the presence of carbon black, however, this antioxidant loses almost all of its effectiveness. There is very little difference between the effect of the acidic and the basic carbon blacks although adsorption by the basic carbon appears to be slightly greater.

CONCLUSIONS

Carbon black has been shown to function as a mild thermal antioxidant for polyethylene at 140°C. The amount of protection increases with concentration and is dependent on the chemical nature of the carbon surface. This antioxidant effect is shown by a variety of carbon blacks with a considerable range of particle size, but very coarse carbons in comparable weight concentration exhibit no antioxidant effect. Recent studies concerned with the chemical nature of the carbon black surface indicate the presence of various oxygenated groupings which may account for the weak antioxidant activity of some carbon blacks.

In all cases examined, conventional amine and

phenol antioxidants in polyethylene are adversely effected by carbon black. This effect can be attributed to adsorption followed by chemical decomposition of the antioxidant on the carbon black.^{5,6} The chemical nature of the carbon black apparently influences the adsorption since the loss in activity of amine antioxidants is much more pronounced with acidic than basic carbon blacks. Whereas the effect of carbon black on antioxidant behavior is observed over a wide pH range, the effect decreases and finally disappears as the particle size of the carbon black is increased.

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References

- (1) V. T. Wallder, W. J. Clarke, J. B. DeCoste, and J. B. Howard, *Ind. Eng. Chem.*, **42**, 2320 (1950).
- (2) B. S. Biggs and W. L. Hawkins, *Modern Plastics*, **31**, 121 (1953).
- (3) J. V. Hallum, *J. Phys. Chem.*, **62**, 110 (1958).
- (4) V. A. Garten and D. E. Weiss, *Revs. Pure and Appl. Chem. (Australia)*, **7**, 67 (1957).
- (5) A. S. Kuzminskii, L. I. Lyubchanskaya, N. G. Khitrova, and S. I. Bass, *Rubber Chem. and Technol.*, **26**, No. 4, 858 (1953).
- (6) J. R. Shelton and W. T. Wickham, Jr., *Ind. Eng. Chem.*, **49**, 1277 (1957).

Synopsis

About 3% by weight of carbon black adequately protects polyethylene against photo-oxidation and, under accelerated test conditions, slightly inhibits thermal oxidation. As a rule small amounts of organic antioxidants are also added to the polymer for optimum protection. Now many of the common phenolic and amine additives have been found to

function much less effectively in polyethylene containing carbon black than in clear polymer. Loss of effectiveness is attributed to adsorption and/or decomposition of the antioxidant by both basic and acidic carbon black.

Résumé

Environ 3% en poids de noir de carbone protège adéquatement le polyéthylène contre la photo-oxydation et, dans le cas d'expériences accélérées, empêche légèrement l'oxydation thermique. Généralement on ajoute aussi au polymère de petites quantités d'antioxydants organiques pour obtenir une meilleure protection. A présent on a remarqué que certains additifs phénoliques et aminés fonctionnent beaucoup moins efficacement dans du polyéthylène contenant du noir de carbone que dans le polymère pur. Cette diminution d'efficacité est attribuée à l'absorption

et/ou à la décomposition de l'antioxydant par le noir de carbone basique et acide.

Zusammenfassung

Etwa 3 Gewichts-% Russ schützen Polyäthylen hinreichend gegen Photooxydation und verhindern unter den Bedingungen einer beschleunigten Prüfung in geringem Masse die thermische Oxydation. In der Regel werden zur Erreichung eines optimalen Schutzes dem Polymeren auch kleine Mengen organischer Antioxydantien zugesetzt. Es wurde jetzt gefunden, dass viele der üblichen Phenol- und Aminzusätze in Polyäthylen, dass Russ enthält, viel weniger wirksam sind als im klaren Polymeren. Der Verlust an Wirksamkeit wird auf Adsorption und Zersetzung des Antioxydants durch basische und saure Russe zurückgeführt.

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