

## The Effect of Carbon Black on Thermal Antioxidants for Polyethylene

T. R. CROMPTON

*Analytical Department, Carrington Research Laboratory, Shell Chemical Company Ltd., Carrington, England*

### Introduction

Oxidation of polyethylene, which results in the loss in physical performance of the polymer, is caused by the effects of heat and ultraviolet radiation. The presence of 2 to 3% of carbon black prevents photo-oxidation and acts as an effective thermal antioxidant. It is customary, however, in polyethylenes containing carbon black, to improve the thermal and processing stability still further by including a thermal antioxidant in the formulation.

Certain carbon blacks, however, markedly reduce the activity of many thermal antioxidants.<sup>1</sup> This work examines the oxidation and degradation of one particular amine antioxidant, *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine, which takes place during the milling of high density polyethylene with carbon blacks of varying pH and particle size.

### Experimental

#### *Determination of Antioxidant*

The methods used for the determination of *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine were modifications of that described in a British Standard (BS).<sup>2</sup> In this method the antioxidant is separated from the polymer by bringing the polyethylene into solution in toluene, followed by precipitation of the polyethylene with alcohol. The mixture is filtered when the antioxidant remains in the filtrate. The antioxidant content of the filtrate is then determined colorimetrically. Oxidation with hydrogen peroxide, in the presence of sulfuric acid, produces a green color with this antioxidant which gradually reaches a maximum intensity. This color is evaluated at 430  $m\mu$  when a maximum depth of color is reached. The oxidation product also shows an absorption in the near infrared region at 830  $m\mu$ , and at this wavelength the absorption is more intense than at 430  $m\mu$ .

#### *Extraction Procedure for High Density Polyethylene*

This work deals exclusively with high density polyethylene and so the BS separation procedure had to be modified because of the low solubility

of this material in toluene. Although high density polyethylene does not dissolve in toluene during a 1 $\frac{1}{2}$ -hr. refluxing period, the polymer granules break up into a nonsticky mass from which the antioxidant separates into the toluene extractant liquid. It was thus possible to modify the BS method by including a reflux step in the procedure. Refluxing is carried out under a nitrogen blanket, and it was found that no oxidation of the antioxidant took place during the extraction process. Some 5% of the antioxidant present remains in the polyethylene, but this is allowed for in the method of calibration, which involves refluxing known quantities of antioxidant with polyethylene, as in the extraction procedure.

#### *Determination of Oxidized N,N'-Di- $\beta$ -naphthyl-*p*-phenylenediamine*

By this modification it was possible to apply the acid oxidation method to the determination of the total content of *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine present in any polyethylene formulation. It was observed, however, that when certain samples were refluxed with toluene the extract was pink in color. Acidification of the alcohol/toluene extract solution resulted in the immediate formation of a green color, although no contact with hydrogen peroxide had taken place. This color did not increase in intensity on standing.

This indicates that the formation of a green color with acid hydrogen peroxide takes place in two stages. The first stage consists of a slow oxidation to give a pink oxidation product, which then immediately changes to green in the presence of acid.

It appeared possible to determine the proportion of antioxidant which was oxidized, therefore, by acidifying the extraction liquid containing the antioxidant with an acid reagent which did not contain peroxide. A green color would thus be formed, which would measure the antioxidant oxidation product.

Application of the acid peroxide reagent to the antioxidant extract produces a color which measures the total of the oxidized and unoxidized fractions

of the antioxidant. The unoxidized fraction of the antioxidant may be determined, therefore, by subtracting the value obtained for the oxidized fraction from the value obtained for total antioxidant obtained by application of the acid peroxide reagent.

#### *Determination of Decomposed or Adsorbed Antioxidant*

These methods were applied to an examination of the stability of *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine antioxidant in the polyethylene formulations containing different types of carbon black. It was found that with clear polyethylene, containing no carbon black, the total of oxidized plus unoxidized *N,N'*-di- $\beta$ -naphthyl-*p*-phenyldiamine corresponded to the quantity of antioxidant which had been milled into the polymer.

When certain types of carbon black were milled into the polyethylene, however, the total antioxidant recovery was considerably less than the quantity of antioxidant added in the formulation. This indicated that some of the *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine had decomposed, with the formation of degradation products which did not produce the usual green color with acid peroxide, or that it had been adsorbed by the carbon black so strongly that it resisted extraction by toluene.

#### *Summary of Methods Used*

The methods which may be used to show how this antioxidant becomes oxidized or degraded during milling are summarized in Table I. These methods were then applied to the study of the influence of various carbon blacks on the stability of this material.

#### **Results and Discussion**

The general formulation examined consisted of 2% carbon black together with 0.18% *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine antioxidant, the mixture being evenly blended by mill massing on a two-roll mill. The carbon black addition was made using the master batch technique, the carbon black content of each master batch being 25%. Each blend was given a standard milling time of 8 min. with a roll temperature between 150 and 160°C. The blends were subsequently analyzed to determine how the antioxidant had behaved during milling in the presence of each of the carbon blacks.

The carbon blacks examined covered a wide range of pH (2.8 to 9.5) and varied in surface area from 42 to 950 m.<sup>2</sup>/g., the particle size varying from 9 to 42  $\mu$ . The analytical data obtained on these blends, directly after the standard milling pro-

TABLE I  
Outline of Analytical Examination

Antioxidant fraction	Determined	Calculated by
Total antioxidant added (A)	Weight addition during formulation	—
Oxidized antioxidant (O)	Acidification in the absence of peroxide	Colorimetric calibration
Oxidized plus unoxidized antioxidant (T)	Acidification in the presence of peroxide	Colorimetric calibration
Unoxidized antioxidant (U)	From difference between colorimetric values	T-O
Unaccounted antioxidant (D)	Antioxidant not accounted for colorimetrically	A-T

cedure, are shown in Table II together with data obtained on a clear reference polyethylene sample, containing no carbon black, but which had been milled with antioxidant in the standard manner.

It is seen that some oxidation of the *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine occurs on milling in the clear reference polyethylene. All the antioxidant added, however, is recovered in the colorimetric analysis. Good recovery of antioxidant is also obtained with the blends containing the furnace blacks. These carbon blacks have a high pH and have a large particle size.

With the acidic channel blacks, however, this is not the case. Considerable oxidation of the antioxidant has taken place with all samples. Also, however, with most of these samples containing acidic blacks some 50% of the antioxidant is unaccounted for by colorimetric measurement and little unoxidized *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine remains.

The small particle size of the carbons in this pH range is also, apparently, connected with the amount of antioxidant which remains unaccounted for in these channel blacks. This may be seen by comparing the results obtained with Monarch 74, Printex U, and CK 3, which all have the same pH value (5.0) but vary in particle size. As the particle size increases so the quantity of unoxidized antioxidant rises while the proportion of antioxidant not determined colorimetrically falls.

Similar tests were then made using the much lower concentration of carbon black of 0.2%. Three channel blacks and one furnace black were examined at this lower level and the results are compared in Table III with those obtained at the higher 2% level. It is seen that, even when present at the 0.2% concentration level, the acid Carbolac 1 of small particle size causes considerable oxidation of the *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine.

Also, a considerable proportion of the antioxidant addition is not determined colorimetrically.

With acid 0.2% Elf 8 and Monarch 74 channel blacks or 0.2% alkaline Sterling SO furnace black the quantity of antioxidant not determined is smaller and the quantity of oxidized *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine is greater than with the corresponding acidic Carbolac 1 channel blacks. From these results and the results obtained on polymers containing 2% of the carbon black, it would appear that acidic carbons accelerate decomposition of the antioxidant by increasing the rate of oxidation, the antioxidant oxidation product being subsequently decomposed to degradation products not detected by colorimetric analysis. Alternatively, with more acidic carbons, some of the *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine and its oxidation product may be so strongly adsorbed onto the carbon black that they resist toluene extraction.

### Conclusions

Colorimetric procedures have been developed for the determination of *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine and of its oxidation product in high density polyethylene.

These procedures have been used to study the stability of this antioxidant during milling in the presence of carbon black. A variety of carbon blacks have been examined, which have varied in pH and particle size. It has been shown that certain grades of carbon black either accelerate the oxidation of *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine and, indeed, bring about appreciable further degradation of this antioxidant beyond the initial stage of oxidation, or alternatively, these grades of carbon strongly adsorb *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine and its oxidation product so that they cannot be isolated from the polymer by solvent extraction. In these cases the total determined *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine and its oxidation product is less than the known antioxidant addition made during manufacture. These grades consist of the acidic channel blacks of small particle size. As the particle size increases this effect decreases.

With the alkaline furnace blacks of large particle size, however, all the antioxidant is determined in the colorimetric analysis. Some oxidation of the antioxidant takes place during the milling of furnace blacks, but this oxidation is of the same order as that which takes place in clear polyethylene.

This work is in agreement with the oxidation studies of Hawkins et al.,<sup>1</sup> who showed that the amine antioxidants are adversely affected by carbon black, particularly acidic carbon blacks of small particle size.

The author wishes to thank Mr. B. Cope for carrying out experimental work and the Directors of Shell Chemical Co. Ltd. for permission to publish this paper.

### References

1. Hawkins, W. L., R. H. Hansen, W. Matreyek, and F. H. Winslow, *J. Appl. Polymer Sci.*, **1**, 37 (1959).
2. Method 405B described in Amendment No. 2 (17.4.59) to British Standard 2782: Part 4, 1958.

### Synopsis

The presence of 2 to 3% of carbon black prevents photo-oxidation of polyethylene but affords only slight protection against thermal oxidation. Small quantities of amine or phenolic antioxidants are also added therefore to prevent thermal oxidation during processing. The influence of various types of carbon black on the decomposition of one particular amine antioxidant, *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine which occurs during milling with polyethylene has been studied in detail. Acidic channel blacks of small particle size have been shown to accelerate the oxidation of the antioxidant. Further degradation, or adsorption onto the carbon black, of this antioxidant also occurs. With the alkaline furnace blacks of large particle size, however, oxidation takes place only to the same extent as that which occurs in clear polyethylene.

### Résumé

La présence de 2 à 3% de noir animal empêche la photo-oxidation du polyéthylène, mais ne fournit qu'une faible protection à l'oxydation thermique. Aussi de faibles quantités d'antioxydants aminé ou phénolique sont ajoutées pour empêcher l'oxydation thermique en cours de réaction. L'influence de différents types de noir animal sur la décomposition d'un antioxydant aminé particulier, à savoir la *N,N'*-di-naphthyl-*p*-phénylènediamine, présente au cours du moulage du polyéthylène, a été étudiée en détail. On a montré que des noirs à caractère acide, dont les particules sont de faible dimension, accélèrent l'oxydation de l'antioxydant. Par après il se produit également la dégradation ou l'adsorption de cet oxydant sur le noir animal. Avec des noirs à caractère alcalin dont les particules sont de grande dimension, l'oxydation se produit seulement sur une étendue semblable à celle qui se présente dans le polyéthylène libre.

### Zusammenfassung

Die Gegenwart von 2 bis 3% Russ verhindert die Photo-oxidation von Polyäthylen, ist aber gegen thermische Oxydation nur schwach wirksam. Daher werden auch geringe Mengen von Aminen oder Phenolen als Antioxydantien zur Verhinderung der thermischen Oxydation während der Verarbeitung zugesetzt. Der Einfluss verschiedener Russtypen auf die Zersetzung eines bestimmten Antioxydans vom Amintyp, *N,N'*-Di- $\beta$ -naphthyl-*p*-phenylendiamin, die während des Mahlens mit Polyäthylen auftritt, wurde genau untersucht. Es wurde gezeigt, dass saure Channelruss von geringer Teilchengrösse die Oxydation des Antioxydans beschleunigen. Weiters tritt auch eine Zersetzung oder Adsorption dieses Antioxydans an den Russ auf. Mit alkalischen Ofenrussen von grosser Teilchengrösse verläuft jedoch die Oxydation nur im gleichen Ausmass wie in reinem Polyäthylen.

Received June 14, 1961