DETERMINATION OF SOME MIXED PHENOLIC ANTIOXIDANTS IN POLYETHYLENE

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The applications of polyethylene have increased enormously in the last decade. Typical of these new uses has been the wrapping of foods with polyethylene film. Small amounts of antioxidants are usually added to protect this plastic against deterioration during processing and to improve its aging characteristics. The most common are phenolic compounds: 4,4'-butylidene-bis-(6-*tert.*-butyl-*m*-cresol) (Santowhite Powder®)*, 2,6-di-*tert.*-butyl-*p*-cresol (BHT), and 4,4'-thio-bis-(6-*tert.*-butyl-*m*-cresol) (Santonox R®). Often these are used in combinations containing Santonox–BHT and Santowhite Powder–BHT. However, before these antioxidants could be utilized to stabilize polyethylene film for wrapping food, methods were required for determining these mixed phenolic antioxidants in polyethylene.

A number of satisfactory methods have been developed for the analyses of polyethylene containing single antioxidants. WADELIN[1] reported a method for the analysis of BHT in polyethylene based on measuring the U.V. absorbance of the potassium salt of BHT in absolute ethanol. HILTON[2] analyzed a number of antioxidants by diazo dye formation. More recently, STAFFORD[3] developed a sensitive spectrophotometric method based on the controlled oxidation of BHT. These methods are not suitable for the direct analyses of mixed antioxidants in polyethylene.

SPELL AND EDDY[4] developed a spectrophotometric method for the analyses of Santonox R and BHT based on the removal of Santonox R by basic extraction and the subsequent U.V. measurement of the separated antioxidants. However, the technique is not applicable to the separation of Santowhite Powder from BHT because Santowhite Powder is too weakly acidic.

The methods described herein involve (1) extraction of the antioxidants from the polyethylene sample, (2) separation of the extracted antioxidants on an alumina chromatographic column and (3) determination of the separated antioxidants by ultraviolet spectroscopy.

EXPERIMENTAL

Reagent and apparatus

1. Aluminum oxide (Merck Reagent grade, Catalog No. 71707) was dried at 120° under 200 mm pressure in a vacuum oven for 20 h.

2. The chloroform and methanol were A.R. grade.

3. The 10 % (v/v) water in methanol reagent was prepared by adding 100 ml of distilled water to 900 ml of methanol.

* ® = trade-mark of Monsanto Chemical Company.

4. Spectrophotometric measurements were made with matched 1 cm silica cells using a Cary Model 11 Recording Spectrophotometer.

5. The chromatographic effluents were monitored by a Gilson Medical Electronics U.V. Scanner (Middleton, Wisconsin) coupled to a Varian Recorder.

Method

1. Sample preparation. If the sample of polyethylene is thicker than approximately $^1/_{16}$ in., it should be thinned by passing it through a conventional rubber or plastics mill. Weigh approximately 2.5 g of a sample containing 0.01 % to 0.3 % of phenolic antioxidant. Dice the sample into small squares (*ca.* 5 mm × 5 mm) and transfer to a bottle with a teflon lined cap. Add 50 ml of chloroform to the sample. If the sample is suspected of having less than 0.02 % antioxidant, add 25 ml of chloroform instead of 50 ml. Place the tightly capped bottle in a 50° oven and let stand for 3 h with intermittent shaking at intervals of approximately 15 min. Remove the sample and cool to ambient temperature.

2. Separation and measurement of antioxidant. Slurry the alumina with equal parts by volume of chloroform. To prepare a 180 mm × 13 mm i.d. alumina column, place just sufficient glass wool in the bottom of the column to support the column packing, fill the column, and place a small pad of glass wool on top of the column to prevent disturbing the column packing when adding the sample. Connect a liter reservoir to the column in such a manner as to provide a 300 mm head of eluant.

Wash the column with 125 ml of chloroform. Add 20 ml of the chloroform extract to the column. Discard the first 10 ml of effluent after beginning addition of the sample to the column.

Trap the next 50 ml of effluent in a 50 ml volumetric flask. The flow rate was found to average approximately 4.6 ml/min. This fraction contains the BHT. Replace the chloroform eluant with 10 % water in methanol eluant. Do not let the top of the column go dry. Start the 10 % water in methanol as the last of the chloroform goes on the column. Trap the Santonox R or Santowhite Powder in a 100 ml volumetric flask. An average flow rate of 2.8 ml/min was found in trapping the second component in a 100 ml volume.

Determine the absorbance at 283 mμ of the BHT fraction *versus* a chloroform blank. Determine the absorbance of the Santonox R fraction at 280 mμ versus a 10 % water in methanol blank. Determine the absorbance at 282 mμ if the Santowhite Powder is present. In order to correct for small absorbances due to polyethylene species, a sample of polyethylene which contains no additives is carried through the procedure in a similar manner.

3. Calculations. The following equation is used to calculate the per cent antioxidant:

$$\% \text{ Antioxidant} = \frac{(A)\ (V_1)\ (V_2)}{a_s\ (V_3)\ (10)\ (\text{g of sample})}$$

where A is the corrected absorbance at the cited wave length, a_s is the specific absorptivity (BHT, 283 mμ, 9.75; Santowhite Powder, 282 mμ, 12.6; Santonox R, 280 mμ, 19.7 l/g-cm), V_1 is the volume of effluent, V_2 is the volume of chloroform extract, and V_3 is the volume of chloroform extract placed on the column. Owing to inherent differences in instruments, a_s values should be determined in each laboratory.

DISCUSSION AND RESULTS

The specific absorptivities were calculated from the slope of linear absorbance *versus* concentration plots for BHT in chloroform, Santowhite Powder, and Santonox R in 10% water in methanol. The ultraviolet spectra of the antioxidants are depicted in Fig. 1.

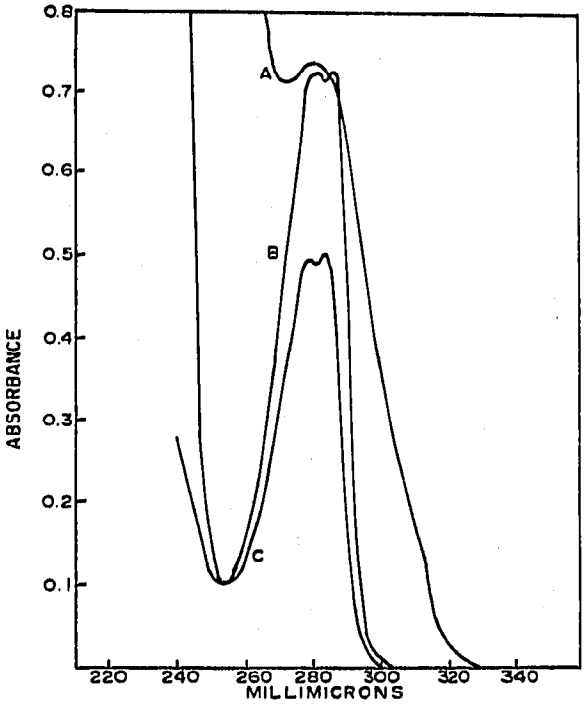

Fig. 1. The U.V. spectra of some antioxidants. A. Santonox R (0.0368 g/l in methanol). B. Santo white Powder (0.0585 g/l in methanol). C. BHT (0.052 g/l in chloroform).

Typical elution chromatograms which show the separation of mixtures of BHT-Santonox R and BHT–Santowhite Powder are depicted in Fig. 2 and Fig. 3, respectively. It is noted that the water–methanol effluent front elutes the bulk of the Santonox R or Santowhite Powder. A large error would result if some of the first part of the

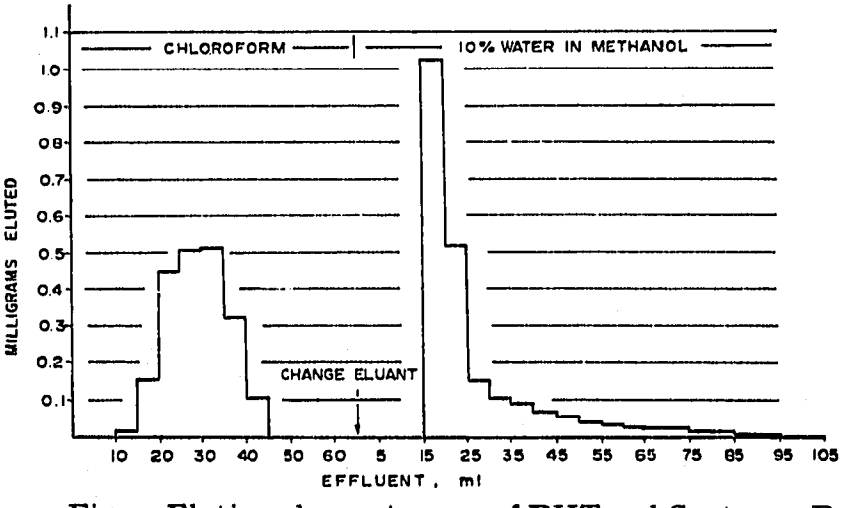

Fig. 2. Elution chromatogram of BHT and Santonox R.

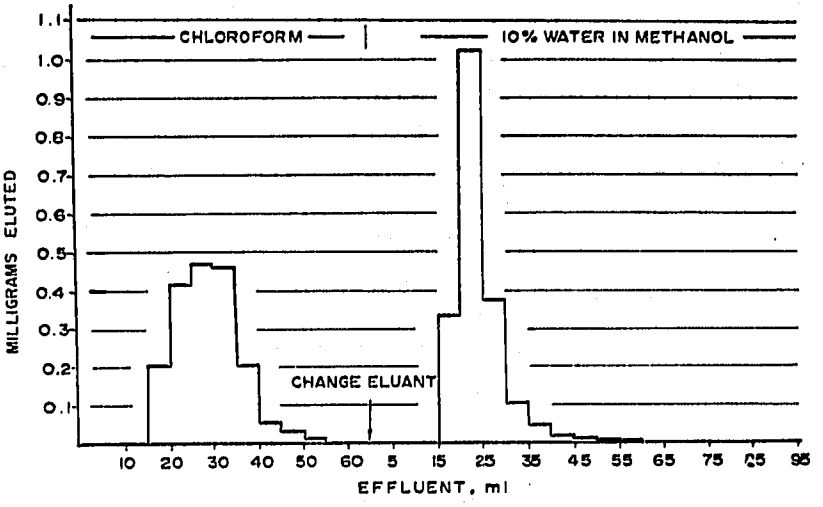

Fig. 3. Elution chromatogram of BHT and Santowhite Powder.

aqueous methanol fraction were discarded. Owing to slight differences in the activity of alumina, it is recommended that the effluent volumes required for separations be determined for each new batch of alumina. An ultraviolet spectrophotometric monitor was found to be a convenient tool for establishing these volumes.

The procedure was verified by analyzing polyethylene samples containing known amounts of antioxidants. These standards were prepared by adding aliquots of known concentrations of antioxidants in ethyl ether to weighed amounts of powdered polyethylene. The ether was allowed to evaporate at room temperature. The mixture was stirred and then pressed for 5 min between two alumina plates at a pressure of 600 p.s.i. at 135°. The analytical results are cited in Table I.

TABLE I

ANALYSIS OF SOME STANDARD POLYETHYLENE SAMPLES

BHT			*Santowhite Powder*			*Santonox R*		
% added	*% found*	*% recovered*	*% added*	*% found*	*% recovered*	*% added*	*% found*	*% recovered*
0.270	0.265	98.0	0.260	0.264	101.3	—	—	—
0.263	0.260	98.8	—	—	—	0.257	0.248	96.5
0.0513	0.0508	99.2	0.253	0.249	98.4	—	—	—
0.0535	0.0534	99.8	—	—	—	0.251	0.245	97.5

Some standard samples were prepared by milling weighed amounts of BHT, Santowhite Powder, and Santonox R in polyethylene at 130°. The analyses of these samples agreed satisfactorily for Santowhite Powder and Santonox R but the BHT concentrations were approximately 30% low. A feasible explanation would be that BHT has a greater volatility than the others, and some BHT was lost due to evaporation during the hot milling process.

Chloroform was chosen as the solvent for extracting the antioxidants from polyethylene because chloroform readily permeates polyethylene and, in addition, it exhibits a favorable distribution coeffcient for phenolic antioxidants[4]. Furthermore, chloroform had the favorable solvent characteristics required of the first eluant in

the adsorption chromatographic separation. The affinity of chloroform for these antioxidants was demonstrated by the fact that essentially none of the antioxidants were extracted from chloroform by 0.1 *N* aqueous sodium hydroxide.

Since short extraction times were desirable, it was found that 3 h of chloroform extraction of the polyethylene samples at 50° gave the results cited in Table I while the same extraction carried out at ambient temperature gave slightly lower recovery.

Chloroform elutes BHT from an alumina column rapidly, but elutes Santonox R and Santowhite Powder slowly enough to permit their complete separation. However, an excessive amount of chloroform (400 ml) was required to completely elute Santowhite Powder and Santonox R. In order to elute these components in a 100 ml volume, it was necessary to change to a more polar solvent system. Methanol eluted Santowhite Powder quite satisfactorily in 100 ml volume, but Santonox R continued to tail. This problem was resolved by using 10 % water in methanol. If desired, additional sensitivity may be obtained by concentrating the fractions under vacuum or using greater path length absorption cells.

In the preparation of certain types of polyethylene, it is necessary to add cross-linking agents such as dicumyl peroxide. Dicumyl peroxide elutes in the first chromatographic fraction and can be determined by U.V. absorption measurements. The method would be applicable to the analyses of mixtures of Santowhite Powder with dicumyl peroxide and Santonox R with dicumyl peroxide, but would not apply to a mixture of BHT with dicumyl peroxide. It should be possible by a slight modification of the method to analyze a mixture containing all three antioxidants. Since Santonox R gives a second absorption maximum at 248 mμ (a_s 45.4) and Santowhite Powder has a minimum at 253 mμ, a two component spectrophotometric system could be used to determine Santonox R and Santowhite Powder in the aqueous methanol fraction. Although the work discussed here was done with polyethylene it seems reasonable that the method would be applicable to other polyolefins.

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SUMMARY

An analytical method was developed for the determination of some mixed phenolic antioxidants in polyethylene. It is applicable to the analyses of mixtures of 4,4'-butylidene-bis-(6-*tert.*-butyl-*m*-cresol) with 2,6-di-*tert.*-butyl-*p*-cresol (BHT) and 4,4'-thio-bis-(6-*tert.*-butyl-*m*-cresol) with BHT in polyethylene in the range of 0.01 % to 0.3 %. The method is based on the separation of the mixed antioxidants by adsorption chromatography with subsequent spectrophotometric determination of the separated antioxidants.

REFERENCES

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