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DETERMINATION OF ANTIOXIDANTS AND THEIR TRANSFORMATION PRODUCTS IN POLYETHYLENE BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

The separation of sterically hindered phenolic antioxidants from polyethylene and their quantitative determination by high-performance liquid chromatography (HPLC) with isocratic elution is described. In the polymer matrix, antioxidants are subjected to oxidation, especially during processing or UV irradiation. The transformation products formed are analysed by HPLC using gradient elution. More than 20 thermal and photochemical transformation products from one of the most common used antioxidants (2,6-di-*tert.*-butyl-*p*-cresol; butylated hydroxytoluene; BHT) have been detected and two of them identified as 2,6-di-*tert.*-butyl-*p*-quinomethane and 2,6-di-*tert.*-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadiene-1-one. The thermal transformation of two other antioxidants has been studied.

INTRODUCTION

Polyolefins, such as polyethylene, are subject to thermal and oxidative degradation. During processing of polymers at high temperatures (200–300°) or subsequent exposure to UV radiation in the presence of oxygen, free-radical chain reactions take place, leading to scission and crosslinking of the polymer chains and consequently to a deterioration of the physical properties of the polymer. To ensure processing and long-term stability, the polymers are protected by antioxidants, mainly sterically hindered phenols.

Analysis of these additives and their transformation products has become increasingly urgent in routine control and particularly in connection with medical plastics and food packaging, where identities and levels of potentially toxic substances must be accurately known and controlled. The difficulties in determining and identifying antioxidants arise from three factors[1]: (1) high reactivity and low stability of antioxidants, (2) the low concentrations (0.1–1 %) at which they are present and (3) the relatively insoluble polymer matrix. Separation of the additives from the polymer, careful handling of the extracts and short analysis times are therefore required if quantitative results are to be obtained.

Howard[2] and Pospisil *et al.*[3] have shown how useful gel permeation chromatography can be for the analysis of polymer additive systems. A shorter analysis time

was obtained by Majors[4] and Wims and Swarin[5] by using liquid adsorption chromatography. Gross and Strauss[6] also applied reversed-phase chromatography to a variety of additives.

In this paper, results are presented for the liquid adsorption chromatographic analysis of phenolic antioxidants and their transformation products in polyethylene using gradient elution. Transformation of antioxidants was carried out by ageing polymer samples with known amounts of additives by either thermal treatment at processing temperatures (200–250°) or exposure to UV radiation in the presence of oxygen. Unknown compounds were identified by mass spectrometry and comparison with synthetic standards.

EXPERIMENTAL

Chemicals

Reagent-grade antioxidants were used. 2,6-Di-*tert.*-butyl-*p*-cresol (butylated hydroxytoluene; BHT) was obtained from Koch-Light, Colnbrook, Great Britain; Irganox 1010 and Irganox 1076 from Ciba-Geigy, Basel, Switzerland; Santonox R from Monsanto, London, Great Britain; and Ionox 330 from Dart Industries, Paramus, N.J., U.S.A.

The polyethylene used for sample preparation was Lupolen 2400 F (density 0.922 g/cm^3) obtained from BASF, Ludwigshafen, G.F.R.

The solvents used were of spectroscopic grade (Merck, Darmstadt, G.F.R.).

Sample preparation

Polyethylene (40 g) was mixed with 0.8 g (2%) of antioxidant at 200° or 250° for different periods (5, 15 or 90 min) in a stainless-steel mixing chamber with temperature control (Brabender, Duisburg, G.F.R.). After cooling to room temperature, the samples were pulverized in an ultracentrifuge mill (Retsch, Haan, G.F.R.) to a particle diameter of less than 0.5 mm. In one instance (BHT), the pulverized sample was exposed to sunlight for 2 weeks.

Extraction procedure

Samples of 5 g were extracted with 50 ml of chloroform under nitrogen in a Soxhlet apparatus for 6 h. The extracts were filtered from polymer material. Eventual losses of solvent by evaporation were adjusted by adding solvent to a total volume of 50 ml. For analysis of transformation products, the extracts were concentrated to 1 ml.

Chromatographic apparatus

HPLC was carried out on a DuPont 830 liquid chromatograph with a gradient elution accessory equipped with a DuPont 837 spectrophotometer. Measurements were carried out at 242 nm. The columns were 25 cm × 4 mm I.D. The chromatographic support was Partisil (mean diameter 5 μm; Chrompack, Middelburg, The Netherlands). The injector was a Valco valve with a 10-μl loop.

Quantitative evaluation

Peak heights were usually measured and the concentrations were obtained from standard graphs constructed by analysing pure antioxidant samples.

RESULTS AND DISCUSSION

Quantitative determination of antioxidants in polyethylene

Polyethylene samples with known amounts of the selected antioxidants (Fig. 1) were prepared by mixing the polymer and the additive at 200° for 5 min. After pulverization, the samples were extracted (Fig. 2) with chloroform and the extraction yields determined every hour by direct HPLC analysis of the extracts (Table I). As shown in Fig. 3, the extraction of BHT was almost complete after 2 h, while quantitative extraction of samples containing Irganox 1076 and Irganox 1010 was ensured after at least 5 h. These differences in extraction times are probably due to the higher solubility of BHT in chloroform. The extraction yields are higher than 90%; the approximately 10% loss of antioxidants is probably due to evaporation during mixing of the components, transformation of antioxidants during the mixing period (Fig. 5) or inclusion of the components in the polymer matrix. Analytical data for the antioxidants together with their detection limits in polyethylene are given in Table I.

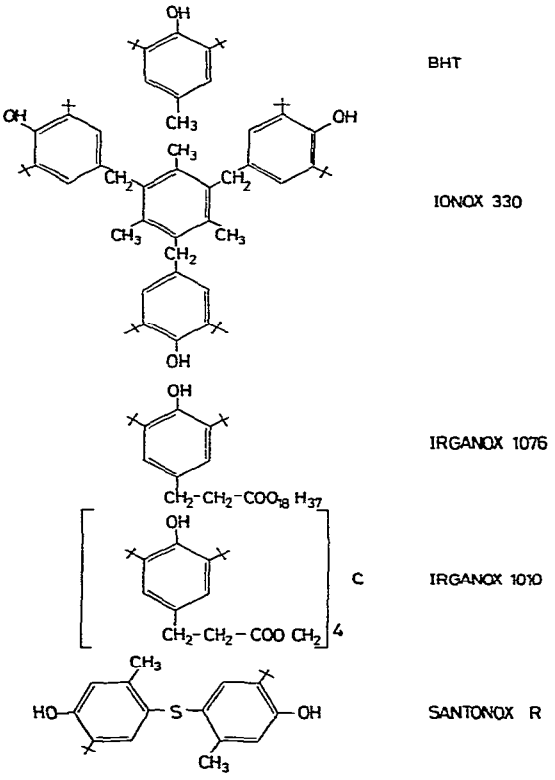

Fig. 1. Structures of antioxidants analysed.

In some practical applications, several antioxidants are used for protection of polymers. In these instances, HPLC analysis of extracts can be performed by applying gradient elution. Fig. 4 shows the separation of the five selected antioxidants in an *n*-hexane–dichloromethane gradient system.

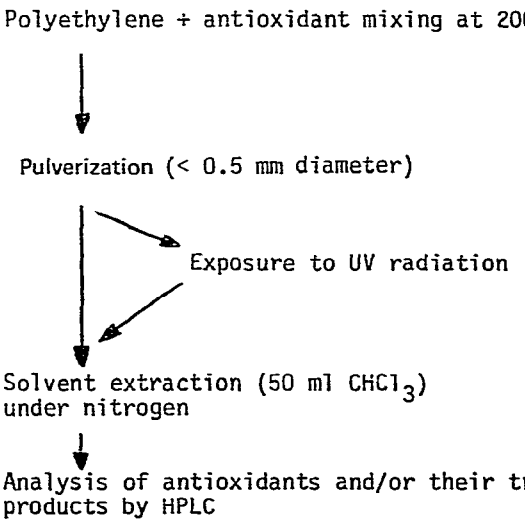

Fig. 2. Sample preparation and extraction procedure for antioxidants in polyethylene.

Oxidation of antioxidants in polyethylene and analysis of their transformation products

Transformation of antioxidants in polyethylene was carried out by ageing polymer samples with known amounts of additives by either thermal treatment at normal polymer processing temperatures or exposure to sunlight in the presence of oxygen.

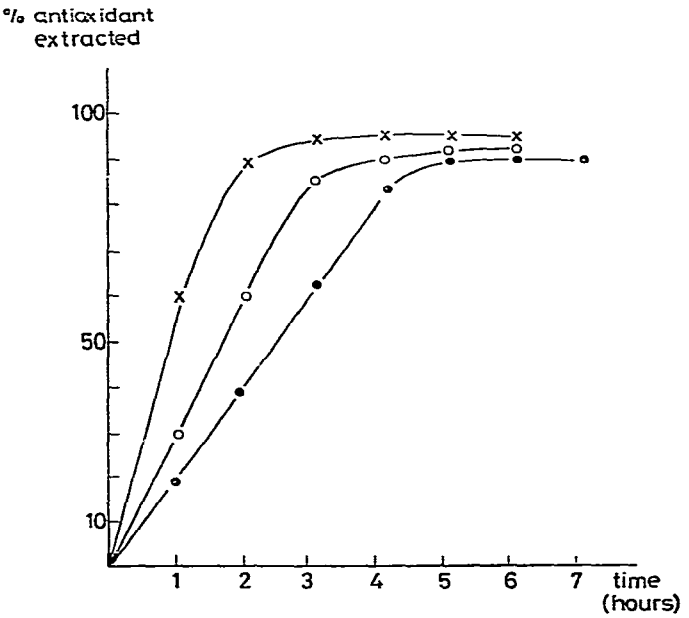

Fig. 3. Extraction yields from antioxidants in polyethylene. Determination by HPLC; for conditions see Table I. ×, BHT; ○, Irganox 1076; ●, Irganox 1010.

TABLE I

DATA FOR ISOCRATIC ELUTION OF ANTIOXIDANTS

Instrument DuPont 830; column, 5-μm Partisil; pressure, 2500 p.s.i.; detection at 242 nm; volume injected, 50 μl.

Antioxidant	*Elution solvent*	*Retention volume (ml)*	*Detection limit (μg antioxidant/g polymer)*
BHT	*n*-Hexane	6.4	20
Ionox 330	*n*-Hexane–dichloromethane (9:1)	7.4	4
Irganox 1076	*n*-Hexane–dichloromethane (8:2)	8.0	20
Irganox 1010	*n*-Hexane–dichloromethane (4:6)	10.1	4
Santonox R	*n*-Hexane–dichloromethane (4:6)	12.0	0.5

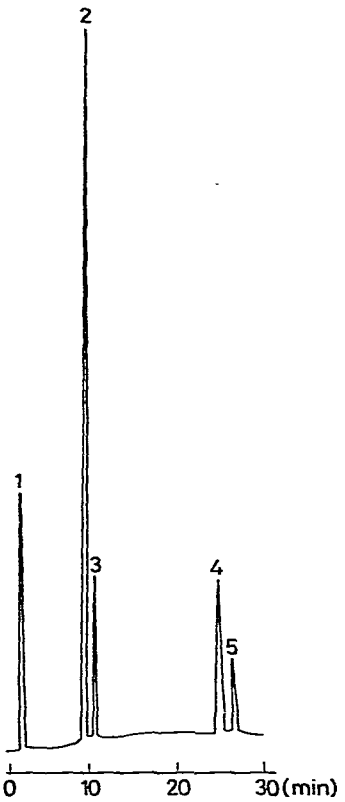

Fig. 4. Analysis of antioxidant in a mixture: (1) BHT; (2) Ionox 330; (3) Irganox 1076; (4) Irganox 1010; (5) Santanox R. HPLC conditions: 3-min isocratic run with 100% *n*-hexane, gradient from 0 to 30% dichloromethane at 2%/min. Column, Partisil (5 μm); detection at 242 nm; pressure, 2000 p.s.i.

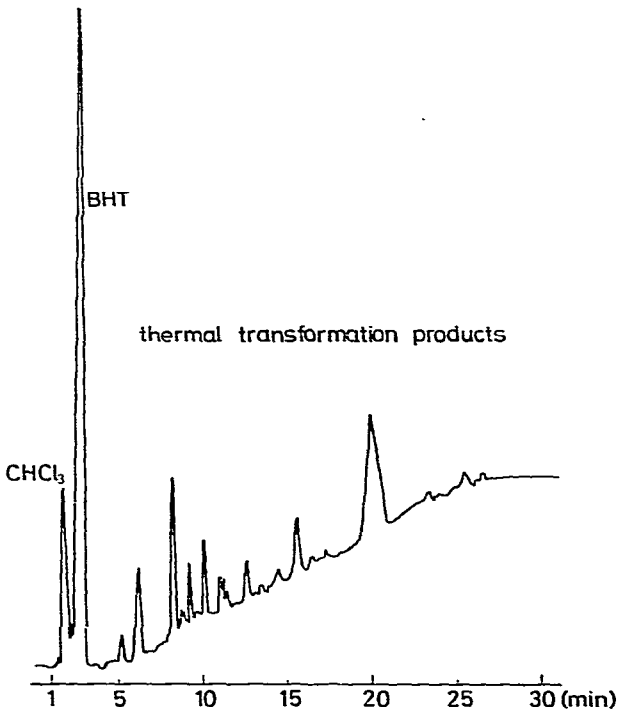

Fig. 5. Chromatogram of extract from polyethylene–BHT sample, treated for 15 min at 200° (extract concentrated to 1 ml). HPLC conditions: 3-min isocratic run with 2% dichloromethane in *n*-hexane, gradient from 2 to 100% of dichloromethane at 5%/min. Column, Partisil (5 μm); detection at 242 nm; pressure, 2500 p.s.i.

The thermal transformation of BHT in polyethylene was tested by continuous treatment (15 min) at 200° after the antioxidant had been added to the polymer. The analysis of the sample extract is shown in Fig. 5. Even after this short thermal treatment of the polymer–additive system trace amounts of transformation products can be detected. Only 80% of BHT was recovered, owing partly to transformation and partly to evaporation during the thermal treatment. Analysis of polyethylene–BHT samples, which had been thermally treated at 200° for 90 min, showed complete loss of BHT (mainly by evaporation), while the amount of transformation products increased only by *ca.* 20%.

The same polyethylene–BHT sample (pulverized), which had been thermally treated at 200° for 15 min, was in addition exposed to sunlight for 14 days. The sample turned slight yellow. HPLC analysis of the extract (Fig. 6) showed a drastic increase in the amount of transformation products. The concentration of BHT had decreased to *ca.* 45% of the original. Owing to photochemical reactions, initiated by polymer peroxy radicals[7], the antioxidants are oxidized, leading to a variety of transformation products. The two main transformation products were isolated and identified by mass spectrometry and by comparison with synthetic standards as 2,6-di-*tert.*-butyl-*p*-quinomethane (6) and 2,6-di-*tert.*-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadiene-1-one (7) (for structures, see Fig. 6).

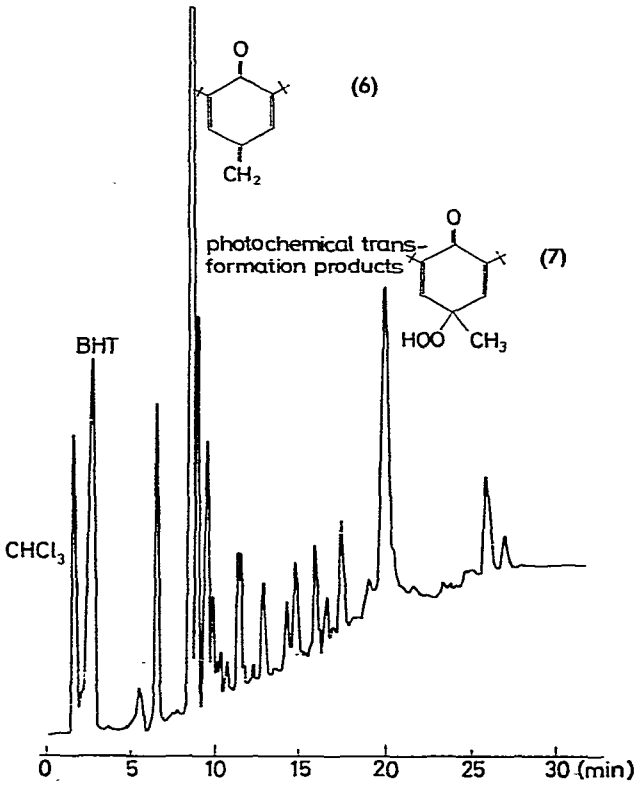

Fig. 6. Chromatogram of extract from polyethylene–BHT sample treated for 15 min at 200° and exposed to UV radiation for 14 days (extract concentrated to 1 ml). HPLC conditions as in Fig. 5.

The thermal transformation of Irganox 1076 and Irganox 1010 in polyethylene was studied. Thermal treatment for 15 min led in both instances to a small amount of transformation products, while in samples treated for 90 min considerable transformation occurred (Figs. 7 and 8).

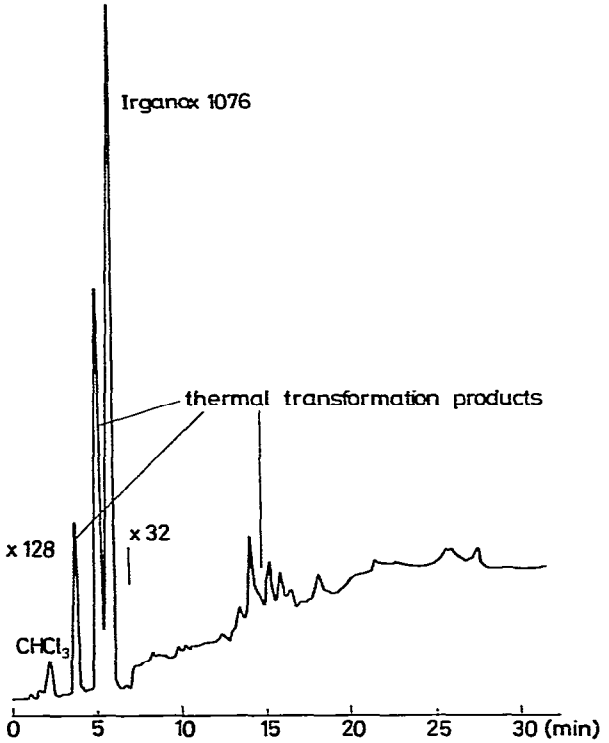

Fig. 7. Chromatogram of extract from polyethylene–Irganox 1076 system, treated for 90 min at 200° (extract concentrated to 5 ml). HPLC conditions: column, Partisil (5 μm); gradient, from 20 to 100% of dichloromethane in *n*-hexane at 5%/min; detection at 242 nm.

CONCLUSIONS

The quantitative determination of antioxidants in polyethylene can be performed by HPLC. Complex mixtures containing thermal and photochemical transformation products from antioxidants can be analysed by applying gradient elution.

Further thermal and photochemical transformation experiments on additives, the identification of transformation products and tests of their mutagenicities are at present being carried out.

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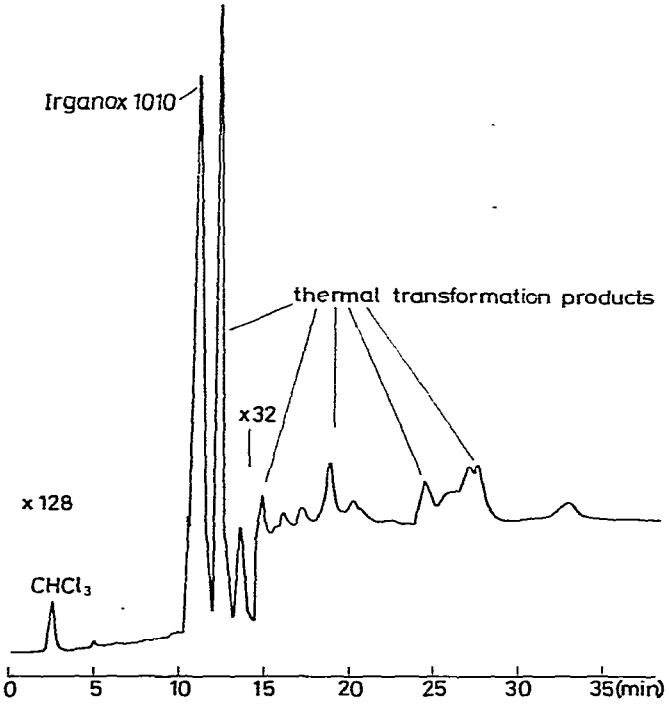

Fig. 8. Chromatogram of extract from polyethylene–Irganox 1010 system, treated for 90 min at 200° (extract concentrated to 5 ml). HPLC conditions: column, Partisil (5 μm); gradient from 40 to 100% of dichloromethane in *n*-hexane at 5%/min; detection at 242 nm.

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