Analysis of Aromatic Antioxidants and Ultraviolet Stabilizers in Polyethylene Using High-Temperature Extraction with Low Boiling Solvent

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SYNOPSIS

A simple procedure for analysis of aromatic antioxidants and UV stabilizers is described: dissolution of polyethylene in *n*-heptane at temperature 160°C and pressure 0.5 MPa, precipitation of the polymer after a cooling of the solution, filtration of the obtained solution into an injection syringe, and injection into a silica gel column flushed with mobile phase *n*-heptane plus polar modifier. The eluted additive is detected with a uv detector. Application of the procedure on quantitative determination of Irganox 1330 in PE-MD demonstrates that the above procedure has high recovery of the antioxidant, good reproducibility of the analysis (σ = 1.9%), and a very low detection limit of 0.013 mg/1 g polymer. The described procedure may be easily adjusted for the analysis of many other additives in semicrystalline polyolefins. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In polymeric materials, the antioxidants play a similar role as vitamins in a living organism: they are present in small concentrations, but their presence decides on long-term stability of the polymeric materials. Thus it is important to known their actual concentration. Their analysis is especially complicated in the most widely used polymeric materials, i.e., in crystalline polyolefins with a worldwide annual consumption in 1994 of 19.2 million tons PE-HD,[1] 26.2 million tons PE-LD and PE-LLD,[2] and 20.8 million tons PP.[3]

The analytical determination of additives in polyolefins is a difficult task, especially due to their solubility at higher temperature only (90–160°C in dependence on solvent) and only in a rather limited number of solvents.

In this paper we will focus our attention on the phenolic antioxidant 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene (Fig. 1). This compound is produced under the registered names Irganox 1330 (Ciba-Geigy, Basel, Switzerland), Goodrite 1330 (B. F. Goodrich, Cleveland, Ohio), Ethyl 330 (Ethyl Corporation, New York, N. Y.), Seenox 326M (Shipro Kasei, Shiraishi, Japan), and Ionox 330 (Shell, London, England).[4] This antioxidant has a broad field of application—it is used for stabilization of polyethylene, polypropylene, polyurethane, polyamide, polyvinylchloride, ABS, polyoxymethylene, and polycarbonate.

Until now, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene was analyzed after isolation from the polymer matrix by soxhlet extraction with solvents such as tetrahydrofuran,[5] chloroform,[5] acetonitrile,[6] or dichloromethane,[7] which do not dissolve the polymer. These extraction procedures require a long time, at least several hours. Nielson[8] introduced ultrasonic and microwave extractions using mixed polar solvents which require only 30–60 min. However, in all these procedures of extraction, usually not 100% of the additive is recovered from the polymeric material. Deliberately, chemical compounds chosen as additives show a low tendency to migrate out of the polymeric matrix. In the case of crystalline polyolefins, the antioxidants are dissolved in the amorphous regions of the poly-

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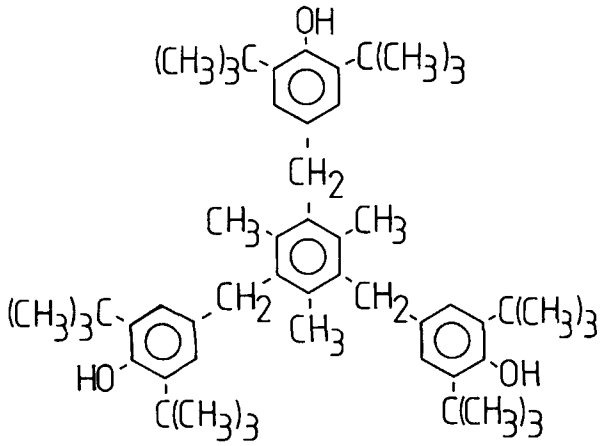

Figure 1 Formula of 1,3,5-trimethyl-2,4,6-*tris*(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene.

mer matrix and may be partially occluded between crystalline lamellae, and thus rendered unextractable.

Schabron, Smith, and Ware[9] dissolved polyethylene and polypropylene pellets in decalin, which is a good solvent for that polymer above 110°C, and reprecipitated the polymer by cooling to room temperature. The analysis of the antioxidant in the supernatant may be complicated by the necessity to evaporate decalin from the filtered solution, however, because this solvent is not always suitable for subsequent HPLC analysis.

As we have first shown,[10] the analysis of aromatic antioxidants in polyolefins may be significantly simplified when the polyethylene is first fully dissolved in a low boiling liquid alkane. We have chosen *n*-heptane, which dissolves PE at high temperature (theta-point for PE is 173.9°C).[11] The boiling point of *n*-heptane is 99°C,[12] i.e., an autoclave has to be used when keeping this solvent at higher temperature. The use of *n*-heptane has the advantage that *n*-heptane is widely used in normal phase liquid chromatography as the main component of the mobile phases, i.e., an *n*-heptane solution containing an antioxidant from polyolefin may be immediately injected into an HPLC column.

EXPERIMENTAL

Chemicals

Irganox 1330, i.e., 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene (Fig. 1) was obtained from Ciba-Geigy, Basel, Switzerland.

The polyethylene pellets without additives were PE-MD (density = 0.934 g/mL, M_w = 120 kg/mol) obtained from Neste Oy Chemicals, Porvoo, Finland. From the same lot, tubes (inner diameter 16 mm, wall thickness 2 mm) were available, which supposingly contained 0.1 wt % of Irganox 1330.

The solvents *n*-heptane (purum) and methanol (p.a.) were bought from Fluka Chemie AG, Buchs, Switzerland.

The standard solution of the additive was prepared by weighing (10 mg Irganox 1339/kg of *n*-heptane).

The mobile phase was prepared volumetrically (*n*-heptane/methanol, 100/0.2, v/v).

Nitrogen (99.999 vol % purity) was obtained from Linde, Stadl-Paura, Austria.

HPLC Apparatus

The mobile phase was pumped out from the solvent reservoir with an LC pump (model 510, Millipore-Waters, Milford, MA) through an injection valve (model 7010, Rheodyne, Berkeley, CA) with 20 μl sample loop into a steel column 25 × 0.4 cm ID (Knauer, Berlin, Germany) packed with normal phase silica gel (Silpearl^R) particle diameter 13 μm (Glass Works Kavalier, Votice, Czech Republic). The composition of the effluent was monitored with a variable-wavelength absorbance UV/VIS detector (model 975, Jasco Co., Tokyo, Japan). The signal of the detector was shown on a recorder (model 540, Kontron, Basel, Switzerland), and digitalized as input into a computer program. The UV spectrum of Irganox 1330 was measured with the above detector.

Prior to injection into the column, the sample solutions were filtered through a glass fiber filter with pore size 3 μm (Tessek, Prague, Czech Republic).

Autoclave

For the dissolution of the polymer samples, an autoclave (Model II, 300 mL/10 MPa, Roth, Karlsruhe, Germany) was used. The autoclave is equipped with thermostat, pressure gauge, magnetic mixer, and two valves. The valves enable purging the contents of the vessel with inert gas. The autoclave vessel has a 300 mL volume. For the determination of the minimum time for complete dissolution of the polymer pellets, the bottom part of the autoclave was modified by installation of two quartz glass windows (3 mm thick, 10 mm diameter, Helma, Freiburg, Germany) and an appropriate optical device for visual inspection (Fig. 2). With this modification, the autoclave could be used up to a pressure of 4 MPa.

For quantitative measurements the autoclave was used without the pressure gauge to avoid conden-

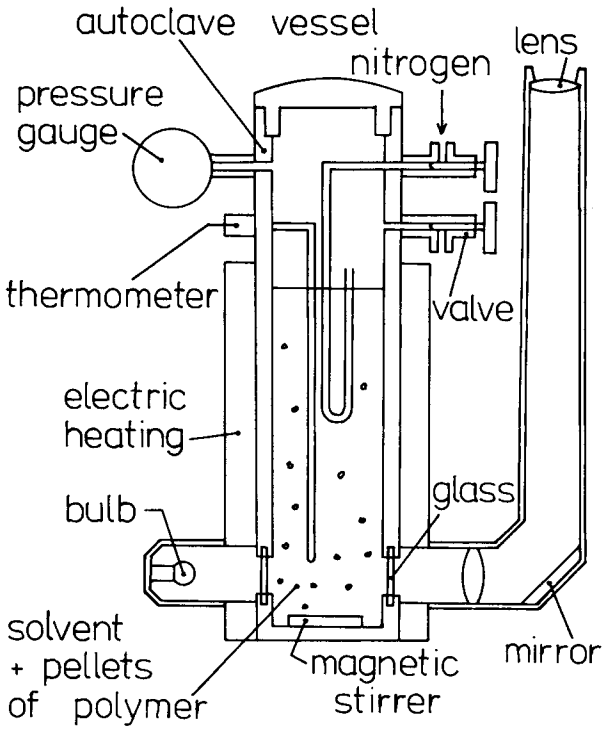

Figure 2 Scheme of the modified autoclave with the glass window used for the determination of the time of dissolution.

sation of solvent within the pressure gauge, which would lead to a considerable systematic error in the determination of concentration.

Procedure of Analysis

The polymer tube was cut in small slices (about 4 mm long and 0.5–1.0 mm thick). One g of the polymer slices, about 100 mL of *n*-heptane (the mass of the added *n*-heptane was determined by weighing), and a magnetic stirrer were put into the pressure vessel. The vessel was closed and purged with nitrogen for 15 min in order to remove all oxygen from the atmosphere above the solvent (Fig. 2). The contents of the vessel were then heated to 160°C within 15 min and then kept for 45 min at 160°C. After this dissolution of the polymer, the autoclave vessel was put into cold water for 40 min. The polyolefin precipitated, the pressure vessel was opened, and its contents transferred into a glass container. The sample of the supernatant was sucked through a glass fiber filter with pore size 3 μm into an injection syringe, and then injected into the LC column.

On the basis of comparison of the peak height (peak area) observed for a standard solution of known concentration (0.010 mg Irganox 1330/g of eluent) with the peak observed for the solution from the autoclave, the concentration of the antioxidant corresponding to 1 g of the polymer was calculated. The base line under each peak was approximated by a third degree polynomial.

On average, about 3 h are needed for performing one complete analysis of a polymer sample.

RESULTS AND DISCUSSION

The UV detector was set to a wavelength of 242 nm, which was chosen on the basis of the respective UV spectrum (Fig. 3). Figure 4(a) shows a chromatogram of the standard solution of Irganox 1330. The tiny peaks at the beginning of the chromatogram correspond to the solvent component and do not disturb the analysis of the additive.

Allen et al.[13] have shown that heating of Irganox 1330 in contact with both polypropylene and oxygen decomposes Irganox 1330 into several products. The heating of Irganox 1330 with PE in *n*-heptane in air atmosphere for about 1 h at 160°C also causes complete decomposition of Irganox 1330, i.e., its characteristic peak did not appear in the corresponding chromatogram. If the air in the autoclave was exchanged for nitrogen prior to heating, the total amount of the added antioxidant was recovered.

Using the modified autoclave with two windows (Fig. 2), we have also determined the minimum time in which the polymer pieces are completely dissolved. After about 25 min at a temperature of 160°C

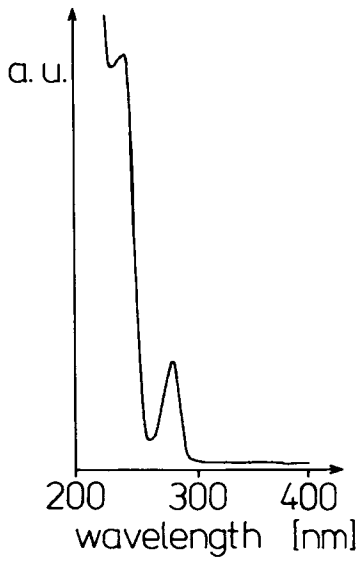

Figure 3 UV spectrum of Irganox 1330 measured at the top of the peak.

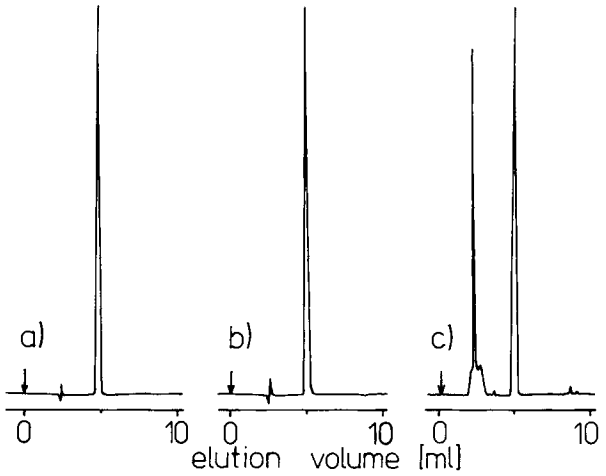

Figure 4 Example of chromatogram (detection at 242 nm; range 0.0025; flow rate 1 mL/min): (a) standard solution of Irganox 1330, concentration 0.010 mg/g; (b) solution of Irganox 1330 taken from the test system; (c) solution of Irganox 1330 isolated from a PE-MD tube.

(plus 15 min needed for the heating of the vessel to 160°C, gives in total 40 min) the solution becomes optically clear, without any visible pieces of the polymer. With this minimum time of dissolution, we have, however, repeatedly obtained only 95% of the additive contained in the respective sample. On the basis of the above result, we have chosen 1 h (including the initial heating to 160°C) as dissolution time for this type of sample. Prolonging the time of heating to 1.5 h did not increase the recovery of the additive.

Taking into account the above results, we first evaluated the recovery and reproducibility of the described procedure by analyzing a test system consisting of 1 g of neat PE-MD, 1 mg of Irganox 1330, and 67.0 g *n*-heptane. This test system has the advantage that the content of the additive is precisely known and is not influenced by inhomogeneity or history of the additive-containing polymer sample.

Finally, we have analyzed a stabilized PE-MD tube. An example of the corresponding chromatogram is shown in Figure 4 and the results are collected in Table I.

As shown in Table I (see lefthand side of Table I), the procedure recovers all antioxidant from the model system. In the PE-MD tube we have found a content of Irganox 1330 which was about 3% higher than stated by its producer (see righthand side of Table I). This may be due to limited precision of the feeders used during compounding.

The described procedure enables us to reach the detection limit (calculated from the height of a peak which is three times higher than noise) of 0.013 mg Irganox 1330/1 g PE, corresponding to the concentration of 0.23 μg Irganox 1330 in 1 gram of the eluent.

The procedure described is, in comparison to known methods, fast and simple—no additional evaporation of the solvent, preconcentration, or redissolution of the additive is necessary.

A literature search showed that a large number of antioxidants and UV stabilizers can be analyzed by liquid chromatography using a mobile phase containing *n*-hexane or *n*-heptane as the main component (Table II).

As a rule, the retention of an additive is controlled by the addition of various polar solvents (isocratically or using a gradient). These combinations of solvents are UV transparent in a broad range of

Table I Mass Content (wt %) of Irganox 1330 Found in the Test System (1 g PE-MD with 1 mg Additive and 67 g *n*-heptane) and in a Polyethylene Tube Made of a PE-MD Formulation with 0.1 wt % of Irganox 1330

	Test System		PE-MD Tube	
Calculated from:	Peak Height	Peak Area	Peak Height	Peak Area
	0.0995	0.0999	0.1039	0.1029
	0.1002	0.1002	0.1019	0.1022
	0.1005	0.1003	0.1043	0.1037
	0.0995	0.0997	0.1062	0.1073
	0.0978	0.1015	0.1016	0.1027
	0.1024	0.1021	0.1025	0.1021
Mean:	0.0999	0.1006	0.1034	0.1035
Standard deviation:	±0.0015	±0.0010	±0.0017	±0.0019
Relative standard deviation (%):	±1.5	±1.0	±1.6	±1.8

Table II Literature on HPLC Analysis of Aromatic Antioxidants and UV Stabilizers Which Were Separated with *n*-Heptane or *n*-Hexane as the Main Component of Mobile Phase

	Additive			
Mobile and Stationary Phase	Code No.	Trade Name	Chemical Name	Reference to Literature
Hexane/dichloromethane (99.8/0.2, v/v) Normal phase silica gel	1	Ionox 220	4,4′-Methylenebis(2,6-di-*tert*-butylphenol)	5
	2	Irganox 1076	octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxy-phenol) propionate	
	3	AO 425	2,2′-Methylenebis(4-ethyl-6-*tert*-butylphenol)	
	4	AO 2246	2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	
Hexane/dichloromethane (75/25, v/v) Normal phase silica gel	5	Santowhite Powder	4,4′-Butylidenebis(3-methyl-6-*tert*-butylphenol)	5
	6	Santanox R	4,4′-Thiobis(3-methyl-6-*tert*-butylphenol)	
	7	DSTDT	Distearyl thiopropionate	
	—	AO 425	(Code No. 3)	
n-Heptane/dichloromethane (gradient)	8	Goodrite 3114	1,3,5-tris(3′,5′-Di-*tert*-butyl-4′-hydroxybenzyl)izokyanurate	9
	9	BHT	2,6-Di-*tert*-butyl-4-methylphenol	
Normal phase silica gel	—	Santanox R	(Code No. 6)	
	10	Topanol CA	1,1,3-tris(2-Methyl-4-hydroxy-5-*tert*-butylphenyl)butane	
	11	Ethyl 330	1,3,5-Trimethyl-2,4,6-*tris*(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene	
n-Heptane/isopropanol (100/0.5, v/v)	12	Irganox 1010	Pentaerythrityl-tetrakis[(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]	10
Normal phase silica gel	13	Irgafos 168	tris(2,4-Di-*tert*-butylphenyl)phosphite	
n-Hexane/dichloromethane (90/10, v/v) Normal phase silica gel	—	BHT	(Code No. 9)	14
	—	Irganox 1330	(Code No. 11)	
n-Hexane/dichloromethane (75/25, v/v)	14	Tinuvin 326	2-(2′-Hydroxy-3′-*tert*-butyl-5′-methylphenyl)-5-chlorobenzotriazole	14
	15	Tinuvin 320	2-(2′-Hydroxy-3,5′-di-*tert*-butylphenyl)-2H-benzotriazole	
	16	Tinuvin P	2-(2′-Hydroxy-5′-methylphenyl)benzotriazole	
n-Hexane/dichloromethane (85/15, v/v)	—	BHT	(Code No. 9)	14
	—	Irganox 1330	(Code No. 11)	
	—	Irganox 1076	(Code No. 2)	
Normal phase silica gel				
n-Hexane/dichloromethane (gradient)	17	Irganox 2246	2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	14
	—	Irganox 1076	(Code No. 2)	
	—	Irganox 1330	(Code No. 11)	
Normal phase silica gel	—	Irganox 1010	(Code No. 12)	
	—	Tinuvin P	(Code No. 16)	
	—	Tinuvin 326	(Code No. 14)	
	18	Tinuvin 320	2-(2′-Hydroxy-3′,5′-di-*tert*-butylphenyl)-benzotriazole	
n-Heptane/di-isopropylether/ isopropanol (gradient) Normal phase silica gel	19	No.nox AN	*N*-Phenyl-1-naphthylamine	15

Table II (*Continued*)

Mobile and Stationary Phase	Additive: Code No.	Additive: Trade Name	Additive: Chemical Name	Reference to Literature
n-Heptane/isopropanol (100/0.5, v/v) Normal phase silica gel	20	Plastanox 2246	2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	16
	33	Chimox 14 Irganox PS 802	β,β'-Thiodi(propionacid-myristylester) (Code No. 7)	
n-Hexane/isopropanol (95/5) Normal phase silica gel	—	Irganox 1076	(Code No. 2)	17
n-Heptane/dichloromethane (gradient) Normal phase silica gel	—	Santanox R	(Code No. 6)	18
n-Hexane/methanol (95/5, v/v) Reversed phase silica gel with amino groups	23	Armostat 400	*N,N′*-Bis(2-hydroxyethyl)-C_{12}-C_{16}-diamine	19
n-Hexane/dichloromethane (gradient) Normal phase silica gel	— —	Irganox 1010 Ionox 330	(Code No. 12) (Code No. 11)	20
n-Hexane/methanol (99.8/0.2, v/v) Normal phase silica gel	—	Ionox 330	(Code No. 11)	21
n-Hexane/dichloromethane (73/27, v/v)	24	Cyasorb UV 1084	2,2′-Thiobis(4-*tert*-octylphenolate)-*n*-butylamine-nickel	22
	—	BHT	(Code No. 9)	
Normal phase silica gel	25	Tinuvin 327	2-(2′-Hydroxy-3′,5′-di-*tert*-butylphenyl)-5-chlorobenzotriazole	
	—	Tinuvin 326	(Code No. 14)	
	45	Irganox 1076	(Code No. 2)	
	26	Cyasorb UV 9	2-Hydroxy-4-methoxybenzophenone	
n-Heptane/dichloromethane (60/30, v/v) Normal phase silica gel	—	Cyasorb UV 1084	(Code No. 24)	23
n-Hexane/chloroform (90/10, v/v)	—	Cyasorb UV 9	(Code No. 26)	24
	29	Cyasorb UV 531	2-Hydroxy-4-*n*-octylbenzofenone	
Normal phase silica gel	30	Uvinul M-410	2-Hydroxy-4-dodecyloxybenzophenone	
	—	Tinuvin P	(Code No. 16)	
	—	Tinuvin 320	(Code No. 18)	
	—	Tinuvin 326	(Code No. 14)	
	—	Tinuvin 327	(Code No. 25)	
	31	Uvinul N35	Ethyl-2-cyano-3,3-diphenylacrylate	
	32	Uvinul N539	1-Ethylhexyl-2-cyano-3,3-diphenylacrylate	
	—	Cyasorb UV-1084	(Code No. 24)	
n-Heptane/dichloromethane (gradient) Reversed phase silica gel with cyano groups	— — —	Irganox 1010 Irganox 1076 Kerobit TBK	(Code No. 12) (Code No. 2) (Code No. 9)	25

Code number refers to the chemical composition of the additive.

wavelengths and allow the detection of very small concentrations of UV absorbing additives. Also, *n*-hexane dissolves polyethylene at high temperature (theta temperature for PE is 133.2°C)[11] and its use for the dissolution of crystalline polyolefins would also require an autoclave (the boiling point of *n*-hexane is 66°C).[12]

If *n*-heptane will be finally evaporated from the obtained solution of additives, then the additives may be redissolved in another solvent (for example, in acetonitrile).[10] In this case, the scope of the method demonstrated above for Irganox 1330 can be expanded far beyond the examples given in Table II.

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