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Note

Analysis of 2-hydroxybenzophenone and 2′-hydroxyphenylbenzotriazole UV stabilizers by high-performance liquid chromatography

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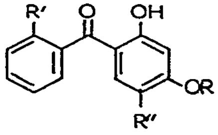
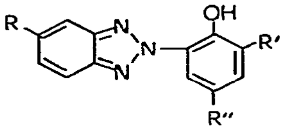
Substituted 2-hydroxybenzophenones (I) and 2′-hydroxy-2-phenylbenzotriazoles (II) are widely used as light stabilizers in polymeric materials to protect the substrate from photo-oxidation by sunlight. In the course of our studies of the reactions of these stabilizers during the autoxidation and photo-oxidation of polymers and model systems it was necessary to determine quantitatively the concentration remaining in the oxidized substrate. In this note a procedure is described for the determination of 2-hydroxybenzophenone and 2′-hydroxy-2-phenylbenzotriazole light stabilizers by high-performance liquid chromatography (HPLC) on silica gel.



I



II

EXPERIMENTAL

Materials

2-Hydroxybenzophenone (Aldrich, Milwaukee, WI, U.S.A.) was purified by column chromatography. 2′-Hydroxy-2-phenylbenzotriazole (Ciba-Geigy, Basle, Switzerland) and 2-hydroxybenzophenone (Cyanamid, Bound Brook, NJ, U.S.A.) light stabilizers, shown in Table I, were recrystallized before use. Reagent-grade methylene chloride was purified by passing through activated (Gr. 1) silica gel and distilled. Isopropanol was spectroscopic grade.

HPLC

HPLC separations were carried out on an isocratic system (Altex 110A pump, Rheodyne loop injection valve with 10-μl loop and Altex 153 UV detector). A 15 cm × 4.6 mm silica gel column (5 μm Spherisorb) and 5 cm pre-column (slurry packed with 5 μm Spherisorb) were used for separations. The mobile phase was 0.1% iso-

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TABLE I

STRUCTURES OF THE PHENOLIC LIGHT STABILIZERS

Additive	*Substituents*		
	R	*R'*	*R''*
2-Hydroxybenzophenones (I)			
2,4-Dihydroxybenzophenone	H	H	H
Cyasorb UV 9	CH_3	H	H
Cyasorb UV 531	n-C_8H_{17}	H	H
Cyasorb UV 24	CH_3	OH	H
Cyasorb UV 207	CH_3	CO_2H	H
Cyasorb UV 284	CH_3	H	SO_3H
2'-Hydroxy-2-phenylbenzotriazoles (II)			
Tinuvin P	H	H	CH_3
Tinuvin 320	H	$C(CH_3)_3$	$C(CH_3)_3$
Tinuvin 326	Cl	$C(CH_3)_3$	CH_3
Tinuvin 327	Cl	$C(CH_3)_3$	$C(CH_3)_3$
Tinuvin 328	H	$C(CH_3)_2CH_2CH_3$	$C(CH_3)_2CH_2CH_3$

propanol in methylene chloride at a flow-rate of 1.0 ml/min. The column was activated by pumping dry diethyl ether (dried with 4A molecular sieve) and the activity maintained for longer periods by inclusion of a 15-cm column packed with a coarser grade of silica gel before the injector.

Derivatization

Approximately 0.5 mg of the phenolic light stabilizer was acetylated by addition of 1.0 ml of a solution of acetic anhydride (2.0 ml) and triethylamine (4.0 ml) in methylene chloride (10.0 ml). The hydroxybenzophenones and Tinuvin P were allowed to stand for 1 h at room temperature whilst Tinuvins 320, 326, 327 and 328 were heated under gentle reflux for 2 h. The solution was then evaporated to dryness under reduced pressure and made up to 5.0 ml with methylene chloride for analysis.

RESULTS AND DISCUSSION

HPLC separation of phenolic antioxidants on silica gel has been applied to the analysis of phenolic antioxidants and their transformation products in polymers[1-3]. However, chromatographic separation of the 2-hydroxybenzophenone and 2'-hydroxy-2-phenylbenzotriazole light stabilizers on silica gel results in broad tailing peaks (Fig. 1) the retention times and peak shapes of which are strongly dependent on the degree of activation of the silica gel and the presence of polar modifiers in the mobile phase. This behaviour is presumably due to strong hydrogen-bonding interaction between the surface silanol groups and the stabilizer molecules (III and IV). (2-Hydroxybenzophenones are known to form strong intramolecular hydrogen bonds[4]). HPLC analysis of these polymer additives would therefore be expected to be improved by suitable derivatization of the phenolic hydroxyl group.

Attempts to methylate the 2-hydroxy group of the 2-hydroxybenzophenones

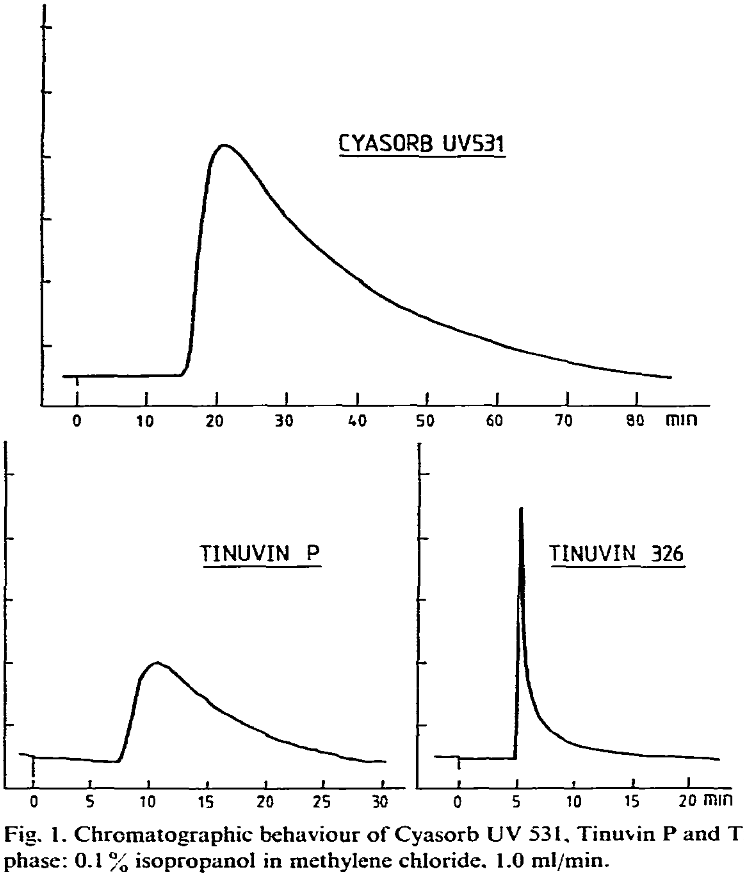
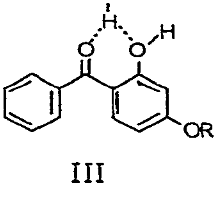
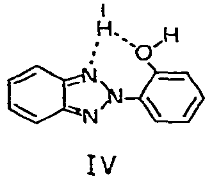


Fig. 1. Chromatographic behaviour of Cyasorb UV 531, Tinuvin P and Tinuvin 326 on silica gel. Mobile phase: 0.1 % isopropanol in methylene chloride, 1.0 ml/min.



III



IV

with diazomethane and diazomethane–boron trifluoride, in ether proved unsuccessful. In each case thin-layer chromatography showed that starting material was recovered unchanged, except for 2,4-dihydroxybenzophenone where 2-hydroxy-4-methoxybenzophenone was obtained on treatment with diazomethane.

Acetylation was more successful and the corresponding acetates chromatographed on silica gel with greatly improved peak shape and reproducibility of retention times. A wide range of retention times was obtained for the commercial additives studied enabling their identification and analysis by this method.

Acetylation of the phenolic light stabilizers was performed under mild conditions using acetic anhydride and triethylamine in methylene chloride. For the hydroxybenzophenones and the unhindered benzotriazole, Tinuvin P (Table I), acetylation was carried out at room temperature and was complete, as verified by HPLC, in less than 1 h. However, for the more hindered benzotriazoles Tinuvins 320, 326, 327 and 328 (see Table I), with a tertiary alkyl group *ortho* to the phenolic hydroxyl group, acetylation was slower and complete reaction, as verified by HPLC, required heating at the boiling point of methylene chloride (40°C).

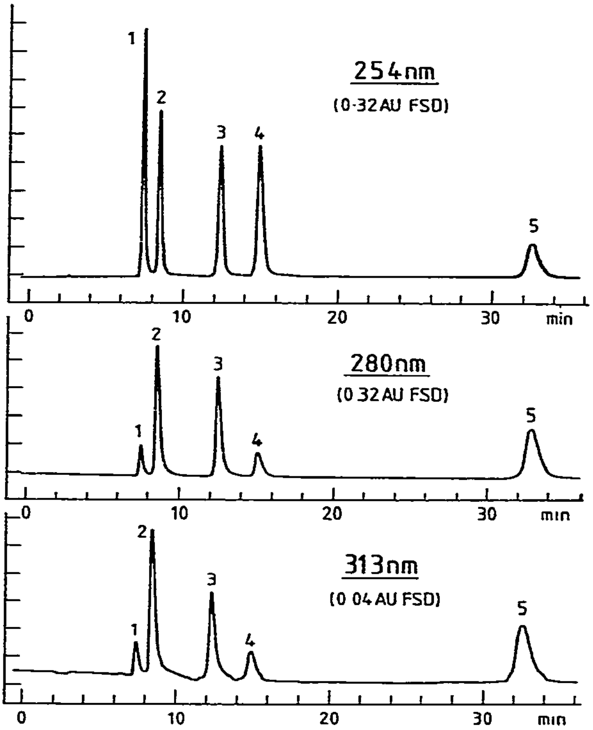


Fig. 2. HPLC separation of 2-hydroxybenzophenone light stabilizers on silica gel after acetylation. Peaks: 1 = 2-hydroxybenzophenone; 2 = Cyasorb UV 531; 3 = Cyasorb UV 9; 4 = 2,4-dihydroxybenzophenone; 5 = Cyasorb UV 24. Column, Spherisorb 5 µm; mobile phase 0.1 % isopropanol in methylene chloride, 1.0 ml/min.

Fig. 2 shows the HPLC separation of several commercial 2-hydroxybenzophenone light stabilizers and 2-hydroxybenzophenone on silica gel after acetylation Cyasorb UV 207 (not shown in Fig. 2) gave a retention time of 6.2 min whilst Cyasorb UV 284 (2-hydroxy-4-methoxy-5-sulphobenzophenone) was not eluted under the conditions employed.

Fig. 3 shows the separation of several commercial 2′-hydroxy-2-phenylbenzotriazole light stabilizers after acetylation. Retention times for the acetates of these additives are shorter than those of the hydroxybenzophenones although the stabilizers are still well resolved. Figs. 2 and 3 show the chromatographic traces at three detector wavelengths (254, 280 and 313 nm). The different spectral

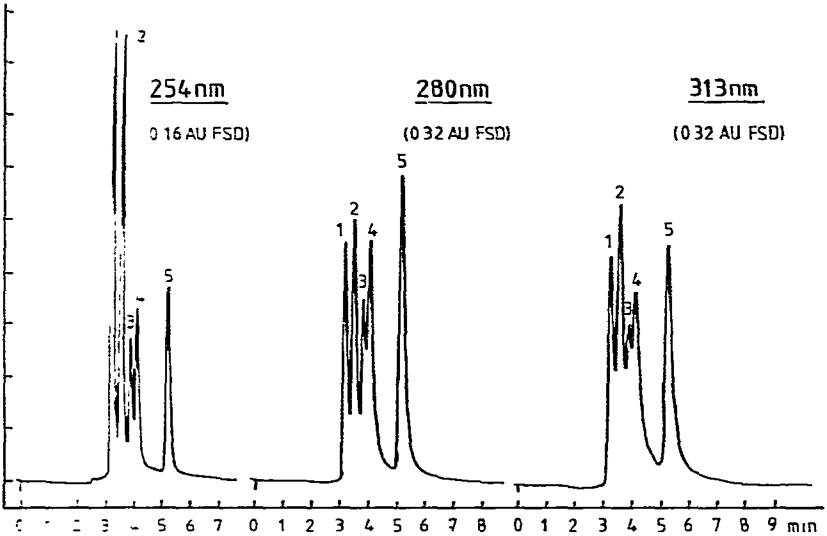


Fig. 3. HPLC separation of 2'-hydroxy-2-phenylbenzotriazole light stabilizers on silica gel after acetylation. Peaks: 1 = Tinuvin 327; 2 = Tinuvin 326; 3 = Tinuvin 328; 4 = Tinuvin 320; 5 = Tinuvin P. Conditions as in Fig. 2.

properties of the individual stabilizer derivatives aid in the characterization of the polymer additive.

The application of the above HPLC method to the determination of extraction yields of hydroxybenzophenone and hydroxyphenylbenzotriazole light stabilizers from polypropylene film is shown in Fig. 4. The extraction of 170 μm melt-pressed

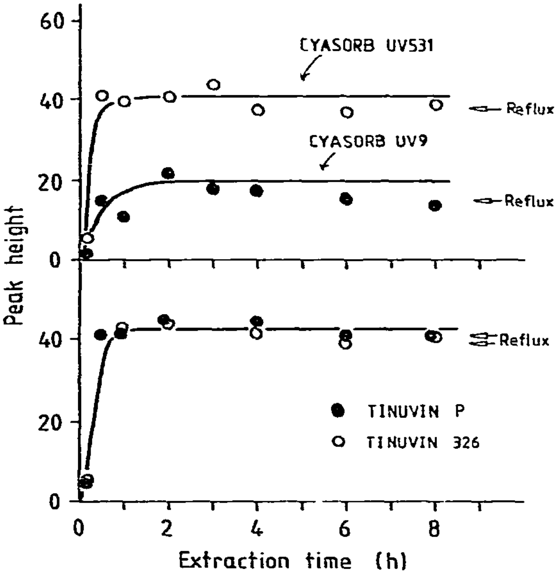


Fig. 4. Extraction yields of phenolic light stabilizers from 170 μm polypropylene films with methylene chloride at room temperature.

films containing 0.5% (w/w) of the additive was carried out by shaking with methylene chloride at a temperature of *ca.* 25°C. The figure shows that the additives were completely extracted from the film in less than 2 h. The same final extraction yields were obtained on refluxing the film sample in methylene chloride for 8 h indicating the complete removal of the additive from the film in the room temperature extractions.

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