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## ANTIOXIDANTS AND STABILIZERS

### LVII\*. BEHAVIOUR OF LIGHT STABILIZERS AND MODEL COMPOUNDS IN GEL CHROMATOGRAPHY

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#### SUMMARY

The gel chromatographic behaviour of a series of derivatives of benzophenone, benzotriazole, salicylic acid and benzoin, some of which are used as light stabilizers for polymers, has been investigated. The elution volumes indicate the effect of the structures of the compounds studied. Gel chromatography can be used to determine the content of light stabilizers in polymer extracts.

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#### INTRODUCTION

Stabilizing systems for polymers contain light stabilizers that act as light screens, UV radiation absorbers or quenching agents, and are used in admixture with antioxidants and synergistic additives. Their content and character are among the decisive factors that determine the lifetime of polyolefins, which are subject to atmospheric ageing. The identification and determination of components in the polymer are not simple, especially if mixtures are involved. Titrimetry<sup>1,2</sup>, spectrophotometry<sup>3</sup> and IR<sup>4,5</sup> and UV<sup>4</sup> spectroscopy have been used, but chromatographic methods have been most frequently employed (paper chromatography<sup>6,7</sup>, thin-layer chromatography<sup>4,6,8–10</sup>, gas chromatography<sup>4,11,12</sup> and gel chromatography<sup>13,14</sup>). Good results were obtained in the analysis of mixtures of stabilizers<sup>14</sup> by gel chromatography, and this technique was used in this investigation of the main types of light stabilizers for polymers, mainly derivatives of benzophenone, benzotriazole and salicylic acid.

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## EXPERIMENTAL

*Chemicals*

Samples of commercial light stabilizers and laboratory-scale model compounds were used. The chemical compositions and trade names are given in Tables I–IV. Commercial stabilizers were obtained from American Cyanamid Co., New York, U.S.A. (Cyasorb), Anchor Chemical Co., Manchester, Great Britain (Uvinul), Chemical Works J. Dimitrov, Bratislava, Czechoslovakia (Dastib), Ciba-Geigy, Basle, Switzerland (Irgastab 2002, Tinuvin), Bayer, Leverkusen, G.F.R. (UV Absorber Bayer 318) and Ward Blenkinsop & Co., Wembley, Great Britain (Uvostat).

*Gel chromatography*

The analyses were carried out with a gel chromatograph built at the Institute of Macromolecular Chemistry (described elsewhere<sup>15</sup>). Tetrahydrofuran was used as the eluent. The columns were packed with a Kopolymer ST-DVB No. VIII (United Chemical and Metallurgical Works, Production Company, Ústí, Czechoslovakia) polystyrene gel, exclusion limit 1200. Volumes of 0.1–0.5 ml of 2–5% solutions of compounds in tetrahydrofuran were injected into the columns. The measurements were carried out at 25°, the flow-rate of the eluent was 30–50 ml/h and the column pressure was 2–4 atm. Elution volumes,  $V_e$  (ml), corresponding to the maximum of the elution peak, were measured (elution volume of excluded molecules,  $V_0 = 124.4$  ml) and are listed in Tables I–IV.

## RESULTS AND DISCUSSION

The determination of light stabilizers by gel chromatography was performed with a series of benzophenone (Table I), benzotriazole (Table II), organic acids esters (Table III) and benzoin (Table IV) derivatives. In addition to commercial stabilizers, model compounds with a modified molecular structure were used and data on the effect of structure on chromatographic behaviour were obtained.

*Benzophenone derivatives*

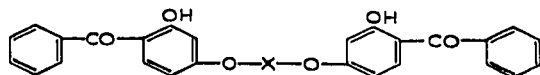
Derivatives of 2-hydroxybenzophenone are well suited for use as light stabilizers (Table I). The hydroxyl group in the 2-position is bonded by an intramolecular hydrogen bond to the carbonyl group. In gel chromatography with tetrahydrofuran as the eluent, free phenolic hydroxyl groups are solvated preferentially<sup>15,16</sup>. In the benzophenone group, this phenomenon can be effective for derivatives with the hydroxyl group in the 4-position. This is clearly seen if  $V_e$  values for 2,4-dihydroxy- and 4,4'-dihydroxybenzophenones are compared (the latter compound has a low elution volume). The etherification of the hydroxyl group in the 4-position interferes with solvation, as shown by etherification with a methyl group (*i.e.*, with a non-bulky alkyl group), which resulted in a pronounced increase in the elution volume (compare 2,4-dihydroxybenzophenone and 2-hydroxy-4-methoxybenzophenone, or 2,4,2',4'-tetrahydroxybenzophenone and 2,2'-dihydroxy-4,4'-methoxybenzophenone). In derivatives that contain a C<sub>7</sub>–C<sub>12</sub> alkoxy group in the 4-position, the steric influence of the increasing alkyl chain length (compare 4-*n*-heptyloxy, 4-*n*-octyloxy and 4-*n*-dodecyloxy derivatives), and especially of its branching (compare *n*- and *iso*-C<sub>8</sub> alkyl groups), plays a

TABLE I

## GEL CHROMATOGRAPHIC BEHAVIOUR OF ACETOPHENONE AND BENZOPHENONE DERIVATIVES

Compound	Molecular weight	$V_e$ (ml)
Acetophenone	120	221.2
Benzophenone	182	209.3
2-Hydroxy-4-methoxybenzophenone (Cyasorb UV 9)	228	201.4
2-Hydroxy-4- <i>n</i> -heptyloxybenzophenone (Uvistat 247)	312	166.9
2-Hydroxy-4- <i>n</i> -octyloxybenzophenone (Cyasorb UV 531)	326	165.9
2-Hydroxy-4-(2-ethylhexyloxy)benzophenone (Dastib 242)	326	160.0
2-Hydroxy-4- <i>iso</i> -decyloxybenzophenone	354	155.0
2-Hydroxy-4- <i>n</i> -dodecyloxybenzophenone	382	154.0
2-Hydroxy-4- <i>n</i> -octyloxy-5- <i>tert.</i> -butylbenzophenone	382	156.0
2-Hydroxy-(2-hydroxyethyloxy)benzophenone	258	174.8
2,4-Dihydroxybenzophenone (Uvinul 400)	214	180.7
2,4-Dihydroxy-5- <i>tert.</i> -butylbenzophenone	270	162.9
4,4'-Dihydroxybenzophenone	214	167.9
2,2'-Dihydroxy-4-methoxybenzophenone (Cyasorb UV 24)	244	186.6
2,2'-Dihydroxy-4,4'-dimethoxybenzophenone (Uvinul 490)	274	168.9
2,4,2',4'-Tetrahydroxybenzophenone (Uvinul D-50)	246	159.0
1,4-Bis-[(3-hydroxy-4-benzoyl)phenoxy]butane	482	154.0
1,8-Bis-[(3-hydroxy-4-benzoyl)phenoxy]octane	538	148.1
1,4-Bis-[(3-hydroxy-4-benzoyl-6- <i>tert.</i> -butyl)phenoxy]butane	594	143.2
1,8-Bis-[(3-hydroxy-4-benzoyl-6- <i>tert.</i> -butyl)phenoxy]octane	650	138.2
1,4-Bis-[(3-hydroxy-4-benzoyl-6- <i>tert.</i> -octyl)phenoxy]butane	702	137.3
1,4-Bis {[3-hydroxy-4-benzoyl-6-(1-phenylethyl)]phenoxy}butane	680	140.2
Bis-[2-(3-hydroxy-4-benzoylphenoxy)ethyl]succinate	598	142.2
Bis-[2-(3-hydroxy-4-benzoylphenoxy)ethyl]adipate	626	140.2
Bis-[2-(3-hydroxy-4-benzoylphenoxy)ethyl]sebacate	682	134.3
Bis-[2-(3-hydroxy-4-benzoylphenoxy)ethyl]3,3'-thiodipropionate	788	138.2

role. The presence of a bulky alkyl group in the position *ortho* to the solvatable hydroxyl group reduces the elution volume.



In derivatives that contain two benzophenone molecules joined by bridges X to form an ether bond with the hydroxyl group in the 4-position, the group X is either a hydrocarbon residue,  $-(CH_2)_n-$ , or an ester group of the type  $-(CH_2)_n-OCO-(CH_2)_m-COO-(CH_2)_n-$  or  $-(CH_2)_n-OCO-(CH_2)_m-S-(CH_2)_m-COO-(CH_2)_n-$ . Although the molecules involved here are rather complicated, changes corresponding to changes in the length and character of the bridge X are still easy to observe in the elution volumes. The effect of the substituent in the 5,5'-positions on the phenolic ring of benzophenone is also reflected in this case. An example can be seen in the  $V_e$  values of derivatives in which X =  $-(CH_2)_4-$  that contain hydrogen atoms or *tert.*-butyl, 1,1,3,3-tetramethyl-butyl (*i.e.*, *tert.*-octyl) or 1-phenylethyl groups in the 5,5'-positions, or of derivatives with X =  $-(CH_2)_8-$  that contain a hydrogen atom or a *tert.*-butyl group in the 5,5'-

positions. The chromatographic behaviour of compounds in which the bridge X forms a group containing a dicarboxylic acid ester is also in accordance with the structure.

#### *Benzotriazole derivatives*

All of the compounds studied (Table II) contain a phenyl group in the 2-position with a hydroxyl group in the 2'-position. The presence of aliphatic substituents of increasing chain length in the 5-position is reflected in a regular decrease in  $V_e$ . In a similar manner to the series of benzophenone derivatives, the 1-phenylethyl group has approximately the same effect as the *tert.*-butyl group on the change in the elution volume.

The influence of a chlorine atom in the 5-position on the elution volume is reflected less markedly in derivatives with a bulkier molecule.

TABLE II  
GEL CHROMATOGRAPHIC BEHAVIOUR OF BENZOTRIAZOLE DERIVATIVES

<i>Compound</i>	<i>Molecular weight</i>	<i>V<sub>e</sub> (ml)</i>
2-(2-Hydroxy-5-methylphenyl)benzotriazole (Tinuvin P)	225	206.4
2-(2-Hydroxy-5-ethylphenyl)benzotriazole	239	194.5
2-(2-Hydroxy-5- <i>n</i> -butylphenyl)benzotriazole	267	183.7
2-(2-Hydroxy-5- <i>n</i> -octylphenyl)benzotriazole	323	166.9
2-(2-Hydroxy-5- <i>n</i> -dodecylphenyl)benzotriazole	379	154.0
2-[2-Hydroxy-5-(1-phenylethyl)phenyl]benzotriazole	315	180.7
2-(2-Hydroxy-3,5-di- <i>tert.</i> -butylphenyl)benzotriazole (Tinuvin 320)	303	168.9
2-(2-Hydroxyphenyl)-5-chlorobenzotriazole	245	189.6
2-(2-Hydroxy-5-methylphenyl)-5-chlorobenzotriazole	259	195.5
2-(2-Hydroxy-3- <i>tert.</i> -butyl-5-methylphenyl)-5-chlorobenzotriazole (Tinuvin 326)	314	179.7
2-(2-Hydroxy-3,5-di- <i>tert.</i> -butylphenyl)-5-chlorobenzotriazole (Tinuvin 327)	357	165.9
2-(2-Hydroxy-3,5-di- <i>n</i> -amylphenyl)-5-chlorobenzotriazole (Tinuvin 328)	385	165.9

#### *Salicylic acid esters*

The ester group of the compounds studied contained a phenyl or naphthyl residue (Table III). The substitution of the phenyl residue in the *para*-position with an alkyl group reduces the elution volume; however, this does not permit bulky isomers to be distinguished in a precise manner (*e.g.*, isomeric 4-octylphenyl derivatives or naphthyl derivatives). The substitution of the *para*-position with chlorine under the conditions used leads to a decrease in the elution volume by 7.9 ml compared with phenyl salicylate; the effect of the presence of a further halogen atom on the phenyl group is not important.

#### *Benzoin*s

The benzoin derivatives used as model compounds (Table IV) contained predominantly methoxyl groups as substituents. The elution volumes permit only compounds with different contents of methoxyl groups to be distinguished; no individual isomers could be discerned.

TABLE III  
GEL CHROMATOGRAPHIC BEHAVIOUR OF SALICYLIC ACID ESTERS

<i>Compound</i>	<i>Molecular weight</i>	<i>V<sub>e</sub> (ml)</i>
Phenyl salicylate	214	194.5
4-Methylphenyl salicylate	244	191.6
4- <i>n</i> -Octylphenyl salicylate	326	161.9
4-(2-Ethylhexyl)phenyl salicylate	326	162.9
4-(1,1,3,3-Tetramethylbutyl)phenyl salicylate	326	165.9
$\alpha$ -Naphthyl salicylate	264	189.6
$\beta$ -Naphthyl salicylate	264	190.6
4-Chlorophenyl salicylate	248	186.6
2,4-Dichlorophenyl salicylate	283	184.7

TABLE IV  
GEL CHROMATOGRAPHIC BEHAVIOUR OF BENZOIN DERIVATIVES

<i>Compound</i>	<i>Molecular weight</i>	<i>V<sub>e</sub> (ml)</i>
Benzoïn	212	185.6
2-Methoxybenzoïn	242	179.7
3-Methoxybenzoïn	242	185.6
4-Methoxybenzoïn	242	180.7
2,2'-Dimethoxybenzoïn	272	165.9
4,4'-Dimethoxybenzoïn	272	180.7
2,3-Dimethoxybenzoïn	272	183.7
3,4,3',4'-Bis(methylenedioxy)benzoïn	300	177.7
2,3,2',3'-Tetramethoxybenzoïn	332	177.7
2,5,2',5'-Tetramethoxybenzoïn	332	213.3
3,4,5,3',4',5'-Hexamethoxybenzoïn	392	167.9

#### *Application of gel chromatography*

The dependence of the peak height in the chromatogram on the concentration of the compound used is linear in the case of refractometric detection. If calibration plots obtained by means of model compounds are used, gel chromatography becomes suitable for the determination of the content of the active component in commercial stabilizers of the benzophenone and benzotriazole type. Its suitability for the determination of the stabilizer content in extracts from polyolefins was verified (extraction techniques were described earlier<sup>14</sup>); the method permits the determination of the losses of stabilizers that occur during processing of the polymers, thus enabling the technological process to be controlled and providing a preliminary estimate of the durability of polymeric products.

In order to extend the possibilities of analyses of light stabilizers in polymers by gel chromatography, we also investigated commercial stabilizers based on esters of unsaturated acids, *viz.*, methyl 4-methoxy- $\beta$ -methyl- $\alpha$ -cyanocinnamate (UV Absorber Bayer 318), ethyl  $\beta,\beta'$ -diphenyl- $\alpha$ -cyanoacrylate (Uvinul N-35) and 3-ethylhexyl  $\beta,\beta'$ -diphenyl- $\alpha$ -cyanoacrylate (Uvinul N-539). The technical samples analyzed were very non-uniform compared with commercial benzophenones and

benzotriazoles. Gel chromatography is not satisfactory for their determination in admixture with other stabilizers in polymer extracts. A similar conclusion was drawn from a study of several samples of UV stabilizers based on chelates of phenolic compounds and nickel(II).

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