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ANTIOXIDANTS AND STABILIZERS

LXXXVII. THE CHROMATOGRAPHIC BEHAVIOUR OF TRANSFORMATION PRODUCTS OF AN ANTIOXIDANT, N,N′-DIPHENYL-1,4-PHENYLENEDIAMINE

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SUMMARY

The antidegradant N,N′-diphenyl-1,4-phenylenediamine, its products formed by atmospheric ageing of polymeric materials and some compounds of related structure were analyzed by thin-layer and liquid chromatography. The colour reactions of the individual compounds with sulphuric acid and aqueous ammonia were also determined. The combination of these analytical methods makes possible identification of the individual compounds in complicated mixtures.

INTRODUCTION

N,N′-Disubstituted derivatives of 1,4-phenylenediamine are the strongest and most widely used inhibitors of the autoxidation and ozonolysis of elastomers. In order to elucidate the mechanism of the protective effect in the ageing of macromolecular compounds, one must identity the transformation products arising under the conditions of the stabilization process. The primary products of oxidation with various agents, including $RO_2^{\cdot}$ radicals, *i.e.*, 1,4-benzoquinone diimines, are known, but the subsequent transformation products or ozonolysis products have not yet been reliably determined.

The identification and determination of antioxidants and antiozonants and their transformation products along with other additives in vulcanized rubbers is a very complicated problem. The results obtained so far are unsatisfactory, even though modern analytical methods were applied[1–6]. The basic problem consists in the lack of suitable reference compounds, without which no characterization of the analyzed mixtures of transformation products could be achieved. Chromatographic methods are of paramount importance in the investigation of this problem.

In this study we combined thin-layer chromatography (TLC) and liquid chromatography (LC) methods with colour tests in a continuation of our work on the effect of amine stabilizers in hydrocarbon substrates[7] and on the analysis of the

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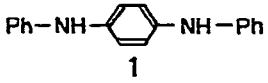
transformation products of amines after oxidation with oxygen[8]. We examined the possibility of resolving the individual transformation products of the antioxidant N,N′-diphenyl-1,4-phenylenediamine, formed by combining oxidation, hydrolysis, reduction and thermally induced reactions. Some of these reactions are also catalyzed by weak acids and proceed, *e.g.*, on the silica gel surface[9], which complicates the TLC and LC analysis and the chromatographic separation of the individual components of mixtures.



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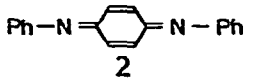

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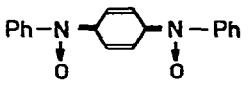

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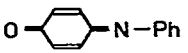

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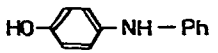

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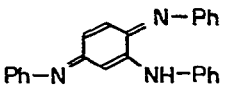

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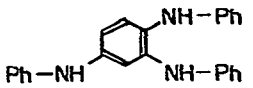

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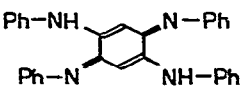

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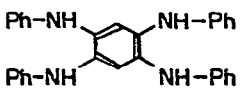

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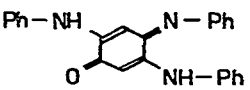

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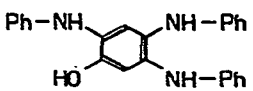

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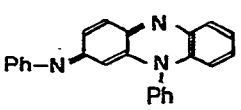

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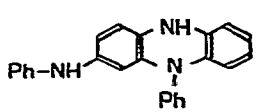

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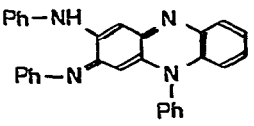

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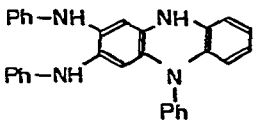

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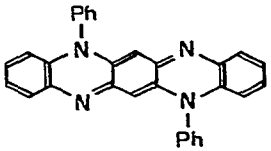

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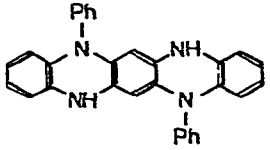

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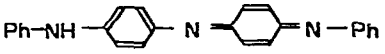

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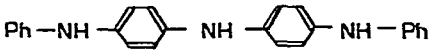

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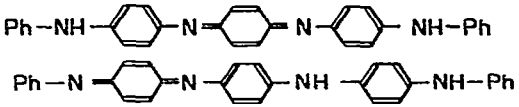

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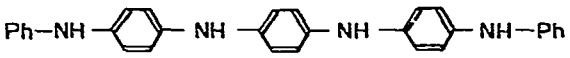

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EXPERIMENTAL

Chromatographically pure compounds were used in the analyses: N,N′-diphenyl-1,4-phenylenediamine (DPPD, 1, recrystallized from commercial Altofane DIP; S.A. Française des Matières Colorantes, St. Denis, France), N,N′-diphenyl-1,4-benzoquinone diimine N,N′-dioxide (3, prepared by oxidation[10]). For the preparation of compounds 4–21 see refs. 9,11. Compounds containing quinone diimine structures ("oxidized forms" of model compounds) were generally prepared from chloroform solutions of the corresponding aromatic amino compounds ("reduced forms" of models) by oxidation with Ag_2O. The reverse process is readily accomplished by reducing a chloroform solution of the respective quinone diimine with one part of a 10% aqueous solution of $Na_2S_2O_4$ and adding one part of ethanol.

Water-dilute H_2SO_4 (1:1) and NH_4OH (1:1) were used as detection agents in

the colour tests. Detection was performed both on a porcelain plate and on silica gel layers.

TLC was performed on silica gel precoated aluminium Silufol with a fluorescence indicator 254 nm (Kavalier, Votice, Czechoslovakia). Detection was with acid $KMnO_4$ and a UV lamp at 254 and 366 nm. Elution systems: S_1 = toluene; S_2 = toluene + 0.1% conc. NH_4OH; S_3 = toluene–diethyl ether (4:1); S_4 = toluene–diethyl ether (4:1) + 0.1% conc. NH_4OH; S_5 = chloroform–diethyl ether (4:1); S_6 = chloroform–diethyl ether (4:1)–0.1% conc. NH_4OH.

Liquid chromatography was carried out on an LC Chrom 50 chromatograph (Laboratory Instruments, Prague, Czechoslovakia), with a stainless-steel column "Separon SI VSK", Type 6009 (silica gel packing, 250 × 6 mm I.D.). Other conditions were: detection with a differential UV analyzer at 254 nm; 25°C; 2 MPa; flow-rate 99 ml/h. Elution systems: mixtures of isopropanol with hexane in various ratios and 0.1% triethylamine (impregnation of the column packing); S_7 = 2% isopropanol in hexane; S_8 = 20% isopropanol in hexane.

RESULTS AND DISCUSSION

An investigation of the mechanism of action of aminic antidegradants requires the knowledge of compounds formed under conditions of the stabilizing effect. Determination of the characteristics of defined products makes possible a better understanding of the data provided by analyses of the extracts of aged stabilized polymers. This study is concerned with a technically important stabilizer, N,N′-diphenyl-1,4-phenylenediamine (1), its primary isolable oxidation products, N,N′-diphenyl-1,4-benzoquinone diimine (2), N,N′-dioxide (3), compounds formed by consecutive transformations of 2 and with model compounds of similar structures, *e.g.*, aromatic amino derivatives (compounds 5, 7, 9, 11, 19, 21), derivatives of quinone imine or diimine (compounds 4, 6, 8, 10, 18 and 20) and compounds with a nitrogen-containing heterocycle (12–17). Some of these compounds are to a limited extent only soluble in the usual solvents. The best results were obtained with chloroform, which also does not interfere with LC analyses (it has a much shorter elution time than the compounds analysed and exhibits a very small UV peak). Compounds 8 and 21 can be dissolved only by heating the chloroform solution.

All the compounds were analyzed by TLC and LC methods. Prior to the chromatographic analyses, detection agents were chosen which were suitable for the whole set of compounds under investigation and gave a characteristic colour with the individual components. Of the agents used, aqueous ammonia and especially sulphuric acid gave the best results (Table I). Solutions of the individual compounds for analysis were deposited on a porcelain plate (unreactive material) and on silica gel plates used in TLC. In both cases the colour of the spots was observed immediately after deposition of the samples and within certain time intervals. No change in colour occurred in compounds deposited on the porcelain plate. On the silica gel plate, several compounds change their colour owing to the acidic character of silica gel combined with the effect of air. Changes occurred predominantly in reduced forms of the compounds, *e.g.*, in 7, 9, 11 and 13, which are very unstable. These aromatic amines must be deposited dropwise on the plates, simultaneously with a freshly prepared $Na_2S_2O_4$ solution, and in a stream of nitrogen.

In TLC, ammonia was added to some elution systems (S_2, S_4, S_6). This prevented formation of elongated spots and deterioration of the reproducibility of analyses (dependence on concentration) in the case of compounds possessing a pronounced basic character. The R_F values measured (Table II) show that S_4 and S_6 give the best results. Stereoisomers, *syn* and *anti*, were distinguished for compound 2 (as shown earlier by LC[12]).

Good separations of aminic and quinoid compounds 1–11 were obtained. Aminic compounds usually have a higher R_F in system S_4 than quinoid ones, while in the system S_6 an opposite sequence has been found. Compounds 12–17 (heterocyclic), which are generally less stable, yield elongated spots. This is mainly observed with the aminic (reduced) forms 13, 15 and 17. Oligomeric amine 19 was easy to identify, but amine 21 gave an elongated spot. Oxidized (quinoid) forms of these two oligomeric compounds, *i.e.*, 18 and 20, are found as a mixture of stereoisomers (two for 18, four for 30), which is reflected in chromatograms in the formation of more spots or of elongated spots.

In liquid chromatography with silica gel columns the acidity of the OH groups of the silica gel had to be adjusted by adding 0.1 % of triethylamine to the eluents. Such impregnation has already proved useful in analyses of aminic antidegradants[8,12]. By changing the isopropanol–hexane ratio in the elution system, it is possible to affect the separability of the individual compounds in a mixture of products. At a low isopropanol content, most compounds remained on the column, but the antidegradant 1 could readily be distinguished from its oxidation products 2 and 3. At higher isopropanol contents the analyses required less time; all the aromatic and quinoid compounds (with the exception of 11 and 21) were eluted, but the elution times of some compounds overlapped. Data selected for Table II were obtained by using elution mixtures containing 2 % (S_7) and 20 % (S_8) of isopropanol. These two systems complement each other fairly well, permitting the analysis even of complicated systems of compounds. The elution times suggest that with an eluent of low polarity (2 % isopropanol) most of the reduced forms of compounds (*i.e.*, aromatic amines) are retained on the column. The *syn* and *anti* stereoisomers of 2 can easily be perceived in both elution systems. Several peaks were obtained in chromatograms of compounds 18 and 20. By analogy with the demonstrasted existence of *syn* and *anti* isomers of 2 and other 1,4-benzoquinone diimines[12], the presence of geometric isomers is also reasonable in these cases. Moreover, quinone diimine 20, formed by the oxidation of amine 21, may exhibit two different positional isomers. This positional and geometrical isomerism increases the complexity of the analysis of mixtures of transformation products of arylenediamine antidegradants.

To identify the peaks of the individual compounds, elution systems with a higher content of isopropanol (4, 6 or 10 % v/v) can be employed. An example of a chromatogram obtained with 4 % isopropanol is shown in Fig. 1. However, the compounds cannot be distinguished in systems with more than 20 % isopropanol.

This investigation has revealed that, to achieve a qualitative analysis of the transformation products of antioxidant 1, one must combine liquid chromatography will several elution systems and the TLC method with specific colour tests. Liquid chromatography alone was found to be useful for quantitative determinations by means of calibration with standards of the individual compounds.

TABLE I

COLOUR TESTS

Compound	*Porcelain plate*			*Silica gel plate*					
	No reagent	H_2SO_4	NH_4OH	*Immediately after deposition*			*After 4 h*		
				No reagent	H_2SO_4	NH_4OH	*No reagent*	H_2SO_4	NH_4OH
1	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Green	Colourless
2	Orange	Carmine	Orange	Orange	Carmine	Orange	Orange	Carmine	Orange
3	Orange	Brown	Orange	Orange	Brown	Orange	Orange	Brown	Orange
4	Orange	Yellow	Orange	Orange	Yellow	Orange	Orange	Green	Orange
5	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
6	Deep orange	Blue-violet	Deep orange	Brown	Blue	Orange	Brown	Blue	Red-brown
7	Colourless	Orange	Colourless	Colourless	Colourless	Colourless	Light yellow	Colourless	Light yellow
8*	Deep orange	Violet-brown	Deep orange	Ochre	Brown-violet	Ochre	Ochre	Brown-violet	Ochre
9	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Yellow	Brown	Yellow
10	Brown-red	Brown	Brown-red	Green-brown	Deep brown	Brown	Yellow-brown	Brown	Yellow-brown
11	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Ochre	Green-brown	Ochre

12	Deep violet	Green	Deep violet	Deep violet	Deep green	Deep violet	Violet	Brown	Violet
13	Colourless	Rose	Colourless	Colourless	Red	Colourless	Orange	Wine red	Orange
14	Deep orange	Deep violet	Deep orange	Carmine	Deep violet	Deep orange	Carmine	Violet	Carmine
15	Colourless	Light green	Colourless	Colourless	Light green	Colourless	Violet-red	Violet	Carmine
16*	Rose	Blue	Rose	Deep blue	Blue	Violet	Blue-violet	Blue	Blue-violet
17	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Blue-violet	Blue	Blue-violet
18	Deep violet	Blue	Deep violet	Deep violet	Blue	Deep violet	Deep violet	Blue	Deep violet
19	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Violet	Blue	Violet
20	Carmine	Violet	Carmine	Red	Brown	Carmine	Red-orange	Light green	Red-orange
21*	Colourless	Colourless	Colourless	Light green	Light blue	Light violet	Green-grey	Green-blue	Grey-violet

* Poorly soluble in chloroform.

TABLE II

R_F VALUES IN TLC IN SYSTEMS S_1–S_6 AND ELUTION TIMES (min) IN LC IN SYSTEMS S_7 AND S_8

Compound	*TLC*						*LC*	
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
1	0.22	0.26	0.55	0.46	0.64	0.74	18.0	6.5
2	0	0.01	0.17	0.33	0.33	0.61	8.0	5.2
		0.06	0.29	0.44	0.50	0.74	9.5	5.5
3	0	0	0.04	0.08	0.48	0.73	—	10.5
4	0.02	0.04	0.31	0.37	0.45	0.68	8.7	6.0
5	0.05	0.05	0.17	0.30	0.28	0.37	9.7	7.5
6	0	0.06	0.29	0.48	0.41	0.78	8.7	5.7
7	0.33	0.37	0.62	0.66	0.66	0.79	—	6.2
8	0.18	0.62	0.71	0.67	0.76	0.84	—	7.5
9	0.35	0.35	0.61	0.70	0.66	0.80	—	6.7
10	0.07	0.12	0.50	0.51	0.65	0.82	—	7.5
11	0.17	0.18	0.50	0.52	0.66	0.71	—	—
12	0	0	0	0.08	0	0.29	23.5	7.7
13	0.06	0.14	0.15	0.16	0.50	0.65	—	8.2
14	0.01	0.06	0.25	0.54	0.48	0.83	17.0	7.0
15	0	0.30	0.50	0.10	0.30	0.35	—	16.7
16	0	0	0.01	0.31	0.67	0.93	16.5	7.5
17	0	0	0	0	0.54	0.83	11.5	7.2
18	0	0	0.07	0.07	0.49	0.71	—	6.0
			0.11	0.22	0.62	0.83		6.5
								7.2
19	0.08	0.11	0.45	0.45	0.73	0.80	39.5	8.5
20	0	0	0.02	0.11	0.37	0.66	—	6.5
			0.05	0.15	0.55	0.75		7.0
21	0.03	0.04	0.37	0.35	0.73	0.80	—	—

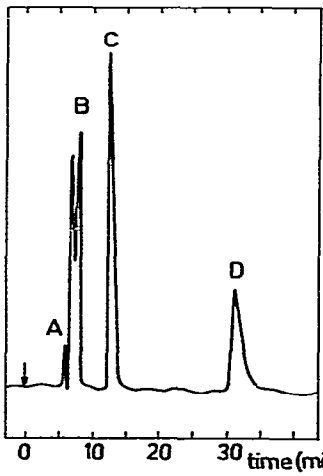

Fig. 1. Chromatogram of a mixture of DPPD (1) and derived primary transformation products 2 and 3. Eluent: 4% isopropanol in hexane. Peaks: A = chloroform; B = mixture of geometrical isomers of 2; C = 1; D = 3.

ACKNOWLEDGEMENT

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