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IDENTIFICATION AND DETERMINATION OF CERTAIN N,N'-DISUBSTITUTED *p*-PHENYLENEDIAMINE ANTIOZONANTS IN CURED STYRENE-BUTADIENE ELASTOMERS

D. THORBURN BURNS

Department of Chemistry, Loughborough University of Technology, Loughborough, Leics. (Great Britain)

and

D. F. COVEY* and E. W. JOHNSON

Rover-Triumph Division, British Leyland Motor Corp., Coventry (Great Britain)

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SUMMARY

A series of columns was examined for the separation of *p*-phenylenediamine antiozonants by gas–liquid chromatography (GLC). Silicone gum rubber was found to give the best separation of model mixtures of antiozonants.

Pyrolysis GLC was examined but was found to be unsuitable due to the complexity of the chromatogram obtained from the pyrolysis products of the major constituents of the elastomers.

An extraction procedure using acetonitrile was used to extract the antiozonants from the elastomers. A 45-min extraction time was found to be insufficient, but further extraction for 45 min yielded 97% of the total extracted after one week. Extracts from model elastomers yielded approximately 80–90% of the amount of antiozonant stated to have been present. The reasons for the apparent loss of antiozonant are described. Thus, a viable method was found for the quantitative determination of the antiozonants examined, except for N,N'-bis-(1-methylheptyl)-*p*-phenylenediamine and N,N'-bis-(cyclohexyl)-*p*-phenylenediamine.

Two thin-layer chromatographic methods were evaluated which successfully overcame the problem of differention between 217 and 26 by GLC.

INTRODUCTION

The deterioration of certain elastomers during storage or service due to reaction with atmospheric ozone is well known[1]. Antiozonants used in the elastomer industry are almost entirely based on *p*-phenylenediamine. The derivations normally used[1–3] belong to the N,N'-disubstituted series in which three basic structures are possible: (a) N,N'-diaryl *p*-phenylenediamines (diaryl), (b) N-alkyl (or cycloalkyl)-N'-

* Present address: Amoco International Laboratories, Stevenage, Herts., Great Britain.

aryl *p*-phenylenediamine (alkyl/aryl), and (c) N,N'-dialkyl (or cycloalkyl) *p*-phenylenediamines (dialkyl). The antiozonants in main use belong to the dialkyl and alkyl/aryl classes. A further class of antiozonants now commercially available, is based on dihydroquinoline, a typical useful member being 6-dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline.

A major problem with the above antiozonants is that they cause staining by contact and migration. Non-staining materials of current interest are tributyl thiourea[4] and benzoxolans[5].

The method of ensuring adequate protection in service consists of accelerated ageing of the elastomer by exposure to an ozone-enriched atmosphere for a certain period of time. The sample is maintained in a stressed condition for 24 h in the normal atmosphere and is then subjected to 25 pphm ozone at 100°F for 5 h (ref. 6). For this reason, it was hoped to develop a rapid analytical technique to determine the concentration of antiozonant in cured elastomers and correlate composition and performance in service or storage.

The analysis of a cured elastomer for any minor constituent presents serious problems. This applies particularly to antiozonants since they are present at the 1% level. To date, the deterioration of antiozonants has basically involved extraction processes which may take up to 16 h to complete. Loss of material by reaction or decomposition is possible during the extraction, and extracts usually contain processing oils, accelerators or other unreacted constituents which may interfere with subsequent analysis. A summary of solvents used for extraction and extraction times is shown in Table I.

TABLE I

SOLVENTS AND EXTRACTION TIMES

Extraction solvent	*Extraction time*	*Reference*
95% methanol or ethanol in an extraction cup	16 h	7
Acetone (room temperature)	10 min (spot test)	8
Benzene, reflux	30 min	9
Ethanol, reflux	16 h	10
Acetone, reflux	16 h	11
Acetonitrile, cold shaking	30 min	12

Several methods have been used to increase sample surface area to weight ratios prior to extraction. These include microtoming[13], grinding the elastomer after cooling with solid carbon dioxide[14], and the use of a Wiley mill[15].

The identification of compounding ingredients without solvent extraction, based on earlier work of Stahl[16], involves the "thermal extraction" of volatile substances from samples[17], with deposition onto a thin-layer chromatography (TLC) plate which is then developed in the normal manner. McSweeney[17] applied the method to the detection of mercaptobenzothiazole, 4-isopropylaminodiphenylamine and polymeric antioxidants. Zijp[18] and Miksch and Prolss[19] laid the foundation for the TLC analysis of antiozonants. A comprehensive review of TLC identification of elastomer compounding ingredients was published by Kreiner[20] in 1971. A particularly

useful paper is that by Kreiner and Warner[21]. Identification of phenyl-2-naphthylamine and N-phenyl-N-isopropyl-*p*-phenylenediamine by TLC (using aluminium oxide layers) and subsequent spectrophotometric quantitative determination has been published by Vinogradova and co-workers[22]. A method described by Cabot Carbon Ltd.[23] distinguishes between staining and non-staining components.

Wise and Sullivan[11] and Emery and Koerner[24] have analysed vulcanizate extracts by gas chromatography but no results on pyrolysis gas chromatography appear to have been reported. The present work has examined this possibility which was discarded in favour of direct gas chromatography and TLC of acetonitrile extracts.

APPARATUS AND MATERIALS

A Perkin-Elmer F11 Mk.2 single-column gas chromatograph with flame ionisation detector (FID) was used.

Pyrolysis was carried out with a Pye Unicam Curie point pyrolyser or a Perkin-Elmer platinum filament pyrolyser.

The antiozonants examined are listed in Table II.

TABLE II

LIST AND ABBREVIATIONS OF ANTIOZONANTS EXAMINED

Chemical name	*Abbreviation*	*Trade name*	*Supplier*
N,N′-Bis-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine	88	UOP 88	Universal Matthey (Enfield, Great Britain)
N,N′-Bis-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine	17	Santoflex 17	Monsanto Chemicals (London, Great Britain)
N,N′-Bis-(1-methylheptyl)-*p*-phenylenediamine	288	UOP 288	Universal Matthey
N,N′-Bis-(1-methylheptyl)-*p*-phenylenediamine	217	Santoflex 217	Monsanto Chemicals
N,N′-Bis-(1,4-dimethylpentyl)-*p*-phenylenediamine	77	Santoflex 77	Monsanto Chemicals
N-(1-Methylheptyl)-N′-phenyl-*p*-phenylenediamine	688	UOP 688	Universal Matthey
N,N′-Bis-(cyclohexyl)-*p*-phenylenediamine	26	UOP 26	Universal Matthey
N-(1,3-Dimethylbutyl)-N′-phenyl-*p*-phenylenediamine	13	Santoflex 13	Monsanto Chemicals
N-Isopropyl-N′-phenyl-*p*-phenylenediamine	IPPD	Santoflex IP	Monsanto Chemicals
6-Ethoxy-2,2,4-trimethyl-1,2,-dihydroquinoline	AW	Santoflex AW	Monsanto Chemicals
6-Dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline	DD	Santoflex DD	Monsanto Chemicals

PRELIMINARY STUDIES

Synthetic mixtures (1% of each component in benzene) were examined under various conditions on the following 2M columns: 2% Versamid 930 on Chromosorb W AW DMCS, 80–100 mesh; 25% Apiezon L on Chromosorb P; 10% silicone grease on Teflon 6, 40–60 mesh; 5% Carbowax 20M with 0.3% NaOH on 0810 Chromosorb

W, 80–100 mesh; 3% silicone gum rubber E 301 on 0810 Chromosorb W, 80–100 mesh. This last column appeared to be the most suitable for the quantitative analysis of *p*-phenylenediamine antiozonants. The peaks were fairly symmetrical and appeared suitable for quantitative treatment. Examination of retention data (see Table III) shows that if an elastomer were analysed it would be difficult to identify positively for example 217. It would be possible to mistake 217 for 26 and *vice versa*. Thus before quantitative analysis was carried out, some other means of positive identification would be necessary, *e.g.* separation on another gas–liquid chromatographic (GLC) column, or qualitative detection using TLC.

TABLE III

RETENTION DATA FOR ANTIOZONANTS OBTAINED USING A SILICONE GUM RUBBER COLUMN

Injection block temperature, setting 7 (approx. 325°C); sample, 0.2 μl of 2% antiozonant in benzene; oven temperature, 250°C; fuel, air at 23 lb./sq.in., hydrogen at 15 lb./sq.in.; carrier gas, nitrogen at 11 lb./sq.in.; recorder, 2.5 mV f.s.d.; chart speed, 5 mm/min.

Antiozonant (abbreviated name)	*Retention time (min after benzene)*
88 and 17 (same composition, different source)	3.7
288 and 217 (same composition, different source)	5.9
77	2.8
688	7.6
26.	5.9
13	3.9
IPPD	2.1
DD	0.8
AW	Three unresolved peaks. Detected at very high sensitivity at 0.8 min, 1.2 min and 3.8 min

PYROLYSIS

Attempts were made to examine cured elastomers by pyrolysis GLC using both Curie point (15 sec at 980°C) and platinum filament (15 sec at 750°C) systems.

The pyrolysis products from cured elastomers yielded complex chromatograms, from which it was extremely difficult to ascertain the presence or absence of antiozonants. The application of direct pyrolysis to a cured elastomer to yield a quantitative analysis of the antiozonant present was considered to be impracticable and extraction procedures were considered.

SOLVENT EXTRACTION STUDIES

The relative FID response of antiozonants 13, 688, 288 and 217 against IPPD were determined so that internal standardisation could be used when examining cured elastomers A–H (Table IV).

TABLE IV

COMPOSITION OF THE CURED* ELASTOMERS EXAMINED QUANTITATIVELY BY GLC

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Cariflex 1605**							150	150
Circosol 380							10	10
Antilux							4	4
Zinc oxide							5	5
Stearic acid							1	1
Vulcafor F	Base = 256 parts by weight of samples A–F						1.5	1.5
TMTD							0.4	0.4
288							1.0	2.0
13	1.5	3.0	—	—	—	—	—	—
688	—	—	1.5	3.0	—	—	—	—
IPPD	—	—	—	—	1.5	3.0	—	—

* Elastomer cured at 307°F for 12 min.
** Cariflex 1605: 100 parts SBR plus 50 parts of carbon black.

The relative response was measured by dissolving 0.5 g of the antiozonant under examination in 10 ml of the appropriate internal standard solution also containing 0.5 g standard. Approx. 0.3 μl of this solution were chromatographed using the conditions given in Table III. Peak areas were measured using a Honeywell Mk.2 precision integrator.

During the initial GLC work a conventional 1-μl syringe (a Hamilton Model 7101 syringe fitted with Chaney adaptor) was used for injecting solutions on to the column. It was found that during the time necessary to eject the sample from the syringe differential volatilisation of the antiozonant under examination and the internal standard occurred. Thus, since adequate manual control of the time during which the needle was in the injection block could not be achieved, the ratio of the areas of the peaks was not constant. The problem was overcome by employing a Hamilton CR 700-20 syringe. This syringe uses a plunger device whereby the needle is rapidly pushed through the injection septum and as soon as it is within the block, a button on the syringe can be pressed, releasing the plunger. The sample is ejected with considerable velocity, before appreciable volatilisation can occur from the needle.

The plunger type syringe described above gave results which were acceptable with regard to repeatability for successive injections; the coefficients of variation on count ratios were 0.2–0.5% on six results.

The elastomer was finely divided by processing through a conventional 12-in. roller mill at room temperature to form a web-like crumble. 5 g of the elastomer crumble were extracted into 25 ml of acetonitrile over 45 min using an automatic shaker. The acetonitrile extract was decanted through a Whatman No. 542 filter. The elastomer was extracted with a further 25-ml portion of acetonitrile for 45 min. The mixture was filtered and the two filtrates combined. The solution was carefully evaporated in a fume cupboard, to a volume of 10 ml, on a hot plate maintained at 60°C. The remaining solution was cooled to −20°C in a fridge and maintained at this temperature for 20 min. This cooling step results in the separation of the processing oils from the extract. The supernatant was decanted, and evaporated in a beaker to dryness

on a hot plate at 60°C. After cooling the beaker and residue, 10 ml of the appropriate internal standard solution containing approx. 0.5 g of internal standard, were added. The resulting solutions were evaporated to a total volume of approximately 5 ml. Aliquots (approximately 0.4 μl) were chromatographed.

If necessary, the internal standard solution concentration was reduced such that 10 ml contained approx. 0.2 g of antiozonant. This was to ensure that the integration counts for both the internal standard and the antiozonant were obtained on the same attenuation range of the FID amplifier.

Results and discussion

The results obtained are tabulated in Table V.

TABLE V
ANALYSIS OF CURED ELASTOMERS

Elastomer code	*Antiozonant present*	*Internal standard*	*Relative response**	*Amount in elastomer (%, w/w)*	*Amount found (%, w/w)*	*Apparent recovery (average) (%)*
A	13	IPPD	1.15	0.58	0.44, 0.49	80.1
B	13	IPPD	1.15	1.16	0.91, 0.96	80.6
C	688	IPPD	0.53	0.58	0.47, 0.49	82.7
D	688	IPPD	0.53	1.16	1.02, 1.00	87.1
E	IPPD	217	1.25	0.58	0.50, 0.51	87.1
F	IPPD	217	1.25	1.16	0.94, 0.91	79.7
G	288	IPPD	0.79	0.58	0.48, 0.49	85.3
H	288	IPPD	0.79	1.16	1.00, 1.01	86.6

* Relative response $= \dfrac{\text{area of antiozonant peak/g}}{\text{area of internal standard peak/g}}$.

Previous work on the efficiency of extraction by reflux with benzene[9], shows a plot or reflux times *versus* per cent recovery for N-(1,3-dimethylbutyl)-N′-phenyl-*p*-phenylenediamine in an oil-extended SBR elastomer. The maximum recovery was 89%, achieved after 30-min reflux. Carlson and co-authors[12] used an extraction time of 30 min with acetonitrile, but the extracts were only examined qualitatively. During the present quantitative work, an extraction of 45 min with acetonitrile yielded approximately 88% of the total maximum extracted after one week. A further extraction for 45 min using another 25 ml of acetonitrile yielded 97% of the total maximum extracted after one week. Detailed results are shown in Table VI for samples E and F.

The reactions of an antiozonant during the curing process result in a diminution in the amount of the antiozonant from that originally present. Because of the reactive nature of the antiozonants, the surface characteristics of the reinforcing agent, and the type and reactivity of the vulcanization agents, it is possible to consume a large percentage of the antiozonant during the curing process. The extent of this loss can be minimized by proper selection of the components of any particular elastomer formulation. However, loss of antiozonant is inevitable.

The type of carbon black used is particularly important since the oxygen contents of the various commercially used carbon blacks vary considerably. A direct relationship between the oxygen content of the carbon black and the extractable anti-

TABLE VI

EFFECT OF EXTRACTION TIME ON RECOVERY OF N-ISOPROPYL-N′-PHENYL-p-PHENYLENEDIAMINE FROM AN SBR ELASTOMER USING ACETONITRILE

Extraction details	*IPPD in extract from E (%)*	*IPPD as per cent of total extracted after 1 week*	*IPPD in extract from F (%)*	*IPPD as per cent of total extracted after 1 week*
(a) 45 min using 25 ml of acetonitrile	0.44	88	0.82	87
(b) Further 45 min using 25 ml of acetonitrile	0.48	96	0.91	97
(c) After further 1-week extraction using 25 ml of acetonitrile	0.50	100	0.94	100

ozonant was shown by Studebaker and co-workers[25]. Cox[26] has demonstrated that the amount of UOP 88 extractable from an SBR stock after vulcanization varied from 60 to 100% of that originally added, depending mainly upon the amount and type of carbon black used. The use of channel blacks causes greater loss of antiozonant than does the use of thermal and furnace blacks, which may be related to the higher oxygen content in the former[26].

The effect of the curing system is also important. It has been shown[27] that thiazole-accelerated, sulphur-cured elastomers containing antiozonant are more ozone resistant than elastomers cured using thiuram disulphides or diphenylguanidine accelerators at the same initial concentration of antiozonant. The variation in ozone resistance of the cured elastomers was again related to the amount of extractable antiozonant[27]. The effect of storage time on extractable antiozonant is difficult to assess. Two changes occurring with regard to the antiozonant are possible, namely (a) the migration of the antiozonant to the surface and (b) the oxidation of the antiozonant by molecular oxygen within the elastomer matrix[26]. The second factor has been shown to be important in elastomers stored for periods of one year, reflected in decreased antiozonant extractability and decreased ozone resistance. The effect is similar to that which occurs on over-ageing of specimens before exposure[28].

With regard to sample preparation, it would seem logical that the factors which could influence the amount of extractable antiozonant are: (a) surface area of the prepared sample; (b) heat generated during the milling or other preparatory steps; and (c) the time lapse between sample preparation and extraction. This effect could be minimised by storing the samples under nitrogen. Little deterioration of the anti-ozonants could be detected by infrared inspection on standing extracted materials in the laboratory atmosphere for 24 h.

The recovery, 95%, using 2 × 45 min extraction times, is sufficient for most purposes, and the overall procedure is simple and rapid.

The analyst can only determine the amount of extractable antiozonant, but it is important to note that the protection afforded a cured elastomer is dependent not upon the amount of the antiozonant originally used in the formulation but on the

extractable antiozonant present in the cured elastomer, and hence the analytical data are meaningful for stability studies. As indicated earlier, before quantitative GLC analysis is carried out on an unknown elastomer extract, it may be necessary to obtain positive identification of the antiozonant, or antiozonants present. TLC is a useful method for obtaining this information and the procedure has been applied earlier to the identification of many of the antidegradants present in elastomers[20–23].

Systems have been evaluated for the examination of elastomer extracts in the present study.

THIN-LAYER CHROMATOGRAPHY

Two TLC procedures were examined in detail, namely (a) a one-dimensional development procedure followed by spraying with benzoyl peroxide solution[22], and (b) a one-dimensional development of duplicate samples followed by spraying one duplicate with antimony pentachloride solution and the other duplicate with bismuth nitrate solution[23].

TLC on aluminium oxide

TLC was carried out on TLC precoated plates Camag aluminium oxide DSF-B, 200 × 200 mm. The bismuth nitrate solution used for spraying was prepared by dissolving 5 g bismuth nitrate (AnalaR grade) in 100 ml 1 *M* nitric acid. The antimony pentachloride was prepared by adding 20 g antimony pentachloride (AnalaR grade) to 100 ml carbon tetrachloride. The acetone and ethyl acetate used were both AnalaR grade.

Procedure. 2% solutions of antiozonants used as standards were prepared in benzene. The elastomers were extracted using the procedure described above, although for qualitative work a single 10-min extraction was used.

The precoated TLC plates were activated by heating in an oven for 1 h at 105°C. After cooling in a desiccator, approx. 5 μl of each sample were applied to the plate using a Drummond micropipette. The original was set at 2 cm from the bottom of the glass plates. The spotted plates were allowed to stand in the laboratory atmosphere, for 5 min, to dry.

The chromotank atmosphere was saturated with eluent vapour, by lining the tank with filter paper which was saturated with *n*-heptane–ethyl acetate (100:20, v/v), the ends of the filter paper sheets being immersed in a small quantity of the solvent.

The plates were placed in the tank ensuring that the saturating solvent did not reach the aluminium oxide layer which would have resulted in the premature start of the chromatographic run; a 1-cm strip of the aluminium oxide layer had been scraped off prior to placing the plate in the tank. After 30 min, sufficient solvent was added to allow the chromatographic run to begin. The solvent front was allowed to run for 20–30 min, a distance of approx. 10 cm from the origin line. The plate was removed and dried for 5 min at room temperature followed by 5 min at 105°C. After cooling, one chromatogram was covered with aluminium foil and the duplicate sprayed with bismuth nitrate solution. The freshly developed chromatogram was covered with the the aluminium foil and the duplicate sprayed with antimony pentachloride solution. The plates were dried for 10 min at room temperature followed by 5 min at 105°C.

During the drying stage the colours developed and the approximate R_F values were determined from the centre of the spot.

The colours observed are reported in the following sequence: (a) prior to spraying, (b) just after spraying, (c) after 10 min at room temperature, (d) after a further 5 min at 105 °C.

Results and discussion. Observations of colour reactions and R_F values for the reference solutions and extracts have been prepared and are shown in Tables VII and VIII. The antiozonants present in the elastomers A, B, C, D, E, F, G and H are shown in Table V. Elastomer I was an SBR elastomer with the same base composition as A–H but the antiozonants present were: 288, 13, 688, and IPPD. All the former were present at a concentration of 0.57% (w/w) in the elastomer. A wide range of colour reactions occurred with sufficient variation in R_F values to enable identification of most of the antiozonants. The R_F values and colour reactions for 77 and 217 are similar, hence positive differentiation between the two is difficult. However, it is not difficult to identify these two antiozonants by GLC.

The procedure to be adopted for identification of an antiozonant in an extract should consist of three steps, namely: (a) Determine R_F values and colour reactions of the antiozonant. (b) Compare these data with the references and hence a list of possible antiozonants can be drawn up. (c) Repeat the test with both samples and references. This will generally enable a positive identification of the antiozonant extracted from the elastomer.

The tables of R_F values and colour reactions should only be considered as a guide. Comparison of data in Tables VII and VIII shows that quite a significant variation in R_F value for an antiozonant can occur, even with strict control of experimental parameters. For this reason, it is essential that step (c) above is carried out. A combination of the TLC procedure described above and GLC enables a qualitative detection and quantitative estimation of the antiozonants tabulated in Table V.

TLC on silica gel

TLC was carried out on precoated silica gel Camag DF-B plates, 200 × 200 mm. The benzene and acetone used were AnalaR grade. The spraying reagent consisted of 4 g benzoyl peroxide in 100 ml benzene. The samples used were solutions of commercial-grade antiozonants (1 %, w/w) in benzene.

Procedure. The plates were conditioned as before. Approximately 5 μl of each sample were applied to the plate using a Drummond micropipette. The spotted plates were allowed to stand in the laboratory atmosphere for 5 min to dry. The chromotank atmosphere was saturated with solvent as before. The development distance was 15 cm.

Benzene–acetone–conc. ammonium hydroxide (100:5:0.1, v/v) was used as the solvent for the one-dimensional development of the antiozonants. This system is described by Kreiner and Warner[21]. After evaporation of the developing solvent, the antiozonants were indicated by spraying with the benzoyl peroxide solution.

Results and discussion. The R_F values and colour reactions of the antiozonants examined are shown in Table IX.

A satisfactory separation of the antiozonants examined was achieved except for the samples containing 17 and 13.

The separation of six of seven *p*-phenylenediamine antiozonants and two hydroquinoline-type antiozonants was achieved on silica gel TLC plates using the parameters described above. Separation of 17 and 13 was not achieved. This creates a problem since these antiozonants are not sufficiently separated during GLC analysis

TABLE VII

IDENTIFICATION OF ANTIOZONANTS BY TLC ON ALUMINIUM OXIDE

Antiozonant	*Bismuth nitrate*					*Antimony pentachloride*			
	$R_F \times 10$	*Prior to spraying*	*Just after spraying*	*Plus 10 min at room temperature*	*Plus 5 min at 105°C*	$R_F \times 10$	*Just after spraying*	*Plus 10 min at room temperature*	*Plus 5 min at 105°C*
A 217	4.8	Pink	Pink	Pink	Pink	4.8	Mauve-pink	Mauve-pink	Mauve-pink
B 88	5.9	Pink	Pink	Pink	Pink	5.8	Mauve-pink	Mauve-pink	Mauve-pink
C 77	4.5	Pink	Pink	Pink	Pink	4.3	Mauve-pink	Mauve-pink	Mauve-pink
D 13	3.4	Yellow	Blue	Blue	Blue	3.4	Purple	Purple	Mauve
E IPPD	2.6	Yellow-green	Blue	Blue	Blue	2.6	Red-brown	Purple	Mauve
F DD	3.8	Buff	Buff	Yellow	Yellow	3.8	Yellow-brown	Yellow-brown	Yellow-brown
G AW	5.8	Light buff	Light buff	Light buff	Light buff	5.8	Light yellow	Light brown	Light brown
H 688	3.9	Yellow	Blue	Blue	Blue	3.9	Red-purple	Purple	Purple
K 26	2.8	Pink	Pink	Pink	Pink	2.9	Pink	Pink	Pink

TABLE VIII

IDENTIFICATION OF ANTIOZONANTS BY TLC ON ALUMINIUM OXIDE

Antiozonants extracted from cured elastomers and internal standard added.

Elastomer reference	*Bismuth nitrate (Series 1)*					*Elastomer reference*	*Antimony pentachloride (Series 2)*			
	R_F *of A.0 ×10*	*Prior to spraying*	*Just after spraying*	*Plus 10 min at room temp.*	*Plus 5 min at 105°C*		R_F *of A.0 ×10*	*Just after spraying*	*Plus 10 min at room temp.*	*Plus 5 min at 105°C*
A1	2.8	Green	Pink	Pink	Pink	A2	2.8	Green	Pink	Pink
	2.2	Grey	Blue	Blue	Blue		2.3	Grey	Brown	Blue-green
B1	2.8	Green	Pink	Pink	Pink	B2	2.8	Green	Green	Buff
	2.4	Mauve	Blue	Blue	Blue-green		2.4	Mauve	Mauve	Mauve
C1	3.2	Green	Mauve	Pink	Pink	C2	3.2	Green	Buff	Buff
	2.5	Mauve	Blue	Green	Blue-green		2.4	Mauve	Mauve	Pink-purple
D1	3.3	Green	Mauve	Pink	Pink	D2	3.2	Green	Mauve-pink	Buff
	2.4	Mauve	Blue	Green	Blue-green		2.4	Mauve	Buff	Mauve
E1	5.5	Pink	Pink	Pink-brown	Brown	E2	5.5	Pink	Pink	Pink
	3.3	Blue	Mauve	Brown	Green		3.2	Blue	Mauve	Mauve
F1	5.4	Pink	Pink	Pink	Green	F2	5.3	Pink	Pink	Pink
	3.3	Blue	Mauve	Mauve	Green		3.2	Blue	Mauve	Mauve
G1	4.4	Mauve	Pink	Pink	Pink	G2	4.3	Pink	Pink	Pink
	2.5	Green	Blue	Blue	Blue		2.5	Red	Purple	Mauve
H1	4.4	Mauve	Pink	Pink	Pink	H2	4.3	Pink	Pink	Pink
	2.6	Green	Blue	Blue	Blue		2.5	Red	Purple	Mauve
	4.5	Mauve	Blue	Blue	Pink		4.6	Mauve	Pink	Pink
I1	3.5	Green	Pink	Pink	Mauve	I2	3.5	Green	Brown	Brown
	2.5	Green	Mauve	Mauve	Mauve		2.5	Green	Buff	Buff

TABLE IX

SEPARATION OF *p*-PHENYLENEDIAMINE ANTIOZONANTS BY ONE-DIMENSIONAL TLC ON SILICA GEL PLATES

Antiozonant	$R_F \times 10$	*Colour reaction*	*Antiozonant*	$R_F \times 10$	*Colour reaction*
217 or 288	2.80	pink	DD	5.40	green
88 or 17	6.25	yellow	AW	8.97	brown
77	1.90	pink	688	7.20	brown
13	6.18	brown-yellow	26	1.03	pink
IPPD	3.46	brown-yellow			

to be positively identified. Thus if this TLC method indicated the presence of 17/13 a further TLC step would be required, for example, by separation on aluminium oxide. Alternatively, the plate may be chromatographed in a second direction using cyclohexane–acetone–conc. ammonium hydroxide (100:5:0.1, v/v), as described by Kreiner and Warner[21], who reported that this procedure was useful in obtaining improved resolution of antiozonants–antioxidants of the multi-component reaction mixture types, for example, the octylated and nonylated diphenylamines.

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