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Note

Behaviour of *p*-phenylenediamine protecting agents in thin-layer chromatography

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The identification and determination of accelerators and protecting agents in vulcanizates has always been one of the more difficult problems in rubber analysis. Various methods have previously been used based on specific colour reactions, column and paper chromatography and absorption spectroscopy, which were often non-specific and time consuming. For these reasons, thin-layer chromatography has been used more recently for the identification and determination of the protecting agents¹⁻¹⁷, since this technique is more rapid, gives better separations and more certain identification, and can easily be coupled with other physico-chemical methods.

N-Substituted derivatives of *p*-phenylenediamine are among the most efficient protecting agents for vulcanizates and the greatest structural variety is encountered in this group. The main types of *p*-phenylenediamine derivatives used in the rubber industry are alkyl-NH-C₆H₄-NH-alkyl, aryl-NH-C₆H₄-NH-alkyl, and aryl-NH-C₆H₄-NH-aryl. At present, there are sufficient convincingly data to conclude that: substitution at both nitrogen atoms with small alkyl groups leads to the maximum activity, but at the same time high volatility and water solubility and an irritant effect restrict their utility; increases in the chain-lengths of the substituents diminish the above disadvantages, while preserving a high efficiency; substitution with two aryl groups decreases the protecting activity (particularly the anti-ozonant effect) and larger aromatic radicals may adversely influence the solubility in rubber; the most satisfactory compromise is probably obtained substituting an alkyl group on the first amino group and an aryl group on the second; and further substitution of the aromatic ring usually decreases the protecting activity.

The usefulness of these protecting agents in the rubber industry together with the advantages of thin-layer chromatography stimulated the authors to study in detail the behaviour of *p*-phenylenediamine derivatives on chromatographic thin layers.

EXPERIMENTAL

The *p*-phenylenediamine derivatives examined are listed in Table I.

Silica gel G (according to Stahl, Type 60), silica gel H (according to Stahl, Type 60), and pre-coated chromatoplates with aluminium oxide GF₂₅₄ (Type E) (all from E. Merck, Darmstadt, G.F.R.) were tested as thin layers.

In general, reasonably constant R_F values are obtained if the layer thickness

TABLE I
***p*-PHENYLENEDIAMINE DERIVATIVES STUDIED**

Symbol Formula

S-1	
S-2	
S-3	
S-4	
S-5	
S-6	
S-7	
S-8	
S-9	
S-10	
S-11	
S-12	
S-13	
S-14	
S-15	

is between 200 and 300 μm , the sample size does not exceed the layer capacity and the elution is performed at constant temperature in a saturated atmosphere. In our work, we used chromatographic layers of 250–300 μm thickness, the sample size was

about 50 μg and the elution was conducted in a saturated atmosphere at room temperature.

The slurry for each layer was prepared from 40 g of adsorbent, 15 g of anhydrous calcium sulphate and 90 ml of water. The applied layer was dried at room temperature and before use was activated for 30 min at 105° in an oven; activated plates were cooled in a desiccator.

The eluents used are listed in Table II; they were prepared from solvents of chromatographic quality. Elution was performed to a distance of 10 cm each time.

The spots were rendered visible with the spray reagents listed in Table III, and applied, as a rule, at room temperature.

TABLE II
ELUENTS TESTED

<i>Symbol</i>	<i>Components</i>	<i>Proportions (v/v)</i>	<i>Reference</i>
E-1	Isopropanol	52	18
	Chlorobenzene	33	
	Water	10	
	Ammonia (25% solution)	5	
E-2	Water	50	18
	<i>n</i> -Butanol	40	
	Acetic acid	10	
E-3	<i>n</i> -Heptane	100	7
	Ethyl acetate	20	
E-4	Benzene	100	9
	Ethyl acetate	5	
	Acetone	2	

TABLE III
SPRAY REAGENTS TESTED

<i>Symbol</i>	<i>Components</i>	<i>Remarks</i>	<i>References</i>
R-1	<i>p</i> -Diazobenzenesulphonic acid, 0.1% in 25% acetic acid	Previous coupling is possible	7, 18
R-2	2,6-Dichloro- <i>p</i> -benzoquinone-4-chloroimide, 0.2% in ethanol	At room temperature	9
R-3	Benzoyl peroxide, 4% in benzene	At room temperature	2, 4
R-4	Sodium nitrite, 10% in water, acidulated with hydrochloric acid	At room temperature	3
R-5	Formaldehyde solution, 40% with sulphuric acid, 1:4 ratio	Heated at 120°	8
R-6	Cobalt(II) chloride (CoCl ₂ ·6H ₂ O), 2% in water	Heated at 105°	19

The characteristic of each *p*-phenylenediamine derivative was noted by its specific R_F value and the colour of the spots.

RESULTS AND DISCUSSION

In order to make use of a thin-layer chromatographic procedure as an independent method, the customary starting point is the finding of spray reagents that give specific colours with each of the substances being studied. Although there seems to be no scarcity of spray reagents for antioxidants²⁰, the finding of a reagent that differentiates between substances with similar structures, such as *p*-phenylenediamine protecting agents, proved not to be a simple task. The most important spray reagents investigated are listed in Table III and the specific coloration obtained with each of the *p*-phenylenediamines studied are listed in Table IV.

According to Table IV, the most suitable spray reagents for our purpose seem

TABLE IV
COLOURS OBTAINED FROM *p*-PHENYLENEDIAMINE DERIVATIVES WITH VARIOUS SPRAY REAGENTS

<i>p</i> -Phenylenediamine derivative	Spray reagent					
	R-1	R-2	R-3	R-4	R-5	R-6
S-1	Beige-brownish	Dark grey	Brown-greyish	Brown-yellowish	Yellow-greyish	Brown-greyish
S-2	Violet-blueish	Grey-blueish	Cyclamen-greyish	Beige-brownish	Grey	Violet-greyish
S-3	Orange-brownish	Grey-blueish	Beige-greyish	Beige-brownish	Grey	Brown-greyish
S-4	Cyclamen	Violet-greyish	Pink-greyish	Beige-brownish	Grey	Cyclamen
S-5	Cyclamen	Violet-greyish	Pink-greyish	Beige-brownish	Grey	Cyclamen
S-6	Cyclamen	Violet-greyish	Pink-greyish	Beige-brownish	Grey	Cyclamen
S-7	Cyclamen	Violet-greyish	Pink-greyish	Beige-brownish	Grey	Cyclamen
S-8	Cyclamen	Violet-greyish	Pink-greyish	Beige-brownish	Grey	Cyclamen
S-9	Blue-greyish	Brown-greenish	Brown-greyish	Red-brownish	Yellow-greyish	Blue-greyish
S-10	Blue-greyish	Brown-greenish	Bright brown	Red-brownish	Yellow-greyish	Blue-greyish
S-11	Blue-greyish	Brown-greenish	Bright brown	Red-brown	Beige-greyish	Blue-greyish
S-12	Blue-greyish	Green-brownish	Bright brown	Red-brownish	Beige-greyish	Blue-greyish
S-13	Blue-greenish	Brown-yellowish	Brown-orange	Brown-reddish	Beige-greyish	Green-blueish
S-14	Cyclamen-violet	Yellow-greenish	Brown	Beige-brownish	Beige-greyish	Blue-greenish
S-15	Pink-orange	Orange-brownish	Pink-beige	Beige-greyish	Grey	Grey-greenish

to be *p*-diazobenzenesulphonic acid (well-known from paper chromatography¹⁸) and 2,6-dibromo-*p*-benzoquinone-4-chloroimide^{3,9}, which, by coupling, give azo and quinoneiminic dyes, respectively, absorbing light in sufficiently different spectral regions.

The next step was the selection of a suitable stationary phase for the thin layer. The testing of all of the eluents and substances on the three types of thin layer led to the conclusion that the most suitable stationary phase was silica gel G. Table V gives

TABLE V

BEHAVIOUR OF SOME *p*-PHENYLENEDIAMINE DERIVATIVES ON VARIOUS CHROMATOGRAPHIC THIN LAYERS

<i>p</i> -Phenylenediamine (PPD) derivatives		Eluent	R_F		
Symbol	Name		Silica gel G	Silica gel H	Aluminium oxide GF ₂₅₄
S-7	N,N'-Di-2-octyl-PPD	E-1	0.88	0.66	0.91
		E-3	0.17	0.38	0.78
S-9	N-Phenyl-N'-isopropyl-PPD	E-1	0.88	0	0.95
		E-3	0.46	0.45	0.33
S-15	N,N'-Di-2-naphthyl-PPD	E-1	0.90	0	0.75
		E-3	0.19	0.14	0.16

results for three derivatives with structures as different as possible for illustrative purposes. Aluminium oxide gave R_F values that were too low or too high, and frequently the spots were tailed or diffuse zones, which affects the precision of the determination (Fig. 1). Silica gel H gave low R_F values and, in some instances, the tested substance was not separated.

In the selection of eluents, mixtures with basic, acidic and neutral properties were tested. Of the large number of tests carried out, only the results obtained on silica gel G, the most suitable stationary phase, are presented here. Table VI shows that the

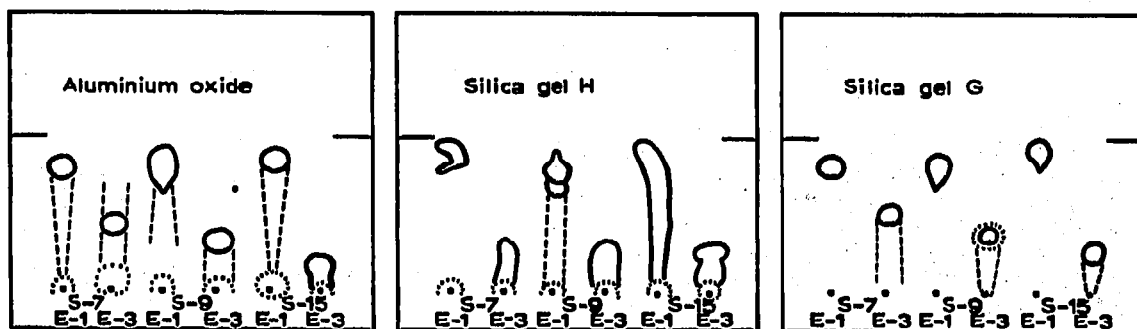


Fig. 1. Comparison of the results obtained with different thin layers. *p*-Phenylenediamine derivatives and eluents are identified as in Tables I and II.

TABLE VI

CHROMATOGRAPHIC BEHAVIOUR OF *p*-PHENYLENEDIAMINE DERIVATIVES ON SILICA GEL G THIN LAYERS

<i>p</i> -Phenylenediamine (PPD) derivative		Eluent			
Symbol	Name	E-1	E-2	E-3	E-4
S-1	<i>p</i> -Phenylenediamine	0.53	0.43	0	0
S-2	N,N'-Dimethyl-PPD	0.54	0.54	0.32	0.58
S-3	N,N'-Diethyl-PPD	0.91	0.82	0.40	0.60
S-4	N,N'-Diheptyl-PPD	0.84	0.84	0.14	0
S-5	N,N'-Di-(1,4-dimethylpentyl)-PPD	0.84	0.84	0.12	0
S-6	N,N'-Di- <i>n</i> -octyl-PPD	0.86	0.84	0	0
S-7	N,N'-Di-2-octyl-PPD	0.88	0.88	0.17	0.20
S-8	N,N'-Di(1-ethyl-3-methylpentyl)-PPD	0.85	0.85	0.12	0.12
S-9	N-Phenyl-N'-isopropyl-PPD	0.88	0.67	0.46	0.49
S-10	N-Phenyl-N'-1,3-dimethylbutyl-PPD	0.87	0.83	0.24	0.20
S-11	N-Phenyl-N'-2-octyl-PPD	0.84	0.83	0.20	0.21
S-12	N-Phenyl-N'-cyclohexyl-PPD	0.87	0.83	0.13	0.13
S-13	N,N'-Diphenyl-PPD	0.87	0.88	0.37	0.35
S-14	Alkylated N,N'-diphenyl-PPD	0.37	0.38	0	0
S-15	N,N'-Di-2-naphthyl-PPD	0.90	0.84	0.19	0.20

most appropriate eluent is the mixture of isopropanol with chlorobenzene and water (eluent E-1) which, except for substance S-14, provides good R_F values. The addition of a small amount of ammonia is recommended to prevent tailing and/or the formation of diffuse zones.

Of the eluents and adsorbents tested, none was proved to ensure a sufficiently fine separation as a function of the nature of the N-substituent, and the colours obtained with the most selective spray reagents make possible only an assignment to one of the broad groups (dialkyl, diaryl or arylalkyl).

In the analysis of unknown vulcanized samples (usually protected with more than one but different anti-ageing agents), after chromatographic separation it is recommended that another physico-chemical method should be used for the identification and determination, e.g., an absorption spectroscopic method.

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