

CHROM. 4279

THE IDENTIFICATION OF RUBBER COMPOUNDING INGREDIENTS USING THIN-LAYER CHROMATOGRAPHY*

J. G. KREINER AND W. C. WARNER

The General Tire and Rubber Company Research and Development Center, Akron, Ohio 44309 (U.S.A.)

(Received July 1st, 1969)

SUMMARY

During 1964-1965, we examined and reported the utility of thin-layer chromatography for the identification of certain rubber compounding ingredients. These ingredients included amine antioxidants and antiozonants, phenolic antioxidants, guanidines, accelerators, and the amines obtained from accelerators. Each of these groups was examined in an effort to determine the solvent and indicator systems most suitable for the separation and, hence, identification of the largest possible number of compounds in each of the above categories. As a result, the systems we have chosen and described herein should make it possible to identify most of the above named types of compounding materials manufactured in the United States.

INTRODUCTION

The five general methods of analysis that have been employed for the identification of rubber compounding materials are spot tests, liquid column chromatography, paper chromatography, and UV and IR spectroscopy. One of the earlier and most comprehensive procedures available was published by ZIJP¹⁰ in 1956. ZIJP subjected extracts of the vulcanizates to various preliminary treatments after which the compounding ingredients or their residues were separated and identified using paper chromatography. Somewhat later, in 1959, GACZYNSKI AND STEPIEN⁷ published a paper chromatographic method for the identification of six most commonly used accelerators (Poland) and N-phenyl-2-naphthylamine.

The analysis of vulcanizates was reviewed in 1959 by BURGER³ and more recently in 1961 by AULER². AULER examined the various methods that had been used for the determination of antioxidants, antiozonants and accelerators with special emphasis on paper chromatography. He evaluated the methods of MIKSCH AND PRÜLSS¹¹ and ZIJP, refined portions of their methods, and included some of his own work.

* A description of this work has been presented at a meeting of the Division of Rubber Chemistry, American Chemical Society, Miami Beach, Fla., May 4th-7th, 1965, and at a technical symposium of the Akron Rubber Group, Inc., October 28th, 1966.

Since the paper chromatographic work of MIKSCH AND PRÖLSS, ZIJP and AULER, the introduction of commercially available apparatus and standard absorbent materials for TLC have provided a new, rapid, and more widely applicable technique for chromatographic separations and identifications. Surprisingly only a few reports^{9,13-15,17} concerning the application of TLC to the identification of compounding ingredients had appeared prior to 1965 and these dealt with a limited number of materials. It was our purpose, therefore, to examine the general usefulness of TLC for the identification of a wide range of compounding ingredients and to develop systems suitable for their identification.

Many schemes, including the excellent procedure by ZIJP, have been presented for the isolation of compounding ingredients from a vulcanizate and the subsequent treatments necessary prior to chromatography or other forms of analysis. Many of these procedures are adequate for a given problem. It is, however, impossible to anticipate all situations, and some of the more challenging rubber compounds might well require development of new procedures. The scope of the work we are reporting does not include additional schemes for the isolation of compounding ingredients from vulcanizates.

Since our original presentation, several other workers have published work dealing with the TLC analysis of compounding ingredients. We have included references to recent work of which we have become aware.^{1,4-6,8,10,12}

EXPERIMENTAL

TLC equipment commercially available from Research Specialties Company and Brinkmann Instruments, Inc., was used for these studies. Silica Gel G from E. Merck AG., Darmstadt, was used for layers. A 2:1 weight ratio of water and Silica Gel G was used to make the slurries for the layer preparation. The layers were dried for 1 h at 110° in a forced air oven and cooled in a desiccator where stored until used.

Reasonably constant R_F values are obtained if the layer thickness is kept between 200 to 300 μ , the sample does not exceed the layer capacity, and chamber saturation is maintained. Our layer thickness was kept between 250 to 300 μ and the sample sizes in most instances were kept between 35 to 45 μg . In general, samples of 5 to 15 μg are used for the above layer thickness. However, the variation in R_F values for our sample size range was found to be small and caused no problem in identification work. A larger sample size was, in fact, found to be more advantageous

TABLE I
MANUFACTURERS OF RUBBER CHEMICALS

Code	Manufacturer	Code	Manufacturer
a	DuPont	i	C. P. Hall
b	UniRoyal	j	Ethyl Corporation
c	Vanderbilt	k	Shell
d	Harwick	m	American Cyanamid
e	Eastman	n	Catalin
f	Universal Oil Products	o	Neville
g	Goodyear	p	Dow
h	Monsanto	q	Pennsalt

APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR AMINE ANTIOXIDANTS AND ANTIOZONANTS

Development on Silica Gel G with benzene-acetone-concentrated ammonium hydroxide (100:5:0.1) as solvent; indicator: benzoyl peroxide. For code to manufacturers, see Table I.

No.	Amine	Trade name	$R_F \times 100$	Color
1	N-Phenyl-1-naphthylamine	Ncozone A (a)	72	Blue-green
2	N-Phenyl-2-naphthylamine	Ncozone D (a)	67	Purple
3	<i>p</i> -(<i>p</i> -Tolyl-sulfonylamido)-diphenylamine	Aranox (b)	18	Orange
4	Nonylated diphenylamines	Polylite (b)	79, 74	Blue and gray
5	Octylated diphenylamines	Age Rite Stalite (c)	78, 74, 71	Blue and gray
6	Octylated diphenylamines	Age Rite Stalite S (c)	77	Blue-gray and brown
7	Octylated diphenylamines	Octamine (b)	79, 76	Blue-gray and brown
8	4,4'-Dimethoxy-diphenylamine	25% of Thermoflex A (a)	51	Red
9	4-Isopropoxy-diphenylamine	Age Rite Iso (c)	64	Green-brown
10	4-Isopropylamino-diphenylamine	Nonox ZA (d)	31	Brown
11	N,N'-Di-isopropyl- <i>p</i> -phenylenediamine	Tenamene 5 (e)	7	Violet
12	N,N'-Di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine	Tenamene 2 (e)	15	Violet
13	N,N'-Bis(1,4-dimethylpentyl)- <i>p</i> -phenylenediamine	Eastozone 33 (e)	21	Violet
14	N,N'-Bis(1-ethyl-3-methylpentyl)- <i>p</i> -phenylenediamine	UOP 88 (f)	47	Violet
15	N,N'-Bis(1-methylheptyl)- <i>p</i> -phenylenediamine	UOP 288 (f)	21	Violet
16	N-Isopropyl-N'-phenyl- <i>p</i> -phenylenediamine	Flexzone 3C (b)	31	Brown
17	N-Cyclohexyl-N'-phenyl- <i>p</i> -phenylenediamine	Flexzone 6H (b)	37	Brown
18	N-(1-Methylheptyl)-N'-phenyl- <i>p</i> -phenylenediamine	UOP 688 (f)	47	Brown
19	N,N'-Diphenyl- <i>p</i> -phenylenediamine	Age Rite DPPD (c)	42	Yellow
20	N,N'-Di-2-naphthyl- <i>p</i> -phenylenediamine	Age Rite White (c)	46	Pink
21	Mixture of diaryl- <i>p</i> -phenylenediamines	Wingstay 100 (g)	59, 55, 51	Yellow
22	Polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline	Age Rite Resin D (c)	54, 45, 34, 26, 23, 12, 8, 5, 3	Gray, blue and brown
23	6-Dodecyl-1,2-dihydro-2,2,4-trimethyl-quinoline	Santoflex DD (h)	67, 40	Tan
24	6-Ethoxy-1,2-dihydro-2,2,4-trimethyl-quinoline	Santoflex AW (h)	44	Brown-green
25	High-temperature diphenylamine-acetone reaction product	BLE (b)	65	Blue and violet
26	High-temperature diphenylamine-acetone reaction product	Age Rite Superflex (c)	65	Blue and violet
27	Low-temperature diphenylamine-acetone reaction product	Aminox (b)	61	Purple
28	Low-temperature N-phenyl-2-naphthylamine-acetone reaction product	Betanox Special (b)	62, 58	Green-brown
29	Aldol-1-naphthylamine	Age Rite Resin (c)	60, 44, 33, 21, 10	Blue, brown and yellow
30	Butyraldehyde-aniline condensation product	Antox (a)	68, 42, 28	Brown and red-brown
31	N,N'-Diphenylethylenediamine	Stabilite (i)	39	Brown
32	N,N'-Diphenylpropylenediamine	Stabilite L (i)	45	Green-brown
33	N,N'-Di- <i>o</i> -tolylethylenediamine	Stabilite Alba (i)	47	Red
34	2,4-Toluenediamine	7.5% of Neozone C (a)	2	Brown
35	4,4'-Diaminodiphenylmethane	Tonox (b)	4	Brown
36	Phenothiazine		51	Green

when working with unknown extracts. In the case of multicomponent materials, the sample size was increased to yield reasonable quantities of the components. Saturation of the developing tank atmosphere was ensured by placing filter paper wet with solvent on the tank walls. The development distance was 15 cm in all cases except for the guanidines, which were developed through a distance of 10 cm. The sample, as a 1% solution, was placed on the layer by means of a platinum wire loop¹⁶ bent at a right angle to the stem of the wire which had been fused into a glass tubing handle. The volume of solution picked up by a loop about 1 mm in diameter was 3.5 to 4.5 μ l. The wire loop method of sample application was preferred since the wire was easily cleaned in a burner flame and gave the required reproducibility for qualitative analysis. All samples were used as obtained from the suppliers. A list of the suppliers is given in Table I.

Amine antioxidants

A solvent of benzene-acetone-conc. ammonium hydroxide (100:5:0.1) was used for the one-dimensional development of the materials listed in Table II and shown in Figs. 1, 2, and 3. After evaporation of the developing solvent, the samples were indicated by spraying with a 4% solution of benzoyl peroxide in benzene. Two-dimensional developments were obtained by developing in the first direction with the benzene-acetone-ammonium hydroxide solvent, drying the plate in a 50° vacuum

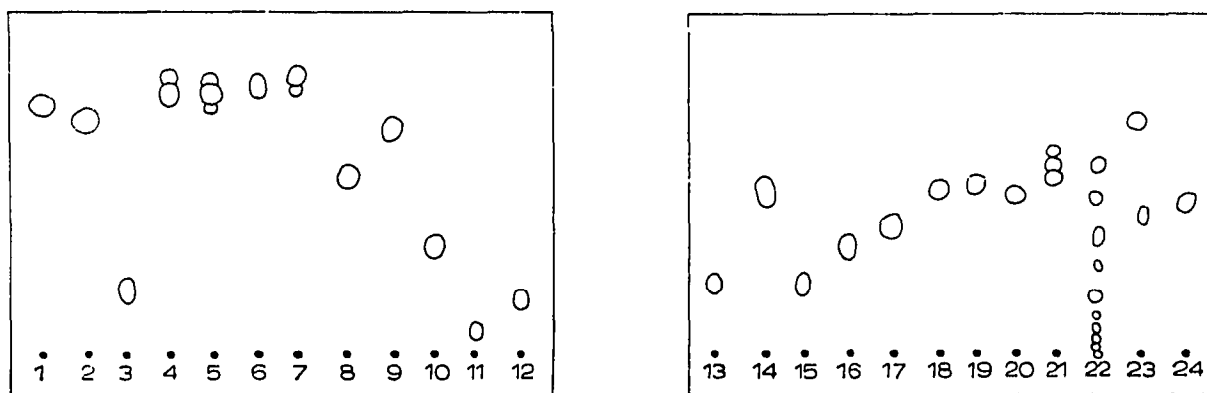


Fig. 1. Separation of amine antioxidants and antiozonants by one-dimensional thin-layer chromatography. Solvent: benzene-acetone-concentrated ammonium hydroxide (100:5:0.1); development distance: 15 cm; indicator: 4% benzoyl peroxide in benzene. 1 = N-Phenyl-1-naphthylamine; 2 = N-phenyl-2-naphthylamine; 3 = *p*-(*p*-tolylsulfonylamido)-diphenylamine; 4 = nonylated diphenylamines; 5 = octylated diphenylamines; 6 = octylated diphenylamines; 7 = octylated diphenylamines; 8 = 4,4'-dimethoxydiphenylamine; 9 = 4-isopropoxydiphenylamine; 10 = 4-isopropylaminodiphenylamine; 11 = N,N'-diisopropyl-*p*-phenylenediamine; 12 = N,N'-di-*sec*-butyl-*p*-phenylenediamine.

Fig. 2. Separation of amine antioxidants and antiozonants by one-dimensional thin-layer chromatography. Solvent: benzene-acetone-conc. ammonium hydroxide (100:5:0.1); development distance: 15 cm; indicator: 4% benzoyl peroxide in benzene. 13 = N,N'-bis(1,4-dimethylpentyl)-*p*-phenylenediamine; 14 = N,N'-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine; 15 = N,N'-bis(1-methylheptyl)-*p*-phenylenediamine; 16 = N-isopropyl-N'-phenyl-*p*-phenylenediamine; 17 = N-cyclohexyl-N'-phenyl-*p*-phenylenediamine; 18 = N-(1-methylheptyl)-N'-phenyl-*p*-phenylenediamine; 19 = N,N'-diphenyl-*p*-phenylenediamine; 20 = N,N'-di-2-naphthyl-*p*-phenylenediamine; 21 = mixture of diaryl-*p*-phenylenediamines; 22 = polymerized 1,2-dihydro-2,2,4-trimethylquinoline; 23 = 6-dodecyl-1,2-dihydro-2,2,4-trimethylquinoline; 24 = 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.

oven at 150 to 250 mm mercury for a few minutes, cooling the plate to room temperature, and then developing in the second direction with cyclohexane-acetone-conc. ammonium hydroxide (100:5:0.1) (Fig. 4).

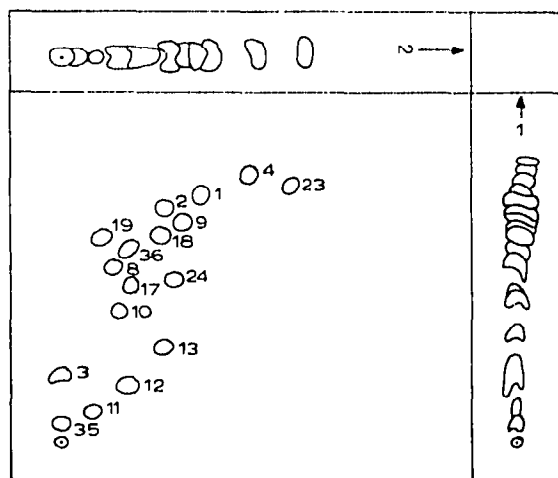
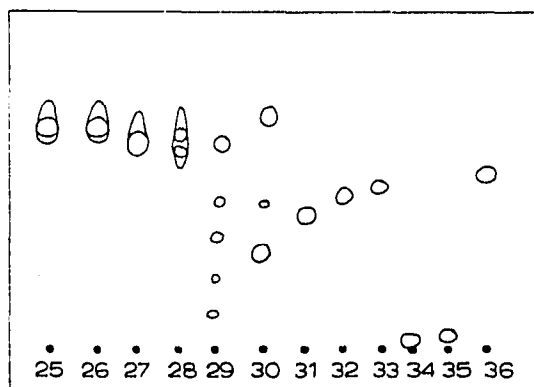


Fig. 3. Separation of amine antioxidants and antiozonants by one-dimensional thin-layer chromatography. Solvent: benzene-acetone conc. ammonium hydroxide (100:5:0.1); development distance: 15 cm; indicator: 4% benzoyl peroxide in benzene. 25 = high-temperature diphenylamine-acetone reaction product; 26 = high-temperature diphenylamine-acetone reaction product; 27 = low-temperature diphenylamine-acetone reaction product; 28 = low-temperature *N*-phenyl-2-naphthylamine-acetone reaction product; 29 = aldol-1-naphthylamine; 30 = butyraldehyde-aniline condensation product; 31 = *N,N'*-diphenylethylenediamine; 32 = *N,N'*-diphenylpropylenediamine; 33 = *N,N'*-di-*o*-tolylethylenediamine; 34 = 2,4-toluenediamine; 35 = 4,4'-diaminodiphenylmethane; 36 = phenothiazine.

Fig. 4. Separation of a mixture of seventeen amines by two-dimensional development. Solvents: (1) benzene-acetone-conc. ammonium hydroxide (100:5:0.1); (2) cyclohexane-acetone-conc. ammonium hydroxide (100:5:0.1). Indicator: 4% benzoyl peroxide in benzene.

The developing solutions used here, while good for purposes of identification, do not resolve the many fractions found in several of the multi-component reaction mixtures. For example, the many components in the octylated and nonylated diphenylamines and the amine-acetone reaction products (Samples 4, 5, 7, 25, 26, and 27)

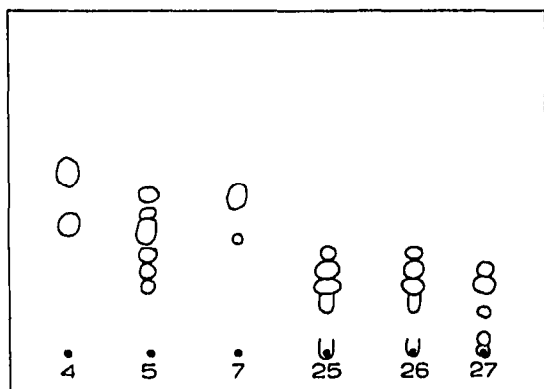


Fig. 5. Separation of amine antioxidants and antiozonants by thin-layer chromatography. Solvent: cyclohexane-benzene-acetone (100:10:1); development distance: 15 cm; indicator: 4% benzoyl peroxide in benzene. 4 = nonylated diphenylamines; 5 = octylated diphenylamines; 7 = octylated diphenylamines; 25,26 = high-temperature diphenylamine-acetone reaction products; 27 = low-temperature diphenylamine-acetone reaction product.

TABLE III
 APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR AMINE ANTIOXIDANTS AND ANTIOZONANTS
 Development on Silica Gel G with cyclohexane-benzene-acetone (100:10:1) as solvent; indicator: benzoyl peroxide. For code to manufacturers, see Table I.

No.	Amine	Trade name	$R_F \times 100$	Color
4	Nonylated diphenylamines	Polylite (b)	53, 39	Blue and brown
5	Octylated diphenylamines	Age Rite Stalite (c)	48, 42, 37, 30, 25, 21	Blue, gray, brown and yellow
7	Octylated diphenylamines	Octamine (b)	46, 34	Blue-gray and brown
25	High-temperature diphenylamine-acetone reaction product	BLE (b)	29, 25, 19, 13, 0	Blue and violet
26	High-temperature diphenylamine-acetone reaction product	Age Rite Superflex (c)	29, 25, 19, 14, 0	Blue and violet
27	Low-temperature diphenylamine-acetone reaction product	Aminox (b)	25, 20, 12, 4, 0	Blue and violet

TABLE IV

APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR PHENOLIC ANTI-OXIDANTS

Development on Silica Gel G with benzene as solvent; indicator: 2,6-dichloroquinonechlorimide. For code to manufacturers, see Table I.

No.	Phenol	Trade name	$R_F \times 100$	Color
1	Hydroquinone monobenzyl ether	Age Rite Alba (c)	7	Blue
2	2,6-Di- <i>tert</i> -butyl-phenol	Ethyl 701 (j)	72	Violet
3	2,6-Di- <i>tert</i> -butyl-4-methyl-phenol	Ionol (k)	74	Creamy yellow
4	2,6-Di- <i>tert</i> -butyl- α -methoxy-4-methyl-phenol	Ethyl 762 (j)	30	Violet-yellow
5	2- α -Methylcyclohexyl-4,6-dimethyl-phenol	Nonox WSL (d)	64	Creamy yellow
6	Butylated hydroxyanisole	Tenox BHA (e)	22	Blue
7	Butylated hydroxytoluene	Tenox BHT (e)	74	Creamy yellow
8	4,4'-Bis(2,6-di- <i>tert</i> -butyl-phenol)	Ethyl 712 (j)	74	Yellow
9	2,2'-Methylene-bis(4-methyl-6- <i>tert</i> -butyl-phenol)	Antioxidant 2246 (m)	62	Yellow
10	2,2'-Methylene-bis(4-ethyl-6- <i>tert</i> -butyl-phenol)	Antioxidant 425 (m)	59	Gray-blue
11	2,2'-Methylene-bis(6- α -methyl-cyclohexyl-4-methyl-phenol)	Nonox WSP (d)	62	Yellow
12	4,4'-Methylene-bis(6- <i>tert</i> -butyl-2-methyl-phenol)	Ethyl 720 (j)	41	Red-violet
13	4,4'-Methylene-bis(2,6-di- <i>tert</i> -butyl-phenol)	Ethyl 702 (j)	76	Red-brown
14	4,4'-Butylidene-bis(6- <i>tert</i> -butyl-3-methyl-phenol)	Santowhite Powder (h)	19	Blue
15	2,2'-Thio-bis(4-methyl-6- <i>tert</i> -butyl-phenol)	CAO-6 (n)	72	Yellow-brown
16	4,4'-Thio-bis(6- <i>tert</i> -butyl-2-methyl-phenol)	Ethyl 736 (j)	45	Red-brown
17	4,4'-Thio-bis(6- <i>tert</i> -butyl-3-methyl-phenol)	Santowhite Crystals (h)	28	Blue-violet
18	4,4'-Thio-bis(3,6-di- <i>sec</i> -amyl-phenol)	Santowhite L (h)	64	Blue and gray
19	N-Butyl- <i>p</i> -amino-phenol	Tenamene 1 (c)	3	Blue
20	Mixture of <i>tert</i> -octyl and <i>tert</i> -butyl cresols	Wingstay T (g)	73	Violet
21	Fortified phenol	Zalba Special (a)	69	Red-brown
22	Alkylated phenol	Naugawhite (b)	69,60	Yellow
23	Alkylated phenol	Nevastain B (o)	64, 29	Blue
24	Alkylated phenol	Stabilite White (i)	76, 59, 50	Blue-gray and brown
25	Alkylated phenol	Age Rite Superlite (c)	69, 54, 47, 43, 39, 30, 26, 18, 9	Violet, blue and gray
26	Substituted styrenated phenol	Phenox (p)	58, 26, 10	Blue
27	Substituted styrenated phenol	Wingstay S (g)	58, 26, 10	Blue
28	Substituted styrenated phenol	Age Rite Spar (c)	58, 26, 10	Blue
29	Substituted styrenated phenol	Wingstay V (g)	67, 61, 56	Blue and cream
30	Tri(nonylated phenyl) phosphite	Polygard (b)	50, 44, 28, 17, 9	Blue, gray, salmon, white
31	Phosphited polyalkylpolyphenol	Age Rite Geltrol (c)	63, 52, 48, 39, 22, 12, 76, 69, 63, 48, 41, 19, 12, 3	Blue, gray, salmon, violet

can be better resolved using a solvent such as cyclohexane-benzene-acetone (100:10:1) (Fig. 5 and Table III).

Phenolic antioxidants

The phenolics (Table IV) were developed with benzene (Figs. 6, 7, and 8). The samples were visualized by spraying with a buffer solution containing 23.4 g sodium tetraborate and 3.3 g sodium hydroxide in 1 l of water followed by a spray of freshly prepared 0.1% 2,6-dichloroquinonechlorimide in methanol.

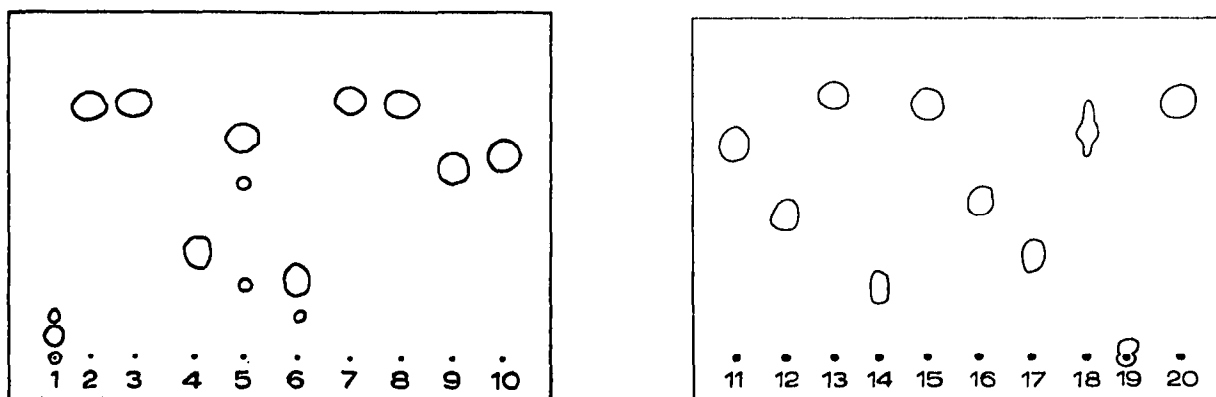


Fig. 6. Separation of phenolic antioxidants by thin-layer chromatography. Solvent: benzene; development distance: 15 cm; indicators: (1) borate buffer; (2) 0.1% 2,6-dichloroquinonechlorimide in methanol. 1 = hydroquinone monobenzyl ether; 2 = 2,6-di-*tert.*-butylphenol; 3 = 2,6-di-*tert.*-butyl-4-methyl-phenol; 4 = 2,6-di-*tert.*-butyl- α -methoxy-4-methyl-phenol; 5 = 2- α -methyl-cyclohexyl-4,6-dimethyl-phenol; 6 = butylated hydroxyanisole; 7 = Butylated hydroxytoluene; 8 = 4,4'-bis(2,6-di-*tert.*-butyl-phenol); 9 = 2,2'-methylene-bis(4-methyl-6-*tert.*-butyl-phenol); 10 = 2,2'-methylene-bis(4-ethyl-6-*tert.*-butyl-phenol).

Fig. 7. Separation of phenolic antioxidants by thin-layer chromatography. Solvent: benzene; development distance: 15 cm; indicators: (1) borate buffer; (2) 0.1% 2,6-dichloroquinonechlorimide in methanol. 11 = 2,2'-methylene-bis(6-*a*-methylcyclohexyl-4-methyl-phenol); 12 = 4,4'-methylene-bis(6-*tert.*-butyl-2-methyl-phenol); 13 = 4,4'-methylene-bis(2,6-di-*tert.*-butyl-phenol); 14 = 4,4'-butylidene-bis(6-*tert.*-butyl-3-methyl-phenol); 15 = 2,2'-thio-bis(4-methyl-6-*tert.*-butyl-phenol); 16 = 4,4'-thio-bis(6-*tert.*-butyl-2-methyl-phenol); 17 = 4,4'-thio-bis(6-*tert.*-butyl-3-methyl-phenol); 18 = 4,4'-thio-bis(3,6-di-*sec.*-amyl-phenol); 19 = *N*-butyl-*p*-amino-phenol; 20 = mixture of *tert.*-octyl and *tert.*-butyl cresols.

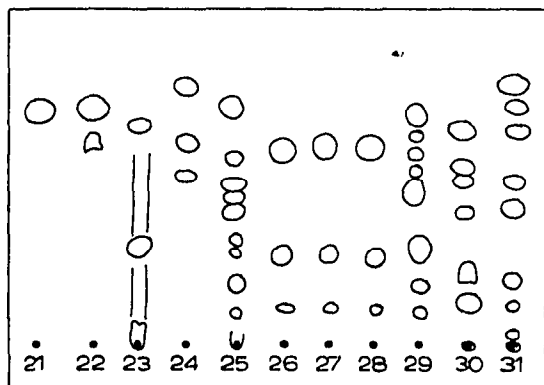


Fig. 8. Separation of phenolic antioxidants by thin-layer chromatography. Solvent: benzene; development distance: 15 cm; indicators: (1) borate buffer; (2) 0.1% 2,6-dichloroquinonechlorimide in methanol. 21 = fortified phenol; 22, 23, 24, 25 = alkylated phenols; 26, 27, 28, 29 = substituted styrenated phenols; 30 = tri(nonylated phenyl) phosphite; 31 = phosphited polyalkyl-polyphenol.

TABLE V

APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR PHENOLIC ANTIOXIDANTSDouble development on Silica Gel G with *n*-hexane-benzene (8:1) as solvent; indicator: 2,6-dichloroquinonechlorimide. For code to manufacturers, see Table I.

No.	Phenol	Trade name	$R_F \times 100$	Color
2	2,6-Di- <i>tert</i> .-butyl-phenol	Ethyl 701 (j)	58	Violet
3	2,6-Di- <i>tert</i> .-butyl-4-methyl-phenol	Ionol (k)	57	Creamy yellow
8	4,4'-Bis(2,6-di- <i>tert</i> .-butyl-phenol)	Ethyl 712 (j)	27	Yellow
13	4,4'-Methylene-bis(2,6-di- <i>tert</i> .-butyl-phenol)	Ethyl 702 (j)	25	Red-brown
15	2,2'-Thio-bis(4-methyl-6- <i>tert</i> .-butyl-phenol)	CAO-6 (n)	30	Yellow-brown
20	Mixture of <i>tert</i> .-octyl and <i>tert</i> .-butyl cresols	Wingstay T (g)	11, 16, 56, 65, 69, 74, 83	Violet, blue and gray
21	Fortified phenol	Zalba Special (a)	5, 47	Red-brown

Since several samples were found to travel similar distances when eluted with benzene a second procedure was devised. The plate was developed with *n*-hexane-benzene (8:1) for a distance of 15 cm, dried in the vacuum oven, and then again developed 15 cm in the same direction with the same solvent system (Fig. 9 and Table V).

Guanidines

Acetone containing 1% concentrated ammonium hydroxide was employed to resolve three guanidines (Table VI). The samples were detected by spraying with 4% sodium hypochlorite (Fig. 10).

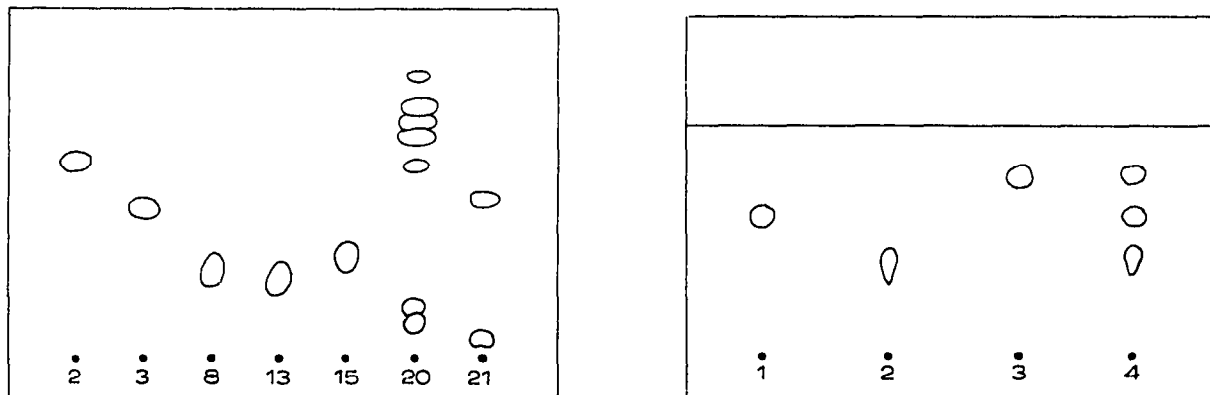


Fig. 9. Separation of phenolic antioxidants by thin-layer chromatography. Solvent: *n*-hexane-benzene (8:1); development distance: 15 cm (twice); indicators: (1) borate buffer; (2) 0.1% 2,6-dichloroquinonechlorimide in methanol; 2 = 2,6-di-*tert.*-butyl-phenol; 3 = 2,6-di-*tert.*-butyl-4-methyl-phenol; 8 = 4,4'-bis(2,6-di-*tert.*-butyl-phenol); 13 = 4,4'-methylene-bis(2,6-di-*tert.*-butyl-phenol); 15 = 2,2'-thio-bis(4-methyl-6-*tert.*-butyl-phenol); 20 = mixture of *tert.*-octyl and *tert.*-butyl cresols; 21 = fortified phenol.

Fig. 10. Separation of guanidines by thin-layer chromatography. Solvent: 1% conc. ammonium hydroxide in acetone; development distance: 10 cm; indicator: 4% aqueous sodium hypochlorite. 1 = diphenylguanidine; 2 = di-*o*-tolylguanidine; 3 = triphenylguanidine; 4 = mixture.

TABLE VI

APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR GUANIDINES

Development on Silica Gel G with 1% concentrated ammonium hydroxide in acetone as solvent; indicator: sodium hypochlorite.

No.	Guanidine	$R_F \times 100$	Color
1	Diphenylguanidine	63	Red-brown
2	Di- <i>o</i> -tolylguanidine	43	Red-brown
3	Triphenylguanidine	80	Yellow-brown

Accelerators

A mixture of benzene-ethyl acetate-acetone (100:5:1) was used to chromatograph the accelerators listed in Table VII and shown in Figs. 11, 12, and 13. Those compounds containing a readily liberated amine were sprayed with 4 *N* hydrochloric acid and placed in a 130° oven for approximately 15 min. The samples were then sprayed with 0.5% solution of ninhydrin in ethanol containing 10% acetic acid and 0.5%

TABLE VII

APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR ACCELERATORS

Development on Silica Gel G with benzene-ethyl acetate-acetone (100:5:1) as solvent; indicators: ninhydrin (1-17 and 22-28) and bismuth nitrate (18-21). For code to manufacturers, see Table I.

No.	Accelerator	Trade name	$R_F \times 100$	Color
1	Tetramethylthiuram monosulfide	Unads (c)	27	Red
2	Tetrabutylthiuram monosulfide	Pentex (b)	53	Red-brown
3	Tetramethylthiuram disulfide	Methyl Tuads (c)	41	Red
4	Tetraethylthiuram disulfide	Ethyl Tuads (c)	57	Red
5	Dipentamethylenethiuram tetrasulfide	Tetronc A (a)	61, 56	Purple
6	Cyclic thiuram	Conac T (a)	17, 12, 8	Yellow-brown
7	Piperidinium pentamethylenedithiocarbamate	Accelerator 552 (a)	54	Purple
8	Zinc dimethyldithiocarbamate	Methyl Zimate (c)	49	Red
9	Zinc diethyldithiocarbamate	Ethyl Zimate (c)	64	Red
10	Zinc dibutyldithiocarbamate	Butyl Zimate (c)	77	Red-brown
11	Copper dimethyldithiocarbamate	Cumate (c)	63	Yellow-green
12	Bismuth dimethyldithiocarbamate	Bismate (c)	32	Red
13	Selenium dimethyldithiocarbamate	Methyl Selenac (c)	56, 51	Red
14	Tellurium diethyldithiocarbamate	Tellurac (c)	60, 48	Red
15	Cadmium diethyldithiocarbamate	Cadmate (c)	47	Red
16	Lead diethyldithiocarbamate	Ethyl Ledate (c)	54	Red
17	2-Benzothiazyl-N,N-diethyldithiocarbamyl sulfide	Ethylac (q)	29	Red
18	2-Mercaptobenzothiazole	MBT (a)	25	Yellow-brown
19	Benzothiazyl disulfide	MBTS (a)	41	Yellow-brown
20	Zinc benzothiazyl sulfide	Zetax (c)	24, 0	Yellow-brown
21	2-Mercaptothiazoline	2-MT (m)	11	Yellow
22	N- <i>tert</i> -Butyl-2-benzothiazole sulfenamide	Santocure NS (h)	45	Creamy yellow
23	N,N-Dispropyl-2-benzothiazole sulfenamide	DIBS (m)	56	Yellow-brown
24	N-Cyclohexyl-2-benzothiazole sulfenamide	Santocure (h)	48	Orange-brown
25	N-Oxydiethylene-2-benzothiazole sulfenamide	Amox (c)	24	Red-violet
26	2-(2,6-Dimethyl-4-morpholinio) benzothiazole	Santocure 26 (h)	31, 23	Tan
27	N,N-Dimethylcyclohexylamine salt of dibutyldithiocarbamic acid	RZ-50-A (h)	72	Red-brown
28	1,1-Methylene-dipiperidine-carbon disulfide reaction product	R-2 Crystals (h)	streaks	Purple

cadmium acetate and returned to the oven for color development. The thiazoles were indicated with a 5 % solution of bismuth nitrate in 1 *N* nitric acid. Since benzothiazole disulfide does not react with the bismuth nitrate until reduced to 2-mercaptobenzothiazole, it was sprayed first with 0.5 % ammonium sulfide. The excess ammonium sulfide was removed by placing the plate in a 50° vacuum oven at 150 to 250 mm mercury for a few minutes. The thiazoles are satisfactorily indicated after the ninhy-

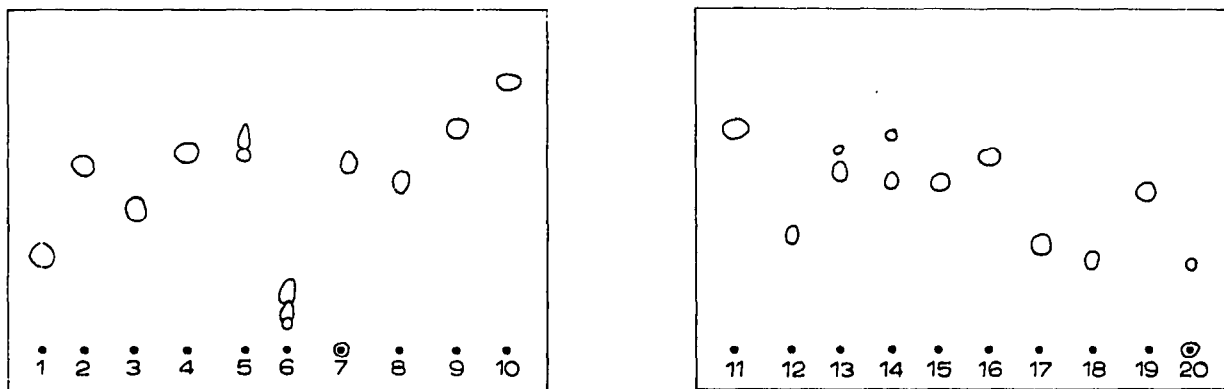


Fig. 11. Separation of accelerators by thin-layer chromatography. Solvent: benzene-ethyl acetate-acetone (100:5:1); development distance: 15 cm; indicators: (1) 4 *N* hydrochloric acid; (2) 0.5 % ninhydrin in ethanol containing 10 % acetic acid and 0.5 % cadmium acetate. 1 = tetramethylthiuram monosulfide; 2 = tetrabutylthiuram monosulfide; 3 = tetramethylthiuram disulfide; 4 = tetraethylthiuram disulfide; 5 = dipentamethylenethiuram tetrasulfide; 6 = cyclic thiuram; 7 = piperidinium pentamethylenedithiocarbamate; 8 = zinc dimethyldithiocarbamate; 9 = zinc diethyldithiocarbamate; 10 = zinc dibutyldithiocarbamate.

Fig. 12. Separation of accelerators by thin-layer chromatography. Solvent: benzene-ethyl acetate-acetone (100:5:1); development distance: 15 cm; indicators: for 11-17: (1) 4 *N* hydrochloric acid; (2) 0.5 % ninhydrin in ethanol containing 10 % acetic acid and 0.5 % cadmium acetate; for 18-20: 5 % bismuth nitrate in 1 *N* nitric acid. 11 = copper dimethyldithiocarbamate; 12 = bismuth dimethyldithiocarbamate; 13 = selenium dimethyldithiocarbamate; 14 = tellurium diethyldithiocarbamate; 15 = cadmium diethyldithiocarbamate; 16 = lead diethyldithiocarbamate; 17 = 2-benzothiazyl-*N,N*-diethylthiocarbamyl sulfide; 18 = 2-mercaptobenzothiazole; 19 = benzothiazyl disulfide; 20 = zinc benzothiazyl sulfide.

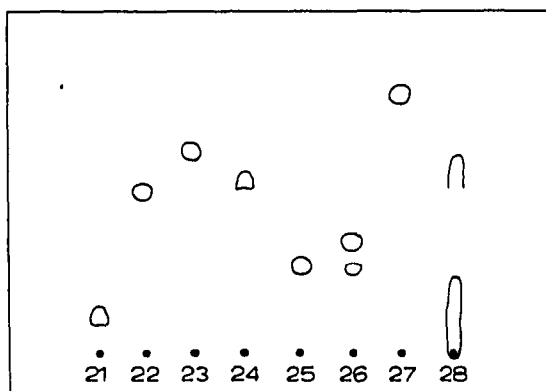


Fig. 13. Separation of accelerators by thin-layer chromatography. Solvent: benzene-ethyl acetate-acetone (100:5:1); development distance: 15 cm; indicators for 21: 5 % bismuth nitrate in 1 *N* nitric acid; for 22-28: (1) 4 *N* hydrochloric acid; (2) 0.5 % ninhydrin in ethanol containing 10 % acetic acid and 0.5 % cadmium acetate. 21 = 2-mercaptothiazoline; 22 = *N-tert*-butyl-2-benzothiazole sulfenamide; 23 = *N,N*-di-isopropyl-2-benzothiazole sulfenamide; 24 = *N*-cyclohexyl-2-benzothiazole sulfenamide; 25 = *N*-oxydiethylene-2-benzothiazole sulfenamide; 26 = 2-(2,6-dimethyl-4-morpholiniothio)benzothiazole; 27 = *N,N*-dimethylcyclohexylamine salt of dibutyldithiocarbamic acid; 28 = 1,1'-methylene dipiperidine-carbon disulfide reaction product.

drin treatment of other compounds on the same plate if they have been masked from the ninhydrin spray by covering with a glass plate. Since one of the sulfenamide amines *tert.*-butylamine, does not yield an especially intense color, the benzothiazole portion can be indicated, after the 4 *N* hydrochloric acid treatment, by further treatment with ammonium sulfide and bismuth nitrate. A second solvent system that has been used to some advantage for accelerators is benzene-ethyl acetate-*n*-butanol (50:1:1).

Amine hydrochlorides

A mixture of *n*-butanol-water-formic acid (5:1:1) was used to separate the amines (Table VIII). After development, the solvent was removed by heating the plate in a 130° forced air oven. When dry, the plate was sprayed with the ninhydrin solution used for the accelerators and returned to the oven to bring out the colors (Fig. 14).

TABLE VIII

APPROXIMATE $R_F \times 100$ VALUES AND COLORS FOR AMINE HYDROCHLORIDESDevelopment on Silica Gel G with *n*-butanol-water-formic acid (5:1:1) as solvent; indicator: ninhydrin.

No.	Amine	$R_F \times 100$	Color
1	Dimethylamine	16	Red
2	Diethylamine	25	Red
3	Diisopropylamine	35	Yellow-brown
4	Di- <i>n</i> -butylamine	52	Red-brown
5	<i>tert.</i> -Butylamine	38	Creamy-yellow
6	Cyclohexylamine	42	Orange-brown
7	Aniline	48	Pink
8	Piperidine	23	Purple
9	Morpholine	18	Red-violet
10	2,6-Dimethylmorpholine	29	Tan

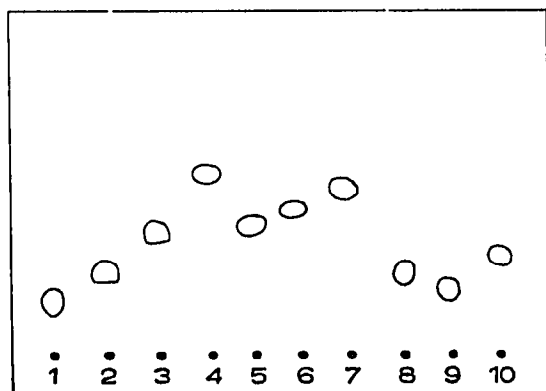


Fig. 14. Separation of amine hydrochlorides by thin-layer chromatography. Solvent: *n*-butanol-formic acid-water (5:1:1); development distance: 15 cm; indicator: 0.5% ninhydrin in ethanol containing 10% acetic acid and 0.5% cadmium acetate. 1 = dimethylamine; 2 = diethylamine; 3 = diisopropylamine; 4 = di-*n*-butylamine; 5 = *tert.*-butylamine; 6 = cyclohexylamine; 7 = aniline; 8 = piperidine; 9 = morpholine; 10 = 2,6-dimethylmorpholine.

RESULTS AND DISCUSSION

In all cases, solvent systems giving the greatest range of R_F values have been chosen. The developing distance in all but one case was 15 cm to give additional space as well as separation since rather large numbers of samples were considered in certain groups. Indicating reagents giving a wide range of colors have also been chosen to permit the identification of the compound in many instances by both color and travel distance. Approximate descriptions of the colors obtained for the compounds we examined have been presented in the accompanying tables. Most of the colors will vary somewhat depending upon the conditions of and time after indication. Many satisfactory indicating reagents other than those chosen by us are available and most can be found in the references we have cited. Approximate R_F values have been tabulated; however, an identification is best made by comparison to known compounds. An unknown compound is identified when, after adjusting the sample spot size to match that of the known, it travels the same distance and gives the same color as the known. If even higher probability is desired, the above procedure may be repeated with a different suitable developing solvent.

Amine antioxidants and antiozonants

The amines are generally quite well spaced with a one-dimensional development (Figs. 1, 2, and 3). One-dimensional development has also been found sufficient to resolve the common commercial mixtures. However, several antioxidants and antiozonants are often mixed for increased effectiveness and some situations may require the use of a two-dimensional development. In Fig. 4, the separation of a mixture of seventeen antioxidants and antiozonants by two-dimensional development is shown. It should be possible to separate and identify almost any combination of antioxidants and antiozonants using the above two solvent mixtures or modifications thereof. The small amount of ammonium hydroxide was added to the developing solutions to minimize the tendency of certain compounds to tail.

Phenolic antioxidants

It has been noted that several of the samples (2, 3, 7, 8, 13, 15, 20, and 21) travel nearly identical distances when eluted with benzene. Samples 3 and 7 not only travel identically, but color the same. Thus BHT (butylated hydroxy toluene) is apparently 2,6-di-*tert.*-butyl-*p*-cresol (IR spectra confirm this conclusion). The 8:1 *n*-hexane-benzene double development separates all but samples 2 and 3 and also shows the several components present in sample 20. The only difference between samples 2 and 3 is a methyl group in the *para* position and a separation of the two would be expected to be somewhat difficult. In this situation, the use of an indicating reagent giving a wide range of colors becomes useful. Since it is not especially common to use more than one phenolic antioxidant in a compound, the above or any other pairing should not be a particularly great problem.

One note of caution: certain components of the complex mixtures, including the phosphites (samples 21 to 31) lag in color development when buffered 2,6-dichloroquinonechlorimide is used as indicator. This can be overcome by warming the plate after application of both spray reagents.

The phosphites were included with the phenolics since they are also non-staining.

Guanidines

Only three compounds are involved and no problems are encountered in the separation.

Accelerators

Since only one or two accelerators are generally used in a rubber compound, a TLC identification should not be too difficult. However, more complex curing systems containing three or four accelerators have been used for certain special applications and the identifications, as expected, become more difficult with increasing sample complexity.

Often it is very difficult and frequently impossible to isolate identifiable amounts of undecomposed or unreacted accelerators from a vulcanizate. In such instances, one can only identify the remaining fragments and reaction products and attempt to reconstruct the original accelerator system based on a knowledge of compounding and the use for which the vulcanizate was intended.

Amine hydrochlorides

A 5:1:1 mixture of *n*-butanol-water-formic acid gave the best separation of the ten amine hydrochlorides. Variation of the ratio of *n*-butanol to water and formic acid (e.g., 3:1:1 to 6:1:1) varies the relative positions of the compounds and may be used to advantage if an overlapping pair is observed. One difficulty experienced with ninhydrin was the light color, a creamy yellow, obtained with *tert.*-butylamine as mentioned above for *N-tert.*-butyl-2-benzothiazole sulfenamide.

CONCLUSIONS

TLC has been shown to be a rapid, reliable, relatively simple, and inexpensive analytical technique of great utility for the identification of rubber compounding ingredients as illustrated above. Although an exhaustive accumulation of all antioxidants, antiozonants and accelerators available in the United States was not made, a major portion of the various types of compounds available were examined to show the general utility of TLC for separation and identification.

ACKNOWLEDGEMENT

The authors wish to thank the General Tire and Rubber Company for permission to publish this work.

REFERENCES

- 1 R. AMOS, *J. Chromatog.*, 31 (1967) 263.
- 2 H. AULER, *Rubber Chem. Technol.*, 37 (1964) 950; *Gummi Asbest Kunststoffe*, 14 (1960) 1024, 1081.
- 3 V. L. BURGER, *Rubber Chem. Technol.*, 32 (1959) 1452.
- 4 J. R. DAVIES AND F. W. KAM, *J. Inst. Rubber Ind. (London)*, 2 (1968) 86.
- 5 J. R. DAVIES AND F. W. KAM, *J. Inst. Rubber Ind. (London)*, 2 (1968) 89.
- 6 R. B. DELVES, *J. Chromatog.*, 26 (1967) 296.
- 7 R. GACZYNSKI AND M. STEPIEN, *Przemysl Chem.*, 38 (1959) 9, 571.
- 8 R. F. V.D. HEIDE, A. C. MAAGDENBERG AND J. H. V.D. NEUT, *Chem. Weekblad*, 61 (1965) 440.
- 9 R. F. V.D. HEIDE AND O. WOUTERS, *Z. Lebensm. Untersuch. Forsch.*, 117 (1962) 129.

- 10 J. JENTZSCH AND R. MARTIN, *Plaste Kautschuk*, 13 (1966) 8, 464.
- 11 R. MIKSCH AND L. PRÖLSS, *Gummi Asbest*, 13 (1960) 250.
- 12 J. H. V.D. NEUT AND A. C. MAAGDENBERG, *Plastics*, 31 (1966) 66.
- 13 E. REY AND L. ERHART, *Elektrotech. Z., B*, 13 (1961) 299.
- 14 A. SEHER, *Fette, Seifen, Anstrichmittel*, 61 (1959) 345.
- 15 D. F. SLONAKER AND D. C. SIEVERS, *Anal. Chem.*, 36 (1964) 1130.
- 16 M. E. TATE AND C. T. BISHOP, *Can. J. Chem.*, 40 (1962) 1043.
- 17 T. YUASA AND K. KAMIYA, *Bunseki Kagaku*, 13 (1964) 966.
- 18 J. W. H. ZIJP, *Rubber Chem. Technol.*, 30 (1957) 705; *Rec. Trav. Chim.*, 75 (1956) 1053, 1083, 1129, 1155.

J. Chromatog., 44 (1969) 315-330