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ANTIOXIDANTS AND STABILIZERS

XLVIII.[*] ANALYSIS OF THE COMPONENTS OF STABILIZATION AND VULCANIZATION MIXTURES FOR RUBBERS BY GEL PERMEATION AND THIN-LAYER CHROMATOGRAPHIC METHODS[**]

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SUMMARY

Amine antioxidants and antiozonants, vulcanization accelerators and some other additives used for the preparation of rubber mixtures were analyzed by combined gel permeation and thin-layer chromatographic methods. Attention was concentrated in the first place on the gel permeation chromatographic method. Elution volumes and relative elution volumes were determined for all compounds under investigation. A flow refractometer combined with a flow UV analyzer was used for detection. Such an arrangement is suitable for the analysis of a mixture of aliphatic and aromatic compounds that have similar elution volumes. Acetone extracts of rubbers and mixtures of technical additives representing the main components of vulcanization mixtures applied in Czechoslovakia were analyzed, and the possibility of the quantitative determination of the individual components in mixtures directly from chromatographic records was investigated.

INTRODUCTION

Synthetic rubbers form complex mixtures of compounds of various types. Besides the basic macromolecular rubber components and intentionally added technical additives (antioxidants, antiozonants, softeners, vulcanization accelerators),

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they contain various amounts of undefined impurities introduced with monomers, catalyst residues, polymerization initiators and regulators and other compounds which may influence vulcanization processes, and above all the degradation of the polymeric material. At the same time, the content and composition of the originally introduced additives vary considerably during both processes. With respect to the general characterization of rubbers and their vulcanizates, it is necessary to know the type and amount of the additives present, and it is also advisable to know the residue content of stabilizers and some transformation products after partial ageing. Hence this analytical problem is very complicated.

The possibilities of a complete and accurate analysis of technical vulcanizates are limited by several factors. Besides a large number of chemically often very similar components, which render the direct determination of the additives practically impossible without a previous separation from the polymer, these factors also result in a difficult and incomplete separation of additives present in the polymer in low concentrations, as well the limited chemical stability of some of these compounds.

The additives are separated from the vulcanization mixtures by a cautious extraction, mostly with polar solvents[1-4] (*e.g.*, acetone, diethyl ether, ethanol and isopropanol). The extracts thus obtained contain, together with the compounds to be analysed, also other extractables, such as oils, waxes and low-molecular-weight components of polymers, which render the analysis difficult. These components must therefore be removed (by precipitation) before analysis. The mixture of additives thus obtained may then be separated into several fractions by further gradual extraction with solvents of different polarity or by column chromatography. For the identification of the additives, the following procedures are used[1-4]: colour tests, colorimetry, IR and UV spectrometry, and frequently chromatographic methods, such as paper chromatography (PC), thin-layer chromatography (TLC) and gas–liquid and gas–solid chromatography (GLC, GSC). A disadvantage of each of the above methods is that they give quantitative and accurate data only sporadically. In all instances, a combination of different analytical techniques should be used in order to obtain accurate results. The difficulties involved in the determination of the additives in rubbers as outlined above have led to a search for more suitable techniques. Of recent chromatographic methods, liquid chromatography (LC) has been used to a limited extent for identifying several antioxidants and softeners[5,6]. Gel chromatography has been applied to the analyses of stabilizers in polyolefins[7,8] and for the investigation of the behaviour of typical amine stabilizers in rubbers[9]. The application of this technique does not exclude extraction; by using a calibration with some appropriately chosen compounds, it is possible to obtain data on the content of some of the components under investigation in the vulcanization mixture.

EXPERIMENTAL

Chemicals and technical materials

The solvents used, tetrahydrofuran (THF), acetone, methanol, benzene, diethyl ether and hexane, were of analytical reagent grade.

Technical samples of rubbers, amine antioxidants and antiozonants, vulcanization accelerators and other rubber additives were used for the analyses. The chemical composition and trade-names of analyzed additives are summarized in Tables I

TABLE I

GEL CHROMATOGRAPHIC BEHAVIOUR OF SELECTED AMINE ANTIOXIDANTS AND ANTIOZONANTS FOR RUBBERS

$V_0 = 124.5\ cm^3$.

Trade-name	*Structure*	*Mol. wt.*	V_e (cm^3)	V_r
Antioxidant 116	Phenyl-2-naphthylamine	219.27	190.6	0.653
PBN	Phenyl-2-naphthylamine	219.27	190.6	0.653
UOP 288	N,N'-Bis-(1-methylheptyl)-*p*-phenylenediamine	332.58	149.1*	0.834
Santoflex IP	N-Phenyl-N'-isopropyl-*p*-phenylenediamine	226.34	172.8*	0.720
Nonox ZA	N-Phenyl-N'-isopropyl-*p*-phenylenediamine	226.34	172.8*	0.720
UOP 688	N-Phenyl-N'-octyl-*p*-phenylenediamine	296.47	156.0*	0.797
Altofane DIP	N,N'-Diphenyl-*p*-phenylenediamine	260.36	169.8*	0.733
JZF	N,N'-Diphenyl-*p*-phenylenediamine	260.36	169.8*	0.733
Antioxidant 123	N,N'-Di-2-naphthyl-*p*-phenylenediamine	360.46	161.0	0.773
DNPD	N,N'-Di-2-naphthyl-*p*-phenylenediamine	360.46	161.0	0.773
Thermoflex A	2:1:1 mixture of phenyl-2-naphthylamine,			
	4,4'-dimethoxydiphenylamine and	—	167.9	0.741
	N,N'-diphenyl-*p*-phenylenediamine		187.6**	0.663
Age Rite Hipar	2:1:1 mixture of phenyl-2-naphthylamine,		167.9	0.741
	p-isopropoxydiphenylamine and	—	176.8	0.704
	N,N'-diphenyl-*p*-phenylenediamine		187.6*	0.663

* Contains some other compounds.

** The presence of 4,4'-dimethoxydiphenylamine was not proved.

and II. The producers are Anchor Chemical Co., Manchester, Great Britain (Antioxidant 123, Age Rite Powder, Antioxidant 116), Arnold, Hoffman & Co., Providence, R.I., U.S.A. (Nonox ZA), J. Dimitrov Chemical Works, Bratislava, Czechoslovakia (PBN, DNPD, Hermat ZDC, Hermat ZDK, Hermat ZDM, Hermat FEDK, Hermat Cu, Antioxidant MB, Pneumax MBT, Rodanin S-62, Pneumax DM, Hermat ZnMBT, Hermat TMT, Herax UTS, Peptazin BAFD, Sulfenax CB/30, dialkyl dithiocarbamates), Établissements Kuhlmann, Paris, France (Altofane DIP), DuPont, Wilmington, Del., U.S.A. (Thermoflex A), Monsanto, St. Louis, Mo., U.S.A. (Santoflex IP, Santocure Moor), R. T. Vanderbilt Co., New York, N.Y., U.S.A. (Age Rite Hipar) and UOP Chemical Co., East Rutherford, N.J., U.S.A. (UOP 288, UOP 688). 2-Phenylbenzothiazole, ISAF carbon black, Triumf, zinc oxide, sulphur, stearin and paraffin (a technical mixture of *n*-alkanes) were from various sources.

Extractions were carried out with commercial samples of styrene–butadiene rubbers of Czechoslovak origin, *viz.*, SBR-1712, Kralex 510 403, SBR-1500, Kralex 010 402, natural rubber PK-RSS-I and polybutadiene rubber *cis*-PB-1220.

Extraction

The rubber samples were cut into strips, weighed and extracted for 16 h in the dark with 150 cm^3 of acetone in an inert atmosphere in a Soxhlet apparatus. The extracts were concentrated in a vacuum evaporator, the oligomers were precipitated with methanol, the filtrates were evaporated to dryness and the solid residues were weighed. The extracts thus obtained were used for chromatographic analyses. The synthetically prepared mixtures of additives containing soluble and insoluble fractions were extracted in the same way for 1 h.

TABLE II

GEL CHROMATOGRAPHIC BEHAVIOUR OF VULCANIZATION ACCELERATORS AND OTHER SELECTED RUBBER ADDITIVES

$V_0 = 124.5$ cm^3.

Trade-name	*Structure*	*Mol. wt.*	V_e (cm^3)	V_r
Hermat ZDM	Zinc N-dimethyldithiocarbamate	305.82	203.4[*]	0.612
Hermat ZDK	Zinc N-diethyldithiocarbamate	361.94	181.7[*]	0.685
Hermat FEDK	Zinc N-ethylphenyldithiocarbamate	458.02	166.9[*]	0.745
—	Nickel N-dimethyldithiocarbamate	299.16	211.3[*,**]	0.589
—	Nickel N-dibutyldithiocarbamate	467.48	156.0[*]	0.797
—	Sodium N-diethyldithiocarbamate	319.56	184.7[*,***]	0.673
Hermat Cu	Copper N-dimethyldithiocarbamate	303.99	207.4[*,**]	0.600
Rodanin S-62	2-Mercaptoimidazoline	102.16	203.4[*]	0.612
Pneumax MBT	2-Mercaptobenzothiazole	167.24	200.5[*]	0.620
Antioxidant MB	2-Mercaptobenzimidazole	150.20	185.6[*]	0.670
—	2-Phenylbenzothiazole	211.29	218.2	0.570
Pneumax DM	Dibenzothiazyl disulphide	332.48	209.3[*,***]	0.594
Hermat TMT	Tetramethylthiuram disulphide	240.45	219.2	0.567
Peptazin BAFD	Di-*o*-benzamidophenyl disulphide	458.62	169.0	0.736
Hermat Zn MBT	Zinc salt of 2-mercaptobenzothiazole	231.61	200.5[*,***]	0.620
Sulfenax CB/30	Benzothiazyl-2-cyclohexylsulphenamide	264.41	188.6[***]	0.659
Santocure Moor	Benzothiazyl-2-morpholylsulphenamide	267.37	208.4	0.597
Herax UTS	Activated hexamethylenetetramine	140.19	183.7[*,***]	0.677
ISAF-black	—	—	[§]	—
Triumf	Mineral oil	—	[§§]	—
—	Zinc oxide	—	[§]	
—	Sulphur	—	304.1[*]	0.409
Paraffin	—	—	[§]	—
Stearin	—	—	152.1	0.817
			157.0	0.792

[*] Partly insoluble in acetone and THF.
[**] Only UV detection.
[***] Contains some other compounds.
[§] Insoluble in acetone and THF.
[§§] Only diffusion UV detection in the range 120–220 cm^3.

Chromatography

Preliminary TLC analyses were performed on Silufol UV$_{254}$ silica gel precoated aluminium foils (Kavalier, Votice, Czechoslovakia). Samples of extracts dissolved in acetone were placed dropwise on these foils and benzene–hexane, benzene–diethyl ether and benzene–ethanol mixtures with ascending development were used for elution. A UV lamp or development of spots by spraying with a hexacyanoferrate(II)–hexacyanoferrate(III) reagent or an acidic solution of potassium permanganate was used for detection.

A chromatograph designed and built at the Institute of Macromolecular Chemistry, Prague, was used for gel chromatographic analyses[9]. The columns were packed with Kopolymer ST-DVB No. VIII polystyrene gel (United Chemical and Metallurgical Works, Production Company, Ústí, Czechoslovakia), grain size 0.040–0.056 mesh. Sample solutions of concentration 2–5% in THF were injected into the columns. The operating temperature in the columns was 25°, the flow-rate of eluent was

30–50 cm^3/h and the pressure in the columns was 2–4 atm. The elution volumes of the samples, V_e (cm^3), were read off from the maxima of the elution peaks of the compounds investigated. In order to characterize the samples, relative elution volumes, V_r, related to the exclusion limit of the chromatographic system, *i.e.*, $V_r = V_0/V_e$, were also calculated.

RESULTS AND DISCUSSION

The gel permeation chromatographic (GPC) analyses of commercial samples of various rubber additives and analyses of extracts of rubber mixtures prepared for vulcanization were based on our previous experience in the gel chromatographic investigation of polymer additives[7–9].

A large group of aromatic amines and diamines and the comparison of their gel chromatographic behaviour with that of model compounds and standards were dealt with in a previous paper[9]. For this study, we selected the most important types of amine antioxidants and antiozonants that are most frequently used in rubber compositions. All were soluble in acetone and THF. Table I gives the values of their elution volumes, V_e. Apart from the main active component indicated by the manufacturer, the stabilizers under investigation almost always contain minor or major amounts of other compounds. For instance, the antioxidant UOP 288 contains at least four other compounds in addition to the main component. On the other hand, the presence of 4,4′-dimethoxydiphenylamine was not detected in a sample of the antiozonant Thermoflex A, which, according to the manufacturer's data, is a mixture of three compounds (Table I). The data presented here indicate that in most instances it is useful for the analyses of rubber mixture extracts to have authentic samples of the technical stabilizers used (which naturally also applies to other additives), in order to obtain more exact conclusions about the content or transformations of the active component.

The individual vulcanization accelerators were also analyzed (Table II; V_e values of the active component are given). It was found that the vulcanization mixtures also consisted of mixtures of several compounds; not only does the composition of the commercial samples often vary with the storage time, but different batches also differ from each other. Sulfenax CB/30 may be cited as an example of such behaviour: in addition to the main component, *i.e.* benzothiazyl-2-cyclohexylsulphenamide, it contained up to 13% of other compounds. Refractometric detection revealed the presence of three, and another seven were found by UV detection; their number and content varied.

Besides 2-phenylbenzothiazole, Antioxidant MB, Santocure Moor, Peptazin BAFD and Hermat TMT, the technical accelerators also contained fractions that were insoluble both in acetone and in THF. Consequently, the insoluble components (which remain in the rubber after extraction) had to be removed by filtration before gel chromatographic analyses; they cannot be determined by the procedure described above.

In order to obtain a wider survey of the complex chromatograms of rubber mixture extracts and the possible interferences that may occur during the determination of stabilizers, the GPC method was also used to analyze some other additives used in rubber mixtures (Table II). All samples of these additives were extracted in the same way as the analyzed vulcanization mixtures. Neither carbon black nor zinc oxide contained any fractions that were soluble in acetone or THF. Sulphur dissolved partly in both extractants when cold. Cooled filtrates of hot acetone and THF sulphur extracts were used for the analyses. Stearin and paraffin were soluble in both extractants only while hot. Paraffin could not be detected in extracts either refractometrically or with a UV analyzer; consequently, it did not interfere in the determination of any of the other components of the mixture.

Samples of additives produced by different manufacturers for which an identical chemical composition is indicated may differ considerably in their contents of the active compounds, and it is often very difficult to determine the individual compounds in such samples. The content of the main active compound and of the other components in a commercial sample may be controlled only by using a calibration with a standard and a defined model compound. In this respect, the GPC analysis provides data that are reproducible and considerably more exact than those obtained by other analytical procedures.

In order to distinguish qualitatively compounds that have the same or a similar elution volume, V_e, and to compare the composition of additives with a declared identical chemical composition but produced by different manufacturers, it is often necessary to use other analytical techniques combined with GPC. We chose TLC for our work; it can be used for preliminary qualitative analyses in combination with colour tests, thus supplementing the results of the GPC measurements. Table III summarizes the results of the TLC analyses of the most important additives used in the rubber mixtures which were investigated in greater detail and for which it was necessary to distinguish qualitatively some components in the mixture that had very similar V_e values (*e.g.*, phenyl-2-naphthylamine PBN and Sulfenax CB/30).

TABLE III

R_F VALUES OF SELECTED RUBBER ADDITIVES (TLC, SILUFOL UV_{254})

S_1 = benzene–hexane (1:1); S_2 = benzene–diethyl ether (3:2); S_3 = benzene–ethanol (95:5).

Additive	R_F		
	S_1	S_2	S_3
PBN	0.22	0.64	0.35, 0.72
Santoflex IP	0	0.31	0.37
Sulfenax CB/30	0.04	0.61	0.61
Santocure Moor	0	0.41	0.29, 0.49, 0.65
Triumf	0.08, 0.58	0.75	0.81

All of the results obtained on separately analyzed technical additives and with the aid of standards or model compounds are a basis for the analysis of mixtures of additives in the extracts of the vulcanization mixtures. The investigation was concentrated on typical mixtures used for car tyre production, two examples of which are given in Table IV. No interference occurred during the GPC determination of the content of the active components of the stabilization and vulcanization mixture. However, it was necessary to compare chromatograms of standards, mixtures of additives and those obtained by model blank analyses, which, in this instance, consisted

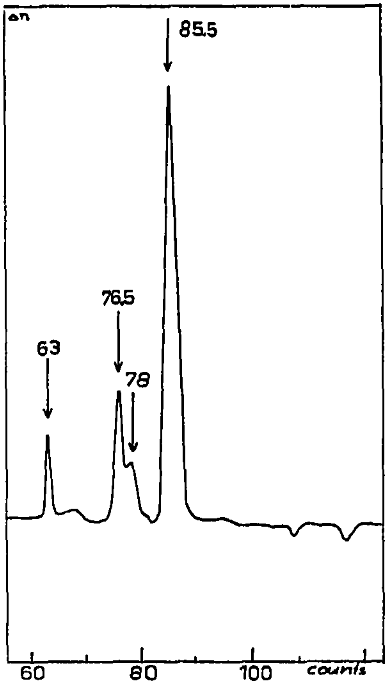
TABLE IV

SELECTED RUBBER COMPOSITIONS

Component	*Proportions (parts by weight)*	
	No. 1[**]	*No. 2*[**]
SBR-1712	60	—
SBR-1500	—	40
SKD[*]	40	—
PB	—	20
PK	—	40
ISAF black	60	—
AXF black	—	50
Triumf	1.3	7
ZnO	3	3
Stearin	2	1.5
Paraffin	1–2	2
PBN	—	1–2
Santoflex IP	1–1.5	1–2
Sulfenax CB/30	1	—
Santocure Moor	—	1
Sulphur	1.8	2.5

[*] Polyisoprene rubber of Soviet origin.

[**] Chromatograms of mixtures Nos. 1 and 2 are shown in Figs. 5 and 6, respectively.



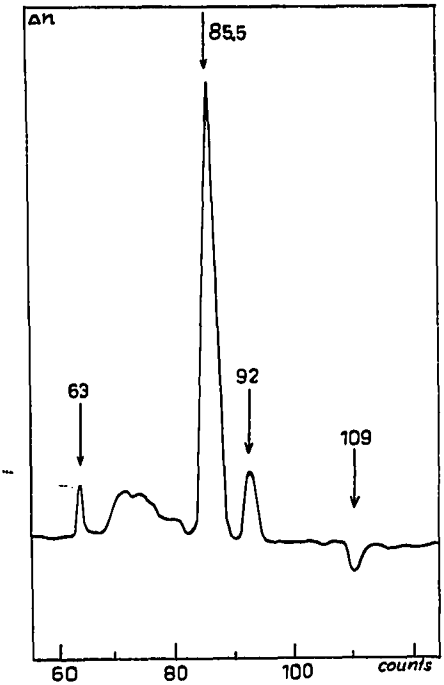
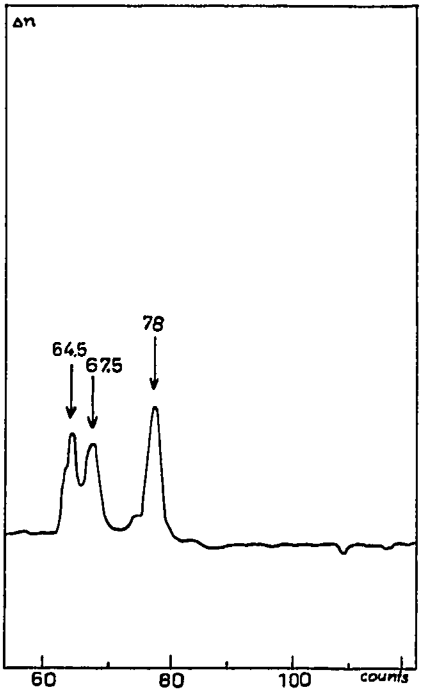


Fig. 1. Chromatogram of an acetone extract of SBR-1712 (refractometric detection; 1 volume count = 1.975 cm^3).

Fig. 2. Chromatogram of an acetone extract of SBR-1500 (refractometric detection; 1 volume count = 1.975 cm^3).

predominantly of analyses of pure rubber bases. Acetone was chosen as the extractant, as it proved to be the most suitable for the required purposes because of its low boiling point and comparatively short extraction time (the additives being readily soluble in it). Most low-molecular-weight organic compounds are extracted with acetone without change; if the extraction is carried out with the exclusion of light and in an inert medium, oxidation of the polymer does not occur. Only a few accelerators (*e.g.*, thiuram compounds) lead to decomposition when acetone is used as the extractant; in the presence of such accelerators, isopropanol was used in the extractions.

Pure rubbers contain small amounts of various compounds that can be extracted with acetone; for instance, the amounts of low-molecular-weight compounds extracted from samples of SBR-1712 rubber, SBR-1500 rubber, PK-RSS-I natural rubber and *cis*-PB-1220 rubber were 6.34, 9.93, 2.46 and 0.42%, respectively. The compounds extracted from synthetic rubbers are mostly monomers and the impurities introduced are oligomers and polymerization additives; an extract of natural rubbers contains compounds of vegetable origin (organic acids and esters, phospholipids, sterols, resins, etc.). Figs. 1–4 show chromatograms of the acetone extracts of rubbers used as a basis for the above vulcanization mixtures, the results being given in volume counts (vol. c.). From the chromatograms obtained by means of a flow refractometer, it can be seen that of the extractable and refractometrically indicated compounds, com-



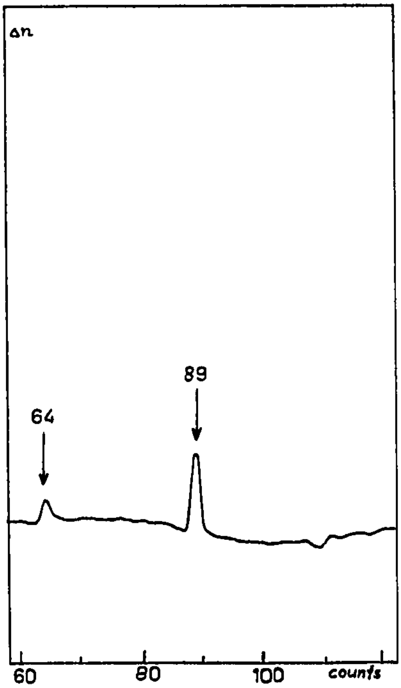


Fig. 3. Chromatogram of an acetone extract of PK (refractometric detection; 1 volume count = 1.975 cm^3).

Fig. 4. Chromatogram of an acetone extract of PB (refractometric detection; 1 volume count = 1.975 cm^3).

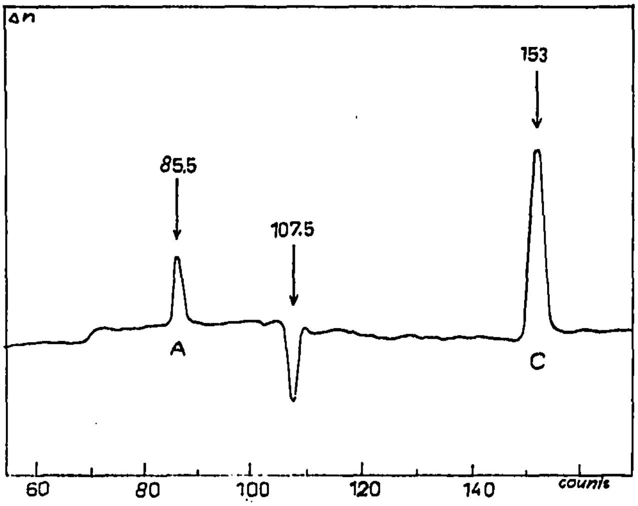


Fig. 5. Chromatogram of an acetone extract of mixture No. 1. A = Santoflex IP; C = sulphur; negative peak = water. (Table IV; refractometric detection; 1 volume count = 1.975 cm^3.)

ponents with $V_e > 75$ vol. c. may interfere with some of the additives. The V_e values of additives are higher in most instances than those of the soluble rubber fractions.

Figs. 5 and 6 show chromatograms of the acetone extracts of two model mixtures of vulcanization additives. The individual components do not interfere during the determination. The quantitative determination was carried out by calibrating the heights of the individual peaks with pure model compounds; agreement was reached in model mixtures between the amount of the active compound used and that determined analytically.

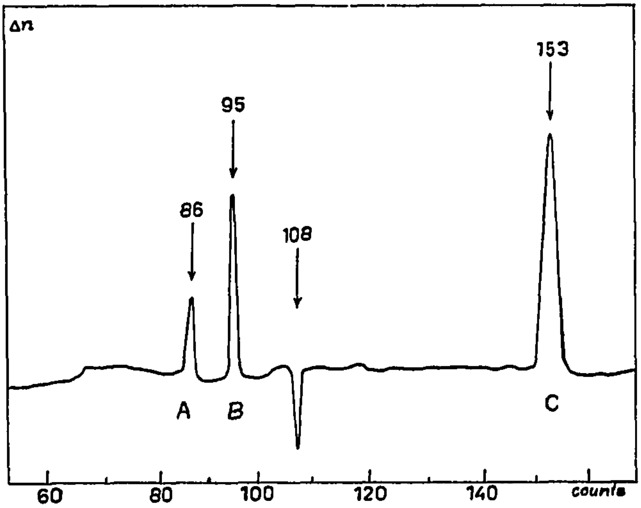


Fig. 6. Chromatogram of acetone extract of mixture No. 2. A = Santoflex IP; B = PBN; C = sulphur; negative peak = water. (Table IV; refractometric detection; 1 volume count = 1.975 cm^3.)

From the examples of the V_e values of various rubber additives obtained from chromatograms of the rubber extracts and of mixtures of additives for technical uses, it can be deduced that the components of the extracts of vulcanization mixtures can be analyzed before the vulcanization process itself.

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