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CHREV. 184

CHROMATOGRAPHIC ANALYSIS OF ELASTOMER ANTIDEGRADANTS AND ACCELERATORS

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CONTENTS

1. INTRODUCTION

The identification of accelerators and antidegradants in rubber mixtures presents some notable difficulties. These are principally due to the relatively small quantity of the materials contained in the mixtures, and to the presence of many other materials, either naturally occurring in the rubber or added during its compounding. Such materials can interfere with the desired identification, especially when traditional methods such as "colour reactions" or fluorometric examinations are used. Often accelerators and antidegradants are difficult or impossible to recover from vulcanizates. They may be altered in the course of mixing and vulcanization, and more completely during subsequent ageing and extraction.

Even in the most favourable cases, the examination of total solvent extracts is uncertain or negative. This is true even if carried out by means of sensitive instrumental analytical methods, *i.e.* ultraviolet (UV) and infrared (IR) spectrophotometry. The spectra obtained are generally very complex and represent the superposition of the spectra of each component, or show the spectra of the components present in greater concentration, which in many cases are not those of interest.

Therefore, as a primary goal it is necessary to achieve the best possible separation of the various components. Considering the low concentrations of the components under examination, their low thermal stability and ease of oxidation, methods based on fractionation by means of solvent or distillation, even if carried out under high vacuum, are not appropriate.

Throughout the last few decades analysts have employed an ever increasing array of techniques to attack the problem of rubber analysis. The advent of chromatographic techniques has provided analysts with a very sensitive simultaneous separatory–identification technique that has enhanced their ability to determine many minor constituents such as accelerators and antioxidants present in vulcanizates.

This review will attempt to cover all relevant chromatographic work pertaining to the analysis of accelerators and antioxidants used in elastomeric compositions.

Periodic reviews[1–20] entitled *Rubber* have appeared in *Analytical Chemistry* and cover the analysis and characterization of rubber by physical, chemical and spectroscopic methods. Methods for the identification and determination of rubber and additives in rubber have been included, but the analysis of additives alone have not.

A number of reviews have appeared in the past but these now largely do not represent current practice or developments. The reviews include:

(i) Analysis of rubber and plastic chemicals by liquid chromatography–spectroscopy (1982)[21].

(ii) Chromatographic detection of accelerators and antioxidants (1966)[22].

(iii) Chromatographic techniques for analysis of rubber (1980)[22].

(iv) Analysis of antioxidants in polymers by liquid chromatography (1980)[22].

(v) Analysis of antioxidants in polymeric materials (1968)[25].

(vi) Gas chromatographic application to rubber analysis (1977)[26].

(vii) Thin-layer chromatographic identification of rubber compounding ingredients (1969)[27].

Several minor reviews[28–33] have also been published between 1959 and 1981.

The second edition of the book by Wake[34] published in 1969 and another book by Crompton[35] give a good account of available analytical techniques of elastomer analysis. The 59th chapter, *Rubber and Rubber Products Analysis*, in the book by Welcher (1963)[36] also provides a useful collection of literature. Haslam and Willis[37], in their book *Analysis of Plastics* (1965), include some material applicable to rubber.

2. VULCANIZATION ACCELERATORS

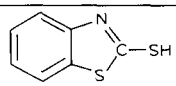
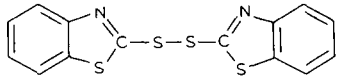
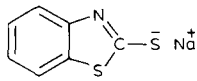
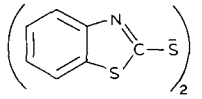
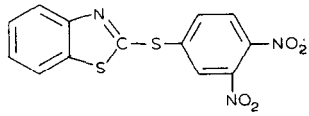
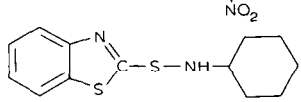
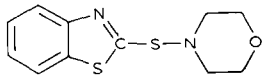
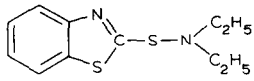
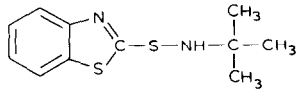
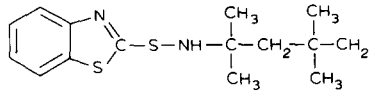
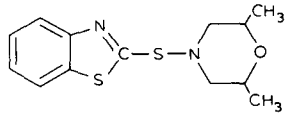
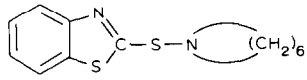
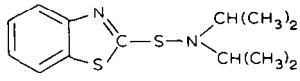
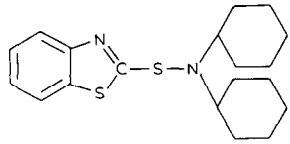
Accelerators are of great economic importance to the rubber industry. They not only reduce vulcanization times from hours to minutes, but they also have important effects on the physical characteristics of rubber stocks in which they are used. These influences on physical properties are important in relation to the final use of the rubber products.

Accelerators in general are made up of several chemical classes as shown in Table 1.

The aldehyde amine condensation products are not usually simple chemical compounds and therefore are not easy to detect or identify. However, they appear to be of diminishing commercial significance, as reflected by the reduction in associated analytical citations. Chemical changes in accelerators during vulcanization have been studied in detail by Campbell and Wise[38,39], using UV spectrophotometry. Mercaptobenzothiazole (MBT) and its derivatives (MBTS, ZMBT, etc.) probably cannot be distinguished from each other in a vulcanizate since all forms may be present in a vulcanizate originally containing only one of them[40]. The same reasoning

TABLE 1

MAJOR CLASSES OF ACCELERATORS

Type	*Formula*	*Chemical name*	*Abbreviation*
Thiazoles		Mercaptobenzothiazole	MBT
		Dibenzthiazyl disulphide	MBTS
		Sodium salt of MBT	SMBT
		Zinc salt of MBT	ZMBT
		2(2,4-Dinitrophenylthio)-benzothizole	–
Sulphenamides		N-Cyclohexyl-2-benzthiazolsulphenamide	CBS
		N-Oxydiethyl-2-benzthiazolsulphenamide	NOBS,MOR
		N,N'-Diethyl-2-benzothiazole sulphenamide	AZ
		N-Tert-butyl-2-benzothiazole sulphenamide	TBBS
		N-2,2,3-Tetramethyl-butyl-2-benzothiazole sulphenamide	TOBS
		2(2,6-Dimethyl-4-morpholino-thio)-2-benzothiazole sulphenamide	MOR-26
		N,N'-Hexamethylene-2-benzothiazole sulphenamide	HBS
		N,N'-Diisopropyl-2-benzothiazole sulphenamide	DPS
		N,N'-Dicyclohexyl-2-benzothiazole sulphenamide	DCBS

(Continued on p. 306)

TABLE 1 (*continued*)

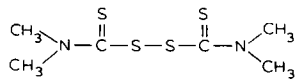
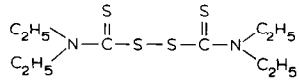
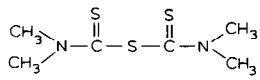
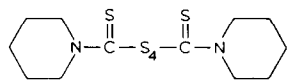
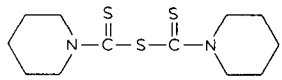
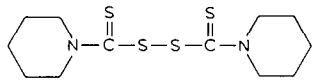
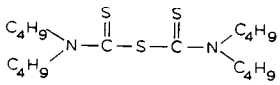
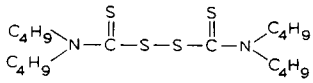
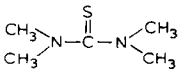
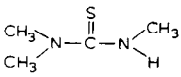
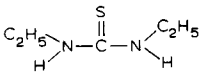
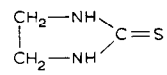
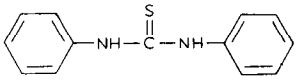
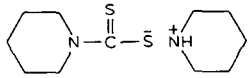
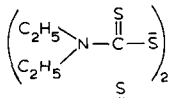
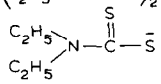
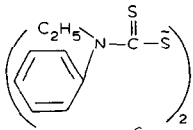
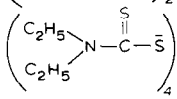
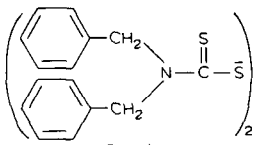
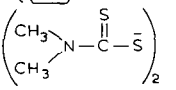
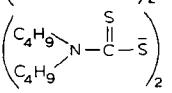
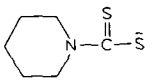
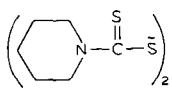
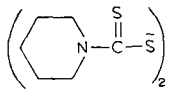
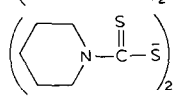
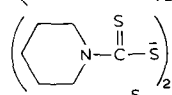
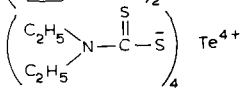
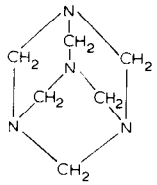
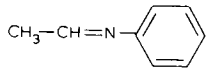
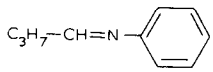
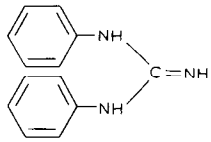
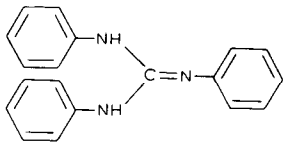
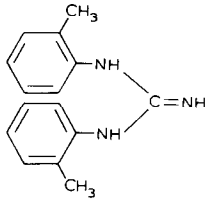
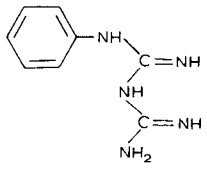
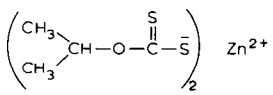
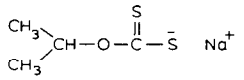
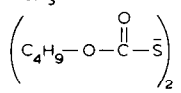
Type	*Formula*	*Chemical name*	*Abbreviation*
Thiuram sulphides		Tetramethyl thiuram disulphide	TMT, TMTD
		Tetraethyl thiuram disulphide	TET, TETD
		Tetramethyl thiuram monosulphide	TMTM
		Dipentamethylene thiuram tetrasulphide	DPTS
		Dipentamethylene thiuram monosulphide	DPM
		Dipentamethylene thiuram disulphide	DPTD
		Tetrabutyl thiuram monosulphide	TBTM
		Tetrabutyl thiuram disulphide	TBTD
Thioureas		Tetramethyl thiourea	TMTU
		Trimethyl thiourea	–
		N,N′-Diethyl thiourea	DMTU
		Ethylene thiourea	EU
		Thiocarbanilide	TC

TABLE 1 (*continued*)

Type	*Formula*	*Chemical name*	*Abbreviation*
Dithiocarbamates		Piperidine pentamethylene dithiocarbamate	PPD
		Zinc diethyl dithiocarbamate	ZDC, ZDEC
		Sodium diethyl dithiocarbamate	SDC, SDEC
		Zinc ethyl phenyl dithiocarbamate	ZEPC
		Selenium diethyl dithiocarbamate	–
		Zinc dibenzyl dithiocarbamate	–
		Zinc dimethyl dithiocarbamate	ZDM
		Zinc dibutyl dithiocarbamate	ZBDC
		Sodium pentamethylene dithiocarbamate	SPD
		Zinc pentamethylene dithiocarbamate	ZPD
		Lead pentamethylene dithiocarbamate	LPD
		Copper pentamethylene dithiocarbamate	CuDD
		Cadmium pentamethylene dithiocarbamate	CPD
		Tellurium diethyl dithiocarbamate	TDEC

(Continued on p. 308)

TABLE 1 (*continued*)

Type	*Formula*	*Chemical name*	*Abbreviation*
Aldehyde amines		Hexamethylene tetramine (hexamine)	HMT
		Ethylidene aniline	EA
		Butryldehyde aniline	BA
Guanidines		Diphenyl guanidine	DPG
		Triphenyl guanidine	TPG
		Di-*o*-tolylguanidine	DOTG
		*o*-Tolyl biguanidine	OTBG
Xanthates		Zinc isopropyl xanthate	ZIX
		Sodium isopropyl xanthate	SIX
		Zinc butyl xanthate	ZBX

applies to dithiocarbamates and to tetraalkyl thiuram sulfide[41–43]. Sulphenamide[28,39] accelerators are also usually completely decomposed to MBT and the amine that was originally combined in the sulphenamide. Guandines are the only class of accelerator that can be detected unchanged. Therefore, the identification of an accelerator system resolves itself into a search for degradation fragments.

When a rubber compound is to be reproduced and the general composition has already been determined, identification of an existing single unknown accelerator can often be made from fragment analysis. The optimum level of accelerator can be independently evaluated using cure rheometer information. However, when two or more accelerators are employed, cure experiments designed to optimize levels become too numerous, and in this case quantitative analytical results are necessary.

3. ANTIDEGRADANTS

By adjusting the various factors making up the curing system of a given stock, it is possible for a rubber compounder to obtain good ageing properties. This requires a proper balance between the amount of sulphur, time of cure, type of accelerator, and the combination of activating materials used. Whilst ageing performance can be improved by using suitable cure systems, the primary retention of properties is made possible using antidegradant chemicals.

In general, antidegradants consist of two major chemical classes *i.e.*, secondary aryl amines and substituted phenols. These can be further classified as shown in Table 2.

The amine type of antioxidants are much more effective in prolonging the life of rubber stocks than the substituted phenols, but during oxidation they form yellow to dark brown compounds which stain materials with which they come into contact[28]. The substituted phenols are particularly free of this disadvantage, but they are much less effective in their protective action[28].

The antioxidants are fairly stable compared with accelerators, but precautions must be taken to minimize oxidation during extraction, otherwise oxidation products will interfere with the subsequent analysis.

4. EXTRACTION OF ACCELERATORS AND ANTIOXIDANTS

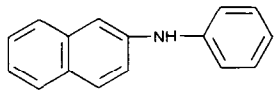
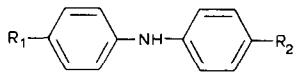
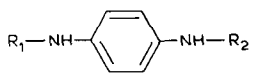
The separation of non-polymeric organic additives from the rubber matrix is the initial step of chromatographic analysis. Most separations that have been reported concern solid–liquid extraction, since the insoluble nature of the rubber matrix precludes the possibility of using the more efficient liquid–liquid extraction.

Quantitative solvent extractions are normally carried out using Soxhlet and Underwriters extraction techniques. Methods for antioxidant extraction from polymers are summarized by Wheeler[25]. The subsequent analyses employed have some degree of versatility, being also useful for other compound ingredients. This topic has also been discussed and reviewed by Schroeder[32], and much of the relevant information on the extraction of accelerators and antioxidants is summarized in Table 3.

It is necessary in most instances to use a solvent system where the maximum amount of organic additives and the minimum amount of the polymer is extracted.

TABLE 2

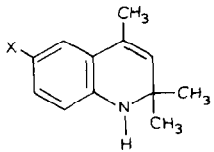
ANTIDEGRADANTS ASSOCIATED WITH VULCANIZATION

Class	*Compound*	*Structure*
I	*Secondary diarylamines Ar-NH-Ar*	
	(A) Phenyl naphthylamines	
	1. N-Phenyl-β-naphthylamine [PBN(A)]	
	2. N-Phenyl-α-naphthylamine [PAN(A)]	
	(B) Substituted diphenylamines	
	1. Nonylated diphenylamine (NDA)	
	2. Octylated diphenylamine (ODA)	
	3. 4,4′-Dimethoxydiphenylamine (MDA)	
	4. Isopropoxy-2-diphenylamine (IDA)	R_1, R_2 usually alkyl C_7–C_9
	(C) Substituted *p*-phenylenediamines	
	1. N,N′-Bis(1,4-dimethylpentyl)-*p*-phenylenediamine (BDPD)	
	2. N,N′-Bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine [BA(M)PD, UOP]	R_1 = alkyl or aryl, R_2 = alkyl or aryl
	3. N,N′-Bis(1-methylheptyl)-*p*-phenylenediamine (BMPD) [N,N′-di-*sec*.-octyl-*p*-phenylenediamine] (DOPD)	
	4. N,N′-Diaryl-*p*-phenylenediamine (DPD)	
	5. N,N′-Di-2-naphthyl-*p*-phenylenediamine (DNPD)	
	6. N,N′-Diphenyl-*p*-phenylenediamine (DPPD)	
	7. N-Cyclohexyl-N′-phenyl-*p*-phenylenediamine (CPPD)	
	8. N-(1-Methylpropyl)-N′-phenyl-*p*-phenylenediamine (Flexzone 5L) [N-*sec*.-butyl-N′-phenyl-*p*-phenylenediamine] (BPPD)	
	9. N-Isopropyl-N′-phenyl-*p*-phenylenediamine (IPPD)	
	10. N,N′-Dimethyl-N,N′-di(1-methylpropyl)-*p*-phenylenediamine [DMD(MP)PD]	
	11. Di-(1-methoxypropyl)-*p*-phenylenediamine [D(MP)PD]	
	12. N,N′-Di-*sec*.-butyl-*p*-phenylenediamine	
	13. N,N′-Di-isopropyl-*p*-phenylenediamine	

II *Ketone (acetone) amine condensates*

(A) Dihydroquinolines, primary arylamine reaction products,

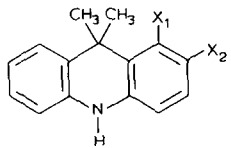
1. Polymerized 1,2-dihydro-2,2,4-trimethylquinoline (PDTQ)
2. 6-Dodecyl-1,2-dihydro-2,2,4-trimethylquinoline (DTQ)
3. 6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (DTEQ)



X = H, alkyl, alkoxy

(B) Secondary diarylamine reaction products,

1. Diphenylamine-acetone
2. N-Phenyl-2-napthylamine-acetone



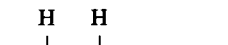
X_1, X_2 = H or phenyl

III *Aldehyde-amine-condensates*

1. Aldol-1-naphthylamine
2. Butyraldehyde-aniline

IV *Alkyl–aryl secondary amines*

1. N,N′-Diphenyl-ethylenediamine
2. N,N′-Diphenyl-propylene diamine
3. N,N′-Di-*o*-tolyl-ethylene diamine



X = ethylene or propylene

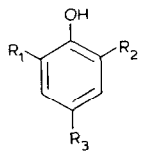
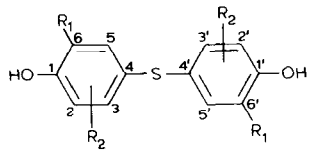
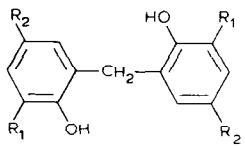
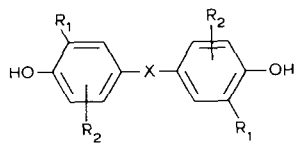
V *Primary arylene diamines*

1. 2,4-Diaminotoluene (TDA)
2. 4,4′-Diamino-diphenylmethane

X = *m*-tolylene or 4,4′-methylenediphenyl

(Continued on p. 312)

TABLE 2 (*continued*)

Class	*Compound*	*Structure*
VI	*Hindered phenols* 1. Alkylated phenol 2. 2,6-Di-*tert.*-butyl-4-methylphenol(2,5-di-*tert.*-butyl-*p*-cresol) (DBCP, BHT) 3. 2,6-Di-*tert.*-butyl-α-dimethylamino-4-methylphenol 4. 2,6-Di-*tert.*-butyl-α-methoxy-4-methylphenol 5. Mixed *tert.*-butyl- and α-octyl-phenols 6. Styrenated (α-phenylethylated) phenol 7. Mixed 2-*tert.*-butyl-4-methoxyphenol and 3-*tert.*-butyl-4-methoxy phenol (BHA)	 R_1 = *tert.*-alkyl or α-phenylethyl R_2 = methyl, substituted methyl, or *tert.*-alkyl R_3 = alkyl or H
VII	*Hindered thio-bis-phenols* 1. 4,4′-Thio-bis(6-*tert.*-butyl-2-methylphenol) (TMTPB) 2. 4,4′-Thio-bis(6-*tert.*-butyl-o-cresol) 3. 4,4′-Thio-bis(6-*tert.*-butyl-3-methylphenol) 4. Thio-bis(di-*sec.*-amylphenol)	 R_1 = *tert.*-butyl or *sec.*-amyl R_2 = methyl in 3 or 2
VIII	*Hindered bis-phenols* (A) *Ortho, ortho′* 1. 2,2′-Methylene-bis(6-*tert.*-butyl-4-ethylphenol) 2. 2,2′-Methylene-bis(6-*tert.*-butyl-4-methylphenol) 3. 2,2′-Methylene-bis(6-α-methylcyclohexyl-4-methylphenol)	 R_1 = *tert.*-butyl or α-methylcyclohexyl R_2 = methyl or ethyl
	(B) *Para, para′* 1. 4,4′-Bis(2,6-di-*tert.*-butylphenol) 2. 4,4′-Methylene-bis(6-*tert.*-butyl-2-methylphenol) 3. 4,4′-Butylidene-bis(6-*tert.*-butyl-3-methylphenol) 4. 4,4′-Methylene-bis(2,6-di-*tert.*-butylphenol) 5. Polybutylated *p,p′*-isopropylidenephenol	 X = alkylidene or may be absent R_1 = *tert.*-butyl R_2 = methyl or *tert.*-butyl in 2 and 2′, or methyl in positions 3 and 3′

(C) Unclassified polymeric phenols
1. 6-Alkyl-2-methylphenol-ketone condensate
2. Butylated butylidene-bis-phenol
3. Butylidene-bis(dimethylphenols)
4. Methylene-bis(dimethylphenols)
5. Methylene-bis(3-isopropylphenol)
6. Trimeric alkylphenol-formaldehyde condensate

IX *Polyhydroxy phenols*
1. 2,5-Di-*tert.*-amylhydroquinone
2. Hydroquinone mono-benzylether

X *Sulphur compounds*
2-Mercaptobenzimidazole

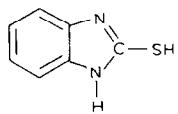


TABLE 3

METHODS OF ACCELERATORS AND ANTIDEGRADANTS EXTRACTION

Substances extracted	*Extracting solvent(s)*	*Details*	*References*
Accelerators and antioxidants	Ethanol–1*N* hydrochloric acid	Refluxed for 2 h and then steam distillation of amines from the extract	44
Antioxidants	Acetonitrile	Finely divided sample is shaken with acetonitrile for 30 min, and cooled to −20°C to separate oil	45
Accelerators and antioxidants	Methyl ethyl ketone–ethanol (3:1)	10 g Sample extracted in Soxhlet	46
Antioxidants and stabilizers	Acetone	For 16 h Soxhlet extraction in the dark under inert atmosphere	47
Accelerators	Isopropanol	Finely divided sample (3 g) extracted with 5 ml of isopropanol by infusion for 1 h at room temperature	48
Accelerators and antioxidants	Acetone	For 8 h in Soxhlet	49,50
Accelerators and antioxidants	Benzene	For 8 h in Soxhlet	51,52
Antioxidants and stabilizers	Ether	2 Days extraction in Soxhlet extraction apparatus	53
Antioxidants and stabilizers	Benzene, acetone, *n*-heptane	24 h Extraction, with benzene or *n*-heptane, or 8 h extraction with acetone	54
Antioxidants	Acetone	24 h Extraction in Soxhlet apparatus in the dark under inert atmosphere	55
Antioxidants	Tetrahydrofuran or chloroform	24 h Extraction in Soxhlet apparatus	56
Antioxidants and stabilizers	Acetone	4 h Extraction in Soxhlet under inert atmosphere, extract was concentrated and oligomers were precipitated with methanol	57
Antioxidants and accelerators	Benzene	Dissolving the uncured polymer in benzene (solvent) and precipitating the polymer with methanol (non solvent)	58

Antioxidants	1. Methanol 2. Chloroform or carbon tetrachloride 3. Isopropanol	1. Extracting with methanol for 4 h or 1–2 h for rapid reflux extraction 2. Shaking with solvent for a short time at temperature (for vulcanizates only) 3. Standing overnight in isopropanol	59
Phenolic antioxidants and cresols	Chloroform	Heat at 50°C for 3 h in a closed container	60
Cresols	Hexane	Heat at 50°C	61
Antioxidants	Toluene	Refluxion to dissolve the polymer in toluene and precipitate with methanol	62–65
Antioxidants	Water	Extraction at 70°C under nitrogen atmosphere	66
p-Phenylenediamine derivative	95% Methanol	For 16 h extraction in an extraction cup	67
Antioxidants	Ether	For 24 h extraction in the dark at room temperature	68
2,6-Di-*tert.*-butyl-*p*-cresol	Cyclohexane	Reflux for 30 min	69
Ketone–amine condensates	Acetone	—	70
Antioxidants	Acetone	—	71,72
Phenolic antioxidants	Compares carbon disulphide with iso-octane	—	73

Various solvents are specified for each polymer type, so that only qualitative analysis of polymer composition is needed before a suitable extraction liquid can be chosen. Where the identity of the elastomer is unknown, a more universal extraction medium may be satisfactory.

Hilton[74] extracted a variety of raw polymers and cured stocks with up to 18 different solvents or solvent combinations for periods ranging from 0.5 to 64 h. Ethanol (95%) was found to be the most versatile solvent but a minimum of 16 h was required for essentially complete extraction. This solvent has several attributes:

(i) It is quite easily removed from the polymer extract because of its low boiling point.

(ii) Most polymers are completely insoluble in ethanol.

(iii) Direct UV analysis can be carried out on the extract.

Parallel experiments[74,75] using Soxhlet and the Underwriters extraction apparatus showed the latter to be more effective during short periods because of the faster rate of solvent recycling. In an overnight run, however, the extraction was complete in both cases for most of the elastomer samples. Other extraction apparatus described include tightly capped bottles in which the sample and solvent are heated under pressure[76], Wiley extractors[67] and flasks in which the sample is merely steeped in solvent[68]. In order to increase the efficiency of extraction, surfactants and ultrasonic devices have been used[77]. An apparatus has been patented[78] where reproducible solubility data for several samples can be obtained simultaneously. A rapid method[79] has also been reported for determining the acetone extractable material in natural rubber (NR) and oil extended NR using a high-speed "Polytron" high-frequency generator.

Yushkevichyute and Shlyapnikov[80] have described an apparatus for the sublimation (*in vacuo*) of several antioxidants present in polymers. Using temperatures of 61–100°C, they were able to achieve satisfactory separation from polymers with molecular weights up to 50,000. In a later publication[55], the same workers reported the extractive separation of certain antioxidants from polymers with distilled water at 75°C under a nitrogen atmosphere.

McSweeney[81] has described a micro-scale procedure for the rapid extraction of compounding ingredients such as accelerators and antioxidants in the rubber using thermal extraction procedures followed by thin-layer chromatographic (TLC) analysis.

Difficult polymers to analyse, because of their insolubility, are polyolefins. The British Standard method[54,55] favoured by some workers, involves dissolution of polymer in boiling toluene under reflux, followed by precipitation of the high-molecular-weight fraction with ethanol. The filtrate then contains the low-molecular-weight organic additives (when toluene and ethanol soluble) and some low-molecular-weight "wax" which normally requires painstaking[61,82] removal. Spell and Eddy[73] considered this procedure too time-consuming. They have studied the extraction of phenolic antioxidants from polyethylenes and find that the required extraction time at room temperature varies linearly with polymer density and particle size and also with the nature of the extraction solvent. They concluded that if polymer is powdered to 50 mesh, 3 h shaking in a wrist-action shaker is sufficient to recover 98% of the antioxidant from the polymer of any density. In support of these findings some correlation has been found between the density of polyethylene and its perme-

ability[83,84] to solvents. The techniques applicable to polyolefins are largely applicable to elastomers due to similar difficulties with the solubility of some types and to the common nature of certain additives.

In conclusion it is quite difficult to conduct extraction techniques quantitatively due to decomposition and loss of additives including antioxidants and accelerators, during extraction[85,86]. In a related work, Crompton[87] determined amine-type antioxidants in polymers using a 1.5-h toluene extraction, refluxing under a nitrogen blanket. Under these conditions no oxidation, or decomposition of the antioxidants occurred, the procedure was demonstrated by separation of N,N-di-β-naphthyl-*p*-phenylenediamine from its oxidation product which is frequently formed during processing or extraction.

An increase in the surface are of polymer sample to be extracted greatly facilitates the rate of solvent extraction. Attempts to increase the polymer surface area–weight ratio before extraction have included the use of ball mills and Wiley cutting mills[64,60,86], microtomes[88] and grinding[89] with solid carbon dioxide.

Schroeder[32] reported that boiling acetone is a good solvent for extracting antioxidants and accelerators from rubbers and vulcanizates, but warned of complications due to stabilizer rearrangements and decomposition. Thus, although oxidation of polymer additives during extraction may occur, there exists a danger that crushing the polymer prior to extraction may lead to a sequence of reactions which affects the chemical structure of the inhibitor. Mechanical degradation of polymers takes the form of chain rupture leading to macroradicals. During cutting at low temperatures Pazowyi *et al.*[90] found radical concentrations related to the area of the new surfaces. In the presence of inhibitors reactions between macro radicals ($\dot{R}$) and inhibitor (I) may occur in the absence of oxygen. As a consequence reaction products of the intermediate inhibitor radical are to be expected

$$\sim\sim\sim\sim \longrightarrow 2\dot{R} + 2I \longrightarrow 2R + 2\dot{I} \longrightarrow I\text{-}I$$

In the presence of oxygen the probability of reaction of the macro radicals with the inhibitor system is increased considerably, particularly if phenolic or amine antioxidants are present.

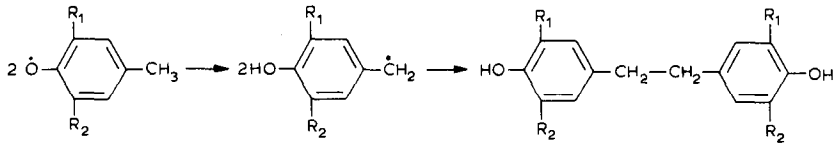
Some of the antioxidants listed in Table 4 are so volatile[74] that direct determination by sublimation[66] is possible. Thus a separation by distillation of the 2,6-di-*tert.*-butyl-4-methylphenol from its dimer deactivation product at 100°C was suc-

TABLE 4

VOLATILITY OF ANTIOXIDANTS[32]

Antioxidant	*Vapour pressure (mmHg)*	*Loss of weight (%) at 150°C*
2,6-Di-*tert.*-butyl-*p*-cresol	22.15	100
2-Benzyl-6-*tert.*-butyl-*p*-cresol	1.83	100
2,2′-Methylene-bis-6-*tert.*-butyl-*p*-cresol	0.169	19–28
Diphenylamine	7.52	100
N-iso-Propyl-N′-phenyl-*p*-phenylene-diamine	0.59	40–53
N,N′-Diphenyl-*p*-phenylenediamine	0.032	2–3

cessful and provided evidence for the isomerization of primarily formed phenoxy radicals to oxybenzyl radicals and their recombination to dioxydiphenyl ethane as shown below.



More commonly, undesirable losses also occur during distillation or evaporation of extracts. When a chloroform solution of 2,6-di-*tert.*-butyl-4-methylphenol was evaporated in a fume cupboard, 63% of the solid was lost; simple open storage of the solid led to 0.75% loss after 24 h[32].

For quantitative estimation of highly volatile compounds, particularly when the type of decomposition products are of interest, enrichment by chromatographic processes should be considered. Polymer separation can be achieved using size exclusion chromatography. By suitable selection of the pore size of the separatory media additives can be separated from polymers in a form suitable for further analysis.

During dissolution, stabilizer degradation does not occur and the polymer is subsequently preferentially precipitated. One should consider solution–precipitant effects on stability, especially of the reaction products of stabilizers or their fragments, with the polymer. Such reaction products have been both determined and isolated with PVC, polyethylene and natural rubber.

Phenolic antioxidants or their decomposition products in part were recovered from polypropylene after oxidative degradation[91]. When rubber vulcanizates containing aromatic amine antioxidants are thermally oxidized amine–rubber derivatives which are resistant to hydrochloric acid extraction are formed[92,93]. Similarly, hydrolysis restistant derivatives are formed between thiol antioxidants and stabilizers[94] and acrylonitrile–butadiene–styrene (ABS) polymer, particularly during high-shear processing.

A simple and comprehensive approach to the identification of the accelerators and antioxidants used in rubber products was described by Brock and Louth[44]. This unusual procedure utilized the tendency of accelerators to decompose during extraction from compounded stocks. The accelerator fragments were isolated using distillation and liquid–liquid extraction procedures given in Fig. 1. The accelerator fragments were identified and the original accelerators used were determined from a knowledge of the decomposition behaviour of known compounds. The antioxidants and guanidine type accelerators are recovered unchanged and can be identified by their UV absorption characteristics and colour reactions.

The separation of additives from mixtures after extraction from the polymer is necessitated by the lack of sufficiently specific methods for the identification of accelerators and antioxidants in the presence of other components. To keep the analytical scheme as simple as possible it is desirable to eliminate this stage. Most separatory techniques, however, also provide a clue to the identity of the components, and in a good scheme of analysis the separatory process forms an important part of

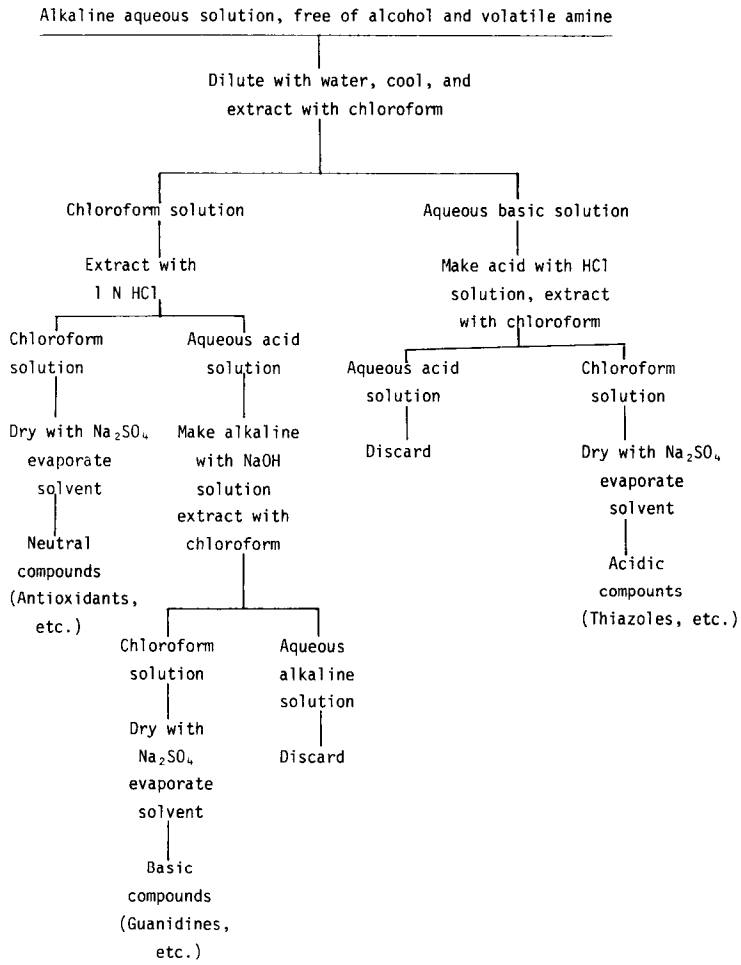


Fig. 1. Separation of non-volatile, neutral, basic, and acidic material[44].

the actual identification procedure. Of all the well-known separatory techniques reported liquid–liquid extraction seems to be the least frequently employed. It has been used mainly to separate antioxidants and accelerators from other organic additives and low-molecular-weight polymer fractions[38,39,44,95,96].

In most commercial rubber stocks, extender oils are used to facilitate processing of the compound. Being in high concentrations they interfere with the analysis of antioxidants and accelerators which are present in much lower concentrations. Here the use of a highly polar extractant such as acetonitrile is recommended[45]. The oil in the acetonitrile extract is precipitated at $-20°C$ thus reducing the ratio of oil to antioxidant from an initial value of 30:1 to approximately equal amounts. In the ASTM TLC method[59], removal of extender oil by pretreatment with light petroleum ether, or by a column chromatographic technique is recommended.

5. COLUMN CHROMATOGRAPHY

Although column chromatography is probably the most exacting chromatographic technique to perform, it has the advantage of being able to handle relatively large samples (50–5000 mg). To save time, preliminary TLC experiments aimed at determining suitable adsorbents and development solvents for achieving a satisfactory separation should be conducted. Suitable conditions can then usually be translated to column chromatography without difficulty. The use of fraction collectors and automatic effluent monitoring devices also reduce time and effort involved in column chromatography.

To identify fractions in which the separated components are concentrated, one can laboriously examine all fractions with IR or UV spectrophotometry. However, by monitoring the column effluent with UV absorption, conductivity, and other monitors, much effort is saved. Some have the disadvantage of being too specific for use with mixtures of compounds of unknown types. Most general purpose monitors are those based on the measurement of the refractive index and thermal effects.

Successful separation of antioxidants from each other was achieved on columns of activated silica by Crompton[35] using benzene as the developing solvent. Adsorbents other than silica gel have also been used for the separation of additives, with Fiorenza *et al.*[97] separating antioxidants and plasticizers in rubber extracts by use of a neutral alumina column. The effluent was monitored with an LBK UV detector at 254 nm. After eluting the fractions exhaustively with carbon tetrachloride, carbon tetrachloride–benzene (50:50), benzene, benzene–ethanol (50:50) and finally ethanol, each component separated was identified by UV or IR spectrophotometry.

Crompton[82] recommends the use of a silica gel column on which the components of the polymer extract can be separated by use of a similar succession of increasingly polar solvents. The effluent was monitored with a JOEL JLC 2A recording chromatograph, which separates by measuring the thermal changes caused by components moving along the column.

A synthetic rubber adsorbent has been used by Berger *et al.*[98] to separate antioxidants. The stationary phase (Silastic 181) was applied to the column as a suspension in light petroleum and the separation carried out with a mobile phase of acetone–water (25:75, v/v). Campbell and Wise[60] used an alumina column to separate phenolic antioxidants with chloroform followed by water–ethanol (10:90). A Gilston Medical Electronics UV scanner was used to monitor the effluent stream.

Another analytical separatory scheme based on column chromatography was reported by Parker[99], where aliquots of the sample solution were chromatographed on γ-alumina columns, each with a different mobile phase. From the position of the components on the various columns after a suitable elution time and from the colours obtained with specific detecting reagents, almost unambiguous identification of antioxidants was claimed.

Bellamy[100] discussed in detail the identification of antioxidants in rubber vulcanizates. Samples extracted were first chromatographed on an alumina column. Separated compounds were detected on the column by UV light and/or by extruding the moist column from the tube and streaking a narrow band down the side of the column with various chromatographic developing reagents such as sulphuric acid, 1% ammonium vanadate in sulphuric acid, 1% potassium dichloromalate in sul-

phuric acid or nitric acid–sulphuric acid (1:3, v/v). Amino and phenolic antioxidants were generally easily eluted from an alumina column with ethanol–benzene (1:99, v/v).

Mann[101] extended the work of Bellamy *et al.*[98] by using IR and UV spectrophotometer for the examination of individual components of vulcanizate extracts (mainly accelerators and antioxidants), after separating from all other compounds present by column chromatography. It was shown contrary to the work of Bellamy, that weak absorption on alumina is not a characteristic feature of antioxidants. Some of the compounds are relatively strongly adsorbed on alumina and require desorption with ethyl alcohol–benzene mixtures nearer to 5:95 (v/v) rather than the 1:99 (v/v) mixture as proposed by Bellamy.

Mann[101] concluded that although IR methods offered a reasonable solution to the problem of the qualitative analysis of vulcanizates for accelerators and antioxidants, it was unlikely that they would be suitable for quantitative work. UV spectrophotometry was suggested to be more amenable to quantitative analysis and more sensitive for accelerator and antioxidant determination.

Parker and Berriman[102] examined the chromatographic behaviour on silica gel–Celite packed columns of 32 accelerators and four antioxidants with methyl chloride as solvent. The separated compounds were identified by viewing the developed column in UV light and by application of various chromatographic streaking regents to the extruded chromatographic column. It was claimed that silica gel– Celite mixtures as adsorbents have certain advantages over alumina as advocated by Bellamy[100] and by Mann[101]. It has weak adsorptive power for accelerators and antioxidants, which permits the chromatography of labile compounds without decomposition. Silica gel–Celite was also claimed to be more suitable for the application of a wide variety of streaking reagents, and is more amenable to the quantitative recovery of adsorbates from the column.

A number of colour reactions which have been reported in the literature are shown in Table 5. Many of these are also suitable for application as streaking reagents. Table 6 lists the streaking reagents used for the detection of compounds.

6. PAPER CHROMATOGRAPHY

Three advantages of paper chromatography over column chromatography are: (i), It is simpler to use; (ii), smaller sample sizes can be used, and (iii), the R_F values are more reproducible. This last advantage is particularly important since it permits some identification of the separated components. Table 7 lists the more important paper chromatographic contributions reported in the literature.

Wheeler[25] reviewed the available literature on the application of paper chromatography in the examination of polymers for antioxidants. It was indicated that because most antioxidants are highly polar, efficient separation on normal paper can only be achieved using highly polar mobile phase. Consequently reversed-phase paper chromatography[107,113–115] or acetylated papers[22,109–111] are usually used to reduce the effect of tailing.

The detecting reagents used are either diazotized amines[22,109] which form coloured products with amines and phenols, or oxidizing agents, since the oxidation products of antioxidants are generally highly coloured[104,109,111]. Sometimes the

TABLE 5

SOME COLORIMETRIC REAGENTS REPORTED IN LITERATURE[102]

Reagent	*Compounds reacting*
$Bi(NO_3)_3$ + 1% NaOH–HNO_3	MBT, thiuram
Aq. $Bi(NO_3)_3$ in acetone	MBT
$AuCl_3$	DPG
Copper oleate in $CHCl_3$	Dithiocarbamates
Ditto, after Na_2SO_3	Thiuram sulphide
Cobalt oleate in benzene	DPG, DOTG, *o*-tolyldiguanide dithiocarbamates, MBT, TMT
$CuSO_4$ aq. + acetone, etc.	Dithiocarbamates, thiurams, etc.
Phenolphthalein	DPG
HCl and phenol or α-naphthol	Diazoaminobenzene
Diazotized *p*-nitraniline	Aromatic amines
NaOH + diazotized *p*-nitraniline	Aromatic amines
Diazotized sulphanilic acid	Aldol naphthylamine
Acetic acid or HCl + *p*-dimethyl amino benzaldehyde	1-Naphthyliminoaldol, PBN
p-Phenylene diamine, Br_2 + NH_3	1-Naphthyliminoaldol, thiuram
p-Phenylene diamine + $DeCl_3$	Primary and various amines
$FeCl_3$ or $CuCl_2$	Aldol–naphthylamine
Aq. NaOCl + phenol (3%)	Aldehyde–aniline condensation products
$SnCl_4$ + amyl nitrite in benzene	Diarylamines and naphthylarylamines
$SnCl_4$ + benzotrichloride in ethylene dichloride	Diarylamine–ketone condensation products
$SnCl_4$ benzoyl peroxide in benzene	Aryl substituted *p*-phenylene diamines
$SnCl_4$ + bromine in ethylene dichloride	Aniline–acetone condensation products, etc.
H_2SO_4 + trace HNO_3	Diphenyl and dinaphthyl *p*-phenylene diamines
H_2SO_4	
H_2SO_4 + SeO_3	
H_2SO_4 + $K_2S_2O_2$	
Concentrated HNO_3	Reactions of 40 commercial antioxidants investigated
Arsenic acid in H_2SO_4	
Ammonium molybdate in H_2SO_4	
10% H_2O_2 in H_2SO_4	
H_2SO_4	
HNO_3	
$(NH_4)_2S_2O_8$ in H_2SO_4	
0.5% MoO_3 in H_2SO_4	Reactions of eight commercial antioxidants investigated
Acetic acid	
Acetic acid + bromide	
1% Ammonium vanadate in concentrated H_2SO_4	
1% Potassium dichromate in concentrated H_2SO_4	Reaction with nine commercial antioxidants recorded
Nitric acid–sulphuric acid (1:3)	

sample solution is treated with the colouring reagent first and the coloured products are then chromatographed. Multiple spots can be obtained from a single antioxidant in this manner as has been demonstrated by Auler[50].

The work of Zijp[109–111] is a major contribution to paper chromatographic methods, a comprehensive scheme for the systematic identification of accelerators and antioxidants being devised. Acetylated paper and different solvent systems were

used for different classes of compounds. Identification was based mainly on the R_F value of each constituent and on the colour produced by various spray reagents. Auler[50] in a detailed survey on the analysis of accelerators and antioxidants was able to reproduce Zijp's work, and in addition applied the same solvent systems to circular paper chromatography with satisfactory results.

Williamson's[22] important work is also based on that of Zijp, but different solvent systems were employed. Before chromatography, sample extracts were evaporated to dryness at 80°C and the residue dissolved in 96% ethanol. Controlled additions of ethanol, strontium chloride and ammonia solutions were made to precipitate fatty acids and other impurities which were then removed by filtration and the clear filtrate examined for accelerators and antioxidants by paper chromatography.

Delves[116] has described a procedure based on paper chromatography for the identification of nitrogen containing antioxidants in synthetic aviation turbine oil formulations which, with minor modification, could be applied to the analysis of antioxidants in polymers. The most succesful solvent system was dipropylene glycol as the stationary phase and cyclohexane saturated with dipropylene glycol as the mobile phase.

The number of antioxidants now commercially available is so great that no single R_F value, even in conjunction with a variety of spray reagents, is likely to be specific enough to identify any component unambiguously. The analyst is therefore required to consider the use of multiple solvent sytems to achieve the necessary specificity. The use of paper chromatography therefore becomes too lengthy a procedure for routine use. Consequently, more recent workers have employed TLC.

7. THIN-LAYER CHROMATOGRAPHY

TLC is an inexpensive and simple method for determining rubber processing ingredients such as accelerators and antioxidants. It is a much more rapid technique than paper chromatography and allows more corrosive spray reagents to be used. Although the reproducibility of R_F values is generally poorer than in paper chromatography[115], Delves[116] and other workers[115–122] have shown that reproducibility can be improved if adequate attention is applied to all of the experimental variables. The more modern technique, high-performance liquid chromatography (HPLC) does not have the disadvantages of TLC, but it requires a longer analysis time and more expensive, immobile instruments.

Wheeler[25] has reviewed the literature on TLC for antioxidant analysis. Gedeon *et al.*[117] recently surveyed the available TLC method for rubber compounding analyses. Table 8 summarizes the more important reports of the use of TLC in the literature.

Schroeder[32] has reported that the greatest success obtained in stabilizer analysis has been with TLC. Good separation efficiency, high separation speed and a great variability of the detection possibilities are the most important advantages of this technique. Variation of carrier material, mobile phase, spray reagents and multistage processes also offer possibilities for the separation of complex stabilizer systems.

TLC separation processes for antioxidants as described by Van der Neut[175] provide a good example. Antioxidants are first separated using benzene on silica gel into six groups of increasing R_F values, and afterwards are separated selectively with

TABLE 6

COLOURS OF STREAKS OBTAINED WITH VARIOUS REAGENTS[102]

Compound	*Sodium hypochlorite in water (30%, w/v)*	*Aqueous $CuSO_4 \cdot 5H_2O$ (5%, w/v)*	*$Bi(NO_2)_2$ in 0.5 N nitric acid (5%, w/v)*	*Bismuth nitrate in 0.5 N acid after reduction*	*Aqueous $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ (5%, w/v)*	*Aqueous lead acetate after reduction*	*$(NH_4)VO_3$ in 60% w/w sulphuric acid (1%, w/v)*	*Mixture of conc. HNO_3 (1 vol.) and conc. H_2SO_4 (3 vols.)*	*Selenium dioxide in conc. sulphuric acid (0.5%, w/v)*
DOTG	dark reddish-brown	nil	nil	nil	nil	nil	nil	nil	nil
DPG	dark reddish-brown	nil	nil	nil	nil	nil	nil	nil	nil
TPG	reddish-brown	nil	nil	nil	nil	nil	nil	nil	nil
TC	pale orange on standing	light brown	yellow	yellow	nil	nil	nil	pale violet fades rapidly	nil
MBT	nil	faint yellow	bright chrome yellow	bright chrome yellow	lemon yellow	lemon yellow	faint green	nil	faint yellow
MBTS	nil	nil	nil	brigth chrome yellow	nil	lemon yelow	nil	nil	nil
TMTD	nil	bright yellow-green	pale lemon-yellow	pale lemon-yellow	nil	nil	v. pale green to faint blue	nil	nil

TMTM	nil	strong yellow	pale yellow	pale yellow	nil	nil	v. pale green to faint blue	nil	nil
TETD	nil	bright yellow green	pale lemon yellow	pale lemon yellow	nil	nil	v. pale green to faint blue	nil	nil
CBS	nil	nil	nil	bright chrome yellow	nil	lemon yellow	faint green	nil	nil
PAN	light orange to orange yellow	nil	nil	nil	nil	nil	prussian blue	dark olive green	blue on standing
PBN	orange	nil	nil	nil	nil	nil	dark brown	green rapidly turning brown	pale greenish yellow
IPPD	orange-pink	nil	pale green or pale blue	nil	nil	nil	dark greenish blue	mauve	deep blue
MTD	orange-brown	yellow-green	nil		nil		pink-brown on standing	faint orange	nil
DPPD	pale orange-yellow	nil	light blue		nil		crimson	magenta	purple

TABLE 7

SEPARATION OF ACCELERATORS AND ANTIOXIDANTS BY PAPER CHROMATOGRAPHIC METHODS

Substances separated	*Stationary phase*	*Mobile phase*	*Derivative or treatment*	*Detection*	*Comments*	*Ref.*
Accelerators and antioxidants	Paper	–	Coupled with *p*-diazobenzene sulphonic acid	Coloured products	–	103
Antioxidants	Paper	Acetic acid–water (1:4)	–	0.2% $Fe_2(SO_4)_3$–0.1% $K_2Fe(CN)_6$ (1:1)	Blue spots	104
Amine antioxidants	Paper	Acetic acid–water–acetone (3:6:1)	React with 3-methyl benzothiazolin-2-one hydrazone HCl–$FeCl_3$ before chromatography	Coloured products	–	105
Antioxidants	Paper	Not given	Heated under reflux with HCl	Sulphanilic acid–sodium nitrite or ninhydrin	–	106
Aromatic amines and phenothiazine antioxidants	Dipropylene glycol on paper	Cyclohexane saturated with dipropylene glycol	–	UV light or *p*-nitrobenzenediazonium fluoroborate	112 μg detected	107
Antioxidants	Whatman acetylated paper No. AC82	Ethanol–benzene–acetyl–acetone (10:10:1)	Antioxidants extracted from accelerators with ethanol	Potassium-*p*-diazobenzene sulphonate	Ascending against the grain (5th)	108
Antioxidants	Acetylated Whatman No. 1	Not reported	Extract into ethanol, add 4 M NH_4OH, 20% $SrCl_2$ and filter	–	–	71
Urea-based stabilizers	Paper	Propanol–methanol–water (2:1:1)	–	*p*-Dimethylamine benzaldehyde	–	89
Basic antioxidants	Acetylated Whatman No. 1	Ethanol (96%)–benzene (1:1)	–	Tollen's reagent, Millen's Reagent		109, 110
Phenolic antioxidants	Acetylated Whatman No. 1	Butyl acetate–pyridine–methanol–water (1:5:1:3)		Tollen's reagent, Millen's Reagent		111
Basic antioxidants	Schleicher and Schull 2043b/45ac	Ethanol (96%)–benzene (1:1)	–	1% Diazobenzene sulphonic acid (DBS) in 25% aqueous acetic acid or 20 mg of DBS in 5 ml of 0.1 *M* NaOH + 5 ml of ethanol (96%)		50

Phenolic antioxidants	Schleicher and Schull 2043b/45ac	Butyl acetate–pyridine–methanol–water (1:5:1:3)	–	Tollen's reagent, Millen's Reagent Phosphomolybdic acid, vanillin or potassium ferricyanide		50
Antioxidants	Paper	Chloroform–acetic acid (99:1)	–	–	Ascending technique in atmosphere from 50% acetic acid	112
Butylated hydroxy anisole	7% liquid paraffin	Light petroleum	–	Ammonical silver nitrate	Descending run (4 h)	113, 115
Catechols	Whatman No. 1 impregnated with formamide + H_3PO_4 dimethyl formamide or liquid paraffin	(a) Isopropyl ether, (b) chloroform, (c) heptane, (d) heptane–benzene (1:1), (e) methanol (80%)	–	–	–	115
Guanidine accelerators	Whatman No. 1 pH = 4	Water saturated butanol	–	4% Sodium hypochloride	Ascending method.	
Thizole type compounds and derivatives of MBT	Whatman No. 1 pH = 10	Water saturated butanol	–	5% Bismuth nitrate + 0.5 N HNO_3	Descending method.	
Thiurams and dithiocarbamates	Whatman No. 1	Butanol saturated with 0.5 *N* HCl	–	Ethanol–carbon-disulphide–triethylamine mixture followed by copper solution of ninhydrin		49
Phenyl 1-naphthylamine and phenyl-2-naphthylamine	Whatman No. 1	Ethanol	–	0.5% Diazotized sulphanilic acid in alcohol–water–8 *N* HCl (1:1:2)	–	51
p-Phenylenediamine derivatives	Whatman No. 1	Ethanol–benzene	–	Benzoyl peroxide	Ascending method	52

TABLE 8

SEPARATION OF ACCELERATORS AND ANTIDEGRADANTS BY TLC

Substances separated	*Stationary phase*	*Mobile phase*	*Detection and spray reagents*	*Refs.*
Phenolic antioxidants	Silica gel G.	Methanol–cyclohexane (1:24)	30% Molybdophosphoric acid + ammonia vapour	61
Antioxidants	Not reported	Acetic acid–diisopropyl ether (1.5:98.5)	20% Molybdophosphoric acid + ammonia vapour	123
BHT	Silica gel	Chloroform	20% Molybdophosphoric acid + ammonia vapour	124
Phenolic antioxidants	Polyamide powder	Methanol–water (3:2) or methanol–CCl_4 (1:9)	Diazotized sulphanilic acid	125
Antioxidants	Polyamide powder	Methanol–acetone–water (6:1:3)	Diazotized sulphanilic acid or molybdophosphoric acid + ammonia vapour	126
Antioxidants	Kieselgel G	–	α,α'-Diphenyl-β-picryl hydrazyl (free radical)	63
Antioxidants	Alumina + 5% Plaster of Paris	Light petroleum (b.p. 40–60°C)–dioxane (10:1)	5% Ethanol, phosphomolybdic acid	127
Antioxidants	Silica gel	Acetone, chloroform, benzene, carbon tetrachloride or binary mixture	–	128
Antioxidants	(1) 10% starch in polyamide powder	Methanol–acetone–water (3:1:1)	–	129
	(b) 10% PVC in polyamide powder	Light petroleum (b.p. 40–60°C)–benzene–acetic acid–DMF (40:40:20:1)	–	
Antioxidants	Silica gel	Light petroleum (b.p. 40–60°C)–ethyl acetate (9:1)	–	81
Sulphenamide accelerators	Kieselgel GF_{254}	(a) Light petroleum (b.p. 40–60°C); (b) toluene–ethyl acetate; (c) light petroleum (b.p. 40–60°C)–triethyl amine (3:1)	The amine residues were identified as their fluorescent 4-chloro-7-nitro-2,1,3-oxa-diazole (NBD-Cl) derivatives	130
Accelerators and antioxidants	Silica gel	(a) Benzene–ethylacetate–acetone (100:5:2) (b) Toluene–ethyl acetate–ammonia (98:2:0.1)	0.2% 2,6-Dibromo-*p*-benzoquinone-4-chloriamide in ethanol	131
Antioxidants	Whatman KC 18R-reversed-phase	(a) *n*-Heptane–ethyl acetate (70:30) (b) Tetrahydrofuran–0.02 *M* NaCl–acetonitrile (5:42:53)	(a) Sulphanilic acid followed by NaOH solution (b) Sodium borate buffer	117
Antidegradants	Silica gel 200–600 μm (30–70 mesh)	(a) Heptane–ethylacetate (95:5) (b) Cyclohexane–diethylamine (75:25) (c) Toluene–*n*-heptane (50:50)	(a) For amine-type antidegradants, diazotized sulphanilic acid (b) For phenolic antidegradants, 0.5% ferric chloride followed by NaOH	59

Accelerators	Silica gel G (Merck)	Benzene–ethylacetate–*n*-butanol (50:1:1)	(a) Dioxane; (b) palladium chloride; (c) phosphomolybdic acid	132
p-Phenylene diamine antidegradants	Silica gel G, silica gel H and alumina GF_{254}	(a) Isopropanol–chlorobenzene–water–ammonia (25%) (52:33:10:5) (b) Water–*n*-butanol–acetic acid (50:40:10) (c) *n*-Heptane–ethyl acetate (100:20) (d) Benzene–ethyl acetate–acetone (100:5:2)	(a) *p*-Diazobenzene sulphonic acid 0.1% in 25% acetic acid (b) 2,6-Dichloro-*p*-benzoquinone-4-chloroimide 0.2% in ethanol (c) Benzoyl peroxide 4% in benzene (d) Sodium nitrite, 10% in water, acidified with HCl (e) Formaldehyde solution 40% with sulphuric acid (1:4) (f) Cobalt (II) chloride ($CoCl_2 \cdot 6H_2O$) 2% in water	133
Antioxidants	Silica gel	(a) Isopropanol–chlorobenzene–water–25% ammonia (52:33:10:5)	*p*-Diazobenzene-*p*-benzoquinone-4-chlorimide, 0.2% in methane)	134
Antioxidants	Silufol UV_{254}-Silica gel	(a) Benzene–hexane (50:50); (b) Benzene–diethylether (60:40) (c) Benzene–ethanol (95:5)	(a) Hexacyano ferrate (II)–hexacyano ferrate (III) regaent (b) (Acidic solution of potassium permanganate	47
Accelerators and antioxidants	Silica gel (Wakogel B-5)	(a) Chloroform–benzene (10:9) (b) Ethanol	Formalin–sulphuric acid (1:4)	135
Accelerators	Silica gel G_{254}	(a) Light petroleum (b.p. 30–40°C)–diethyl ether (110:20) (b) Benzene–ethyl acetate–acetone (100:7:2) (c) Cyclohexane (d) Toluene–ethylacetate–ammonia (100:5:0.1) (e) Cyclohexane–diethyl amine (75:25) (f) Chloroform–benzene (100:90) (g) Acetone–ammonia (100:1)	(a) Iodoplatinate solution (*i.e.* 3 ml of 10% platinum chloride mixed with 97 ml of aqueous potassium iodide) (b) Dibromo benzoquinone chloride 1% solution in methanol (c) Sodium hypochloride, 4% solution in water (d) 1% Sodium bicarbonate solution	148
Thiuram and dithicarbamate accelerators	Silica gel	Benzene–ethyl acetate	3% Aqueous cupric sulphate	136
Accelerators and antioxidants	Silica gel	(a) Light petroleum (b.p. 40–60°C) (b) Light petroleum (b.p. 40–60°C) + ether (60:40)	2,6-Dibromo-*p*-benzoquinone-4-chlorimine	81
Amine type antioxidants	Silica gel	(a) Benzene–acetone–conc. ammonia (100:5:0.1) For two dimensional TLC cyclohexane–acetone–conc. ammonia (100:5:0.1)	4% solution of benzoyl peroxide in benzene	137

(Continued on p. 330)

TABLE 8 (*continued*)

Substances separated	*Stationary phase*	*Mobile phase*	*Detection and spray reagents*	*Refs.*
Phenolic antioxidants	Silica gel G	Benzene	2.34% sodium tetraborate + 0.33% NaOH aqueous solution followed by 0.1% 2,6-dichloroquinone chlorimine in methanol.	138
Thiazole type accelerators		Benzene–ethyl acetate–acetone (100:5:1)		
Thiazole type compounds		Benzene–ethyl acetate–acetone (100:5:1)	4 *N* HCl, 0.5% ninhydrin in ethanol containing 10% acetic acid and 0.5% cadmium acetate	
Sulphenamide		*n*-Butanol–water–formic acid (5:1:1)	5% Bismuth nitrate in 1 *N* nitric acid ninhydrin	
Guanidines		Acetone + 1% conc. ammonia	4% Sodium hypochloride	
Antioxidants and stabilizers	Kiesel gel GF_{254} (Merck)	Benzene–ethyl acetate–acetone (100:5:2)	2,6-Dichloro-*p*-benzoquinone-4-chlorimine	139
Antioxidants	Silica gel G + Silicayl G + 5% Dow silcone (reversed phase)	(a) Ethanol–water (3:1) (b) Cyclohexane–methanol (50:1)	30% Phosphomolybdic acid in ethanol–water mixture	140
Accelerators and antioxidants	Silica gel (No. 13181) with fluorescent indicator	(a) Benzene–ethylacetate (95:5) (b) Benzene (c) *n*-Heptane–ethylacetate (d) Acetone	2,6-Trichloro-*p*-benzoquinoneimine, 2,6-trichloro-*p*-benzoquinone chlorimine	58
Phenolic antioxidants and their oxidation products	Silica gel layers with gypsum binder	Hexane–ethyl acetate (9:1)	3.5-Dichloro-*p*-benzoquinonechlorimide or molybdophosphoric acid (for phenols) with 2,4-dinitrophenylhydrazine (for quinones) and with Fe(II)NH_4SCN (for peroxide)	141
Antioxidants	Silica gel G (activated at 120°C for 0.5 h) (gypsum bound 0.3 mm thick)	(1) Benzene–ethyl acetate (98.5:1.5) (2) Toluene–propanol (88:12) (3) Benzene–light petroleum (b.p. 60–80°C) mixture (4) Cyclohexane–benzene–methanol (88:10:2)	Methanolic 3,5′-dibromo-*p*-benzoquinonechlorimine or methanolic iodine and 3,3′-dimethylnaphthidine	142
Antioxidants	Silica gel G	Cyclohexane–ethyl acetate (1:1) and (17:3)	Diazotized-4-nitroaniline or diazotized 2,4-dinitrophenylhydrazine	143
Phenolic antioxidants		Hexane–benzene (1:3) or hexane–benzene–methanol (15:29:6)	0.5% 3,5-Dichloro-*p*-benzoquinone-chlorimine in isopropanol	
Amine antioxidants	Silica gel G (0.25 mm thick)	Pentane–diethyl ether (10:1)	1% Ethanolic-4-dimethylaminobenzaldehyde or 0.5% 4-nitrobenzenedi-	144

			azonium fluoroborate solution in 5% acetic acid solution	
BHT	Alumina–silica (1:1) ($CaSO_4$ as binder) activated at 110°C for 2 h	Chloroform	Iodine vapour or methanolic iodine solution	145
Phenolic antioxidants	Silica gel G (0.3 mm thick)	Chloroform–benzene–methanol–light petroleum (b.p. 40–60°C) (12:4:3:1)	Citric acid–H_3BO_3, ammonium oxalate ammonium molybdate or Folin-Ciocalteu reagent	146
Phenolic antioxidants	Silica gel G	Light petroleum (b.p. 60–80°C)–chloroform	–	147
Antioxidants	Silica gel	Benzene or chloroform	By heating at 160°C	148
	Silica gel–Kieselguhr	Hexane–acetic acid (4:1)		
Phenolic antioxidants	Activated Kieselgel 60	Light petroleum (b.p. 40–60°C)–benzene–acetic acid (2:2:1)	Ethanolic 3.5% molybdophosphoric acid or bleaching with NH_3 or ethanolic 3,5-di-chloro-*p*-benzoquinonechlorimine and aq. $Na_2B_4O_7$	149
p-Phenylene diamine and its oxidation products	Silica gel G	Xylene, benzene, benzene–methanol (19:1), benzene-1-4-dioxan, or ethanol–aq. NH_3–water (20:1:2)	Modified Ehrlich reagent	150
Phenolic antioxidants	Silica gel (0.25 mm)	Cyclohexane–ethyl acetate (4:1)	aq. 5% $FeCl_3$	151
BHT	Silica gel G impregnated with $AgNO_3$	Light petroleum (b.p. 60–80°C)–liquid paraffin (9:1)	Exposing 360 nm radiation for 10 min	152
Phenolic antioxidants	Silica gel G (activated at 110°C for 1 h)	Hexane–acetic acid (9:1)	Folin-Ciocalteu phenol reagent	153
MBT and its impurities	Silufol UV 254 Silica gel	CCl–$CHCl_3$–diethyl ether–acetone (70:30:5:3)	0.2% $PdCl_2$ solution of 0.02% bromophenol blue solution in 1% aq. $AgNO_3$	154
Phenolic antioxidants	Silica HR-25-UV-254	–	Boute reaction (nitrozo derivative)	156
BHT and BHA	Silica gel	Hexane–anhydrous acetic acid (9:1)	Folin-Ciocalteu reagent	156
Phenolic antioxidants	BD-Cellulose DEAE-cellulose Polyethylenimine-cellulose Dowex 50-X4 (H^+) AGl-X4 (CH_3COO^-)	Methanol–water (3:1) or 1 *M* acetic acid in methanol for AGl-X4	Alcoholic 1%, 3,5-dichloro-*p*-benzoquinonechlorimine	157
Antioxidants	Silica gel G (0.5 mm layer)	Benzene	–	158
Antioxidants	Silica gel G	Benzene	0.2% 3,5-dichloro-*p*-benzoquinonechlorimine in isopropanol	159
Phenolic antioxidants	Silica gel or polyamide	Light petroleum–benzene–acetic acid or (2:2:1) or hexane–acetone–acetic acid (11:8:3) or methanol–acetone–water (3:1:1)	$FeCl_3$–2,2-bipyridyl and 3,5-dibromo-*p*-benzoquinonechlorimine	160
Antioxidants	Kiesel G	Benzene–acetic acid (15:4, 7:3, 5:6)	0.1% 3,5-Dichloro-*p*-benzoquinonechlorimine and NH_3 vapour	161

(Continued on p. 332)

TABLE 8 (*continued*)

Substances separated	*Stationary phase*	*Mobile phase*	*Detection and spray reagents*	*Refs.*
Phenolic anti-oxidants	Polyamide–silica gel (8:15) (0.25 mm)	1:4 mixture of anhydrous acetic acid with $CHCl_3$, CCl_4 or benzene	Ammonical $AgNO_3$ solution	162
BHT	Silica gel (0.5 mm layer)	Hexane–ethyl acetate (10:1)	3,5-Dichloro-*p*-benzoquinonechlorimine	163
Phenolic antioxidants	Silica gel (0.5 mm) activated at 105°C for 1 h	Chloroform	10% Ethanolic molybdophosphoric acid	164
Antioxidants	Kieselgel H–magnesium silicate (9:1)	Chloroform–methanol–aq. ammonia (13:7:1) and chloroform–acetone–acetic acid–water (10:4:2:)	–	165
BHT, BHA	Silica gel	Hexane	Folin-Ciocalteu reagent	166
Antioxidants	Kieselgel HF_{254}	Hexane–ethylmethyl ketone–butyl ether (34:7:6)	0.65% $FeCl_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$ in 1 *N* HCl and heated at 40°C or 0.25% of 2,2′-bipyridyl and 0.1% of $FeCl_3 \cdot 6H_2O$	167
Antioxidants	Kieselgel G (0.3–0.55 mm thick)	Benzene–light petroleum (b.p. 30–50°C) (7:3) or benzene–light petroleum (b.p. 50–60°C)–acetic acid (7:3)	2,2′-Diphenyl-1-pirylhydrazyl, 3,5-dichloro-*p*-benzoquinonechlorimine and K_2PtI_5	168
Antioxidants	Silica gel	Benzene	1% Ethanolic linoleic acid, exposed to UV radiaton, sprayed wityh 0.1% N,N-di-methyl-*p*-phenylenediamine in $CHCl_3$–CH_3COOH–H_2O (5:5:1)	169
BHT	Alumina	2,2,4-Trimethylpentane–ethylether (9:1)	Iodine vapour	170
Antioxidants	Silica gel (Merck)	Cyclohexane–diethyl ether (4:1)	0.01% methanolic 1,1-diphenyl-2-picryl-hydrazyl	171
Antioxidants	Silica gel (0.25 mm layer)	Heptane–benzene (7:3)	7 g of $(NH_2)_2SO_4$ $FeSO_4 \cdot 6H_2O$ in 50 ml of 10% aq. NH_4SCN acidified with 0.5 ml of H_2SO_4.	172
Antioxidants	Silica gel	$CHCl_3$–acetic acid	20% Molybdophosphoric acid	173
Antioxidants	Silica gel G impregnated with 1,2-bis-(2-aminoethoxy)-ethane-N,N,N′,N′-tetraacetic acid (disodium salt)	Benzene–chloroform–polyoxyethylene glycol 1000 (50:25:6) and diisopropyl ether–anhydrous formic acid–water (297:23:10)	–	174
1,4-Phenylenediamine derivatives	Silufol (activated at 100°C for 1 h)	*n*-Hexane–ethanol or *n*-hexane-ethanol–0.1% triethylamine in varying ratios	Iodine vapour	119

another nine eluent systems and identified using four spray reagent systems. This scheme is comparable with that devised for the identification of metals via groups. Rueda and Fernandez[176] also developed an analytical scheme for identification of twenty common antioxidants using TLC. Newly developed antioxidants can be easily inserted into these schemes. However, the success of this system depends to a large extent on the reproducibility of the R_F values, and the authors do not describe their experimental procedure.

In contrast, Crompton[35,81] provided an excellent account of the experimental TLC examination of polymer additives. A 1% solution of the sample was applied as a continuous band along the bottom of two 20 × 20 cm plates, one of silica gel G254 (Merck) and the other silica gel GF254 containing a fluorescent indicator. After development, the plates were examined with radiation at 254 or 366 nm so that any substances on the plate which absorb radiation at wavelengths greater than 230 nm would appear on the fluorescent silica gel as dark areas on a blue fluorescent background. Any substance which itself is fluorescent appears on the non-fluorescent plate. After the position of the substances revealed have been marked, the plates were sprayed with aggressive spray reagents to reveal any additional components. Further identification was achieved by spraying additional plates with more specific reagents and by simultaneously analysing known antioxidant standards on the chromatogram. Crompton reported that many commercially available grades of silica contain traces of organic impurities which interfere by reacting with the spray reagent or by absorbing the UV or IR. These effects can be avoided, however, by first developing the plate in a highly polar solvent which moves the impurities to the solvent front. The plate can then be redried and used for the analysis of polymer extracts.

Kreiner and Warner[138] have described a useful TLC procedure for the identification of antioxidants and accelerators in which solvent systems giving the greatest range of R_F values are used. The developing distance in all cases was 15 cm to give additional space as well as separation, since a large number of samples were considered in certain groups. Indicating reagents giving a wide range of colours were chosen to permit identification of the compound, in many instances by both colour and travel distance. Most of the colours will vary somewhat depending upon the conditions of time after indication. Many satisfactory indicating reagents, other than those used by these workers, are available.

Simpson and Currel[139] used TLC in the determination of additives such as antioxidants and accelerators. Comparatively small samples of polymer materials are required, and by means of the techniques described it was possible to identify additives in extracts containing several different components. The method can be used to detect additives in low concentration *i.e.* 1–10 μg per sample, and both qualitative and quantitative determinations of greater accuracy are possible. Slonaker and Sievers[61] and Hoggon *et al.*[63] reported similar work and were able to detect between 300 and 900 ppm of antioxidants in polymers.

Millingen[48] applied TLC successfully to the analysis of accelerators in unvulcanized rubber compounds by introducing a new spray reagent. Higgins and McSweeney[130] developed a TLC method for identification of sulphenamide accelerators by mean of the NBD-Cl derivative of amine residues. Gedeon *et al.*[117] recently reported a reversed-phase C_{18} adsorbent for reversed-phase TLC analysis of antioxidants.

8. GAS CHROMATOGRAPHY

The attraction of gas chromatography (GC) lies in its ability to simultaneously separate, and estimate sub-milligram quantities of complex mixtures, and it would therefore seem to be the complete answer to the problems of additive analysis. More recently the method has been extended to the analysis of high boiling and thermally unstable compounds, including rubber antioxidants and accelerators. The developments include the use of GC columns containing low levels of thermally stable liquids and highly inert supports which has allowed the range of analysis of high-boiling mixtures to be greatly extended. Highly reactive compounds can often be analysed with on-column injections in all-glass systems. An enormous amount of GC data which has been published over the last few years refer to antioxidants and accelerators, some reports being listed in Table 9. This table shows that many of the works do not represent current practice particularly with regard to the stationary phases used.

There are, however, serious limitations to the GC method. Day-to-day reproducibility of GC is less satisfactory with most instruments when operated at high temperatures and retention varies considerably with the condition of the column at such temperatures.

Since many antioxidants and accelerators are of low volatility[25] low stationary phase loadings are used to reduce retention times to reasonable values. This leads to large areas of uncoated solid support which may lead to bonding with phenols and amines on the column, resulting in distortion of peaks and lengthening of retention times. There are, however, measures which can be taken to meet these difficulties. Relative retention times are more reproducible than unadjusted retention times and non-volatile components can be converted into more volatile derivatives such as trimethylsilyl ethers[186,204,208], methyl ethers[147] or trifluoroacetates[203] which also helps to reduce bonding to columns. The solid support can also be treated (for example with hexamethyl disilazane) to reduce the number of active sites on the column available for bonding[187], or inactive supports are freely available.

With the use of high temperatures or temperature programming coupled with higher carrier-gas flow-rates and low stationary phase loadings it may be possible to chromatograph relatively high-molecular-weight substances. Knight and Siegel[185] and Crompton[82] have been able to chromatograph the antioxidant 1,3,5-trimethyl-2,4,6-tri(3,5-di-*tert.*-butyl-4-hydroxybenzyl)benzene, which has a molecular weight of 775 (vapour pressure 0.014 mm at 180°C) with a retention time of less than 10 min. The first report where GC was used for amine-type antioxidant analysis was by Wise and Sullivan[182]. For quantitative analyses, a known concentration of an internal standard expected to elute near the unknown, was added to the acetone extract of the raw or vulcanized rubber. A temperature range of 220–310°C with an Apiezon L grease column is suitable for all the common amine stabilizers. Good separation of many amines is obtained for identification purposes, while some phenols can also be determined. Dual-column operation and a sensitive detector are essential for this type of work. Apiezon L[182] was found to be a suitable stationary phase while the now obsolete alternate materials Dow Corning 701 silicone fluid and butanediol were too volatile at the maximum operating temperature of 310°C. Dimethyl polysiloxane rubbers did not exhibit as high a degree of resolution as Apiezon L. It was found

TABLE 9

SEPARATION OF ANTIDEGRADANTS AND ACCELERATORS BY GC

Substances separated	*Stationary phase*	*Column temperature (°C)*	*Other details*	*Refs.*
Phenolic antioxidants	5% SE-30 on 80-90 Anakron adsorbent	290	H_2 carrier gas	81
BHT	25% LAC 2R/466 (adipate ester) +	135	H_2 carrier gas, flame ionization detection,	177
2-(2-Hydroxy-5-methyl-phenyl) benzotriazole	2% H_3PO_4 on chromosorb		(FID), error ± 1%	
BHT, 2,6-di-*tert.*-butyl phenol, 2,4-tri-*tert.*-butyl phenol, diphenyl amine	10% Apiezon N on celite 545	164	He carrier gas, FID, 10^{-3} M No interference from other substances	178
BHT and PBN	Apiezon		FID	179
Halogenated bisphenols	10% DC-710 Silicone oil on chromoport XXX 80–100 mesh	225–250	12 × 0.5 in O.D. glass column, carrier gas He, 130 ml/min	180
Low-boiling phenols	Capillary column coated with 10% xylenolphosphate	125	FID	181
Amine antioxidants	20% Apiezon L on 30–60 mesh chromosorb W.	300	2 × 0.5 in O.D. column	182
Phenols and 5-*tert.*-butyl derivtives	Silicone oil 550–carbowax 400 (3:2)	200	Mean deviation, 0.4%	183
Phenols and cresols	5% (w/w) of various phosphate esters of phenols	110	120 cm × 4.5 mm column	184
Phenolic antioxidants	(a) 20% DC-710 silicone oil on chromosorb (b) 2% SE-30 silicone gum on chromosorb	200–300 10°C/min	(a) 12 × 3/16 in. column (b) 12 × 1/16 in. column	185
Low-molecular-weight phenols	Silicone-coated capillary column	–	Converted to trimethylsilyl ethers before chromatography	186
BHT	20% SE-30 on HMDS treated 60 mesh Chromosorb W	200	Electron-capture detection (ECD)	187
Amine and phenolic antioxidants	5% Apiezon N on 60–80 mesh chromosorb Z	250	5 ft. × 0.5 in. I.D. stainless-steel column, FID	188
Accelerator fragments and antioxidants	80–100 Gas Chrom. Q coated with UCW-98	88–250 6°C/min	Amine residues were converted to trifluoro acetamide derivative before chromatography	189
BHA and BHT	Apiezon L	220	–	190

(Continued on p. 336)

TABLE 9 (*continued*)

Substances separated	*Stationary phase*	*Column temperature (°C)*	*Other details*	*Refs.*
Antioxidants	Silicone oil Apiezon L	220 190	H_2 carrier gas up to 0.5% antioxidant would be detected	191
Phenolic antioxidants	1% Methyl vinylsilicone Lucoprene G-1000 on Chromaton N AW DMCS	100–280 12°C/min	N_2 (30 ml/min) carrier gas, FID	192
Hindered phenols	10% SE-30 on 40–60 mesh Chromosorb W	330	He carrier gas, FID	193
Phenolic antioxidants	10% Silicone gum rubber E301 on 80–100 mesh Diatomite CQ	250 or 300	Argon carrier gas (45 ml/min), FID, 2.5 ft. × 0.25 in. column	194
MBT	30% Poly(ethanedioladipate) on Celite 545	160	H_2 carrier gas (65 ml/min), katharometer detector	195
BHT and BHA	5% XE-60 on Gas Chrom Q (60–80 mesh)	150	N_2 carrier gas (45 ml/min), FID	196
Hydrogenated *p*- and *m*-phenylene-diamines	10% Sorbitan mono-oleate on Celite 545	–	He carrier gas (60 ml/min), 1.2 m × 1.5 mm column	197
Cresols	2.5% Bis-(3,3,5-trimethylcyclohexyl)phthalate on Chromosorb W (80–100 mesh)	125	N_2 carrier gas (25 ml/min), 4 m × 3 mm column	198
Phenolic antioxidants	SP-2340	–	FID	199
BHT	5% SE-30 on hexamethyldisilane-treated Chezasorb	150	N_2 carrier gas, FID, 2 m × 4 mm column	200
Phenolic antioxidants and their methyl ethers	SE-30 or polyethanediol adipate	150–220	N_2 carrier gas (45 ml/min), FID	147
BHT and BHA	SE-30	280	–	201
Phenylenediamines	3% LAC-796 on Gas Chrom 9 (60–80 mesh)	140–215 16°C/min	FID, 3 m × 4 mm column	202
BHT, BHA and the trifluoroacetate of BHA	5 or 10% SE-30 on Chromosorb W AW DCMS (80–20 mesh)	160 and 175	N_2 carrier gas, FID, 1.5 m × 3 mm columns or Ar–CH_4 (9:1) (40 ml/min) ECD	203
Antioxidants	OV-17 on Anakrom ABS (80–90 mesh)	160–260, 10°C/min	N_2 carrier gas (30 ml/min), FID, 2 m × 0.125 in. column	157
Phenolic antioxidants as their trimethylsilyl derivatives	3% SE-54 on Gas Chrom Q (100–200 mesh) and 3% SP 2100 on Chromosorb W HP (100–120 mesh)	150–280, 2°C/min, 132°C	He carrier gas (21 ml/min) He carrier gas (8 ml/min), 2 m × 3 mm columns	204

Phenolic antioxidants	10% FFAP and 5% DEGS–1% H_3PO_4 on Chromosorb W AW DMCS	140–210 3°C/min	N_2 carrier gas, FID	205
BHT and its oxidation products	3% SP-2100 on Supelcoport	140	He carrier gas (40 ml/min), FID, 1.83 m × 3.2 mm column	206
Phenolic antioxidants	25% SKTN-1 on Chromaton N	160	FID, 1 m × 3 mm column	207
Phenolic antioxidants and their trimethylsilyl derivatives	Glass wool pre-column	–	–	208
BHT	Squalene-supported on Chromosorb G	–	–	209
Pyrolysis products of antioxidants	30% SE-30 on Diatomite S	220	N_2 carrier gas (120 ml/min), FID, 2 m × 4 mm column	210
Antioxidants	Fused-silica cap—illary columns coated with 0.15-μm layer of SE-30	170–250 5°C/min	He carrier gas, 25 m × 0.3 mm column	211
BHT	10% Carbowax 20 M on Celite (100–120 mesh) or QF-1 on Chromosorb W	–	N_2 carrier gas	212
Antioxidants	20% SE-31 silicone on Celite 545	200	He carrier gas (22 ml/min)	213
Antioxidants	LAC-2R-446 on Chromosorb G AW	200	N_2 carrier gas, FID	165
Antioxidants	1% Methyl vinyl silicone Lucoprene G-1000 on Chromotom N AW DMCS	100–280 12°C/min	N_2 carrier gas (30 ml/min), FID, 1 m × 3 mm column	214
BHT	20% SE-30 on Chromosorb W HMDS (60–80 mesh)	200	N_2 carrier gas (70 ml/min), FID and ECD, 2 m × 0.55 in. column	215
BHT	15% Silicone FM 1322/300 on fire brick	220	6 m × 4 mm column	216
BHT and BHA	5% Apiezon L and 10% of QF-1 on Gas Chrom Q	–	FID (4 ft. and 6 ft. × 4 mm two columns)	217
BHT and BHA	10% Apiezon M on Celite 545	175	Ar carrier gas (70–80 ml/min) β-ray ionization detector	218
Phenolic antioxidants	3% GE-XE-60 on Gas Chrom-Q (60–80 mesh)	1. 100–150 10°C/min 2. 100–165 10°C/min 3. 165–250 16°C/min	N_2 carrier gas (125 ml/min), FID, 2 m × 0.25 in column	219

that this method was very satisfactory in the absence of interfering compounds, but processing and extender oils now in common use usually produced interfering peaks. Gaeta[188] later developed a GC method for antioxidant analysis for use in the presence of extending oils.

Tyler[28] used the same principle for the determination of the purity of N,N′-substituted *p*-phenylenediamines and found that materials tend to decompose or oxidize slightly when injection is made into a flash heater, but this problem was minimal with on-column injection. A small hump on the front of the peak often persists, even with highly purified N,N′-diphenyl-*p*-phenylene diamine.

Fewer reports of the application of GC for accelerator analysis exist. It is not possible to apply GC directly for the analysis as most are thermally unstable and decomposition may occur during analysis. However, a GC method has been reported by Patel[189] where accelerators have been identified via their decomposition products, carbon disulphide, amines and mercaptobenzthiazole (MBT). Vulcanizate rubber was extracted in a Brock and Louth's apparatus[44] containing 1.5 *N* HCl and ethanol. Carbon disulphide trapped in 0.2 *N* alcoholic potassium hydroxide was detected by the copper xanthate reaction when thiuram and dithiocarbamates were converted into their trifluoracetamide derivatives while MBT was converted to the methyl thioether for GC detection.

The formation of derivatives before chromatography however, often leads to some sample loss and the appearance of spurious peaks. Lack of specificity can be overcome using a variety of columns in the manner described for paper chromatography and TLC. It is concluded that although GC will play an important part in the analytical scheme of play an important part in the analytical scheme of additives such as antioxidants and accelerators, it is not likely to replace TLC as the basic method at the present time.

The possibility of using pyrolysis GC has also been considered[210,220]. Fragmentation of polymers and in one case the analysis of a polyurethane type cross-linker in natural rubber products has been described[221]. The procedure employs chemical cleavage of the compound or polymer at an amenable functional group using alkaline procedure and subsequent examination of the fragments or their derivatives by gas, liquid or gel permeation chromatography. The work follows from extensive studies of alkaline fusion by Siggia[222] and Haken[223] and co-workers.

9. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

While GC has been of limited success in the analysis of accelerators and antioxidants, high-performance liquid chromatography (HPLC) offers many potential advantages, particularly with the high boiling compounds of limited thermal stability concerned.

The most important advantages of HPLC in the application of interest in addition to its use with non-volatile and non-thermally stable compounds is the ease of variation of the eluent with a corresponding alteration of the elution sequence. The limitations of GC due to volatility has been reported by Leitch and Kirkland[224] who suggest that 85% of all compounds are not amenable to GC.

Conventional liquid chromatography, primarily used as a preventative procedure, is a slow technique, sometimes requiring hours or even days for a complete

analysis. HPLC, with efficiencies approaching those of GC, has become possible over the last decade by the development of high-pressure equipment with low-dead-volume detectors and highly efficient packings.

Analysis time in HPLC can be shortened considerably without loss of peak resolution by optimising the parameters of column length and diameter, flow-rate, sample size and support particle size. Table 10 summarises the more important literature on the application of HPLC for the determination of accelerators and antioxidants.

The most important contribution to the application of HPLC to the determination of antioxidants and plasticizers has been made by Majors[53]. He examined the applicability of commercially available silica supports to applications relevant to this work with columns (1000 × 2.1 mm I.D.) of Zipax, Corasil I and OPN–Durapak. Since the surface area of Zipax, 0.65 m^2/g and Corasil I 7.0 ± 1.0 m^2/g are drastically different, no attempt was made to keep the film thickness equivalent. Both were impregnated with 0.52% (w/w) with β,β'-oxydipropionitrile comparisons with OPN–Durapak.

A number[243–249] of comparisons were made with the packings relevant to amine antioxidant separation. Although the relative elution order is the same on all three columns, the selectivity for each peak relative to N,N′-diethylaniline appears to be affected. Selectivity for each solute (elution volume of solute divided by that of N,N′-diethylaniline) was the highest on OPN–Durapak and lowest on β,β'-oxydipropionitrile–Zipax. However due to the increased column efficiency of Zipax, resolution of the amine solutes on β,β'-oxydipropionitrile–Zipax are comparable. In all cases β,β'-oxydipropionitrile–Corasil I has the best peak resolution. Height equivalent to a theoretical plate (HETP) values of less than a millimetre are obtained for the weakly retained solutes on Zipax and Corasil I.

Durapak gives plate heights an order of magnitude greater. The decreased efficiencies observed with this support are possibly due to slow solute mass transfer in the porous Corasil backbone at the higher flow-rate or from the resistance of mass transfer due to the large amount of the chemically-bonded liquid film or combination of these effects.

The increase in peak resolution for Corasil I, and distinct tailing of all peaks, suggests that the silica surface of the bead is contributing to the separation mechanism, even though the active sites should be covered with the polar β,β'-oxydipropionitrile liquid. This effect could be beneficial when using Corasil I for certain applications, but the mechanism governing the separation may be a combination of liquid–liquid partitioning and liquid–solid adsorption.

For "true" liquid–liquid chromatography without the adsorption effects from the siliceous surface of Corasil I it would be desirable permanently to deactivate the support. The manufacturer suggests heating the material overnight at 300–400°C. A portion of Corasil I after deactivation at 350°C and coated wtih 0.5% by weight of β,β'-oxydipropionitrile was packed into a 1000 × 2.1 mm I.D. column. Comparing the separation of this column and the deactivated column, it is apparent that for amine antioxidants, tailing is partially eliminated as evidenced by the increased tailing factors. Likewise, the elution volumes are decreased and close to those obtained for these solutes on the Zipax column. In addition, the resolution of solutes relative to N,N-diethylaniline is decreased when compared to undeactivated Corasil I.

TABLE 10

ANALYSIS OF ACCELERATORS AND ANTIDEGRADANTS BY HPLC

Compounds separated	*Column and stationary phase*	*Mobile phase*	*Column Pressure*	*Flow-rate (ml/min)*	*Concn.*	*Other details*	*Refs.*
(a) MBT, MBS, PBNA	1 m, ODS Permaphase	(a) Dioxane–water (40:60)	1100 p.s.i.	0.33	1 mg/ml	830 (DuPont) liquid chromatograph equipped with a 3000 p.s.i. pump and 254-nm UV detector and 1-mV recorder	58
(b) Styrenated phenol	1 m, ODS Permaphase	(b) Dioxane–water (50:50)	1200 p.s.i.	0.33	2 mg/ml		
(c) TMTD, TMTM	1 m, ODS Permaphase	(c) Dioxane–water (7.5:92.5)	1000 p.s.i.	0.44	2.5 mg/ml		
(d) DMB, PPD	1 m, Corosil - II	(d) Chloroform–hexane (12:88)	200 p.s.i.	1.30	2 mg/ml		
(e) DPG	1 m, Corosil II	(e) Isopropanol–hexane (45:55)	300 p.s.i.	1.00	0.5–10 μg/ml		
(f) MBT	1 m, Corosil - II	(f) Isopropanol–hexane (2:98)	200 p.s.i.	1.38	0.5–1.0 μg/ml		
Aromatic amine type antioxidants	(a) Zipax (1000 × 2.1 mm I.D. column packed with 0.5% β,β′-oxidipropionitrile on 20–37 μm Zipax support	Isooctane	–	0.31	9.5 μg/ml	5000 p.s.i. pump, Refracto-Monitor Model 1103 (LDC) with cell volume of 3 μl and refractive index (RI) 1.3–1.55 and UV monitor UV Absonce Monitor (LDC) with 8 μl cell volume	53
Aromatic amine type antioxidants	(b) Corasil (1000 × 2.1 mm I.D. column packed with 0.5%, β,β′-oxidipropionitrile on 37–50 μm Corasil support)	Isooctane	–	0.50	–		
Aromatic amine type: antioxidants	(c) OPN–Durapak (1000 × 2.1 mm I.D. column packed with 3.7% OC_4H_4CN bonded with 36–75 μm Porosil C	Isooctane	–	2.24	–		
Hindered phenolic type: antioxidants	(d) Corosil II (1000 × 2.1 mm I.D. packing 37–50 μm Corasil II activated at 110°C)	1% Isopropanol in hexane	–	0.95	0.54 mg/ml		

Antioxidants	300 × 4 mm I.D. glass column packed with SG-10-Silica gel.	Isopropanol–*n*-hexane (15:85)and(4:96) + 0.1% triethylamine	1–1.5 MPa	0.55–1.5	5 · 10^3 mol/l	Detection was by UV detector at 254 nm	225
Antioxidants	(a) 200 × 3 mm I.D. stainless-steel column packed with Separon SE	(a) *n*-Heptane	–	0.83	–	UV detector at 230 nm	55
Antioxidants	(b) 200 × 8 mm I.D. stainless-steel column packed with Separon SE	(b) Methanol–*n*-heptane (97:3)	–	0.76	–	Refractive index detector	
Antioxidants	(c) 300 × 3 mm I.D. glass column packed with Separon SE	(c) Water–methanol–diethylether (10:55:35)	–	0.55	–	UV detector at 270 nm	
Accelerators and antioxidants	(d) 300 × 3 mm I.D. glass column packed with Separon SE	(d) –		0.45	–	UV detector at 254 nm	
Antioxidants	(e) 300 × 3 mm I.D. glass column packed with Separon SE	(e) –	–	0.58	–	UV detector at 254 nm	
MBT	Bondapak-Alkyl-Ph	Gradient of methanol–water (55:45) to (90:10)	–	2.0	–	UV detection at 320 nm(limit 0.1ppm)	226
Phenolic and amine antioxidants	Alkyl phenyl-lined (Bondpak), reversed-phase	Gradient elution of 0.05 *M* H_3PO_4 in acetonitrile	–	–	–	UV detection	227
Toluene diamines	1 m, SCX-Zipax®	Water	800 p.s.i.	1.0	–	Ambient temperature	228
Toluene diamines	1 m 1% Cyano-silicone on Zipax®	*n*-Heptane	900 p.s.i.	1.5	–	UV photometer at 254 nm	
Chloro aromatic amines	1 m × 3.2 mm I.D. column, 1.75 trimethylene glycol (TMG) on Zipax	TMG saturated with heptane	–	1.6	–		
Xanthate accelerators	1 m ODS-Zipax®	35% THF in water	1500 p.s.i.	0.7	–		
Antioxidants	25 cm column packed with Zorabax-SIL	(a) Hexane + 0.2% methylenechloride (b) 0.9–70% CH_2Cl_2 gradient elution	–	1.0	–	UV and RI detectors	56

(Continued on p. 342)

TABLE 10 (*continued*)

Compounds separated	*Column and stationary phase*	*Mobile phase*	*Column Pressure*	*Flow-rate (ml/min)*	*Concn.*	*Other details*	*Refs.*
Phenolic antioxidants	Sil × 11 - Octadecyl	Methanol–water (9:1, 8:2, 7:3)	–	0.9	0.2%	Retention times increases with the water–methanol ratio	229
Cresols	25 cm × 2.1 mm column packed with Zorbax SIL (5 μm)	Cyclohexane–CH_2Cl_2 (15:2)	2500 p.s.i.	0.6		Operation at 48°C, UV detection at 254 nm	198
Phenolic antioxidants	30 cm × 4 mm column packed with μBondapak C_{18}	Gradient of methanol 55–85%	–	–	–	–	230
Antioxidants and their transformation products	25 cm × 4 mm column packed with Partisil (5 μm)	Gradient elution CH_2Cl_2 in hexane	–	–	–	UV detector at 242 nm	231
BHT	Column (1 m × 2.1 mm) Permaphase ODS	Water–methanol (9:11)	300 p.s.i.	0.3	–	UV detector at 254 nm	232
Phenols and BHT	Sephadex LH-20 column	Cyclohexane–chloroform (1:1)	–	–	–	–	233
Phenolic antioxidants	Column (25 cm × 1.5 mm) of Micropack Si 10	2,2,4-Trimethylpentane–ethylacetate–CH_2Cl_2 (19:3:3)	–	–	–	UV detector at 292 nm limit of detection 9–21 ng	234
MBT	Column (15 cm × 0.46 cm) of Merckosorb SI 60 (5 μm)	Ethanol–2,2,4-trimethylpentane (1:9)	–	1	0.3 mg/l	UV detector at 325 nm, detection limit 0.03 mg l^{-1}	235

Phenolic antioxidants	Column (30 cm × 3.9 mm) of μPorasil (10 μm)	5 min, elution gradient 100% heptane to 100% CH_2Cl_2	–	–	–	UV detection at 280 nm, limit of detection 0.0006–0.004%	236
Phenolic antioxidants	Column 25 cm × 3 mm) of LiChrosorb RP-18 (10 μm)	Gradient elution with 5% acetic acid initially in aq. acetonitrile or methanol	–	1	–	UV detection at 280 nm	237
Phenolic antioxidants	Column (30 cm × 3.9 mm) of μBondapak C_{18} and (30 cm × 3.0 mm) column of Co:Pell ODS (30–38 μm)	Gradient programme from 50 to 90% of methanolic 1% acetic acid	–	1.5	–	–	238
Phenolic antioxidants	Columns (25 cm × 6 mm) of Separon SE	70–100 Methanol	–	1	–		239
Phenolic antioxidants	Column (25 cm × 6 mm) of Separon Si-C_{18}	Aq. 97% methanol	–	1	–	UV detector at 270 nm	240
Phenolic antioxidants	Column of Lichrosorb RP-18 (10 μm)	80% Methanol	–	1	–	UV detector at 254 nm	241
Phenolic antioxidants	Column of Partisil PXS 10/25 ODS-2 and LiChrosorb RP-18	0.05 *M* $LiClO_4$ in aq. 30, 65 and 85% methanol	–	–	–	Fluorescende at 370 nmUVdetector at 230 and 280 nm, electrochemical detector	242
BHT	1-m column of Corasil II	Heptane	–	–	–	–	166
1,4-Phenylene-diamine	Column (2.6 mm O.D.) of Silpearl (10–30 μm) (Kavalier)	*n*-Heptane–ethanol	–	1.5	–	UV detector at 254 nm	119

Majors[53] also reported the separation of hindered phenolic antioxidants by HPLC. Corasil II of surface area 14 ± 2 m^2/g was used and it was suggested that this material should facilitate the direct extrapolation of TLC data to moderate (15–500 p.s.i.) and high (> 500 p.s.i.) pressure liquid–solid chromatography[35,250]. To illustrate this possibility, Majors separated three phenolic antioxidants on silica gel plates conditioned for 1 h at 110°C, and on 1000 × 2.1 mm Corasil II column.

Pugh[228] used HPLC for the first time for the separation of amine antidegradants. Subsequently, Sullivant *et al.*[58] applied HPLC for the separation of accelerators and antioxidants extracted from unvulcanized rubber stocks. Some accelerator decomposition was observed in the rubber during mixing. TLC was used as an adjunct to HPLC for the identification of the individual additives.

Guenter *et al.*[226] determined MBT in rubber baby bottle nipples by HPLC. The mean release of MBT was 3 ppm with 30 μg/l from some samples with the limit of detection 0.1 ppm. The release of MBT should be controlled because of its bitter taste.

A comparison of liquid adsorption chromatograph (LAC) with gel permeation chromatography (GPC) was made by Wims *et al.*[56], who reported that both GPC and LAC are very good for routine monitoring techniques. LAC can be used when a factor analysis of antioxidants is required.

Guergens[227] *et al.* also used HPLC for antioxidant analysis. Amine and phenolic stabilizers, present in rubber articles, were separated in an alkyl-phenyl-lined (Bondapak) reversed-phase column, with gradient elution by 0.05 *M* orthophosphoric acid in acetonitrile.

Smejkal *et al.*[55] used HPLC for the separation of antioxidants with different sterically shielded polar groups. A selective interaction solute–mobile phase was utilized and liquid–liquid chromatography (LLC) achieved by means of utilization of the various interaction profiles of some solvents. LLC with the macroporous gel Separon SE was used to determine the retention of some antioxidants and to analyse these compounds in polymers.

10. SIZE EXCLUSION CHROMATOGRAPHY

GPC also known as size exclusion chromatography (SEC), has long been used as a method for the determination of polymeric molecular weight distributions, for the analysis of polymer additives, preparative fractionation and sample clean-up. However, techniques formerly used, required long columns and low linear velocities (*i.e.* flow-rates) in order to achieve a required resolution. Following the development of microparticulate columns for ion-exchange, liquid–solid and bonded-phase chromatography in the early 1970's, microparticles also became available for the exclusion chromatographic mode, allowing more rapid chromatographic separations. The SEC microparticles resulted in shorter columns (30–50 cm *vs.* 120 cm), consuming less solvent and permitting more convenient thermostatting.

Relative to other LC modes, the advantage of exclusion techniques is its apparent simplicity. Often one merely dissolves the sample and injects it. In contrast to the other LC modes, all sample components should elute between the excluded volume and the total permeation volume, each compound appearing at a fixed time (volume) interval. Thus little operator experience in chromatography is required and the in-

terpretation of the chromatogram is fairly easy. The only decision to be made is in choosing optimum pore size which can be selected by a knowledge of the molecular weight operating range of the column (or columns) and matching it with the suspected molecular weight range of the sample.

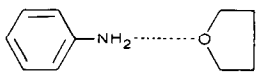
The most important contribution to the application of SEC for the separation of antioxidants and accelerators has been made by Protitová and co-workers[47,54,57,251]. Table 11 summarises the more important literature on the application of SEC to antioxidant and accelerator analysis.

Protivová and Pospíšil[251] have reported on the behaviour of some amine antidegradants (see Table 12) and some model substances (phenols, aromatic hydrocarbons and amines) during SEC and have applied their technique, as described below, to the analysis of rubber extracts. Čoupek *et al.*[54] and Protivová *et al.*[47] have previously discussed the application of SEC to stabilizers of various types but have not discussed the use of this technique quantitatively.

Since the size exclusion method does not allow a direct determination of the molecular weights or molar volumes of the samples under investigation, calibration was made by using standard compounds in the form of a graphic dependence of their molar volume on the elution volume[251]. Normal hydrocarbons and aliphatic esters were used as standards. The molar volumes (ml/mole) were plotted against elution volumes, V_e (ml), in the calibration curves, as shown in Table 13. The molar volumes were calculated from the atomic volumes and structural coefficients[253].

The results of SEC measurements by Protivová and Pospíšil[251] on the elution volumes of aromatic amines, their molecular weights, calculated molar volumes and the effective molar volumes observed and read from the calibration curves are given in Table 12. A comparison of the calculated and effective molar volumes revealed deviations in the behaviour of all the amines investigated, compared to similar aliphatic hydrocarbons.

The behaviour of the compounds in tetrahydrofuran solution and in contact with a swollen gel is affected by several factors. Protivová and Pospíšil deduced from the literature data[254–256] and from experimental data obtained by measurements of various types of compounds that, similarly to phenols, the gel chromatographic behaviour of aromatic amines is predominantly affected by the formation of solvates due to intermolecular hydrogen bonds between the amine and ether groups of tetrahydrofuran.



Solvation with tetrahydrofuran leads to an increase in the volume of the molecule of the aromatic amine and a decrease in V_e. To compare the behaviour of aromatic amines, data on selected alkyl phenols are given in Table 14 measured under comparable conditions.

The increase in V_e is affected by changes in the pore size of the gel during the flow of the sample through the columns. If the gel comes into contact with compounds that can be readily hydrated (*e.g.* amines), a transitional decrease in the gel pores is observed due to the contact with water molecules (the so-called trapping

TABLE 11

SEPARATION OF ANTIDEGRADENTS AND ACCELERATORS BY GPC

Compounds separated	*Columns used*	*Mobile phase*	*Column pressure (atm)*	*Flow-rate*	*Other details*	*Refs.*
Antioxidants and stabilizers	S-Gel-832 (UMCH, CSAV Czechoslovakia) was packed into 9 (1.2 m × 8 mm) stainless-steel columns connected in series	Tetrahydrofuran	5	35 ml/h	Flow differential refractometer and UV detectors	54
Antioxidants and stabilizers	Six stainless-steel columns packed with styrene divinylbenzene gel, Copolymer ST DVB No. 1X grain size 0.040–0.056 mesh; connected in series	Tetrahydrofuran	5	35–45 ml/h	Differential refractometers and UV detectors	57
Phenolic and aminic anti-oxidants and their model compounds	Six stainless-steel columns (1200 × 8 mm) packed with copolymer ST-DVB No. 1X polystyrene gel 0.040–0.056 mesh	Tetrahydrofuran	5	35–45 ml/h	30°C temperature, differential refractometer and UV detector (254 nm)	251
Antioxidants	Four Styragel columns with porosities 250, 100, 60 and 60 Å, connected in series	Tetrahydrofuran	–	1 ml/min	Differential refractometer detector	56
Low molecular weight additives, including antioxidants	Micropak TSK columns packed with cross-linked polystyrene of 8–10 μm particle diameter Micropak TSK 3000 H (50 cm × 8 mm I.D.) Micropak TSK 2000 H (50 cm × 8 mm I.D.) Micropak TSK 1000 H (80 cm × 8 mm I.D.)	Tetrahydrofuran	–	0.5 ml/min	UV detector at 215 nm	252
Accelerators and antioxidants	Columns (1200 × 8 mm) packed with co-polymer ST-DVB No. VIII polystyrene gel, grain size 0.040–0.056 mesh.	Tetrahydrofuran	2–4	30–40 ml/h	25°C temperature UV and RI detectors	47

TABLE 12

THE BEHAVIOUR OF AMINE ANTIOXIDANTS, ANTIOZONANTS AND MODEL COMPOUNDS IN SEC[251]

Chemical structure	*Molecular weight*	V_e *(ml)*	*Molar volume (ml/mole)*		*Deviation*
			Calculated	*Effective*	
Aniline	93.12	238	110.2	150.3	+40.1
4-Methylaniline	107.15	238	132.4	150.3	+17.9
2,3-Dimethylaniline	121.18	247	154.6	115.6	−39.0
2,4,6-Trimethylaniline	135.20	232	168.8	183.2	+14.4
2,3,5,6-Tetramethylaniline	149.24	247	199.0	115.6	−83.4
N-Methylaniline	107.15	253	133.9	95.9	−38.0
N,N-Dimethylaniline	121.18	278	156.1	44.2	−111.9
1-Naphthylamine	143.18	242	161.8	134.9	−26.9
2-Naphthylamine	143.18	241	161.8	139.0	−22.8
Diphenylamine	169.22	229	200.3	201.0	+0.7
Phenyl-2-naphthylamine	219.27	235	251.9	166.7	−85.2
o-Phenylenediamine	108.14	238	124.4	150.3	+25.9
m-Phenylenediamine	108.14	220	124.4	266.1	+141.7
p-Phenylenediamine	108.14	248	121.4	111.4	−10.0
4-Aminodiphenylamine	184.23	221	214.5	257.6	+43.1
4,4′-Bis(dimethylamino)-diphenylamine	255.41	228	320.5	212.3	−108.2
Benzidine	184.23	217	213.0	291.7	+78.7
o-Tolidine	212.28	224	257.4	234.4	−23.0
N,N′-Dimethyl-*p*-phenylene-diamine	136.22	247	171.8	115.6	−56.2
N,N′-Diethyl-*p*-phenylene-diamine	164.14	222	216.2	249.5	+33.3
N,N′-Di-*sec.*-butyl-*p*-phenylenediamine	220.38	236	305.0	162.2	−142.8
N,N′-Diisoheptyl-*p*-phenylenediamine	305.4	202	438.2	462.4	+24.2
N,N′-Diisooctyl-*p*-phenylenediamine	332.58	200	482.6	495.5	+12.9
N,N,N′-trimethyl-*p*-phenylenediamine	150.28	252	186.0	98.9	−87.1
N,N′-Dimethyl-2-methyl-*p*-phenylenediamine	150.28	250	186.0	105.2	−80.8
N,N′-Diphenyl-*p*-phenylenediamine	260.36	208	304.6	384.5	+79.9
N,N′-Dinaphyl-*p*-phenylenediamine	360.46	205	415.2	421.7	+6.5
N-Isopropyl-N′-phenyl-*p*-phenylenediamine	226.34	222	282.6	249.5	−33.1
N-Isobutyl-N′-phenyl-*p*-phenylenediamine	240.36	214	304.8	319.9	+15.1
N-Cyclohexyl-N′-phenyl-*p*-phenylenediamine	266.41	206	326.8	410.2	+83.4
N-Octyl-N′-phenyl-*p*-phenylenediamine	296.47	206	393.6	410.2	+16.6
N,N′-Bis-4-(N,N′-dimethylamino)-phenyl-*p*-phenylenediamine	346.55	218	424.8	283.1	−141.7

TABLE 13

THE BEHAVIOUR OF STANDARD COMPOUNDS IN SEC AND MOLAR VOLUMES CALCULATED[253]

Compound	*Molecular weight*	*Molar volume (ml/mole)*	V_e *(ml)*
n-Pentane	72.15	118.4	246
n-Hexane	86.18	140.6	239
n-Heptane	100.20	162.8	233
n-Dodecane	170.33	273.8	220
n-Hexadecane	226.43	362.6	212
n-Octadecane	254.48	414.4	206
Octyl adipate	270.14	495.4	200
Octyl sebacate	326.24	613.8	192

effect[255]). Another factor which greatly contributes to a considerable increase in V_e is the aromatic character of the compounds. An example can be seen in the behaviour of several aromatic hydrocarbons in Table 14. Deviations in the V_e values compared to the assumed molar volumes have been found by Čoupek *et al.*[257]. Since a com-

TABLE 14

THE BEHAVIOUR OF SELECTED AROMATIC HYDROCARBONS AND PHENOLS IN SEC[251]

Chemical structure	*Molecular weight*	V_e *(ml)*	*Molar volume (ml/mole)*		*Deviation*
			Calculated	*Effective*	
Benzene	78.11	278.0	96.0	44.2	−51.8
Toluene	92.14	256.0	118.2	87.5	−30.7
m- and *p*-Xylenes	106.16	255.0	140.4	90.2	−30.2
Ethylbenzene	106.16	247.0	140.4	115.6	−24.8
Mesitylene	120.18	255.0	154.6	90.2	−64.4
Pseudocumene	120.18	254.0	154.6	92.7	−61.9
Cumene	120.18	241.0	162.6	139.0	−23.6
p-Cymene	134.21	245.0	184.8	122.5	−62.3
1,2,4,5-Tetramethylbenzene	134.21	252.0	184.8	98.9	−85.9
tert.-Butylbenzene	134.21	242.0	184.8	134.9	−49.9
Naphthalene	128.16	255.0	147.6	90.2	−57.4
Diphenyl	154.20	241.0	162.6	139.0	−23.6
Phenol	94.11	240.0	105.9	142.9	+37.0
o-, *m*- and *p*-Cresols	108.13	237.0	128.1	157.4	+28.7
2- and 4-Ethylphenols	122.16	235.0	100.3	166.7	+16.4
2-*n*-Propylphenol	136.19	229.0	164.5	201.0	+36.5
2,4-Dimethylphenol	122.16	233.0	150.3	177.9	+27.6
2,3-Dimethylphenol	122.16	238.0	150.3	150.3	0.0
2,6-Dimethylphenol	122.16	239.0	150.3	147.9	−2.4
2,4,6-Trimethylphenol	136.19	237.0	164.5	157.4	−7.1
2- and 4-Phenylphenols	170.20	233.0	194.5	177.9	−16.6
2-Naphthol	144.16	251.0	157.5	101.6	−55.9
o-Aminophenol	109.12	242.0	130.1	134.9	+4.8
m-Aminophenol	109.12	226.0	130.1	221.3	+91.2
p-Aminophenol	109.12	242.0	130.1	134.9	+4.8
Tetrahydrofuran	72.10	–	88.3	–	–

parison with a series of amine compounds was necessary Protivová *et al.*[47] repeated the measurements under conditions when different absolute V_e values wer found. The comparison of relative relationships showed a negative difference between the calculated and the determined molar volumes in all cases. This is true for both mononuclear and binuclear aromatic hydrocarbons. The aromatics associate with the gel, which is also aromatic; owing to sorption, they remain in the gel pores much longer than similar non-aromatic compounds. Steric effects also play their part especially in the case of bulky substituents.

The same factors are met in the analysis of aromatic amines. As can be seen from Table 12 the minimum deviation between the calculated and effective molar volumes appeared in the case of diphenylamine; here, influences tending to increase and to decrease the molar volume occurred at the same time as result of the presence of two aromatic nuclei and one amino group. The maximum negative deviation was observed with N,N′-di-*sec*.-butyl-*p*-phenylenediamine and N,N′-bis-4-(N,N′-dimethylamino)phenyl-*p*-phenylenediamine.

Some basic findings about the effect of the structure of the compounds investigated in the work of Protivová *et al.*[47] on the SEC behaviour are as follows: the deviation between the observed and calculated molar volume of benzene was −51.8. Substitution of a benzene ring not containing any solvatable group with small alkyls was reflected in deviations in the range from −23 to −86. Introduction of one –OH or $-NH_2$ group into the benzene ring increases the calculated, as well as the effective, molar volume of benzene by approximately the same value. The deviation between the calculated and the effective molar volume is also comparable. It is interesting to compare the behaviour of the benzene derivatives containing two solvatable groups. The effective molar volumes of *o*- and *p*-aminophenols differ little from the calculated volume. A high solvation took place in the case of *m*-aminophenol. A similar trend was found in the series of isomeric phenylendiamines. In this case, however, there is a striking difference between the *o*- and *p*-isomers, the latter exhibiting a negative deviation.

In the case of primary amines with one benzene ring and small substituents in the ring, hydrogen bonds between amine groups and tetrahydrofuran can play a specific role. A comparative investigation of the SEC behaviour of selected monoalkylphenyls showed that in all cases, even if the less bulky substituent was at position 2, solvation took place. The same holds for 2,4-xylenol. The effective molar volume for all other dialkylphenols was the same or smaller than the assumed volume. The effect of the substituent in anilines similarly substituted in the ring with a methyl group was less regular. A marked difference is seen when 2,4,6-trimethylphenol and 2,4,6-trimethylaniline are compared and for which a similar trend in the solvation effect might have been assumed an irregular effect on the volume due to solvation can be observed when comparing 2,4,6-trimethylaniline and 2,3,5,6-tetramethylaniline. Less regular influences on the retention time of the substitution of simple aromatic amines, in comparison with phenols, has also been observed in column liquid chromatography[258].

The presence of two condensed aromatic nuclei has a strong effect as in the naphthalene series. Introduction of the solvatable group is either virtually not reflected in a decrease in the negative deviation from the calculated molar volume (*cf.*, 2-naphthol), or the solvation makes the effective molar volume only approximate to the calculated volume (both examples were isomeric naphthylamines).

Substitution with one polar group in the diphenyl series (4-phenylphenol) brings the effective molar volume somewhat nearer to the calculated one. The effect of solvation is particularly marked in the presence of two amino groups, as can be seen in the example of benzidine. Experimental data show, however, that hindrance due to a mere methyl group in *o*-toluidine suppresses the effect of solvation in this case.

If aliphatic substituents are bonded to a nitrogen atom, the possibility of solvation decreases and the aromaticity of the compound plays the predominant role in SEC analysis. This can be demonstrated for the series aniline, N-methylaniline and N,N-dimethlaniline. If nitrogen in aniline is substituted by an aromatic residue, a decrease in the observed molar volume can be expected compared to the calcualted one, owing to the concurrent effect of the decreased solvation power and increased portion of the aromatic groups. This assumption is valid for phenyl-2-naphtylamine or N,N′-bis(4-dimethylamino)diphenylamine, but not for diphenylamine. In accordance with the preliminary data, the presence of a solvatable group in diphenylamine will raise the value of the molar volume observed (*e.g.* 4-aminodiphenylamine). In a similar fashion to the aniline series, a decrease in solvation due to substitution at the nitrogen atom must also be assumed for the phenylenediamine series. In the group of aliphatically N,N′-disubstituted derivatives compounds were studied by Protivová *et al.*[47] which differed to a great extent in the volume of the substituent. However, with the exception of compounds substituted with methyl groups (the conclusions hold also for N,N′-dimethyl-2-methyl-*p*-phenylenediamine and N,N,N′-trimethyl-*p*-phenylenediamine) and with *sec.*-butyl, the assumption concerning limited solvation was not fulfilled. Further interactions among molecules of analysed compounds, eluent and gel packing probably occur specifically in the system studied.

Completely anomalous behaviour was exhibited by the N,N′-disubstituted derivatives of *p*-phenylenediamine, in which one of the substituents on the nitrogen atom or both of them were aromatic. For these derivatives, larger elution volumes than those found were assumed, as the aromatic substituents on the nitrogen atom are capable of restricting the formation of hydrogen bonds with tetrahydrofuran.

Some of the amine compounds investigated by Protivová *et al.*[47] exhibited negative peaks with refractometric detection (that is, they had a lower refractive index increment than tetrahydrofuran) or the shape of the peaks was unusual. To prevent errors due to an incorrect determination of the peak of a compound, a combination of refractometric and UV detection proved useful.

The literature would suggest that the SEC technique is ideally suited to the analysis or purification of a wide variety of antioxidants and accelerators from polymers. Often, for low-molecular-weight additives, resolution is such that they can be determined directly. In some cases the technique can be used to provide a prefractionation or clean-up with the actual separation being carried out with a secondary chromatographic method such as reversed-phase LC. For such work, SEC columns have the advantage of low peak dilution.

11. SUMMARY

The use of various chromatographic methods in the analysis of all classes of elastomer antidegradants and accelerators is reviewed. The review of extraction methods is also included.

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