Identification of antioxidants and accelerators in gum and carbon black-filled rubbers by thin-layer chromatography

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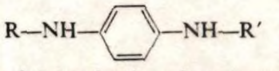
INTRODUCTION

THE types of organic accelerator used for natural rubber and other polymers can be represented by the following classes, (a) aldehyde-amine condensates (b) guanidines and thiocarbanilides, (c) Thiazoles; sulphenamides; thiurams; xanthates and dithiocarbamates.

Typical thiazole accelerator types are 2-mercaptobenzothiazole (MBT) and benzothiazyl disulphide (MBTS), which are closely related to the sulphenamide types which are widely used in the rubber industry, being manufactured from mercaptobenzthiazole and a selected amine eg *t*-butylbenzthiazyl-2-sulphenamide. Various types of compounds, given the general terminology " antioxidants " are also used in rubber compounds to minimise degradation of polymer materials due to the effect of oxygen and ozone. Chemically these antioxidant compounds are represented by the following classes, (a) amines and their derivatives which include ketoamine and aldehyde-amine condensates and secondary aromatic amines, (b) phenols and their derivatives and (c) dithiocarbamates and other sulphur compounds.

Typical examples of the amine types are polymerised 2,2,4-trimethyl 1,2,dihydroquinoline (' Flectol ' H), phenyl-β-naphthylamine (PBN) and para-phenylenediamine derivatives based on the general formula

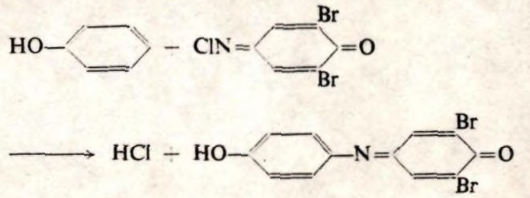


The identification and determination of accelerator and antioxidant in vulcanisates has always been one of the more difficult problems in rubber analysis. The quantitative determination of accelerator or antioxidant is often possible once it has been shown by qualitative tests to be present, but it by no means follows that the amount found after vulcanisation is the same as that originally added. Various methods have been previously used based on specific colour reactions[1], column and paper chromatography[2, 3] and absorption spectroscopy[4], which were often non-specific and time consuming. For this reason the technique of thin-layer chromatography was applied to this problem of identification of antioxidants and accelerators in vulcanised rubbers.

EXPERIMENTAL

Examination of commercially available antioxidants and accelerator compounds

The various samples, as received from the manufacturer, were examined by TLC using 0·1, 0·5 or 1·0 per cent w/v solution in appropriate solvents (normally acetone or carbon tetrachloride). Five microlitre aliquots were pipetted on to silica gel plates and developed with benzene/ethyl acetate/acetone 100/5/2 v/v. Toluene/ethyl acetate/ammonia 98/2/0·1 v/v can also be used. The spots were located by spraying with 2,6-dibromo-*p*-benzoquinone-4-chlorimide (0·2 per cent in ethanol) and heating gently with a hot-air blower, giving specific and well defined colours with the various types of antioxidant and accelerator. The usefulness of this spray reagent is illustrated by the fact that even elemental sulphur is detected as a pink spot. The reagent appears to function in a dual capacity of acting as a mild oxidising agent which can oxidise certain compounds such as the secondary amines to give coloured Wurster salts or by a coupling reaction to give a coloured product. With phenolic compounds indophenols are formed.



RESULTS

Typical chromatograms are shown in Figs. 1 and 2 and th specific colours and R_F values are given in Table I.

TABLE I—Typical R_F values and colours for antioxidants and accelerators, using Benzene/Ethyl Acetate/Acetone 100/5/2 as solvent

		R_F	*Spot colours*
1.	N,N′-Dimethyl-N-N′-di-(1-methyl propyl)-*p*-phenylenediamine (' Eastozone ' 32) ...	0·28	deep purple
2.	N-N′-Di-Sec.octyl *p*-phenylenediamine (' Tenamene ')	0·50	choc. brown
3.	Phenyl α-Naphthylamine (PAN)	0·78	orange brow
4.	Phenyl β-Naphthylamine (PBN)	0·76	brick red
5.	N-isopropyl N′ phenyl *p*-phenylenediamine (' Nonox ' ZA)	0·43	yellowish brown
6.	N,N′Diphenyl-*p*-phenylenediamine (' Nonox ' DPPD)	0·69	,,
7.	N-cyclohexyl-N′-phenyl-*p*-phenylenediamine (CPPD)	0·53	brown
8.	Polymerised 2,2,4 trimethyl 1,2 dihydroquinoline (' Flectol ' H)	0·72	light brown
		0·61	blue
		0·49	,,
		0·40	,,
		0·31	,,
9.	Phenyl-β-Naphthylamine/Diphenyl-*p*-phenylene diamine (HFN) 90/10/w/w ...	0·75	brick red
		0·69	yellow
10.	Diphenylamine-acetone reaction product (BLE)	0·78	deep gree (tailing)
11.	N,N′-Di-β-Naphthyl-*p*-phenylenediamine ...	0·65	orange bro
12.	2-Mercaptobenzothiazole (MBT)	0·42	orange
13.	Benzothiazyl-disulphide (MBTS)	0·65	light brown
14.	N-cyclohexyl-2-benzothiazole sulphenamide (' Santocure ' CBS)	0·65	grey
15.	*Tetramethyl thiuram disulphide (TMTD)* ...	0·57	pinkish gre
16.	2,5-di(*tert*.amyl) hydroquinone (' Santovar ' A)	0·68	grey
17.	Substituted styrenated phenol (' Wing Stay ' S)	0·78	purple
		0·57	purple
18.	2,2′-Methylene-bis-(4-methyl-6-*t*-butyl phenol) (' Antioxidant ' 2246)	0·74	yellow
19.	Elemental sulphur	0·95	pink
20.	Zinc dibutyl dithiocarbamate (ZD_BC) ...	0·55	brown (ta

Reasonably constant R_F values are obtained if the thickne the silica gel layer is kept between 200 and 300μ and the cha saturation is maintained. The small variation in R_F values ca no problem in identification work as the indicating reagent ga wide range of colours which permitted identification of the va compounds both by colour and distance travelled. Althoug exhaustive testing of all commercially available antioxidants

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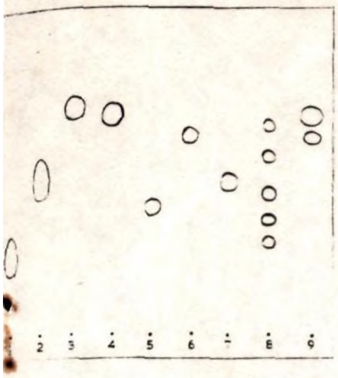


Figs. 1 and 2. Chromatograms of typical commercial antioxidants and accelerators. Solvent: benzene/ethyl acetate/acetone, 100/5/2; Spray: 0.2% 2,6 dibromo-p-benzoquinone-4-chlorimide in ethanol.

See also Table 1.

ccelerators was not made. a portion of the various types available ere examined to illustrate the general usefulness of TLC fqr eparation and identification. It is also a useful way of assessing ie purity of the commercial compounds, since small amounts of npurities can be detected using this technique.

xamination of antioxidants and accelerators in um and carbon black-filled natural rubbers

The customary starting-point for any examination of the antioxidant and accelerator system of a rubber compound is an extracon procedure, giving an extract which is a complex mixture of aterials initially present in the rubber, vulcanising and other gredients added during compounding, together with reaction and reakdown products of these. For the extraction of natural ibber, whether raw or vulcanised, acetone extraction is always pecified as it fulfils most of the criteria for a good extractant. These re that the polymer should be swollen slightly by the solvent but ould not be soluble in it: it is convenient that it should boil well elow any extracted material so that it can be easily removed from ie extract without any extract loss; the solvent should also be ert to any possible ingredients of the extract and not be objectionble by virtue of excessive toxicity, inflammability or odour.

Acetone has been widely used in the rubber industry but does ave certain disadvantages in that it causes decomposition of ertain accelerators[5]. This effect will give no real problem in lentification of accelerator types used in a rubber compound, but ili, of course, make quantitative measurements on accelerators ither difficult; as, however, most of the organic accelerators used ecompose during vulcanisation, only qualitative measurements re really meaningful. Some workers have used isopropyl alcohol room temperature as the extractant but work in the laboratory iowed that incomplete extraction was often observed.

The rubber samples, compounded according to the formulations Tables II and III, both in the uncured and cured state were lightly illed to facilitate extraction and cut into small pieces. A one-gram imple (±0·01g) was extracted for 12 hours with acetone under eflux, the acetone was then distilled off and the residue was dissolved 0·5 ml of carbon tetrachloride. Aliquots (normally 5 μl) were ipetted on to silica gel plates and developed with solvent mixture nd sprayed with spotting reagent as previously described.

RESULTS

Typical chromatograms are shown in Figs. 3 and 4. The following general observations were made.

TABLE II—Formulation for various rubber samples

Gum mix	*Sample No.* 1	2	3	4	5	6
Natural rubber (RSS1) ...	100	100	100	100	100	100
Stearic acid	2·0	2·0	2·0	2·0	2·0	2·0
Zinc oxide	5·0	5·0	5·0	5·0	5·0	5·0
Sulphur	2·5	2·5	2·5	2·5	2·0	2·0
N-cyclohexyl-2-benzothiazole-sulphenamide (' Santocure ' CBS)	1·0	1·0	1·0	1·0	—	—
Diphenylguanidine (DPG) ...	—	—	—	—	0·5	0·5
Benzothiazyl-disulphide (MBTS)	—	—	—	—	1·0	1·0
*N-isopropyl N-phenyl-p-*phenylenediamine (' Nonox ' ZA)	—	2·0	—	—	—	—
Phenyl β-Naphthylamine (PBN)	—	—	2·0	—	—	2·0
Polymerised 2,2,4 trimethyl 1,2 dihydroquinoline (' Flectol ' H)	—	—	—	2·0	—	—

TABLE III—Carbon Black-filled mix

	Sample No. 1	2	3	4	5	6
Natural rubber (SMR 5 Y.O.)	100	100	100	100	100	100
Carbon black (HAF)	50	50	50	50	50	50
Zinc oxide	3·5	3·5	3·5	3·5	3·5	3·5
Stearic acid	2·5	2·5	2·5	2·5	2·5	2·5
Sundex 1585 oil	4·0	4·0	4·0	4·0	4·0	4·0
Sulphur	2·5	2·5	2·5	2·5	2·0	2·0
N-cyclohexyl-2-benzothiazole-sulphenamide (' Santocure ' CBS)	0·5	0·5	0·5	0·5	—	—
Diphenylguanidine (DPG) ...	—	—	—	—	0·5	0·5
Benzothiazyl disulphide (MBTS)	—	—	—	—	1·0	1·0
N-isopropyl N′-phenyl-*p*-phenylenediamine (' Nonox ' ZA)	—	2·0	—	—	—	—
Phenyl β-Naphthylamine (PBN)	—	—	2·0	—	—	2·0
Polymerised 2,2,4 trimethyl 1,2 dihydroquinoline (' Flectol ' H)	—	—	—	2·0	—	—

The cured samples were heated at 140°C for 30 minutes.

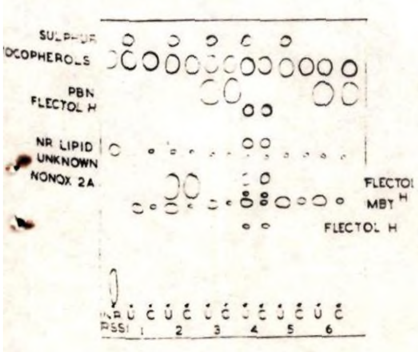
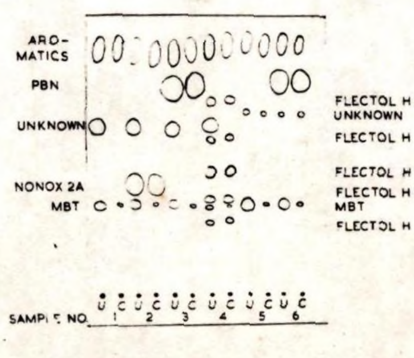


Fig. 3. Chromatogram of a Gum Rubber Extract; Developing Solvent Benzene/Ethyl Acetate/Acetone, 100/5/2 v/v. U—uncured; c—cured

Fig. 4. Chromatogram of a Carbon-Black Filled Rubber Extract; Developing Solvent Benzene/Ethyl Acetate/Acetone, 100/5/2. U—uncured; c—cured



Gum Rubbers. (Fig. 3)

In the uncured and cured rubber extracts, certain phenolic components were detected which were found in raw natural rubber, being identified as the tocopherol and tocotrienol class of compounds. The relative amounts appeared to be independent of the type of accelerator or antioxidant system used.

In all the uncured samples free elemental sulphur (R_F 0·95; pink spot) and free MBT (R_F 0·42; orange spot) were detected, the MBT being formed by decomposition of either the sulphenamide (CBS) or the disulphide (MBTS) accelerator on compounding. The relative amounts depended on the accelerator system ie the greater amount of MBTS used gave more MBT: but also rather surprisingly the amount of free MBT appeared to vary with the type of antioxidant present. This appeared to suggest that some secondary reaction was taking place between the acidic thiol group in MBT and the basic amine antioxidants.

However, in the cured samples only traces of free MBT were found due to the reaction of MBT with zinc oxide to give ZMBT, which was not extracted from the rubber by acetone. Once again there appeared to be relatively more MBT formed from the MBTS/DPG/S system.

The relative amounts of antioxidants in the uncured and cured rubbers appeared very comparable and identification of the various types was possible from the R_F value and colours. There appeared to be little or no loss of free antioxidant on compounding or curing.

Carbon black-filled rubbers (Fig. 4)

The phenolic type of compounds found in natural rubber were not detected in the uncured or cured states, probably due to adsorption on to the surface of the carbon black.

Elemental sulphur could be detected in the uncured samples (R_F 0·95: pink). However, a second component of comparable R_F value was also detected in the uncured and cured rub extracts, which appeared to be associated with the aroma components found in the processing oil ('Sundex' 1585). found with the gum rubbers, free MBT (R_F 0·42) could be detec in the uncured samples, the relative amounts depending on accelerator systems and antioxidant type. On curing only tr amount of MBT could be detected, the relative amount being grea for the DPG/MBTS/S accelerator system.

Identification of antioxidant type was again possible both in uncured and cured state, the relative amounts in each case be virtually identical, suggesting that there was little or no loss of f antioxidant on compounding or curing. From previous work loss of free antioxidant depended markedly on the type of carb black and the basicity of the antioxidant ie the more basic antioxidant, the greater the adsorption on the surface of the carb black.

From the above general observations, it is seen that identificati of antioxidant and accelerator type in gum or carbon black-fil rubbers is possible by comparing R_F value and spot colour w those of the standard compounds. Although occasionally deco position of accelerators takes place either by curing or extracti procedures, identification of the decomposition products is possi eg thiuram accelerators decompose to dithiocarbamates which detected as the zinc dithiocarbamates by R_F value and colour.

This work forms part of a programme of research undertaken the Natural Rubber Producers' Research Association.

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