Studies on the Reactions between Thiocarbamyl Sulfenamide and 2-(Iminodithio)benzothiazole Accelerator System in the Early Stage of Vulcanization of NR

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Synopsis

Investigations on the interactions of the synergistic pair of accelerators comprising of thiocarbamyl sulfenamide and 2-(iminodithio)benzothiazole have been carried out through hplc. *N*-cyclopentamethylene thiocarbamyl-*N'*-oxydiethylene sulfenamide, *N*-oxydiethylenethiocarbamyl-*N'*-cyclopentamethylene sulfenamide (OTCS), 2-morpholinodithiobenzothiazole, and 2-piperidinodithiobenzothiazole (PDB) have been selected as the reactants which, when suitably combined, provide most effective accelerator systems capable of generating heat and age resistant vulcanizates. The OTCS–PDB system has been found to yield vulcanizates which exhibit the greatest crosslink density, scorch safety, and highest modulus and tensile strength. An attempt has been made to explain the higher activity of the binary systems studied as compared to that obtained from comparable thiocarbamyl sulfenamide plus dibenzothiazyl disulfide system. Zin–dithiocarbamates have been found to influence the curing reactions depending upon the composition of the mixed accelerators. Cyclohexyl thiophthalimide, a versatile cure retarder, reacts with the accelerators to yield cyclohexyl thiomorpholine and cyclohexyl thiopiperidine, as the case may, which also have a profound effect upon cure retardation as noticed in the present investigation.

INTRODUCTION

While carrying out the investigations on thermal and age-resistance properties of NR gum vulcanizates in the EV systems it was found[1] that 2-morpholinodithiobenzothiazole (MDB) and *N*-oxydiethylenethiocarbamyl-*N'*-oxydiethylene sulphenamide (OTOS) in 3 : 6 molar ratio yielded vulcanizates having notable heat and age resistance properties. In the present investigation it is our endeavor to gather further information regarding the accelerating property of this binary system and have an insight into the mode of action of this type of accelerator combination particularly with regard to the isolation of some intermediate compounds formed *in situ* and their characterization through high performance liquid chromatography (hplc).

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EXPERIMENTAL

Materials

N-cyclopentamethylenethiocarbamyl-N'-oxydiethylene sulfenamide, N-oxydiethylenethiocarbamyl-N'-cyclopentamethylene sulfenamide, dicyclopentamethylenethiuram disulfide, di-N-oxydiethylenethiuram disulfide, zinc–di-N-pentamethylene dithiocarbamate, zinc–di-N-oxydiethylene dithiocarbamate, zinc–dibutyl dithiocarbamate, and MDB were prepared and purified according to the procedures reported elsewhere[1] with some modifications. N-cyclopentamethylene benzothiazole sulfenamide,[2] 2-benzothiazyl-1-piperidyl thiocarbamyl monosulfide,[3] bis(cyclopentamethylene) thiuram

TABLE I
List of Compounds Used

Chemical name	Abbreviation
2-benzothiazyl-1-piperidyl thiocarbamyl disulfide	BPTD
2-benzothiazyl-1-piperidyl thiocarbamyl monosulfide	BPTM
Cyclohexyldithio benzothiazole	CDB
Cyclohexyl thiomorpholine	CM
Cyclohexyl thiopiperidine	CP
N-cyclopentamethylene benzothiazole sulfenamide	CPBS
N-cyclopentamethylenethiocarbamyl cyclohexyl disulfide	CPTCD
Dicyclopentamethylenethiuram disulfide	CPTD
Bis(cyclopentamethylene) thiuram monosulfide	CPTM
N-cyclopentamethylenethiocarbamyl–N'-oxydiethylene sulfenamide	CTOS
Cyclohexyl thiophthalimide	CTP
Dithiodimorpholine	DTDM
Dithiodipiperidine	DTDP
2-Mercaptobenzothiazole	MBT
Dibenzothiazyl disulfide	MBTS
2-Morpholinodithiobenzothiazole	MDB
N-oxydiethylenebenzothiazole sulfenamide	OBTS
N-oxydiethylenethiocarbamyl–N'-cyclopentamethylene sulfenamide	OTCS
Di-N-oxydiethylenethiuram disulfide	OTD
N-oxydiethylenethiocarbamyl–N'-oxydiethylene sulfenamide	OTOS
2-Piperidino dithiobenzothiazole	PDB
N-piperidyl-N'-morpholinyl thiourea	PMTU
Tetramethyl thiuram disulfide	TMTD
Zinc–dibutyl dithiocarbamate	ZBD
Zinc–di-N-oxydiethylene dithiocarbamate	ZOD
Zinc–di-N-pentamethylene dithiocarbamate	ZPD
Zinc dithiocarbamate	ZDC

monosulfide,[4] N-piperidyl-N'-morpholinyl thiourea,[5] cyclohexyl thiopiperi-dine,[6,7] and cyclohexylthiomorpholine[6,7] were prepared in the laboratory. 2-Piperidino dithiobenzothiazole[8] was synthesized following a method for the preparation of MDB with necessary modifications. OTOS, N-oxydiethylene-benzothiazole sulfenamide, dibenzothiazyl disulfide, dithiodimorpholine, and cyclohexyl thiophthalimide were commercial samples used either as such or after necessary purifications. A list of chemical compounds and their abbreviations used in the present investigation are given in Table I.

IDENTIFICATION OF PRODUCTS THROUGH HPLC

Identification of various compounds formed in the reaction of the accelerators heated at 140°C for definite time interval both in the presence and absence of rubber in the solid phase was done using hplc technique. The solid residue obtained on heating was extracted with acetonitrile–water (70 : 30 v/v) solvent mixture which served as the eluent for the hplc system. The reaction products were identified using a 25 cm waters, C_{18} Bondapack, reverse phase chromatography column by retention time as well as co-injection of the authentic samples. A Varian UV detector operating at 254 nm was used. The flow rate of the solvent was maintained at 0.5 cm^3/min.

In the comparison of peak areas of the component(s), the fixed weight of the accelerators corresponding to different millimolar ratios were heated at 140°C for 2 min. The molten mass obtained in each case was extracted with acetonitrile–water (70 : 30 v/v) mixture and the volume made up to 5 cm^3. An aliquot of 2 mm^3 of the clear solution was injected onto the column, and the chromatograms were obtained. In the rubber medium, spacers were used to have very thin sections of grossly undercured stocks. In order to keep the proportions of the accelerators same, a calculated amount of molten mass (undercured stocks) taken on a filter paper (Whatman 42 ashless) in thin layer was extracted with boiling acetone for 1 h. Acetone was removed under vacuum and 5 cm^3 of acetonitrile–water (70 : 30 v/v) was added to the dry residue. Chromatograms were then obtained by injecting 2 mm^3 of the clear solution onto the hplc column.

PREPARATION OF VULCANIZATES AND MEASUREMENT OF PHYSICAL PROPERTIES

Zinc oxide (5 phr), extrapure stearic acid (2 phr), and G.R. grade sulfur (0.5 phr) were used. The vulcanizing ingredients were incorporated in the rubber on a Berstorff laboratory mixing mill of size 203 × 102 mm. The whole compounding cycle was 18 min. The cure characteristics of the different stocks were obtained using the the Monsanto Rheometer R-100 at 140 and 170°C and are presented in Tables I and II. The stocks were cured under pressure at 140°, and the vulcanizates were kept for 24 h at ambient temperature before the measurement of modulus at 200% elongation and tensile strength according to ASTM D 412-51T using dumbbell-shaped test pieces in an Amsler (Sweden) tensile tester.

In the aging experiment, vulcanizates obtained at optimum cure were aged at 100 ± 1°C in an oven provided with forced air circulation for 72 h. The

TABLE II
Physical Data of Cured Stocks Obtained at 140 And 170°C[a]

Mix. no. and composition (mmol)	Extent of cross linking R_∞ (N m)	Scorch safety, t_2 (min)	Optimum cure time t_{90} (min)	200% modulus (MPa)	Tensile strength (MPa)
1. CTOS 9	4.30	4.50	29.00	0.94	16.07
	(4.35)	(1.25)	(6.50)		
2. CTOS 6	5.05	8.00	21.00	1.01	20.30
MDB 3	(4.25)	(1.75)	(3.75)	(1.16)[+]	(19.67)[+]
3. CTOS 3	4.70	10.00	22.50	0.99	19.53
MDB 6	(3.85)	(1.75)	(2.75)		
4. MDB 9	3.70	14.50	35.00	0.73	17.26
	(2.90)	(2.00)	(4.75)		
5. OTOS 9	3.10	5.50	26.00	0.55	12.15
	(3.37)	(1.25)	(11.00)		
6. OTOS 6	4.95	9.25	20.50	1.03	18.61
MDB 3	(4.22)	(2.00)	(3.50)	(1.23)[+]	(18.51)[+]
7. OTCS 9	4.45	9.00	38.50	0.84	16.52
	(3.72)	(1.50)	(6.00)		
8. OTCS 6	5.45	10.50	21.50	1.16	22.70
PDB 3	(5.00)	(2.00)	(4.00)	(1.35)[+]	(20.83)[+]
9. PDB 9	5.40	9.50	20.50	1.06	19.93
	(4.80)	(2.25)	(4.00)		
10. CPTM 3	4.95	8.75	20.00	0.89	19.41
MDB 6	(3.25)	(1.75)	(3.25)		
11. CPTD 3	5.00	7.75	18.75	0.98	20.01
MDB 6	(4.20)	(1.25)	(3.50)		

[a]Values in parentheses indicate those obtained at 170°C except those indicated by +, which denote the corresponding results obtained after aging at 100°C.

specimens thus aged were kept for a further period of 24 h at room temperature before measuring the modulus and tensile strength.

Modulus, tensile strength, torque, etc. of the vulcanizates generally decrease with rise in temperature; hence retention of these physical properties for the vulcanizates obtained at elevated temperature was considered to be a measure of heat resistance of the cured products.

RESULTS AND DISCUSSION

Thiocarbamyl sulfenamides are greatly activated by MDB, and this phenomenon of cure synergism is recorded in Table II for the mixes 1–6. Figure 1 depicts the curing behaviour of CTOS, a representable thiocarbamyl sulfenamide, when it is progressively replaced by MDB keeping the total millimolar concentration of the mixed accelerators at a constant level of 9 mmol phr. As is the case with CTOS–MBTS system,[1] maximum synergism is obtained with the recipe (mix 2) containing CTOS and MDB in 6 : 3 millimolar ratio. The behavior of OTOS (mix 6) in this regard is similar to that of CTOS, and somewhat longer scorch safety is observed in the former case.
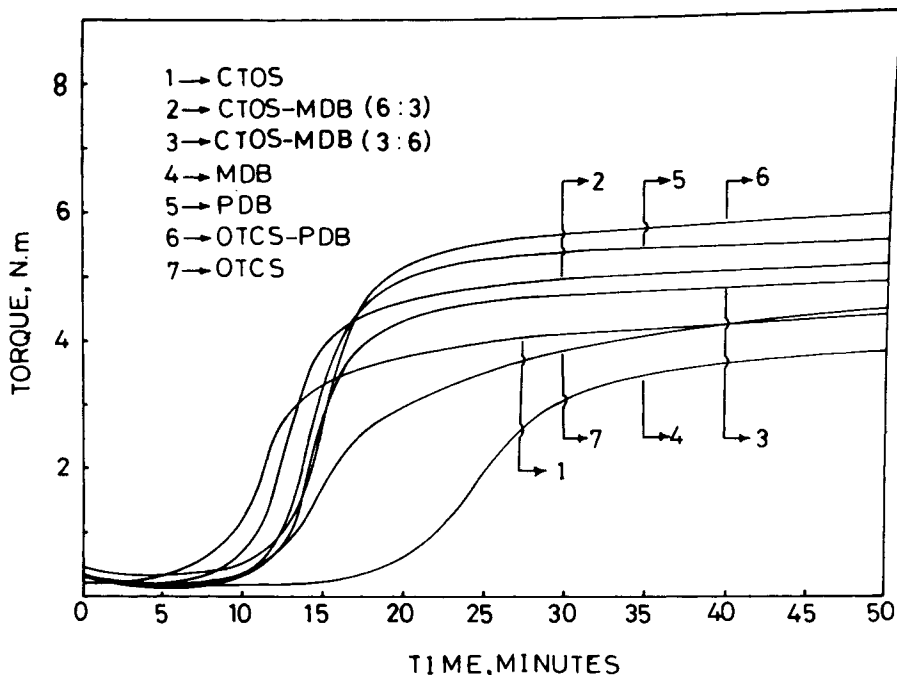
Fig. 1.   Rheographs of NR gum stocks cured at 140°C: (1) CTOS; (2) CTOS–MDB (6:3); (3) CTOS-MDB (3:6); (4) MDB; (5) PDB; (6) OTCS–PDB; (7) OTCS.

We have observed that OTOS and CTOS react separately with MBTS[5] and in both the cases MDB could be detected, and that it has a positive effect upon OTOS and CTOS is quite clear from the preceding discussion. Likewise it was decided to study the effect of PDB, the piperidine analog of MDB upon its parent compound, i.e., OTCS. The results are given in Table II (mixes 7–9). The action of PDB on OTCS is noteworthy. It can be seen that PDB exhibits mutual activity in the presence of OTCS. The curing cycles for the three combinations are also shown in Figure 1. It is evident from Table II and Figure 1 that OTCS–PDB combination presents better extent of cure, scorch safety, modulus, and tensile strength than those given by CTOS–MDB combination.

Higher activity of the mixed accelerators than the individual component associated with the significant changes in the kinetics of crosslinking as evinced from the rheographs is indicative of some sort of interaction between the two accelerators which eventually react with the rubber. Thus it becomes imperative to study the chemical reactions of the accelerators both in the absence and presence of NR. The products formed were analyzed through hplc as reported earlier.

Figure 2 shows the decomposition of MDB at the curing temperature (140°C). In the absence of rubber it seems that the compound is mostly stable, although minute amounts of MBT, DTDM, OBTS, and MBTS could be detected [Fig. 2(a)]. But the reverse is true when MDB dispersed in rubber is heated even for a shorter period (2 min) at 140°C. Here, it exhibits itself as a
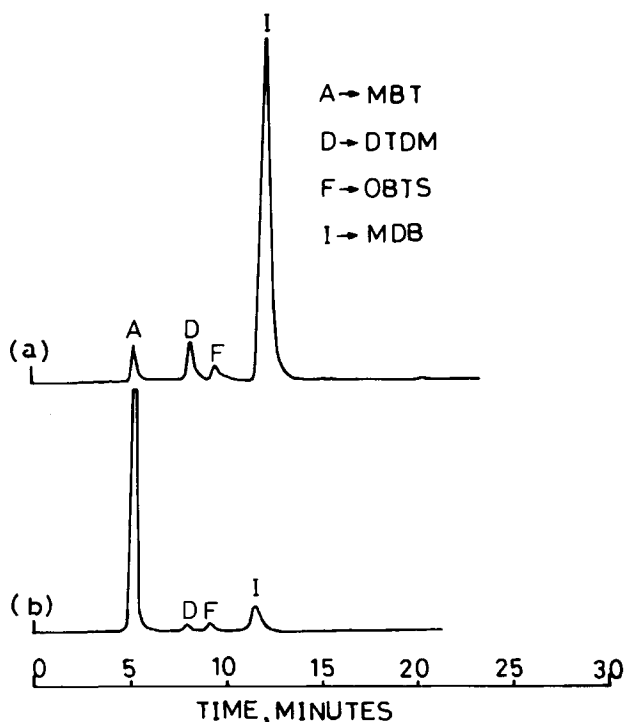
Fig. 2. (a) High performance liquid chromatogram of MDB (6 mmol) when heated at $140°C$ for 2 min; (b) high performance liquid chromatogram of undercured vulcanizate obtained at $140°C$ for 2 min. Stock composition: NR 100, zinc oxide 5, stearic acid 2, sulfur 0.5, and MDB (6 mmol). (A) MBT; (D) DTDM; (F) OBTS; (I) MDB.

highly reactive compound and large amount of MBT could be detected in the reaction [Fig. 2(b)].

CTOS in conjunction with MDB seems to be highly reactive, and even in the absence of rubber we observe that vigorous reaction sets in when these two components are heated at $140°C$ for 2 min. The results are depicted in Figure 3(a), which suggests the formation of large amount of CPTM and CPTD. Also, MBT, PMTU, DTDM, OBTS, and BPTD could be detected in the mixture after the reaction. From the chromatogram it thus becomes apparent that MDB facilitates decomposition of CTOS which, when heated alone under identical condition, has been observed by us to yield CPTD, PMTU, and CPTM but to a lesser degree.[5] Figure 3(b) depicts a chromatogram obtained with CTOS–MDB combination dispersed in NR. The characteristics of the reaction are reflected in the abundant generation of MBT as well as the depletion of CPTD and CPTM. The concentrations of PMTU and BPTD, as are noticed from the chromatogram, remain practically unaltered as compared to those obtained in the absence of rubber. Facile formation of MBT in the rubber medium obviously arises from the reactions [eqs. (1)–(4)] leading to rubber-bound intermediates prior to the vulcanization of NR as

depicted below:

$$2R_1\text{-}S\text{-}S\text{-}R_3 \longrightarrow R_1\text{-}S\text{-}S\text{-}R_1 + R_3\text{-}S\text{-}S\text{-}R_3 \quad (1)$$
$$\text{(MDB)} \qquad\qquad \text{(MBTS)} \quad \text{(DTDM)}$$

$$2R_2\text{-}S\text{-}R_3 + R_1\text{-}S\text{-}S\text{-}R_1 \longrightarrow R_2\text{-}S\text{-}S\text{-}R_2 + 2R_1\text{-}S\text{-}R_3 \quad (2)$$
$$\text{(CTOS)} \qquad \text{(MBTS)} \qquad\quad \text{(CPTD)} \qquad \text{(OBTS)}$$

$$R_1\text{-}S\text{-}R_3 + KaH \xrightarrow{S_8} Ka\text{-}S_x R_3 + R_1\text{-}S H \quad (3)$$
$$\text{(OBTS)} \qquad\qquad\qquad\qquad\qquad \text{(MBT)}$$

$$R_1\text{-}S\text{-}S\text{-}R_1 + KaH \xrightarrow{S_8} Ka\text{-}S_x R_1 + R_1\text{-}S H \quad (4)$$
$$\text{(MBTS)} \qquad\qquad\qquad\qquad\qquad \text{(MBT)}$$

where

$$R_1= \text{(benzothiazolyl)} \quad\quad R_2 = \text{(piperidyl-N-C(=S)-S-)}$$

$$R_3 = \text{(morpholino-N-)} \qquad\qquad KaH = Rubber.$$

As for the notable decrease in the concentration of CPTD and CPTM, it can be reasonably said that CPTD and CPTM are also formed in the rubber medium in substantial quantities, but these are rapidly converted into dithiocarbamates in the presence of zinc oxide also present in the medium. Zinc dithiocarbamates (ZDC) quickly react with rubber and form rubber-bound intermediate as well. It should be mentioned here that the CTOS–MBTS system under the same conditions of experiment usually provides a greater amount[5] of BPTD which is likely to be formed[9] from CPTD and MBTS. Conversion of CPTD into crosslink precursors via ZDC is thus impaired for a while, and this is reflected in the scorch safety which is, in fact, higher for CTOS–MBTS system (t_2 = 10.5 min) than that obtained with the CTOS–MDB binary combination (t_2 = 8 min).

From the hplc study it is indicated that MDB influences decomposition of CTOS, the resultant effect being the formation of CPTD or CPTM. It is reported[10] that tetramethyl thiuram disulfide (TMTD)–MDB system provides useful vulcanizates. As members of the thiuram class, CPTD and CPTM are apt to influence vulcanization in the presence of MDB. Thus several stocks were prepared and the cure behavior of the products was studied. The results are shown in Figure 4. From the rheographs it is evident that MDB mitigates the scorchy behavior of the stocks containing either CPTD or CPTM. Moreover, it greatly improves the speed of reaction and enhances the number of crosslinks. From an examination of the physical data (Table II) obtained with recipes (2), (10), and (11) it can be seen that these three systems have very close R_∞, t_2, and t_{90} values. Thus it may be inferred that same type of crosslinking reactions is involved in these systems. Further from a comparison
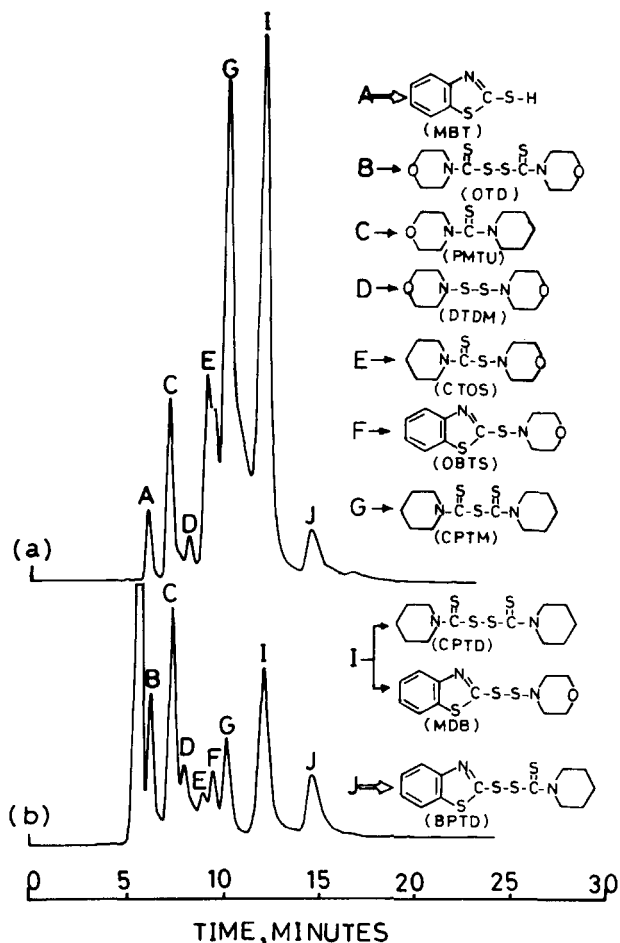
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Fig. 3. (a) High performance liquid chromatogram of CTOS (6 mmol) and MDB (3 mmol) combination when heated at 140°C for 2 min; (b) high performance liquid chromatogram of undercured vulcanizate obtained at 140°C for 2 min. Stock compostion: NR 100, zinc oxide 5, stearic acid 2, sulfur 0.5, CTOS (6 mmol), and MDB (3 mmol).

of the retention of physical properties at an elevated temperature, namely, 170°C, it is evident that the vulcanizates obtained from mixes 2, 6, and 11 gave the best results. Our results are consistent with those observed by earlier workers [10] in the EV system containing TMTD and MDB, where the synergistic property of the binary system associated with the heat resistance property could be observed.

From the rheographs presented in Figure 4 it is apparent that CPTD provides greater R_∞ than the recipe containing CPTM (compare curve 3 with curve 4). Also, the stock containing CPTD is found to be somewhat scorchy. It is revealed from a comparison of the two chromatograms (Fig. 5) that the recipe containing CPTD and MDB produces a greater amount of BPTD than that containing identical concentrations of CPTM and MDB. Also, we have observed[9] that BPTD formed *in situ* in a system containing MBT and CPTD
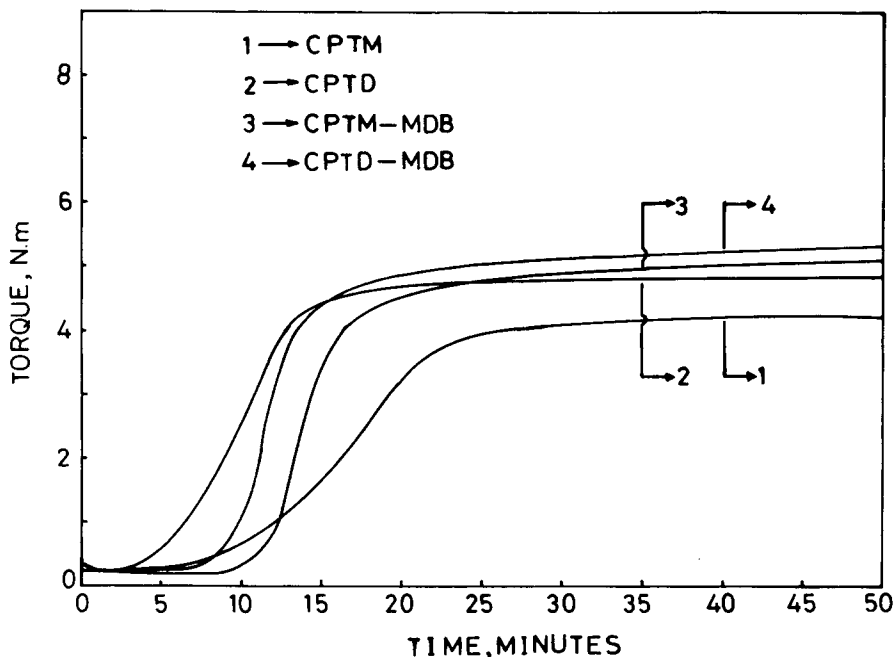
Fig. 4.   Rheographs of NR gum stocks cured at 140°C: (1) CPTM; (2) CPTD; (3) CPTM–MDB; (4) CPTD–MDB.

exhibited scorchy behavior, which might be the case for the mix containing CPTD and MDB as presented above.

The involvement of thiuram compounds in the vulcanization of NR inevitably generates ZDC which as pointed out by us in our earlier communication[1] greatly influences the fate of vulcanization. The results obtained with thiocarbamyl sulfenamide–MDB systems along with ZDCs are summarized in Table III (mixes 1–4). It can be seen from the table that addition of 1 mmol ZPD increases the physical properties. The action of ZOD in this respect is singular in that a reduction in the torque value as recorded by the rheometer is indicated from the very beginning for mixes 2 and 4. It is worth mentioning at this stage that similar system CTOS–MBTS–ZOD, having identical proportions of the ingredients as those contained in the recipe 2 (Table III) enhances the maximum rheometric torque values during vulcanization of NR. The results suggest that MDB has some peculiarity of its own. In fact from hplc studies we observe that when the reactions are carried out outside rubber medium, the CTOS–MDB system is capable of generating OTD only in the presence of ZOD (Fig. 6). However, in the presence of rubber, facile formation of OTD is observed even in the absence of ZOD [Figs. 3(b) and 7]. It has been pointed out earlier [Fig. 3(a)] that the CTOS–MDB combination heated at 140°C for 2 min in the absence of rubber does not show any indication of the formation of OTD, but copious formation of CPTD is well indicated. CPTD thus formed in the rubber medium produces ZPD which is likely to influence the reaction. So, it can be reasonably assumed that ZDCs are responsible for bringing about the reaction in which CPTD formed from CTOS is trans-

formed into OTD in the presence of MDB. Both CTOS and MDB have the same morpholine moiety on the sulfenamide N-atom and we believe that, in the formation of OTD, MDB provides this amine moiety since OTD could not be detected in the CTOS–MBTS–ZOD combination under the same experimental conditions.[5] From a comparison of the chromatograms it is evident that formation of OTD is more in rubber medium (compare Fig. 6 with Fig. 7). So, it is likely that with the progress of cure a significant amount of ZOD via OTD obtained from the thiocarbamyl sulfenamide–MDB–ZOD systems is thus formed in the vulcanizates. The probable reactions occurring in rubber medium are given in the following scheme:
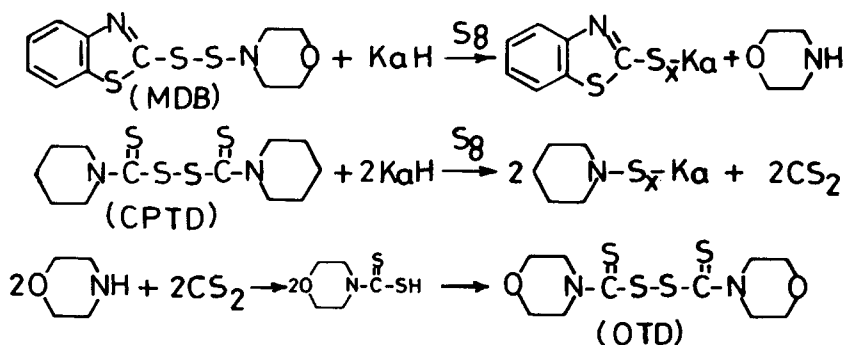
Where,

$$KaH = Rubber$$

With the incorporation of a further amount of ZOD in the recipes it might so happen that the critical concentration of ZOD exceeds the limit (1 mmol phr) in the mixes, and thereby a fall in the physical properties might be observed.[1] ZPD also is expected to promote the formation of OTD from the mixes concerned. Under the experimental conditions this concentration of OTD presumably remains below the critical value of ZOD. The deleterious effect upon the physical properties consequent upon the generation of ZPD also could not be noticed in other systems as a much more higher concentration[1] of this component is needed to meet the same catastrophic disaster brought about by ZOD.

EV systems constituting high accelerator and low sulfur ratio impart better utilization of sulfur than the conventional NR vulcanization system. The crosslinks formed in the former system are predominantly monosulfidic and are believed to be responsible for the heat resistance property of the vulcanizates. Since the torque recorded by rheometer during vulcanization can be considered as a measure of crosslink density, the data for R_∞ in parentheses in Table II provide a measure for the heat resistance properties of the various systems. The three binary systems, CTOS–MDB (mix 2), OTOS–MDB (mix 6), and OTCS–PDB (mix 8), are seen to possess notable heat resistance properties at 170°C. The best value is, however, obtained from the OTCS–PDB system. It needs mentioning that stock containing PDB alone (Table II, mix 9) has a good heat resistance property. The vulcanizates
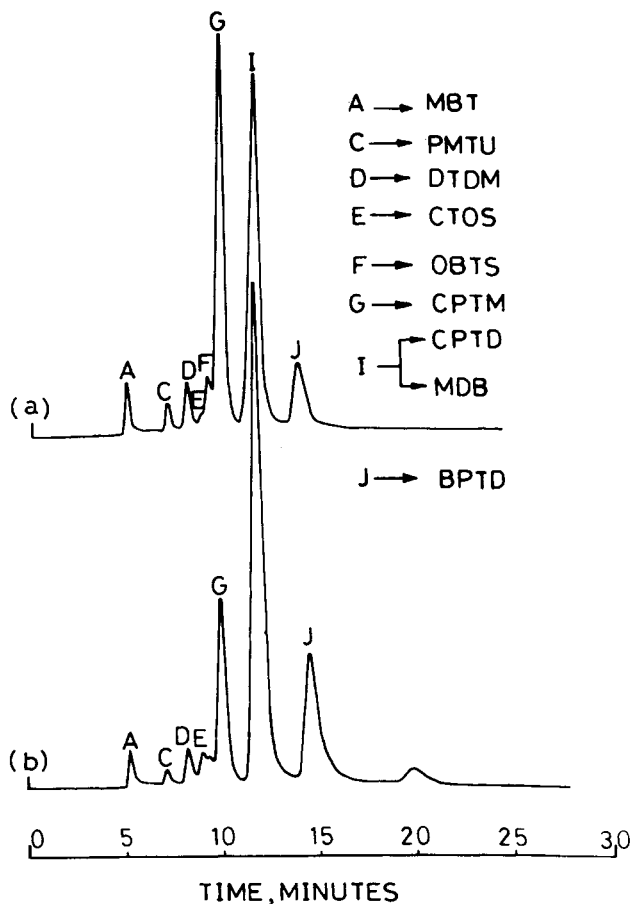
Fig. 5. High performance liquid chromatogram obtained by heating the accelerators at 140°C for 2 min: (a) CPTM (3 mmol) and MDB (3 mmol); (b) CPTD (3 mmol) and MDB (3 mmol). (A) MBT; (C) PMTU; (D) DTDM; (E) CTOS; (F) OBTS; (G) CPTM; (I) CPTD;MDB; (J) BPTD.

obtained from the mixes 2, 6, and 8 are seen to be quite capable of resisting the heat aging at 100°C for 72 h (also recorded in Table II). Here also, the OTCS–PDB combination gives the best results insofar as the modulus and tensile strength are concerned.

It has been observed by us that the early stage of vulcanization thiocarbamyl sulfenamide and 2-iminodithiobenzothiazole, both in the presence and absence of rubber, yield several products of which thiuram disulfide, thiazole sulfenamide, and dithiodiamine seem to govern the crosslinking reaction of NR. Thus the OTOS plus MDB combination produces OTD, OBTS, and DTDM; the CTOS plus MDB system gives CPTD, OBTS, and DTDM, whereas the binary system comprised of OTCS and PDB generates OTD, N-cyclopentamethylene benzothiazole sulfenamide (CPBS), and dithio dipiperidine (DTDP).

It has been observed by Dogadkin and co-workers[11] that DTDP provides a greater crosslink density of rubber vulcanizates than that obtained from

<div align="center">

TABLE III

Physical Data of Cured Stocks Obtained at 140 and 170°C[a]

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Mix. no. and composition (mmol)	Extent of cross linking R_∞ (N m)	Scorch safety, t_2 (min)	Optimum cure time t_{90} (min)	200% modulus (MPa)	Tensile strength (MPa)
1. CTOS 6 MDB 3 ZPD 1	5.20 (4.50)	6.25 (1.50)	19.00 (3.25)	1.02	20.53
2. CTOS 6 MDB 3 ZOD 1	4.80 (4.30)	6.00 (1.00)	17.50 (2.50)	1.06	18.64
3. OTOS 6 MDB 3 ZPD 1	5.05 (4.70)	7.25 (1.75)	21.50 (4.25)	1.01	18.56
4. OTOS 6 MDB 3 ZOD 1	4.50 (4.05)	14.00 (2.25)	38.00 (5.25)	0.85	16.36
5. CTOS 6 MDB 3 CTP 2	4.55 (3.65)	10.50 (2.25)	26.00 (4.50)	0.83	16.42
6. OTOS 6 MDB 3 CTP 2	4.40 (3.80)	20.50 (2.75)	35.00 (5.50)	0.86	16.51

[a]Values in parentheses indicate those obtained at 170°C.

Fig. 6. High performance liquid chromatogram of CTOS (6 mmol), MDB (3 mmol), and ZOD (1 mmol) combinations when heated at 140°C for 2 min: (A) MBT; (B) OTD; (C) PMTU; (D) DTDM; (E) CTOS; (F) OBTS; (G) CPTM; (H) BPTM; (I) CPTD; MDB; (J) BPTD.

DTDM. This difference in crosslinking behavior lies in the basicity[12] of the amine moiety. Piperidine being a stronger base is likely to generate more crosslinks than morpholine. Hence binary combination containing PDB is expected to generate more crosslinks than its morpholine analog, i.e., MDB. Actually this has been observed. The activity of the mixed accelerators from the three combinations (Table II, mixes 2, 6, and 8) can also be understood from the rheometric studies of the combinations OTD plus OBTS, CPTD plus OBTS, and OTD plus CPBS (Fig. 8). From the rheographs it is evident that the OTD–CPBS system (2:4 mmol) provides vulcanizates which have a greater crosslink density than that obtained from the CPTD–OBTS or OTD–OBTS combinations having the same millimolar ratios of accelerator. These observations lend support to the superior properties with regard to torque, modulus, tensile strength of the vulcanizates obtained from OTCS–PDB (6 : 3 mmol) combinations. It should be mentioned at this stage that the CTOS–MDB combination is better than CTOS–MBTS insofar as torque, modulus, and tensile strength are concerned. This is due to the fact that in the former combination DTDM is formed (Fig. 2) through the cleavage of the S—S bond as depicted below:
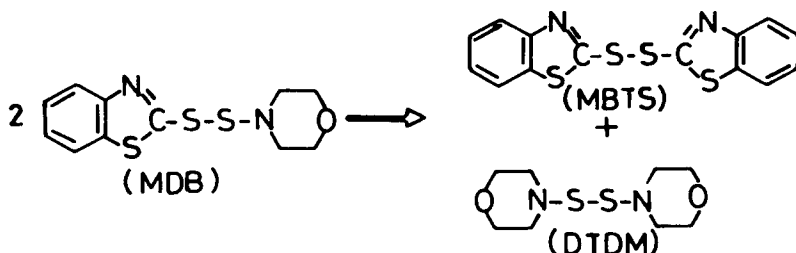
whereas in the latter combination formation of DTDM is possible through the rupture of the stronger C—S bond
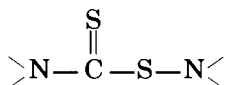
of CTOS. Probably for this reason we could not detect any dithiodiamine in the decomposition of thiocarbamyl sulfenamides.[5]

From the foregoing studies it is apparent that the CTOS plus MDB and OTOS plus MDB binary systems of accelerators can produce vulcanizates which in many respects are superior to those obtained from CTOS and MBTS. However, these stocks are found to be somewhat scorchy. Thus it was necessary to investigate the action of CTP upon these systems. The results are summarized in Table III (mixes 5 and 6). It is seen that incorporation of CTP in the CTOS–MDB combination enhances the t_2 value (compare mix 2, Table II) while there occurs a reduction in the values of R_∞, modulus, and tensile strength. It should be mentioned here that similar proportions of CTOS, MBTS, and CTP in the combination[13] had very little effect upon scorch safety. CP generated in this reaction medium was considered responsible for
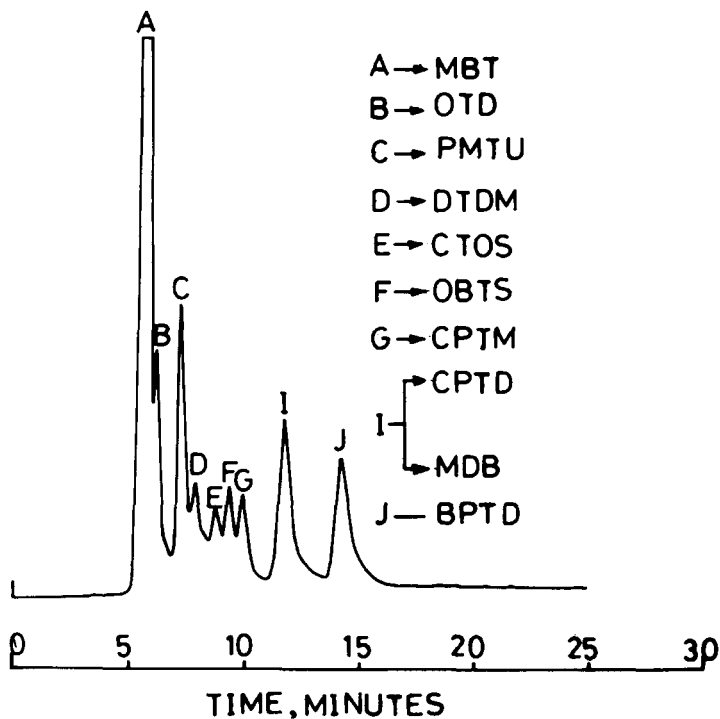
Fig. 7. High performance liquid chromatogram of undercured vulcanizate obtained at 140°C
for 2 min. Stock composition: NR 100, zinc oxide 5, stearic acid 2, sulfur 0.5, CTOS (6 mmol),
MDB (3 mmol), and ZOD (1 mmol). (A) MBT; (B) OTD; (C) PMTU; (D) DTDM; (E) CTOS; (F)
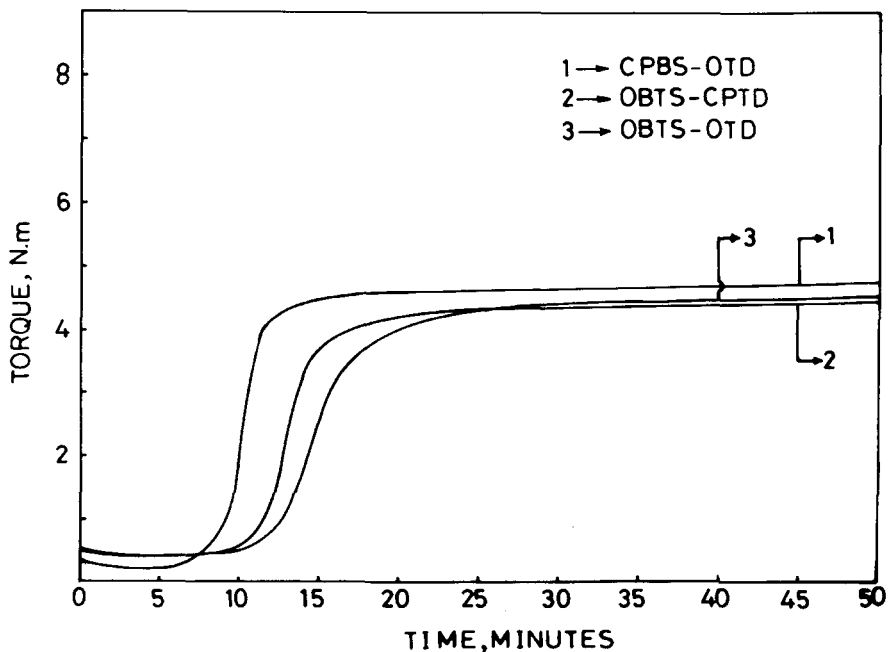OBTS; (G) CPTM; (I) CPTD; MDB; (J) BPTD.

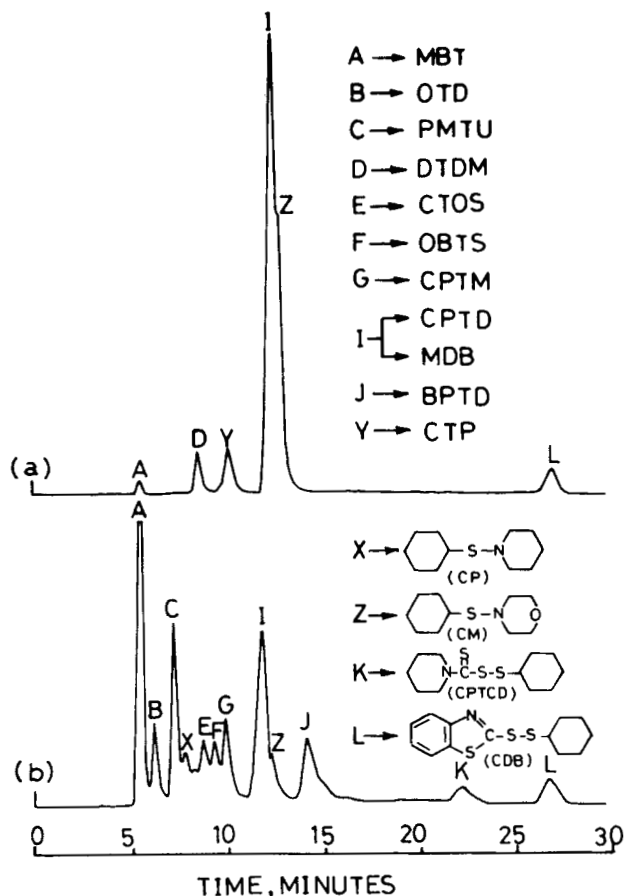Fig. 8.   Rheographs of NR gum stocks cured at 140°C: (1) CPBS–OTD; (2) OBTS–CPTD; (3)
OBTS–OTD.

Fig. 9. (a) High performance liquid chromatogram obtained by heating a mixture of MDB (6 mmol) and CTP (1 mmol) at 140°C for 2 min; (b) High performance liquid chromatogram of undercured vulcanizate obtained at 140°C for 2 min. Stock composition: NR 100, zinc oxide 5, stearic acid 2, sulfur 0.5, CTOS (6 mmol), MDB (3 mmol), and CTP (1 mmol). (A) MBT; (B) OTD; (C) PMTU; (D) DTDM; (E) CTOS; (F) OBTS; (G) CPTM; (I) CPTD; MDB; (J) BPTD; (Y) CTP.

this change owing to its scorchy behavior. From Figure 9(b) it is obvious that the stock containing CTOS, MDB, and CTP forms CM in addition to CP in the rubber medium. Thus the increase in t_2 exhibited by the CTOS–MDB–CTP combination is due to the retarding effect of CM. The fact that CM is generated from the reaction between MDB and CTP is more explicit from the chromatogram a in Figure 9. The OTOS–MDB combination in the presence of CTP can generate only CM as the intermediate retarder, which, as usual, shows its activity (mix 6) by prolonging the onset of cure, enhancing t_{90}, and attenuating the modulus and tensile strength. Our results are thus in direct contradiction with those of earlier workers,[10,14] who concluded that CTP practically had no effect upon the physical properties of the vulcanizates. It needs mentioning here that the reaction of CTP with MDB and CTOS in the combination also shows the formation of cyclopentamethylenethiocarbamyl cyclohexyl disulfide (CPTCD) and cyclohexyldithio benzothiazole (CDB). CPTCD behaves as a scorchy accelerator while CDB, as observed by us,[13]

functions as a very poor accelerator. The early part of vulcanization of NR in the present study involves various reactions among the compounding ingredients whereby intermediate accelerators and retarders are formed. The products thus formed pass through complex reaction steps with sulfur and rubber hydrocarbon and pave the way for vulcanization. The observed scorch delay is, therefore, dependent upon the formation of accelerators and retarders as well as their involvement in vulcanization.

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