

# Studies on the Effect of Thiuram Disulfide on NR Vulcanization Accelerated by Thiazole-Based Accelerator Systems

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## SYNOPSIS

Thiuram disulfides form synergistic combinations with thiazole and thiazole-based accelerators, namely, *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 2-mercaptobenzothiazole (MBT), and 2-mercaptobenzothiazyl disulfide (MBTS). Unfortunately, widely used thiuram disulfides (TD) generate carcinogenic *N*-nitrosoamine. It is reported that the nitrosamines from *N*-methylpiperazine and dibenzylamine are free from this menace. So, some investigations were carried out with the binary combinations of each of bis(*N*-methylpiperazino)thiuram disulfide (MPTD), tetrabenzylthiuram disulfide (TBzTD), and tetramethylthiuram disulfide (TMTD) separately with CBS, MBT, and MBTS. It was observed that all the TD are activated by the CBS, MBT, or MBTS in the combinations studied. The intensity of activation is manifested in the enhancement of torque, modulus, tensile strength, cure rate, hardness, and decrease of elongation at break values and is very much dependent upon the ratio of the accelerators used. Considering the torque, modulus, tensile strength, and the elongation at break values, it appears that MPTD and TBzTD are capable of competing with the hitherto unbeaten TMTD as suitable accelerators for the vulcanization of rubber. Some investigations in respect to heat- and age-resistance behavior have also been carried out and the observed differences in the activities of various binary combinations have been explained through a mechanism. The results obtained with filled vulcanizates indicate that the binary systems comprising TD and MBTS provide fruitful results of which the TBzTD-MBTS combination seems to give the best cure and physical data for practical vulcanizates. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Thiuram disulfides (TD), either alone or in conjunction with the thiazole group of accelerators,<sup>1,2</sup> have been immensely important and popular during last three decades in the rubber industry for their efficient crosslinking capacity, leading to the preparation of vulcanized articles of desired technological properties. Recent concern for the potential health hazard of different rubber chemicals has thrown the subject quite open to the scientist. The thiuram compound, e.g., tetramethylthiuram disulfide (TMTD), as derived from secondary amine has

been reported<sup>3</sup> to have generated carcinogenic nitrosoamine. TD are so important in the rubber industry that their absence could not be thought of. Again, there remains the slogan "Save the environment and provide pollution-free and workable industrial atmosphere." Naturally, unsafe TD are to be replaced by safe ones without changing their major activity.

Chemical compounds for the rubber industry contain carcinogenic nitrosoamines if they are obtained from the secondary amines like dimethylamine, diethylamine, morpholine, and piperidine. A more general solution of the nitrosoamine problem in the rubber industry requires the introduction of new rubber chemicals which cannot be nitrosated or which form noncarcinogenic nitrosoamines. With

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this in mind, we chose in the present study safe TD, e.g., bis(*N*-methylpiperazino)thiuram disulfides (MPTD) and tetrabenzylthiuram disulfides (TBzTD) derived from safe<sup>4</sup> *N*-methylpiperazine and dibenzylamine and evaluated their vulcanizing activity in combination with other safe accelerators like *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 2-mercaptobenzothiazole (MBT), and 2-mercaptobenzothiazyl disulfide (MBTS). The effect of MPTD and TBzTD separately with CBS, MBT, and MBTS on the resultant vulcanizate has been compared with the corresponding TMTD compounds in light of the physical properties of the vulcanizates. Also, it was our endeavor to investigate the thermal- and age-resistance behavior of the vulcanizates obtained from these binary combinations.

As the process of vulcanization is an extremely complicated process, gum vulcanization has been deliberately chosen for its simplicity and thus to understand the process clearly. After gathering some information in this direction, filler was incorporated to simulate the composition for the filled stocks generally employed in the rubber industry. Further, to avoid the complexity of the network, a ratio of a moderately high (9 mmol phr) concentration of accelerator to a low concentration of sulfur (0.5 phr) was chosen.

## EXPERIMENTAL

*N*-Cyclohexyl-2-benzothiazole sulfenamide (CBS)<sup>5</sup> and bis(*N*-methylpiperazino)thiuram disulfide (MPTD)<sup>6</sup> were prepared in the laboratory. 2-Mercaptobenzothiazole (MBT), 2-mercaptobenzothiazyl disulfide (MBTS), tetramethylthiuram disulfide (TMTD), and tetrabenzylthiuram disulfide (TBzTD) were commercial samples and were used as such or after necessary purification.

A list of chemical compounds with their abbreviations and structures are given in Table I. The compositions of the accelerators for the various stocks are provided in Tables II–IV.

The vulcanizing ingredients [5 phr zinc oxide, 2 phr stearic acid, 0.5 phr sulfur, accelerator(s)] were incorporated into the untreated natural rubber (NR) (RMA-1X) on a laboratory mixing mill. The total concentration of accelerator(s) was kept at 9 mmol phr. The cure characteristics of the different stocks were obtained using the Monsanto Rheometer R-100 at 140, 160, and 170°C. The data for torque  $R_\alpha$ , scorch time ( $t_2$ ), and optimum cure time ( $t_{90}$ ) are presented in Tables II–IV. The modulus at 200%

elongation, tensile strength, and elongation at break of different stocks are also recorded in Tables II–IV. In the filled vulcanizates, 40 phr carbon black and 10 phr paraffin oil were used. The cure and physical data of the filled vulcanizates and their aging property are recorded in Table V.

As the temperature increases, modulus, tensile strength, torque, etc., of the vulcanizates decrease. Hence, retention of these physical properties for the vulcanizates obtained at an elevated temperature was considered to be a measure of heat resistance of the cured products. The data at higher temperature are recorded in Table VI.

In the aging experiment, vulcanizates obtained at optimum cure were aged at  $100 \pm 1^\circ\text{C}$  in an oven provided with forced air circulation for 72 h. The specimens thus aged were kept for a further period of 24 h at room temperature before measuring the modulus and tensile strength.

## RESULTS AND DISCUSSION

The synergistic activity of the binary mixtures is discussed stepwise as presented below.

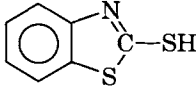
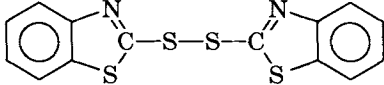
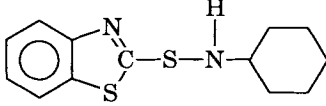
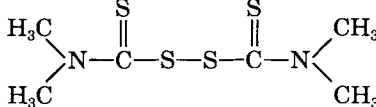
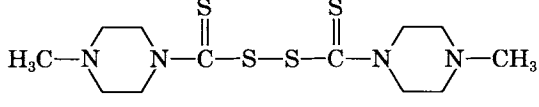
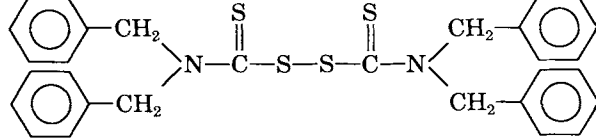
### Binary Combination with CBS and Thiuram Disulfide

The cure and physical data of the vulcanizates when cured at 140°C are recorded in Table II. It is evident from the results (mixes 1–13) that all the TD in the presence of CBS exhibit a synergistic effect in respect of the torque. It is observed that maximum rheometric torque ( $R_\alpha$ ) of these TD when used alone (9 mmol phr) differs from one another and follows the order

$$\text{TBzTD} > \text{TMTD} > \text{MPTD}$$

The change in  $R_\alpha$  value is dependent upon the MPTD : CBS accelerator ratio. Replacing MPTD by CBS, some increase in  $R_\alpha$  values is observed for mixes 2–4 over the individual combinations (mixes 1 and 5). The lowest  $R_\alpha$  value is attained in the combination comprising MPTD : CBS in the molar ratio of 6 : 3 and highest  $R_\alpha$  value observed in the MPTD : CBS molar ratio of 3 : 6 and 4.5 : 4.5. As regards scorch safety, the  $t_2$  value of the MPTD-accelerated stock, quite expectedly, is lowest. This is the general character of thiuram vulcanization. In this regard, the mix containing CBS exhibits the highest cure delay. However, when a mixture of the

Table I List of Compounds Used

Structure	Abbreviation	Chemical Name
1. 	MBT	2-Mercaptobenzothiazole
2. 	MBTS	2-Mercaptobenzothiazole disulfide
3. 	CBS	<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide
4. 	TMTD	Tetramethylthiuram disulfide
5. 	MPTD	Bis( <i>N</i> -methylpiperazino)thiuram disulfide
6. 	TBzTD	Tetrabenzylthiuram disulfide

two is obtained, the stock containing the relatively highest proportion of MPTD shows the maximum scorch safety. The behavior is more or less reflected in the  $t_{90}$  values of the mixes.

The binary system containing TBzTD and CBS (mixes 5–9, Table II) is somewhat different from the MPTD–CBS system. It is evident from the  $R_\alpha$  data that CBS is activated by TBzTD, but the intermediate combinations cannot surpass the  $R_\alpha$  value of the TBzTD-accelerated stock. As regards the  $t_{90}$  values obtained in the binary combinations of TBzTD and CBS, the behavior is similar to that of the MPTD–CBS combinations. The  $t_{90}$  values of CBS-accelerated and TBzTD-accelerated stocks (mixes 5 and 9) are very close to one another. But their combinations considerably lower the  $t_{90}$  values (mixes 6–8), which, incidentally, are very close to one another.

Synergism with respect to torque is evident for the TMTD–CBS combinations (mixes 5, 10–13)

and, in fact, the highest  $R_\alpha$  is obtained for mix 11 having a TMTD : CBS molar ratio of 6 : 3. The  $t_2$  and  $t_{90}$  values of the binary mixes as in the former combinations lie between those obtained with either accelerator alone.

It is evident from the results that mutual activity in respect of the modulus is absent for all the combinations. However, synergism is very small for tensile strength values of some vulcanizates in the cases of MPTD–CBS and TBzTD–CBS accelerated stocks. However, the tensile strength and modulus values of the stocks containing a binary mixture of TD and CBS is not harmonic with the respective torque value ( $R_\alpha$ ). Comparing all the combinations of the TD–CBS system, it is clear that the TMTD–CBS system offers maximum torque, modulus, and tensile strength and proves its own superiority compared to other TDs. So, the choice of the TBzTD–CBS and/or the MPTD–CBS system in place of the

**Table II Physical and Cure Data of Stocks (Gum) Cured at 140°C**

Mixture No. and Composition (mmol)	Maximum Torque $R_\alpha$ (nm)	Scorch Safety $t_2$ (min)	Optimum Cure Time $t_{90}$ (min)	Modulus at 200% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1. MPTD-9	3.60	2.0	11.5	0.80	14.7	820
2. MPTD-6 CBS-3	4.00	7.0	13.5	0.58	14.5	860
3. MPTD-4.5 CBS-4.5	4.25	6.0	14.0	0.67	14.2	840
4. MPTD-3 CBS-6	4.25	4.5	13.0	0.65	14.9	840
5. CBS-9	3.45	15.5	27.5	0.52	12.8	900
6. CBS-6 TBzTD-3	4.20	7.5	17.0	0.67	13.2	700
7. CBS-4.5 TBzTD-4.5	4.10	9.5	16.0	0.61	14.2	710
8. CBS-3 TBzTD-6	4.20	8.5	15.0	0.61	15.5	710
9. TBzTD-9	4.30	5.0	27.0	0.87	15.2	680
10. TMTD-9	3.90	3.0	10.0	0.86	18.5	800
11. TMTD-6 CBS-3	4.50	5.0	13.5	0.72	16.2	840
12. TMTD-4.5 CBS-4.5	4.30	6.5	14.0	0.67	16.4	840
13. TMTD-3 CBS-6	4.20	6.5	13.5	0.59	15.5	860

TMTD-CBS system would be judged considering a small sacrifice of physical properties of the vulcanizates in order to achieve beneficial factors that prevent the formation of carcinogenic nitrosoamines in addition to the enhancement of scorch safety.

The vulcanizates obtained from the CBS-accelerated stock (mix 5) exhibit the highest elongation at break (900%). MPTD- and TMTD-accelerated stocks (mixes 2 and 10) also show about 800% elongation at break. TBzTD-accelerated stock (mix 9) is an exception, and in this case, 680% elongation at break is obtained. The intermediate combinations for all the stocks, however, show values which lie in between the parent combinations as is evident from the data of Table II.

#### Binary Combination with MBT and Thiuram Disulfides

The cure and physical data concerning this study are presented in Table III. It is evident from the results that the torque values of the mixed system of accelerators are affected by the ratio of the ac-

celerators used. Though synergism with regard to torque is observed in the combinations of MPTD, TBzTD, and TMTD with MBT, the magnitude of mutual activity is very small. In fact, significant activation of MBT by each of these thiurams, so far as torque is concerned, can be seen. The activity of TBzTD is very near to that of TMTD in this respect. The results suggest that maximum synergism with regard to torque is observed at the thiuram : MBT ratio of 6 : 3 (mixes 2, 8, and 11, Table III).

It can be seen that the scorch safety of mix 1 containing MPTD only is a minimum among the combinations presented in Table III. But incorporation of a portion of MBT into the stock first increases the  $t_2$  values (mix 2). With the incorporation of a greater amount of MBT, the  $t_2$  values more or less become steady. This trend is also reflected in the  $t_{90}$  values of the combinations (mixes 2-4). It is evident from the results that TBzTD in the presence of MBT provides some scorch safety (mixes 6-9) and thus also influences the  $t_{90}$  values provided in the table. Similar results of same kind but of different degree are obtained with TMTD-MBT combinations (mixes 10-13).

**Table III Physical and Cure Data of Stocks (Gum) Cured at 140°C**

Mixture No. and Composition (mmol)	Maximum Torque $R_\alpha$ (nm)	Scorch Safety $t_2$ (min)	Optimum Cure Time $t_{90}$ (min)	Modulus at 200% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1. MPTD-9	3.60	2.0	11.5	0.80	14.7	820
2. MPTD-6 MBT-3	3.90	5.0	16.0	0.72	15.5	820
3. MPTD-4.5 MBT-4.5	3.80	4.5	18.0	0.63	14.6	850
4. MPTD-3 MBT-6	3.70	4.5	17.0	0.56	13.5	850
5. MBT-9	1.35	5.0	33.0	—	01.6	900
6. MBT-6 TBzTD-3	3.75	7.0	26.0	0.59	13.2	700
7. MBT-4.5 TBzTD-4.5	4.10	7.5	30.0	0.69	14.7	700
8. MBT-3 TBzTD-6	4.30	7.5	31.0	0.75	16.2	700
9. TBzTD-9	4.30	5.0	27.0	0.87	15.2	680
10. TMTD-9	3.90	3.0	10.0	0.86	18.5	800
11. TMTD-6 MBT-3	4.65	5.0	14.5	0.82	17.8	800
12. TMTD-4.5 MBT-4.5	4.30	6.0	18.0	0.72	17.4	820
13. TMTD-3 MBT-6	3.85	5.0	16.0	0.57	14.6	850

As regards the modulus values of the vulcanizates, there occurs a decrease with the progressive replacement of TBzTD or TMTD or MPTD by MBT. The thiuram compounds have a pronounced effect upon the activation of MBT in this regard and the highest activity is observed for the TD : MBT ratio of 6 : 3 in each combination. However, the vulcanizates obtained in the binary systems of TMTD plus MBT (mix 11) exhibit the highest modulus. This is also true for the tensile strength of the respective combinations.

Thiuram compounds are notable for yielding vulcanizates that possess high modulus, torque, tensile strength, and low elongation at break values. The results presented in Table III corroborated these well-established earlier observations. The results of the mixed system of accelerators using safe thiuram compounds indicate that the activity of TBzTD in the presence of MBT is somewhat superior to that of MPTD. It is evident from the data that the activity of TBzTD : MBT in a 6 : 3 molar concentration is close to that of the TMTD : MBT combination having a similar concentration.

#### Evaluation of Synergistic Interaction Between Thiuram Disulfide and MBTS

After studying the vulcanizing effect of the TD-CBS and TD-MBT systems, our next attempt was to explore the efficiency of the TD-MBTS system in the vulcanization of rubber. The cure data of several mixes and the physical properties of the corresponding vulcanizates are recorded in Table IV and the progress of cure is depicted in the rheographs (Figs. 1-3). It is evident from the results as well as from Figure 4 that maximum rheometric torque for all the three TD-MBTS compounds is attained at the millimolar ratio of 4.5 : 4.5 (mixes 3, 7, and 12). It is evident from the results that the scorch time ( $t_2$ ) and the optimum cure times ( $t_{90}$ ) for these TD-MBTS systems are somewhat higher than the corresponding values obtained in the TD-CBS and TD-MBT systems (Tables II and III). Like the torque values, the 200% modulus values of TD-MBTS systems vary with a gradual change of proportion of TD and MBTS and attain a maximum value at the millimolar ratio of 4.5 : 4.5. The results indicate that TD-MBTS combinations definitely improve the

Table IV Physical and Cure Data of Stocks (Gum) Cured at 140°C

Mixture No. and Composition (mmol)	Maximum Torque $R_\alpha$ (nm)	Scorch Safety $t_2$ (min)	Optimum Cure Time $t_{90}$ (min)	Modulus at 200% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1. MPTD-9	3.60	2.0	11.5	0.80	14.7	820
2. MPTD-6 MBTS-3	4.70	7.5	21.0	0.81	14.7	700
3. MPTD-4.5 MBTS-4.5	4.75	6.5	19.5	0.91	15.3	660
4. MPTD-3 MBTS-6	4.00	8.0	20.5	0.60	13.7	720
5. MBTS-9	3.20	16.0	45.0	0.45	11.3	900
6. MBTS-6 TBzTD-3	4.40	10.5	32.0	0.84	14.8	670
7. MBTS-4.5 TBzTD-4.5	4.65	9.0	28.5	0.91	15.6	640
8. MBTS-3 TBzTD-6	4.60	9.5	33.0	0.89	14.4	650
9. TBzTD-9	4.30	5.0	27.0	0.87	15.2	680
10. TMTD-9	3.90	3.0	10.0	0.86	18.5	800
11. TMTD-6 MBTS-3	4.40	6.0	22.5	0.75	14.9	670
12. TMTD-4.5 MBTS-4.5	4.55	7.5	21.0	0.80	15.1	670
13. TMTD-3 MBTS-6	4.30	8.0	20.5	0.75	13.4	690

modulus values of the vulcanizates compared to TD-CBS or TD-MBT binary systems. As for the tensile strength, maximum values for MPTD-MBTS, TBzTD-MBTS, and TMTD-MBTS accelerated systems are also obtained at the equimolar concentration of the accelerators, but the results are more or less at par with those obtained from TD-MBT or TD-CBS accelerated stocks. It needs mentioning here that the elongation-at-break (%) values for TD-MBTS-accelerated vulcanizates are significantly low as compared to those mentioned earlier (compare the data of Table II or Table III with those of Table IV). It is clear from Table IV that the  $R_\alpha$  values of TD-MBTS system follow the order

$$\begin{array}{l} \text{MPTD} - 4.5 > \text{TBzTD} - 4.5 > \text{TMTD} - 4.5 \\ \text{MBTS} - 4.5 > \text{MBTS} - 4.5 > \text{MBTS} - 4.5 \end{array}$$

However, the tensile value follows the order for the combinations

$$\begin{array}{l} \text{MPTD} - 4.5 > \text{TMTD} - 4.5 > \text{TBzTD} - 4.5 \\ \text{MBTS} - 4.5 > \text{MBTS} - 4.5 > \text{MBTS} - 4.5 \end{array}$$

The results discussed so far clearly indicate that positive synergism is prominent in the TD-MBTS system, the cure and physical data of which establish the supremacy of this system over both TD-CBS and TD-MBT systems employed in the present study.

It is now an established fact that both MBTS and CBS decompose in the rubber medium; the former is transformed into MBT while the latter generates both MBT and cyclohexyl amine.<sup>7</sup> It has been shown by previous workers<sup>1,2</sup> that the MBT-TMTD system provides mutual activity. The synergistic effect observed in the MBTS-TMTD and CBS-TMTD systems thus arises from the generation of MBT and perhaps reorientation of the effective combination of TMTD-MBT. So, it is expected that systems comprising TD-MBT, TD-CBS, and TD-MBTS would exhibit a similar type of synergistic activity. The foregoing results also indicate some differences in the mutual activity of these systems. Apparently, this is not expected since all three systems essentially contain an equivalent amount of TD and MBT and these are highly active accelerators. To understand clearly the difference in the mutual activity

**Table V Physical and Cure Data of Stocks (Filled<sup>a</sup>) Cured at 140°**

Mixture No. and Composition (mmol)	Maximum Torque $R_a$ (nm)	Scorch Safety $t_2$ (min)	Optimum Cure Time $t_{90}$ (min)	Modulus at 200% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Shore-A Hardness
1. MPTD-4.5 CBS-4.5	5.60	4.5	11.5	4.0 (6.7) <sup>b</sup>	23.4 (16.3)	650 (320)	62.5 (67.5)
2. TBzTD-6 CBS-3	6.40	4.5	19.0	4.8 (7.2)	22.0 (13.6)	460 (290)	66.0 (68.0)
3. TMTD-6 CBS-3	6.05	4.5	13.5	4.1 (6.0)	23.6 (17.3)	650 (380)	62.5 (67.5)
4. MPTD-6 MBT-3	5.35	3.5	16.0	3.8 (5.1)	21.8 (14.3)	640 (370)	65.0 (66.0)
5. TBzTD-6 MBT-3	6.25	3.5	29.0	4.9 (6.5)	21.5 (12.1)	440 (280)	65.0 (67.0)
6. TMTD-6 MBT-3	6.25	3.5	19.0	4.4 (7.0)	21.7 (14.1)	610 (300)	65.0 (70.0)
7. MPTD-4.5 MBTS-4.5	6.15	4.0	17.5	4.4 (6.6)	21.2 (14.5)	480 (310)	62.5 (70.0)
8. TBzTD-4.5 MBTS-4.5	6.65	4.5	26.0	5.3 (7.5)	21.3 (13.7)	430 (280)	66.0 (70.0)
9. TMTD-4.5 MBTS-4.5	6.75	3.7	17.5	5.3 (7.3)	21.5 (13.2)	450 (260)	65.0 (70.0)

<sup>a</sup> 40 phr carbon black and 10 phr paraffin oil.

<sup>b</sup> Values in the parentheses are the aged property of the vulcanizates at  $(100 \pm 1)^\circ\text{C}$  for 72 h.

**Table VI Physical and Cure Data of Stocks (Gum) Cured at 140, 160, and 170°C**

Mixture No. and Composition (mmol)	Maximum Torque $R_a$ (nm)	Scorch Safety $t_2$ (min)	Optimum Cure Time $t_{90}$ (min)	Modulus at 200% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Temperature (°C)
1. MPTD-4.5 MBTS-4.5	4.75	6.5	19.5	0.91	15.3	660	
2. TBzTD-4.5 MBTS-4.5	4.65	9.0	28.5	0.91	14.6	640	140
3. TMTD-4.5 MBTS-4.5	4.55	7.5	21.0	0.80	15.1	670	
1. MPTD-4.5 MBTS-4.5	4.28	2.0	5.5	0.85	15.2	740	
2. TBzTD-4.5 MBTS-4.5	4.10	2.5	6.0	0.83	14.5	720	160
3. TMTD-4.5 MBTS-4.5	4.50	2.5	8.0	0.77	14.2	750	
1. MPTD-4.5 MBTS-4.5	4.05	2.0	3.5	0.71	14.8	740	
2. TBzTD-4.5 MBTS-4.5	4.10	1.5	4.5	0.70	14.3	740	170
3. TMTD-4.5 MBTS-4.5	4.40	2.0	5.0	0.75	14.0	760	

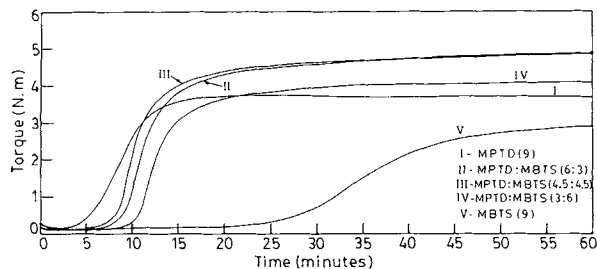


Figure 1 Rheographs of NR gum stocks cured at 140°C.

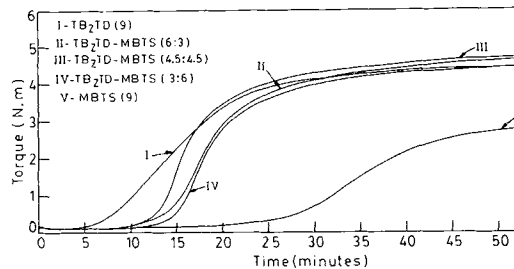
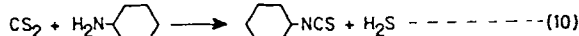
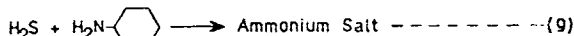
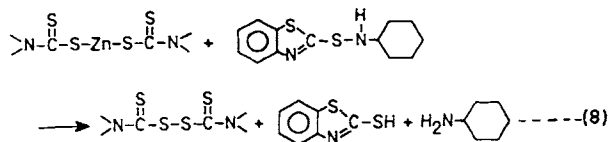
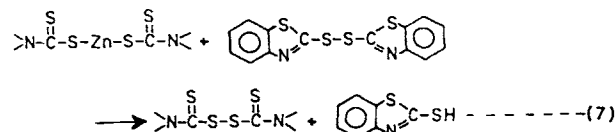
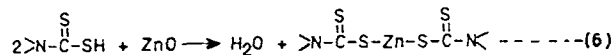
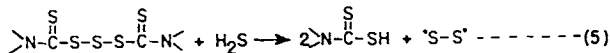
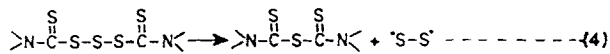
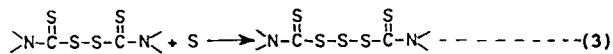
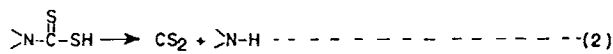
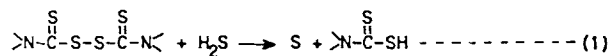


Figure 2 Rheographs of NR gum stocks cured at 140°C.

between the TD-MBTS and TD-CBS systems, the following reaction scheme is presented:



The scheme depicts the probable paths (steps 1–8) for the transformation of zinc dimethyl dithiocarbamate (ZDC) under the influence of MBTS and CBS in the presence of H<sub>2</sub>S that is formed<sup>8</sup> during the process of vulcanization. Steps 1, 4, and 5 lead to crosslinking<sup>7</sup> of rubber, while steps 7 and 8 indicate the regenerative path for TMTD.<sup>9</sup> It needs mentioning<sup>9</sup> here that MBT formed in the medium produces a higher amount of TMTD from ZDC than

that obtained with MBT added to the system as such. The cyclohexylamine generated from CBS (path 8) is likely to form the effective sulfurating complex<sup>10</sup> in the presence of ZnO and sulfur and thus CBS is expected to show higher vulcanizing activity as compared to that exhibited by MBTS. But this is not observed. This phenomenon may be explained by the reaction of cyclohexylamine with H<sub>2</sub>S (path 9) and CS<sub>2</sub> (path 10).<sup>11</sup> The capture of H<sub>2</sub>S by cyclohexylamine not only prevents cyclohexylamine from complex formation but also severely affects the paths 7–5. As a result, there occurs a fall in the concentration of sulfur crosslinks. There is also another way (path 10) for the depletion of cyclohexylamine. This further decreases the concentration of the sulfurating complex and thus the number of sulfur crosslinks in the case of TMTD-CBS-accelerated vulcanizates. Dimethylamine is generated from TMTD during vulcanization. Like cyclohexylamine, it is also expected to react with H<sub>2</sub>S. But it may be assumed that the effect is nearly the same in both MBTS-TMTD and CBS-TMTD systems. It thus appears that cyclohexylamine plays a vital role in determining mutual activity. Obviously, in the absence of the reactions due to paths 9 and 10 in the MBTS-TMTD system, a comparatively higher amount of crosslinks are likely to be generated in this system which evidently exhibits

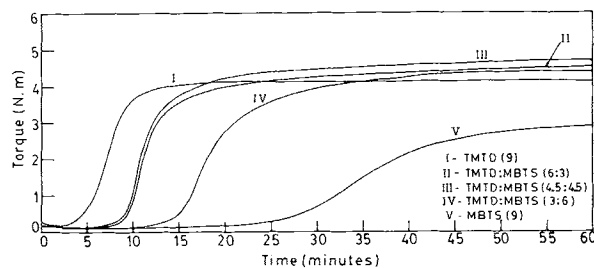
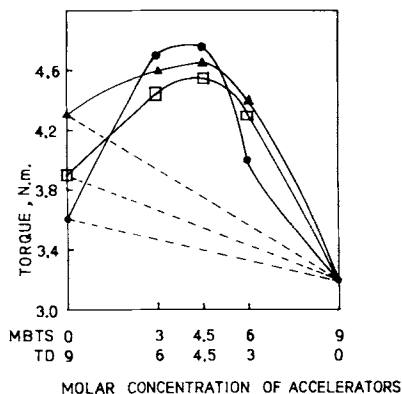


Figure 3 Rheographs of NR gum stocks cured at 140°C.





**Figure 4** Effect of the ratio of TD to MBTS on the torque obtained from rheographs: (●) MPTD; (▲) TBzTD; (□) TMTD.

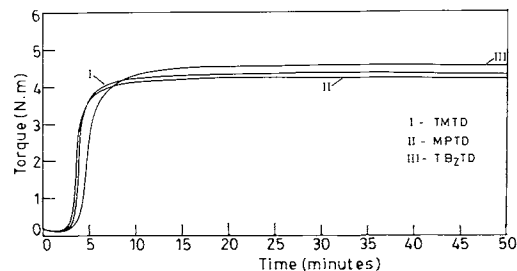
higher synergistic activity as compared to that observed in the CBS-TMTD system.

It is also observed from Tables II-IV that the highest  $t_2$  value is obtained from TBzTD-accelerated stock in all three binary systems. This is due to the lower basicity<sup>12</sup> of the dibenzylamine. The  $t_{90}$  values of TBzTD-accelerated stocks in all the above three systems (Tables II-IV) are also higher. This is probably due to the steric hindrance<sup>12</sup> offered by the bulky amine moiety of TBzTD.

### The Effect of Cure Temperature on Thiuram-MBTS Systems

It is well known that as the cure temperature is increased the efficiency of vulcanization decreases. The TD-MBTS system shows exactly the same decrease in efficiency, i.e., loss of modulus with increasing cure temperature. This decrease in efficiency with increasing cure temperature is considered to be partly due to an increase in the rate of breakdown of crosslink precursors, which are an accelerator moiety attached to the rubber through polysulfidic linkages before they have reacted to form a crosslink.<sup>13-15</sup> Loss of accelerator activity and shortening of the lifetime of the accelerator complex are the two factors responsible for decreasing the cure efficiency at high temperature.

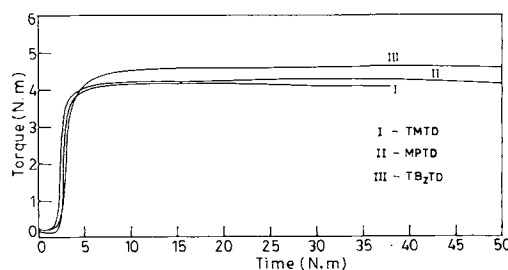
For studying the efficiency of vulcanization at higher temperature, TMTD-MBTS, MPTD-MBTS, and TBzTD-MBTS systems (molar ratio 4.5 : 4.5) were taken and their vulcanization efficiency was measured in respect to torque, modulus, tensile strength, and elongation at break at 140, 160, and 170°C. These data are recorded in Table VI. The results indicated that with increase of temper-



**Figure 5** Rheographs of NR gum stocks cured at 160°C.

ature, as expected, the cure rate increases (Figs. 5 and 6) for all the stocks. But at the same time, there occurs a considerable shortfall in torque, scorch safety, and optimum cure time. The decrease of modulus values at 200% elongation, as is evident from Table VI, is also small up to 160°C, but by increasing the temperature to 170°C, a sharp fall in modulus values is observed for the binary systems containing TBzTD and MPTD. The TMTD-accelerated binary system (mix 3) is an exception to this, and in this case, the decrease is not much. Tensile strength and rheometric torque ( $R_\alpha$ ) of all three stocks decreased with increase of temperature. However, elongation at break increases with increasing temperature.

The reversion of TD-MBTS systems was studied in respect of torque by taking the torque value at different temperatures for longer periods of time. This is important as thick natural rubber articles require a long cure time for the central portion of the articles to reach optimum cure. We observed good reversion resistance as reflected by the rheographs in Figures 5 and 6. The good reversion resistance is due to formation of a sufficient number of thermally stable monosulfidic crosslinks in our system. Actually, polysulfidic linkages impart the fatigue properties to the vulcanizates and monosulfidic linkages impart heat-resistance properties.



**Figure 6** Rheographs of NR gum stocks cured at 170°C.

Unfortunately, fatigue properties have become progressively poorer as one goes from polysulfidic to disulfide and thereafter to monosulfidic crosslinks.<sup>16</sup> Thus, in practice, a compromise between thermal stability and fatigue resistance is reached for each particular application.

### Vulcanization Characteristic of Filled Stocks and Their Age-resistance Behavior

Having gathered the information that several safe TD in conjunction with MBTS, CBS, and MBT effectively function as accelerators for the gum vulcanization of natural rubber, our attention was next focused on the performance of these binary combinations in carbon black-loaded compounds. So, some mixes were prepared and the physical and cure data were obtained. These are recorded in Table V. From the table, it is evident that the torque values depend on the accelerator ratios and are found to follow the order

TD-CBS system:

$$\begin{array}{c} \text{TBzTD} > \text{TMTD} > \text{MPTD} \\ \text{CBS} > \text{CBS} > \text{CBS} \end{array}$$

TD-MBT system:

$$\begin{array}{c} \text{TBzTD} = \text{TMTD} > \text{MPTD} \\ \text{MBT} = \text{MBT} > \text{MBT} \end{array}$$

TD-MBTS system:

$$\begin{array}{c} \text{TMTD} > \text{TBzTD} > \text{MPTD} \\ \text{MBTS} > \text{MBTS} > \text{MBTS} \end{array}$$

It is evident from the table that the highest torque value is obtained from TD-MBTS-accelerated stocks (mixes 7-9, Table V). The results indicate that scorch safety, which is very important for rubber compounds of practical utility, is more or less same for the combinations studied and it varies from 3.5 to 4.5. The optimum cure time ( $t_{90}$ ) values are related to the rate of cure. It is seen from the table that in all the cases stocks containing TBzTD have the highest  $t_{90}$  value, as is evident from the following presentation:

TD-CBS system:

$$\text{TBzTD} > \text{TMTD} > \text{MPTD}$$

TD-MBT system:

$$\text{TBzTD} > \text{TMTD} > \text{MPTD}$$

TD-MBTS system:

$$\text{TBzTD} > \text{TMTD} = \text{MPTD}$$

The modulus values of the vulcanizates TD-CBS- and TD-MBT-accelerated systems follow the order for  $t_{90}$  values just mentioned above. But in the TD-MBTS system, the modulus values vary in the following order:

$$\text{TBzTD} = \text{TMTD} > \text{MPTD}$$

Considering the modulus values, it is seen from Table V that the TD-MBTS system is the best among the systems studied. However, as to the tensile strength values, this order is not followed. The TD-CBS system has the highest tensile strength value compared to the other two systems (TD-MBT and TD-MBTS). The TD-MBT and TD-MBTS systems have nearly the same tensile strength value. The elongation at break follows the order shown below:

$$\begin{array}{c} \text{TD-CBS} > \text{TD-MBT} > \text{TD-MBTS} \\ \text{system} \quad \quad \quad \text{system} \quad \quad \quad \text{system} \end{array}$$

The elongation-at-break values for the TBzTD-accelerated stocks are the lowest in the respective binary systems. As can be seen from Table V, the highest Shore-A hardness (66) is exhibited by TBzTD-CBS- and TBzTD-MBTS-accelerated stocks (mixes 2 and 8), while the lowest value (62.5) is obtained in the MPTD-MBT-, TMTD-MBT-, and MPTD-MBTS-accelerated stocks (mixes 1, 3, and 7). The vulcanizates derived from the rest of the stocks (mixes 4-6 and 9) have the same Shore-A hardness value (65).

The oxidative aging of rubber vulcanizates is one of utmost importance for practical purposes. The performance of the vulcanizates of the carbon black-filled stocks (TD-CBS, TD-MBT, TD-MBTS) during aging was tested and the results are shown in the parentheses of Table V. It can be seen from the results that during aging both modulus and Shore-A hardness values are increased. The order of activity with respect to modulus values is found to follow the order

TD-CBS system:

TBzTD > MPTD > TMTD

TD-MBT system:

TMTD > TBzTD > MPTD

TD-MBTS system:

TBzTD > TMTD > MPTD

The highest modulus value is obtained in the TBzTD-MBTS-accelerated stock and the lowest in the MPTD-MBT-accelerated stock. However, this trend is not followed in the case of Shore-A hardness values. The TD-MBTS system and the TMTD-MBT system yield vulcanizates that possess the highest Shore-A hardness (70), while for the rest of the vulcanizates, this value is found to lie between 66 and 68. The tensile strength values for all the vulcanizates decrease considerably after aging. The retention of tensile strength is more or less the same for all the stocks (about 70%) except for the TBzTD-accelerated stocks, where retention of tensile strength is less (about 60%). The elongation-at-break values also diminish considerably in every case within the stipulated time.

It was also noticed by an earlier worker that TD in the presence of zinc oxide is converted into zinc dithiocarbamates which act as accelerators as well as antidegradants.<sup>17-19</sup> Good heat resistance as well as age resistance exhibited by all the combinations thus might be due to formation of various zinc dithiocarbamates produced from the three types of TD used. As to the increase in modulus of the vulcanizates of NR during aging, it may be assumed that prolonged heating at 100°C is apt to cause postvulcanization, thereby generating more crosslinks that are also responsible for the increase in hardness values during the aging of the rubber vulcanizates. With increase in the number of crosslinks, the network becomes rigid and thus may restrict the elongation at break and, actually, this is observed for all the vulcanizates subjected to hot-air aging.

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