

Sulfur Vulcanization of Natural Rubber Accelerated with 2-Mercaptobenzothiazole plus Tetramethylthiuram Disulfide

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Synopsis

The sulfur vulcanization of NR by a MBT-TMTD mixed accelerator system both in the presence and absence of ZnO and stearic acid with or without DCP has been studied. The rate of decomposition of DCP in the presence of both MBT and TMTD is quite similar to that in the MBT system alone. The reduction in crosslinking due to DCP is dependent mainly on MBT. The decomposition product of TMTD may contribute to it only at the later stage of vulcanization. Though TMTD has no influence on the decomposition rate, it reacts with MBT at least in the initial stage of vulcanization and suppresses the retardation caused by MBT on DCP vulcanization in accordance with the free sulfur decrease, the nature of crosslinking formation both in the presence and absence of DCP, and the methyl iodide treatment of the vulcanizates. The vulcanization process of the MBT-TMTD-S-NR system has been interpreted in terms of both free radical and polar mechanisms. The domination of either of these depends on the dominant amount of either MBT or TMTD in the accelerator ratio. According to the initial high rate of crosslink formation, free sulfur decrease and also the initial additiveness of crosslinking in stocks containing DCP, the vulcanization process of MBT-TMTD-ZnO-St. acid-S-NR system has been explained in terms of an ionic mechanism. The pronounced synergistic nature of such systems has been interpreted by the enhanced activation of MBT-S-ZnO-St. acid complex due to the dithiocarbamate ion formed in the initial stages of vulcanization, and also by the activation of TMTD accelerated vulcanization due to the mercaptobenzothiazyl ion.

INTRODUCTION

Vulcanization of rubber with combined accelerators has attracted widespread interest due to its quicker rate and higher efficiency. Though a great deal of work has been done on the mechanism of vulcanization using single accelerators, slight attention has been paid to the chemistry of vulcanization with combined accelerator systems. Dogadkin et al.¹ classified the binary systems into three groups according to their power of acceleration. Jones² suspected that the action of bases, which are generally used as secondary accelerators with thiazole-type accelerators, was similar to that of fatty acids. This explanation³ cannot properly explain the fact that, with increase in proportion of a basic secondary accelerator up to the molar equivalence with the primary accelerator, the rate of vulcanization considerably increases. No comprehensive mechanism of binary acceleration has been put forward.

Our recent investigations⁴ with 2-mercaptobenzothiazole (MBT) and diphenylguanidine (DPG) have produced some valuable information. The present investigations using 2-mercaptobenzothiazole (MBT) and tetramethylthiuram

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disulfide (TMTD) have been undertaken to throw more light on the subject. Dicumyl peroxide (DCP) has been used for the determination of the radical or polar nature of the reactions.

EXPERIMENTAL

The materials used and the experimental procedures followed have been described in an earlier communication.⁴ The compound formulations used in the present investigation are given in Table I and can be summarized into the following four groups: (1) natural rubber, DCP (1 phr), and accelerators (variable); (2) natural rubber, sulfur (2 phr), and accelerators (variable) in the presence and absence of DCP (1 phr); (3) natural rubber, zinc oxide (5 phr), stearic acid (3 phr), sulfur (2 phr), and accelerators (variable) in the presence and absence of DCP (1 phr); (4) a fixed amount of the single accelerator (MBT = 0.7 phr or TMTD = 0.3 phr) in the presence and absence of activators (ZnO = 5.0 phr or stearic acid = 3 phr) with or without DCP (1 phr).

The compounds containing identical compositions with or without DCP are denoted by the same letter with the addition of a subscript to that letter in compounds containing DCP. Each of the curves denoted by the combination of two letters in Figures 6(b) and 7(b) is the theoretical additive curve of the two curves corresponding to the two letters.

RESULTS AND DISCUSSION

The logarithm of free DCP concentration as a function of cure time is plotted in Figure 1. The straight lines indicate that the decomposition of DCP follows first-order kinetics in all cases. From the slope of these curves, the rate constants (K_d) for the decomposition process have been calculated (Table II). The K_d values correspond almost to those reported earlier⁵ for the MBT accelerated system. The K_d values are about 50% higher than those for the NR-DCP system and are practically independent of the amount of MBT and TMTD or their ratio and the presence or absence of sulfur, zinc oxide, and stearic acid.

It is well-known that DCP decomposes predominantly through homolytic cleavage leading to the generation of free radical, and the higher K_d values may be due to induced decomposition of DCP by the benzothiazyl sulfide radicals.⁵ The inertness of TMTD toward decomposition of DCP may be ascribed mainly to the interaction of TMTD with the MBT, which will be discussed later in connection with crosslink density.

Free Sulfur

In stocks without zinc oxide and stearic acid (Fig. 2), free sulfur falls gradually up to 70 min and then becomes constant. Free sulfur decrease gradually, accelerates with increasing TMTD:MBT ratio up to a limiting ratio (MBT:TMTD = 1.42:1.0 mole/mole), and then with further increase in TMTD:MBT the free sulfur decrease lessens (curve K). Free sulfur decrease is somewhat more in stocks containing DCP (not shown in the figure) than in the stocks without it. Both the rate and the total amount of decrease in free sulfur are higher in a mixed system than in the system containing either accelerator separately.

With the addition of zinc oxide and stearic acid (Fig. 3), the rate of decrease

TABLE I
Compounding Formulations

Material	A	B	C	D	E	F	G	H	I	J	K	H ₁	I ₁	J ₁	K ₁	
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	—	—	—	—	1.0	1.0	1.0	1.0	1.0
Sulfur								2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MBT	1.0	1.0	1.0	1.0	1.0	0.2	0.5	0.9	0.7	0.5	0.3	0.9	0.7	0.5	0.3	0.3
TMTD	0.2	0.5	1.0	1.0	1.5	1.0	1.0	0.1	0.3	0.5	0.7	0.1	0.3	0.5	0.5	0.7
	L	M	N	O	L ₁	M ₁	N ₁	O ₁	P	P ₁	Q	Q ₁	R	R ₁	S	S ₁
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	—	—	—	—	1.0	1.0	1.0	1.0	—	1.0	—	1.0	—	1.0	—	1.0
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MBT	0.9	0.7	0.5	0.3	0.9	0.7	0.5	0.3	0.7	0.7	—	—	0.7	0.7	—	—
TMTD	0.1	0.3	0.5	0.7	0.1	0.3	0.5	0.7	—	—	0.3	0.3	—	—	0.3	0.3
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	—	—	—	—	—	—	5.0	5.0
Stearic acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	—	—	—	—	3.0	3.0	3.0	3.0

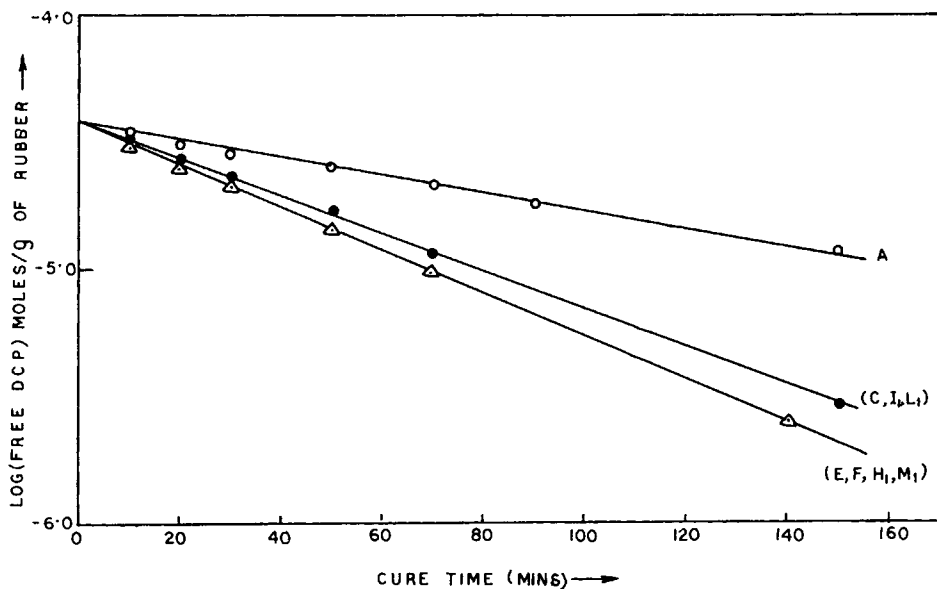


Fig. 1. Decrease of dicumyl peroxide according to first-order time law at 140°C.

TABLE II
Rate Constants of DCP Decomposition at 140°C

Stock	A	C	E	F	H ₁	I ₁	L ₁	M ₁
$K_d \times 10^3$, min ⁻¹	12.70	19.80	20.15	20.10	20.25	19.95	19.65	20.20

in free sulfur becomes rapid during the initial period, and within 8–10 min almost all sulfur is consumed. Here it is also noted that with increasing TMTD:MBT ratio, free sulfur decrease gradually becomes greater up to the limiting ratio (MBT:TMTD = 1.315:1.000 mole/mole), and beyond that the initial rate of free sulfur decrease is slightly lowered, though the final consumption is identical with other systems. The presence of DCP slightly increases the initial rate of free sulfur decrease.

Formation of Zinc Sulfide

The kinetics of ZnS formation (Fig. 4) have been measured in four stocks containing MBT: TMTD in high ratio (stock L); in low ratio (stock O); optimum ratio (stock N) and in optimum ratio with DCP (stock N₁). In stock O, the ZnS formation is lowest at the initial stage of vulcanization but highest at the final stage. In stock L, the initial ZnS formation is slightly higher than in stock O, but it is lower at the final stage. Stock N, containing an optimum proportion of accelerators, shows a greater amount of ZnS up to 50 min of vulcanization than in any other case, but the ZnS formation is less in the final stage of vulcanization than in stock O. The presence of DCP (stock N₁) does not affect the formation of ZnS at the initial stage of vulcanization, but only the final amounts of its formation are lower in a system containing DCP. A comparison of these curves with those in Figure 7(a) reveals that the formation of ZnS follows more or less the same pattern as the formation of crosslinks.

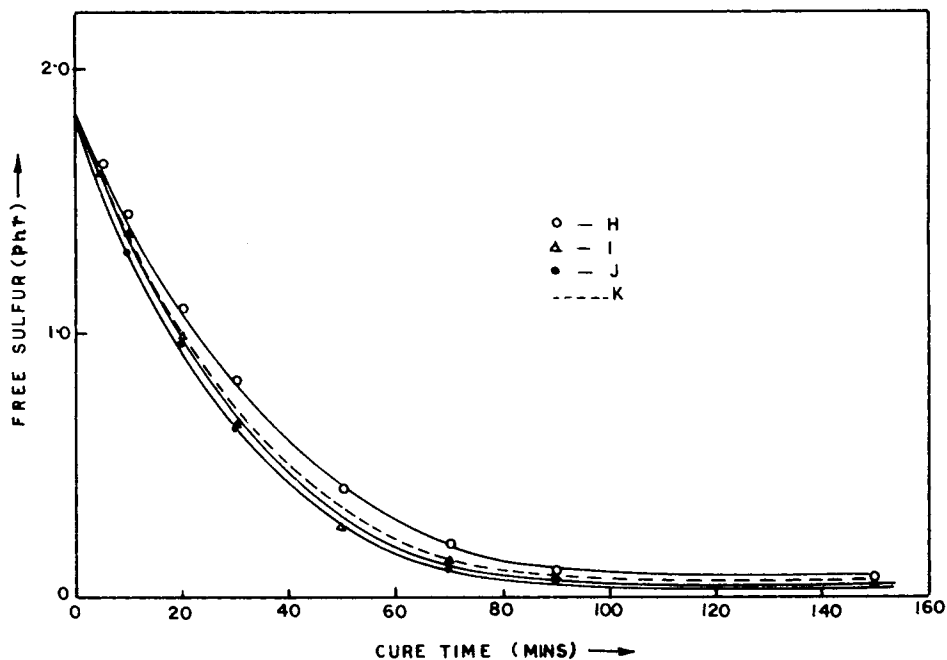


Fig. 2 Variation of free sulfur with cure time in systems without zinc oxide and stearic acid.

Crosslink Density

MBT, TMTD, and DCP

The kinetics of crosslink formation in the presence of variable amounts of TMTD with a constant level of MBT and DCP (curves B, C, D, and E) and in the presence of variable amounts of MBT with a constant amount of TMTD and DCP (curves F, G, and D) are shown in Figure 5. It is interesting to note that with a constant level of MBT and DCP, increase in the concentration of TMTD always increases the initial crosslink density up to a certain period of vulcanization (30–40 min) but lowers the final crosslink densities. This initial increase in crosslink density gradually becomes prominent as the MBT:TMTD ratio is decreased. To summarize, the compounds with high MBT:TMTD ratio give rise to low initial crosslink density but comparatively high final crosslink maxima, but with low MBT:TMTD ratio it is just the reverse. This fact does not agree with the findings of the 2-mercaptobenzothiazole (MBT) + diphenylguanidine (DPG) system,⁴ where with constant MBT and DCP increment in DPG concentration steadily increased the crosslink density from the very beginning to the final stage of vulcanization.

However, with a constant level of TMTD and DCP, an increment of MBT steadily decreases the crosslink formation. It should be mentioned here that all these accelerators, when present alone, reduce the crosslink density due to DCP, depending on their concentration.⁵⁻⁷

These observations clearly indicate that in a mixture of DCP, MBT, and TMTD, MBT is the most effective scavenger of free radicals due to DCP at the initial stage of cure, and TMTD inhibits the action of MBT, either by scavenging the free radicals due to MBT or by reacting initially with it. However, in the latter stage of cure, TMTD also becomes an effective radical scavenger along with

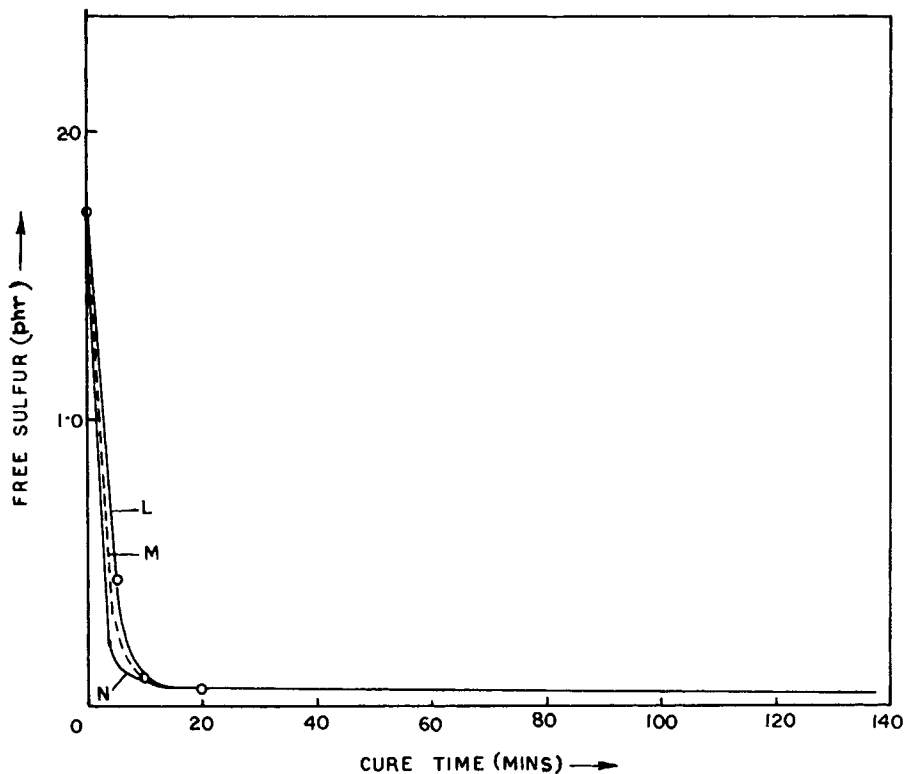
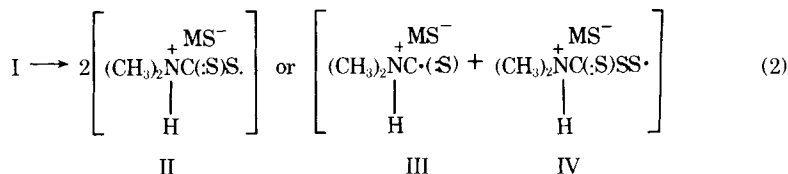
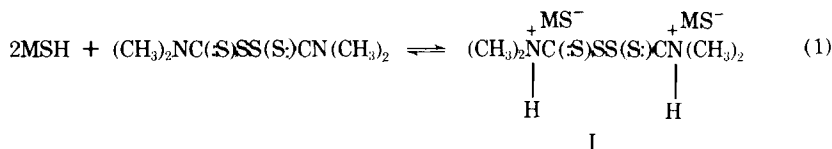


Fig. 3. Variation of free sulfur with cure time in systems with ZnO and Stearic Acid.

MBT, thus destroying the free radicals due to DCP. These experimental facts may very well be explained by the following reactions reported earlier for the MBT system⁵ and the following reactions:



The inhibiting action of TMTD on MBT, at the initial stage of vulcanization, may be explained by reaction (1) where an acid-base type equilibrium reaction between MBT and TMTD may occur. It has already been found that a similar type of acid-base type molecular binding may occur in a MBT-DPG system.⁴ As observed from an experiment on latter stages of vulcanization, this complex (I) may break to generate free radicals II, III, and IV. This can further scavenge the free radicals due to DCP, thus lowering final crosslinks. This difference in

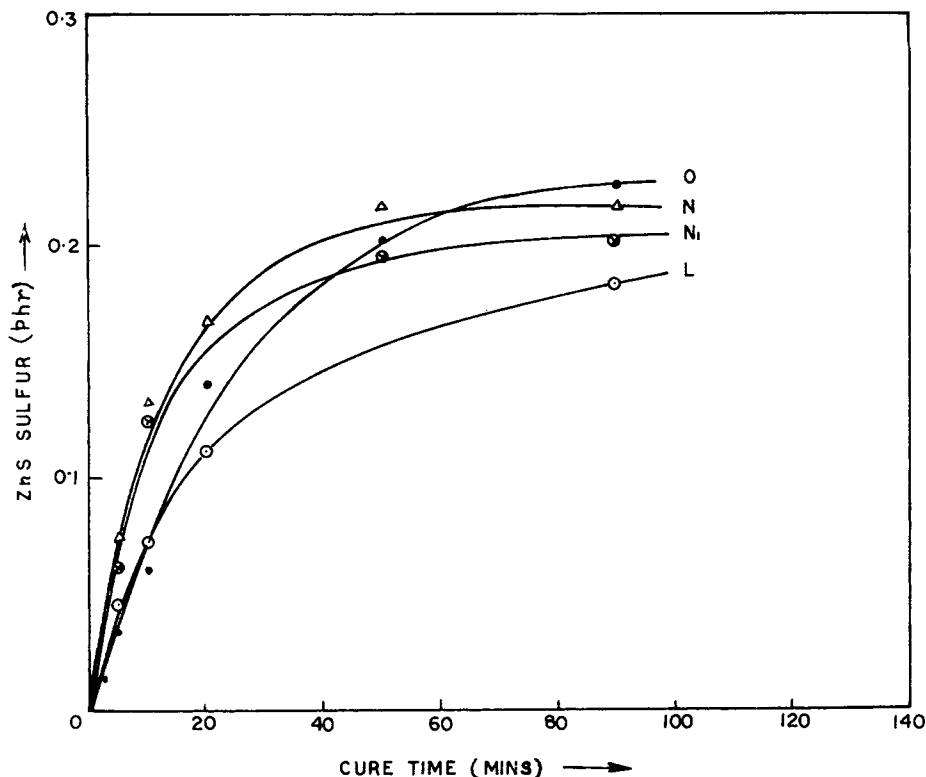


Fig. 4. Variation of the zinc sulfide sulfur with cure time.

behavior between complex I and the MBT-DPG molecular complex may be ascribed to the fact that TMTD is thermally less stable than DPG.

MBT, TMTD, Sulfur, and Natural Rubber in the Presence and Absence of DCP

The kinetics of crosslink formation for these systems without DCP are shown in Fig. 6(a) (curves H, I, J, and K). The characteristic features of these curves are the initial steady formation of crosslinks up to a maximum value within 60 min followed by a slow reversion. With the increase in TMTD: MBT ratio, up to a limiting ratio, the rate of crosslink formation and the maximum amount of crosslink gradually increases, but beyond this limiting ratio both fall off (curve K). Free sulfur decrease also follows the same trend. This limiting ratio is found to be approximately MBT:TMTD = 0.5:0.5 g/g, or 1.42:1.00 mole/mole. The behaviors of MBT (0.7 phr) and TMTD (0.3 phr) separately and in combination are shown in curves P, Q and I, respectively [Fig. 6(b)]. The crosslink density is much higher and the initial rate of crosslink formation is much faster in combined systems. These facts suggest that in a MBT-TMTD accelerated sulfur vulcanization system, accelerators are activated by the presence of each other

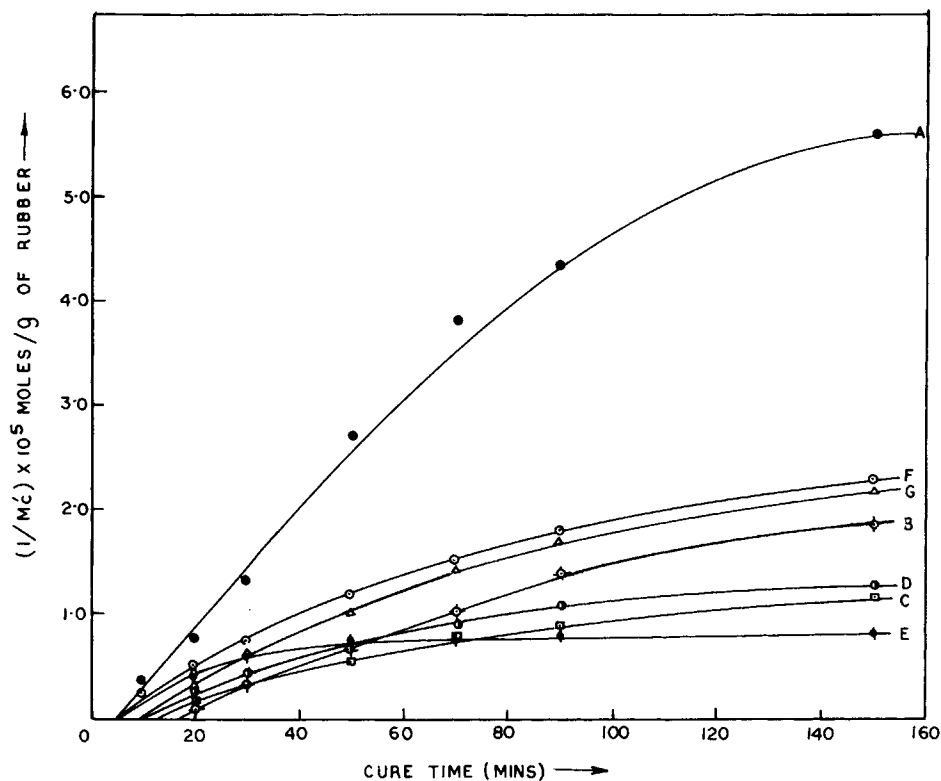


Fig. 5. Variation of physical crosslink density ($1/M'_c$) with cure time in systems containing MBT-TMTD-DCP.

and the activation is maximum when the molar proportion of MBT predominates in the system.

The addition of DCP in the above systems changes the nature of the curves of crosslink formation [curves H₁, I₁, J₁, and K₁ in Fig. 6(a)]. These curves are quite similar to those of the NR-DCP system (curve A), except that the initial crosslink densities are higher in these systems while the final crosslinks are lower than in the NR-DCP system. The initial rate of crosslink formation and the initial amount of crosslink are increased gradually with increasing TMTD:MBT proportion up to a limiting ratio. This limiting ratio is found to be MBT:TMTD = 0.3:0.7 g/g, i.e., approximately 1.0:1.5 mole/mole, which is in contrast to the limiting ratio of MBT:TMTD = 1.42:1.0 mole/mole for similar systems without DCP. It is interesting to note that only in stocks with approximately this limiting ratio of MBT:TMTD (1:1.5 mole/mole), the initial crosslink densities are additive for quite an appreciable period (up to 30-35 min), and the crosslink density of the MBT-TMTD-DCP-S-NR system is the summation of the crosslink densities of the DCP-NR and MBT-TMTD-S-NR systems. The mixed nature of crosslinking leading to both carbon to carbon (C-C) and sulfide types of crosslinkages is supported by the reaction of the vulcanizates with methyl iodide, which is known to destroy all types of sulfide linkages (Table III). In the systems with lower TMTD:MBT proportion than the limiting ratio, though additiveness is not found, both sulfide and C-C types of crosslinks are found to be formed. The amounts of sulfide crosslinks (obtained by deducting the C-C crosslinks

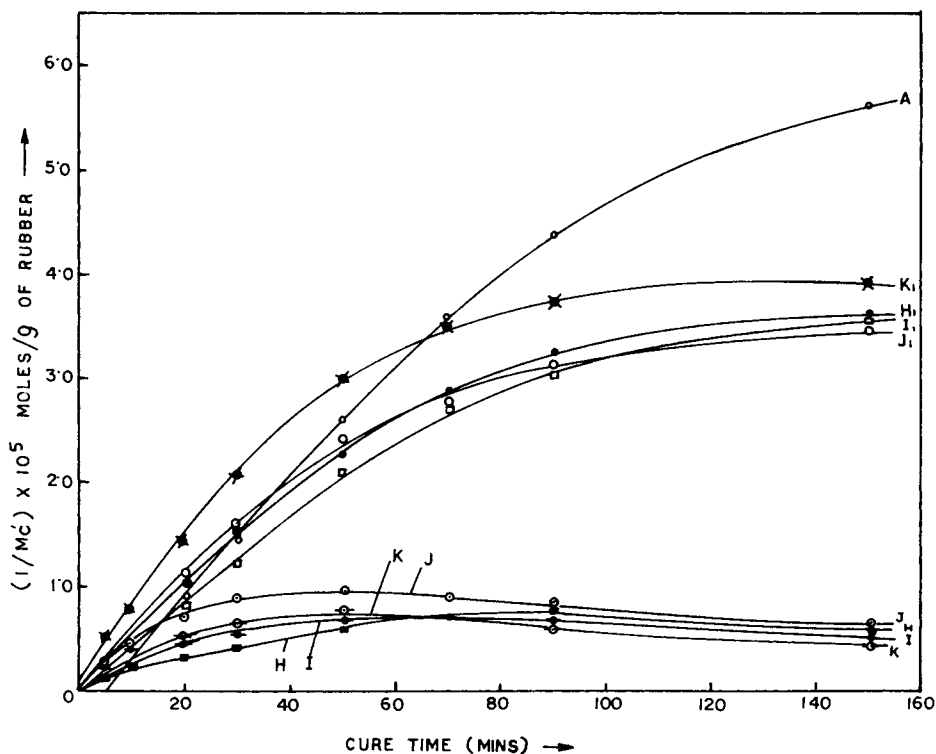


Fig. 6. (a) Variation of physical crosslink density ($1/M_c$) with cure time in systems containing MBT-TMTD-S both in presence and absence of DCP. (b) Comparison of crosslink density formation between single and binary accelerated systems containing no zinc oxide and stearic acid. Dotted curves are theoretical additive curves.

from the total crosslinks) in stocks containing DCP are much lower than in stocks without it, and also the C-C crosslinks are lower than in the NR-DCP system. Both the sulfide and C-C crosslinks are increased with an increment in TMTD:MBT ratio until the additiveness is found in the vicinity of TMTD:MBT = 1.5:1.0 mole/mole. In the presence of DCP also, the combined system has a higher efficiency than the additive effect of the two accelerators functioning separately at least at the initial stages of vulcanization [cf. curves PQ_1 , P_1Q , and I_1 in Fig. 6(b)].

All the above experimental findings can be explained by a reaction scheme where both free-radical and ionic mechanisms are operative. First, MBT alone may form a sulfur complex^{5,8} which generates free radicals and finally forms sulfur crosslinks with rubber. But in the presence of DCP, there are mutual reactions between these free radicals and the radicals from DCP, thus lowering both types of crosslinks in stocks containing DCP. Secondly, the MBT may combine initially with TMTD, as shown in eq. (1), and the resulting MS^- may lead to the ionic cleavage of the sulfur octet ring which finally forms sulfur crosslinks as proposed by Bateman and co-workers¹²:

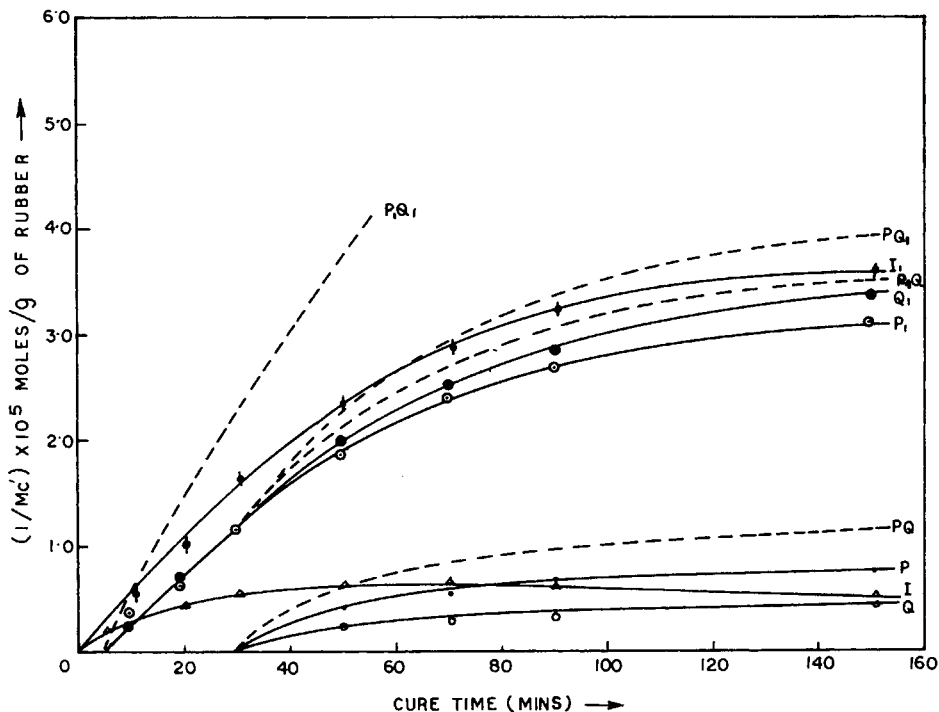
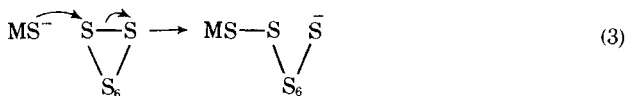


Fig. 6. (Continued from previous page.)



The first process predominates as long as the proportion of MBT is high in the accelerator ratio, while the second process is more important when TMTD is present in higher proportion. In our recent study with the MBT-DPG binary accelerator system,⁴ it was found that the molecular complex formation between the two accelerators and reaction (3) were the major causes for the formation of sulfur crosslinks. The difference in behavior may be ascribed to the lower basicity of TMTD than that of DPG. The formation of the complex between the accelerators becomes much more favorable with increase in TMTD concentration, and thus at higher TMTD:MBT ratio the vulcanization mainly proceeds via the ionic mechanism.

MBT, TMTD, Sulfur, Zinc Oxide, Stearic Acid, and Natural Rubber in the Presence and Absence of DCP

Figure 7(a) (curves L, M, N, and O) shows the plot of crosslink densities against cure times for such systems in the absence of DCP. The introduction of zinc oxide and stearic acid causes an increase in the initial rate of crosslink formation and the free sulfur decrease. The characteristic nature of these curves is the

TABLE III
 Degree of Crosslinking Before and After Treatment with Methyl Iodide

Stoc- k	Vulcanizate corresponding to cure time, min	Methyl iodide of vulcanizates (96 hr at 80°C), g/g	$(1/M'_c) \times 10^5$ before treatment	$(1/M'_c) \times 10^5$ after treatment
A	10	1.50	0.38	0.37
	20	1.50	0.75	0.74
	150	1.50	5.61	5.32
H ₁	10	1.50	0.47	0.24
	20	1.50	0.81	0.40
	150	1.50	3.58	2.93
J ₁	10	1.50	0.58	0.30
	20	1.50	1.02	0.52
	150	1.50	3.64	3.02
K ₁	10	1.50	0.76	0.39
	20	1.50	1.44	0.77
	150	1.50	3.91	3.10
L ₁	10	2.0	8.01	0.41
	20	2.0	8.06	0.76
	150	2.0	9.80	4.21
N ₁	10	2.0	10.94	0.40
	20	2.0	10.75	0.74
	150	2.0	13.41	4.87

initial fast rate of crosslink formation leading to a maximum value within 5–8 min followed by a comparatively quick reversion within 20 min and then a very slow and steady reversion throughout the later stages of vulcanization. This is present only when neither of the accelerators is present in high amount. It is observed that with increase in TMTD:MBT ratio, the initial rate of vulcanization and the crosslink maxima gradually increase up to a limiting accelerator ratio. This limiting accelerator ratio obtained from the plot of initial rate of crosslink formation against the accelerator ratio (curve I in Fig. 8), is found to be MBT:TMTD = 0.48:0.52 g/g. Beyond this limiting ratio, an increment in TMTD:MBT ratio decreases the initial rate of crosslink formation and the crosslink maxima.

Comparison with single accelerators [Fig. 7(b)] shows that the crosslink density in a combined accelerator system is much higher in the initial period (up to 15 min) than the additive crosslink densities of these two systems taken separately (cf. curves RS and M). The synergistic nature of the MBT–TMTD system is also evident from Figures 7(b), 8, and 9(a), which also shows that MBT becomes more activated in the presence of TMTD than the activation of TMTD by MBT.

Curves L₁, M₁, N₁, and O₁ [Fig. 7(a)] depict the kinetics of crosslink formation for similar systems containing DCP. As observed for the systems without DCP, the initial rate of crosslink formation gradually increases [curve II in Fig. (8)] with TMTD:MBT ratio up to the limiting ratio which is identical with that for a similar system without DCP. Then the rate of crosslink formation gradually increases, though at a slower rate instead of reversion. The final crosslink density is found to be more with increasing TMTD:MBT proportion up to the limiting ratio; and beyond the ratio it also increases, but to a much less extent. The presence of DCP does not alter the synergistic nature of this binary accelerator

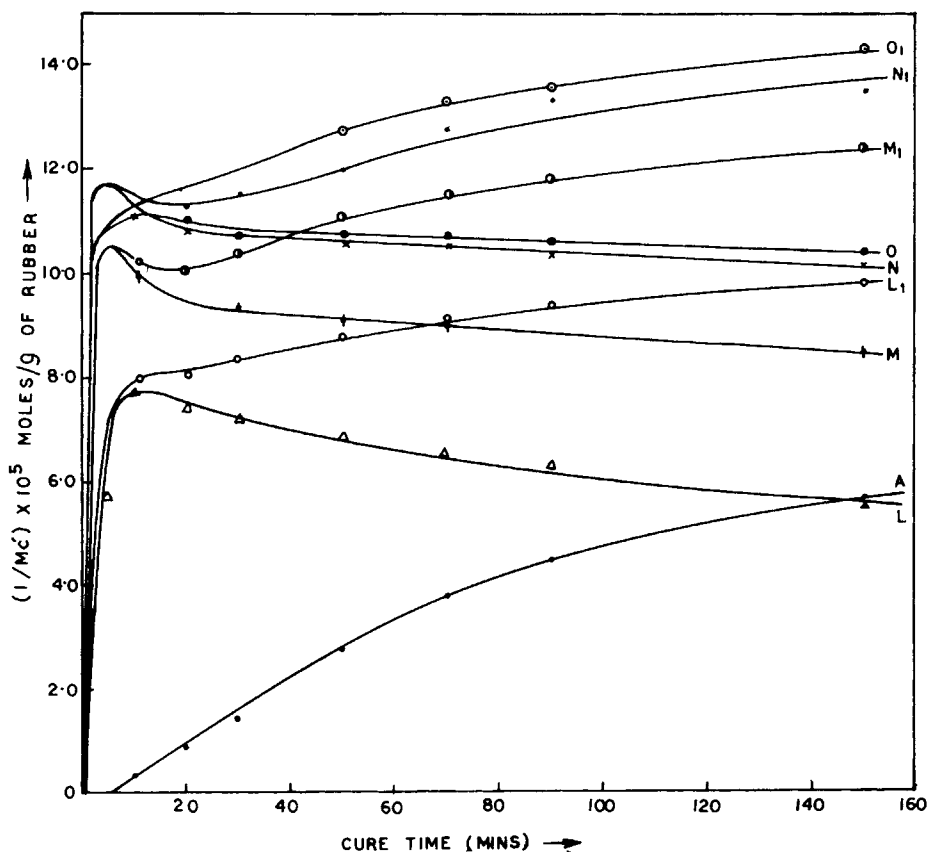


Fig. 7. (a) Variation of physical crosslink density ($1/M_c$) with cure time in systems containing MBT-TMTD-S-ZnO and stearic acid both in presence and absence of DCP. (b) Comparison of the crosslink density formation between single accelerated and binary accelerated system containing zinc oxide and stearic acid. Dotted curves are theoretical additive curves.

system [Fig. 9(b)]. Comparison with single accelerated systems containing DCP shows that the efficiency of the combined accelerator system with DCP is much higher, at least in the initial period of vulcanization [curves R_1S , RS_1 , and M_1 in Fig. 7(b)].

The most interesting point is that for a particular cure time in the initial period of rapid crosslinking in any of the stocks (L_1 , M_1 , N_1 , and O_1) containing both sulfur and DCP, the number of crosslinks can be represented by the summation of that due to similar stocks without DCP (L , M , N , and O) and the stock (A) with only DCP. This mixed vulcanization is further supported by treatment of the vulcanizates with methyl iodide (Table III). It is observed that final C-C crosslinks are more in number as TMTD:MBT ratio increases.

DCP does not interfere with the initial and principal stages of sulfuration of NR by the MBT-TMTD binary accelerator system. In the later stages, vulcanization by DCP becomes the main source of crosslink formation, though at a slower rate, and this balances the slow reversion observed in the absence of DCP while causing an overall increase in the crosslink density. The retardation is due to the unreacted MBT, but the decomposition products of TMTD may also contribute to it.

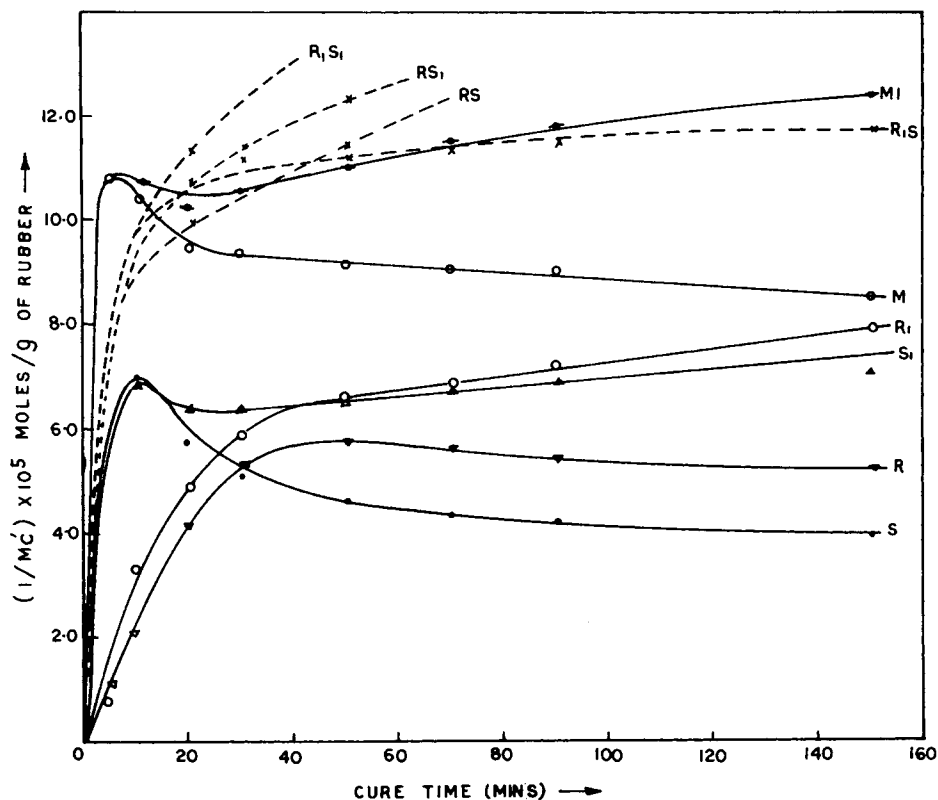


Fig. 7. (Continued from previous page.)

These experimental findings strongly demonstrate that MBT-TMTD binary accelerated sulfuration in the presence of zinc oxide and stearic acid follows an ionic mechanism with the mutual activation of one accelerator by the other. The activation becomes greatest with the accelerator ratio MBT:TMTD = 0.48:0.52 g/g, which conforms to 2.84×10^{-3} : 2.16×10^{-3} mole/mole, i.e., 1.315:1.000 mole/mole. It is generally accepted^{7,11} that two thirds of the thiuram disulfide, which is introduced initially, is converted during the initial stage of vulcanization in the presence of excess zinc oxide to zinc dimethyl dithiocarbamate (ZDMC), independent of the concentration of TMTD. If it is true, we can write the ratio of MBT to ZDMC formed as 1.315:0.666 mole/mole. MBT is also generally known⁵ to form the zinc salt of MBT (ZMBT) at the initial stages of vulcanization for which 2 moles of MBT are converted to 1 mole of ZMBT. If this is also true, then we can write ZMBT:ZDMC = 1:1 mole/mole (approx.). Thus it appears that at the initial stage of vulcanization both MBT and TMTD are converted to zinc salts and the ZMBT proceeds to form the sulfur complex.⁵ With the partial structure of the accelerator-zinc complex, the role of ZDMC can be il-

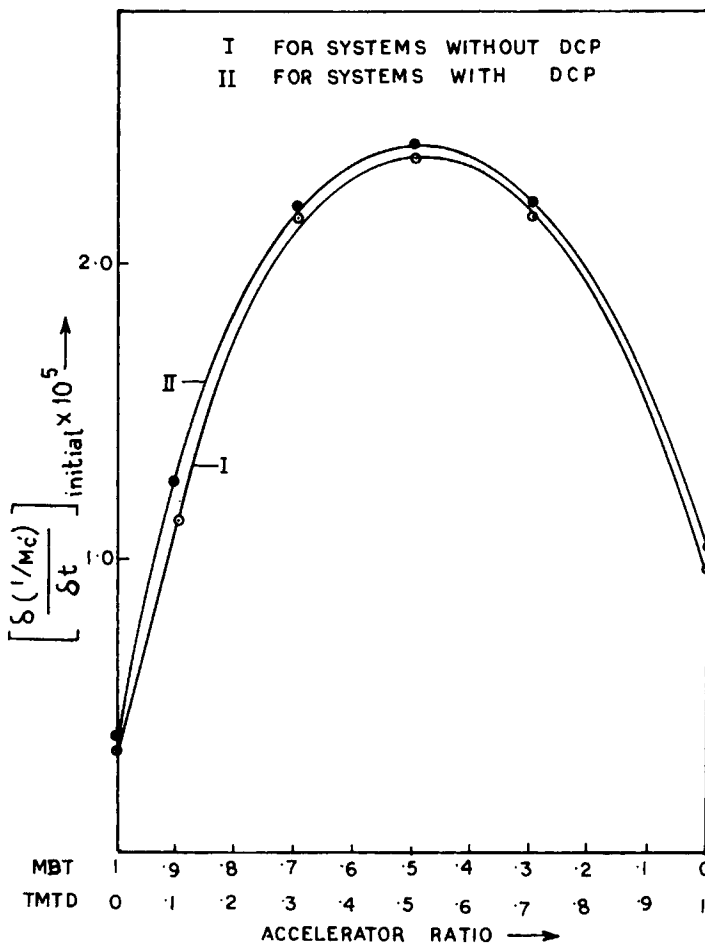
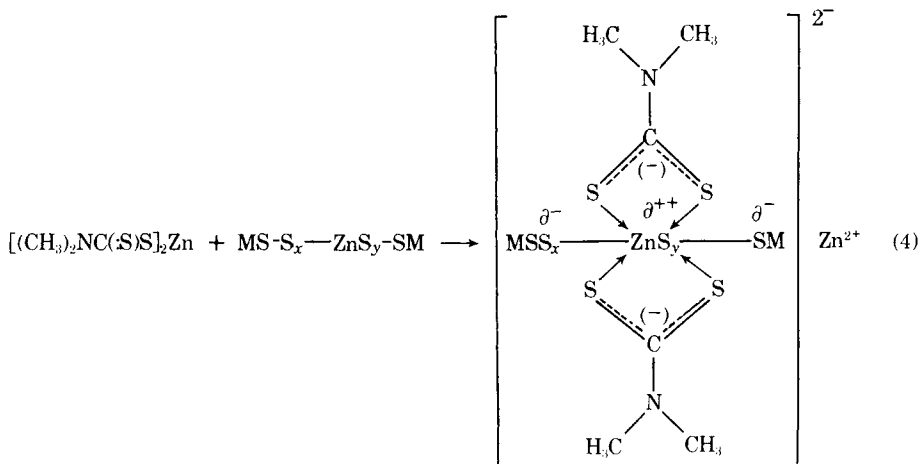


Fig. 8. Dependence of initial rate of crosslink formation [calculated from Fig. 7(a), curves L to O and L₁ to O₁] on the MBT:TMTD ratio.

lustrated as follows:



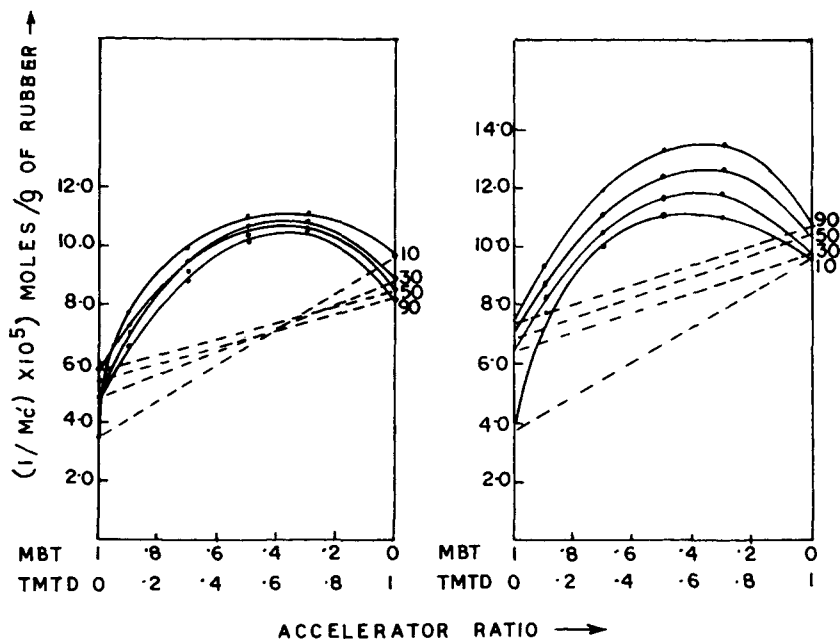


Fig. 9. Change in crosslink density during vulcanization in NR-MBT-TMTD-S-ZnO-stearic acid system [Fig. 9(a)] and NR-MBT-TMTD-S-DCP-ZnO-stearic acid system [Fig. 9(b)]. Numbers on the curves indicate minutes of cure time, points on dotted curves indicate theoretical additive values of the two accelerators.

This structure conforms to the molar ratio of ZMBT and ZDMC formed in the initial vulcanization period. As the ZDMC anion forms a strong ligand, the bond between Zn and the $MS-S_x-$ and MS_y- groups will be weakened by spreading or destroying the positive charge on the metal. The result will be more nucleophilicity of MSS_x^- , and hence, there will be an enhanced sulfuration rate. This explains how TMTD activates MBT in the combined accelerated vulcanization.

However, it is not very clear how MBT activates TMTD though the activation by MBT on TMTD is not very pronounced (Fig. 8). It is generally accepted^{7,11} that in the initial phase of vulcanization by TMTD, the nucleophilic attack of a basic oxy anion from ZnO on the thiocarbon atom of TMTD takes place; and finally, higher polysulfides are formed which then, on interchange with ZDMC, form an actual sulfurating complex. The MS^- formed in the initial stage of vulcanization may act as a nucleophilic agent and thus help in the formation of higher polysulfides.

CONCLUSIONS

MBT and TMTD, when present together in a vulcanization system of NR, may interact with one another. The sulfur vulcanization of NR, accelerated jointly by MBT and TMTD in the absence of zinc oxide and stearic acid, proceeds simultaneously through free-radical and polar mechanisms. The vulcanization in the presence of MBT, TMTD, S, ZnO, and stearic acid is of a synergistic nature and mainly follows a polar mechanism.

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