

Studies on Cure Synergism. I. Effect of Safe Zinc Dithiocarbamates on NR Vulcanization Accelerated by Thiazole-Based Accelerators

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SYNOPSIS

Investigations have been carried out on the effect of several zinc dithiocarbamates in the presence of thiazole-based accelerators in the vulcanization of natural rubber (NR), keeping in mind the possibility of introducing safe dithiocarbamates derived from safe amines. Mutual activity is observed in all the binary systems studied, the highest being observed in the zinc dibenzylthiocarbamate-dibenzothiazylsulfide (ZBEC-MBTS)-accelerated system. The effect of zinc diisopropyl dithiophosphate, reportedly a safe rubber additive, which is recognized as an age-resistant agent for NR, on cure has also been studied. The study reveals that thiuram disulfide and MBT are always formed from the reaction either between zinc dithiocarbamate (ZDC) and MBTS or between ZDC and *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS). It has been conclusively proved that 2-mercaptobenzothiazole (MBT) generated from MBTS or CBS reacts with ZDC and produces tetramethyl thinram disulfide (TMTD). The observed mutual activity has been discussed based on the cure and physical data and explained through the results based on HPLC and a reaction mechanism. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Most of the secondary amines have been shown to produce nitrosoamines, which are believed to be carcinogens.¹ A significant amount of rubber chemicals is obtained from these secondary amines. In fact, a recent survey shows that these rubber additives and the vulcanizates obtained from these chemicals contain varying proportions of nitrosoamines.² The present investigation aims at finding some rubber accelerators based on zinc dithiocarbamates (ZDCs) that are widely used in the preparation of technological vulcanizates, especially in latex goods and cable compounds. ZDCs do not impart odor or taste to the resulting vulcanizates that exhibit good aging behavior. It has been reported³ that ZDCs act as booster accelerators when they are combined with *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 2-mercaptobenzothiazole (MBT),

and dibenzothiazylsulfide (MBTS). These binary systems of accelerators find applications in the vulcanization of diene elastomers and slow-curing butyl rubber. However, systematic investigations in this regard are lacking and the available information is very scanty. In the present investigation, it was our endeavor to prepare ZDCs from safe amines and to study their boosting effect in the presence of other accelerators during the vulcanization of rubber.

EXPERIMENTAL

Materials

N-Cyclohexyl-2-benzothiazole sulfenamide (CBS),⁴ zinc(*N*-methylpiperazino)dithiocarbamate (ZPDC),⁵ and zinc diisopropylthiophosphate (ZDP)⁶ were prepared in the laboratory and purified according to the procedures reported elsewhere. 2-Mercaptobenzothiazole (MBT), dibenzothiazylsulfide (MBTS), zinc dimethylthiocarbamate (ZDMC), and zinc dibenzylthiocarbamate (ZBEC) were

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Table I List of Compounds Used

Chemical Name	Structure	Abbreviation
(1) 2-Mercapto-benzothiazole		MBT
(2) Dibenzothiazyl-disulfide		MBTS
(3) <i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide		CBS
(4) Zinc(<i>N</i> -methyl-piperazine)-dithiocarbamate		ZPDC
(5) Zinc dimethyl-dithiocarbamate		ZDMC
(6) Zinc dibenzyl-dithiocarbamate		ZBEC
(7) Zinc diisopropyl-dithiophosphate		ZDP

Table II Physical Data of Cured Stocks (Gum) Obtained at 140°C

Mixes and Composition (mmol)	Maximum Torque R_α (Nm)	Scorch Time t_2 (min)	Optimum Cure Time t_{90} (min)	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1. ZDMC 9	1.5	1.5	7.5	0.14	3.5	820
2. ZDMC 6 MBTS 3	3.35	5.0	17.5	0.53	12.4	740
3. ZDMC 4.5 MBTS 4.5	4.13	6.0	19.5	0.71	14.6	710
4. ZDMC 3 MBTS 6	4.15	7.0	17.5	0.67	14.9	700
5. MBTS 9	3.2	16.0	45.0	0.45	11.3	900
6. CBS 9	3.45	15.5	27.5	0.52	12.8	800
7. CBS 6 ZDMC 3	3.6	3.0	8.5	0.52	13.6	760
8. CBS 4.5 ZDMC 4.5	3.65	4.0	11.0	0.57	14.2	790

Table II (Continued from the previous page)

Mixes and Composition (mmol)	Maximum Torque R_{α} (Nm)	Scorch Time t_2 (min)	Optimum Cure Time t_{90} (min)	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
9. CBS 3 ZDMC 6	3.3	3.0	10.0	0.46	13.6	800
10. MBT 9	1.35	5.0	33.0	—	1.6	900
11. MBT 4.5 ZDMC 4.5	3.1	3.0	13.5	0.44	12.4	810
12. MBT 4.5 ZPDC 4.5	2.8	4.0	17.5	0.36	10.4	830
13. ZPDC 9	0.9	1.5	6.5	0.07	2.0	900
14. ZPDC 6 MBTS 3	3.05	6.0	17.5	0.37	11.7	800
15. ZPDC 4.5 MBTS 4.5	3.8	7.0	22.0	0.61	13.4	740
16 ZPDC 3 MBTS 6	3.8	8.0	19.0	0.60	13.3	710
17. CBS 6 ZPDC 3	3.45	4.5	10.0	0.44	13.5	800
18. CBS 4.5 ZPDC 4.5	3.45	4.5	11.0	0.51	13.6	810
19. CBS 3 ZPDC 6	2.93	3.5	9.0	0.37	11.5	820
20. ZBEC 9	1.27	2.5	17.5	0.07	3.25	850
21. ZBEC 6 MBTS 3	3.9	6.0	26.0	0.67	15.3	720
22. ZBEC 4.5 MBTS 4.5	4.3	7.0	25.5	0.74	14.14	670
23. ZBEC 3 MBTS 6	4.3	8.0	24.0	0.74	15.0	720
24. ZBEC 6 CBS 3	3.25	3.5	11.5	0.51	12.2	790
25. ZBEC 4.5 CBS 4.5	3.6	4.5	16.0	0.53	13.28	760
26. ZBEC 3 CBS 6	3.9	4.0	12.0	0.58	14.5	740
27. ZDP 9	1.4	5.5	25.5	0.03	2.3	850
28. ZDP 6 MBTS 3	3.7	10.5	33.5	0.52	14.8	770
29. ZDP 4.5 MBTS 4.5	3.9	10.5	28.0	0.67	14.2	730
30. ZDP 3 MBTS 6	3.85	13.0	30.5	0.60	14.3	740
31. CBS 6 ZDP 3	3.6	6.0	17.5	0.48	13.2	800
32. CBS 4.5 ZDP 4.5	3.5	6.0	17.0	0.45	12.3	790
33. CBS 3 ZDP 6	3.45	6.5	19.0	0.45	13.1	780

commercial samples used either as such or after necessary purifications. A list of chemical compounds, their structures, and their abbreviations used in the present investigation are given in Table I.

Preparation of Vulcanizates and Measurement of Physical Properties

Zinc oxide (5 phr), extrapure stearic acid (2 phr), G.R. grade sulfur (0.5 phr), and accelerator (s) were

incorporated into 100 g of rubber on a Berstorff laboratory mixing mill of size 203×104 mm using an 18 min compounding cycle. The total concentration of the accelerator(s) were kept at 9 mmol phr. The cure characteristics of different stocks were obtained using the Monsanto Rheometer R-100 at 140°C and the cure data are presented in Table II. The stocks were cured under pressure at 140°C for optimum cure time and the vulcanizates were kept for 24 h at ambient temperature before measuring the modulus at 200% elongation and tensile strength according to ASTM D 412-51T using dumbbell-shaped test pieces in an Amsler (Sweden) tensile tester. The physical data concerning modulus, tensile strength, and elongation at break of the vulcanizates are also provided in Table II.

Identification of Products Formed in the Early Part of Vulcanization Through HPLC

Various compounds formed in the early part of vulcanization at 140°C were identified using a 25 cm Waters Bondapack C_{18} reverse-phase chromatography column by retention time as well as co-injection of authentic samples. A Varian UV detector operating at 254 nm was used. The flow rate of the solvent was maintained at $0.5 \text{ cm}^3/\text{min}$.

Very thin sections of grossly undercured samples of desired compositions were obtained using spacers. Prior to compounding, natural rubber (NR) was extracted with hot acetone for 72 h. The samples were extracted with an acetonitrile:water (70 : 30) solvent mixture for 24 h using a shaker. The mixture was filtered and the filtrate was ready for analysis. In the case of a sticky product, a thin film of the material was prepared on chromatography paper, which was then extracted in accordance with the procedure just mentioned above. Chromatograms were obtained by injecting the requisite volume of the clear solution obtained in each case onto the HPLC column.

RESULTS AND DISCUSSION

Gum stocks were selected in order to understand better the effect of ZDC in the vulcanization of rubber. It has been observed that in the vulcanization low sulfur and a high accelerator ratio produces network structures of very little main-chain modification. Since this modification complicates the fine structure of the rubber vulcanizates and thus affects adversely the properties of the network structures,

a low sulfur (0.5 phr) and high accelerator (9 mmol) ratio was used throughout the investigation.

First of all, the binary combinations of accelerators composed of ZDMC plus MBTS, ZDMC plus CBS, and ZDMC plus MBT were tried for their vulcanizing activity. It is evident from Table II that with the progressive replacement of ZDMC by MBTS (mixes 1–5) marked mutual activity with regard to torque (R_α) could be noticed as the cure progresses. This synergistic effect is also observed for the modulus and tensile strength values of the vulcanizates. The scorch safety, elongation at break, and optimum cure values for the intermediate compositions, however, are found to be in between those separately obtained with ZDMC and MBTS alone. The mutual activity in respect of R_α , modulus, and tensile strength is also pronounced for the binary systems composed of ZDMC and CBS (mixes 1, 6–9). It is evident from Table II that mutual activity for the two systems, ZDMC + MBTS and ZDMC + CBS, is of same kind but differs slightly in degree, the former exhibiting somewhat higher activity than that of the latter.

Some investigations have also been carried out on the effect of MBTS–ZDC binary combinations upon the vulcanization of NR. The results are shown in Table II (mixes 1, 10–13). It is evident that, like MBTS and CBS, MBT is also capable of exhibiting enhanced activity with regard to torque, modulus, and tensile strength in the presence of ZDMC or ZPDC. ZDMC is obtained from unsafe dimethylamine, and, thus, the accelerator itself suffers from the drawback of generating unsafe nitrosoamines. As the nitrosoamines from *N*-methylpiperazine and dibenzylamine are reported to be safe, it was decided to investigate the effect of ZPDC and ZBEC separately in combination with MBTS and CBS upon cure. The results are given in Table II (mixes 5 and 6, 13–26). ZPDC along with MBTS exhibits cure characteristics (R_α , t_2 and t_{90}) similar to those obtained with ZDMC plus MBTS. This is also true for the physical properties like modulus, tensile strength, and elongation-at-break values of the vulcanizates. The cure data and physical data for the binary combinations composed of ZPDC and CBS also point out a similar trend as observed for ZDMC and CBS systems. From Table II, it can be further seen that ZBEC can be effectively utilized by combining separately with MBTS and CBS to produce vulcanizates that exhibit the highest torque, modulus, and tensile values for the intermediate compositions (mixes 5, 6, 20–26).

In this comparative study, ZDP was included since this safe rubber additive⁷ (originating from

bis[diisopropyl]thiophosphoryl disulfide [DIP-DIS]) along with thiazole accelerators yields NR vulcanizates of notable age resistance.⁸ The results are summarized in Table II (mixes 5, 6, 27–33). It is evident from the table that synergism occurs as ZDP is gradually replaced either by MBTS or by CBS. The results are similar to those obtained with ZDMC, ZPDC, and ZBEC and vary only in degree. The gum stocks for ZDP–MBTS combinations (mixes 28–30) show the highest t_2 and t_{90} values among the combinations. This is also true for ZDP–CBS-accelerated stocks as compared to ZDC–CBS systems. The results discussed so far clearly indicate synergism for the binary systems of accelerators employed in the present study.

To understand the mutual activity of the MBTS–ZDC and CBS–ZDC systems, some investigations were carried out. It has been observed by us that both these systems generate MBT and tetramethyl thinram disulfide (TMTD). This phenomenon is clearly depicted in the HPLC chromatograms (Figs. 1 and 2). 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 cyclohexylamine.⁹ It may be reasonably expected that MBT thus formed may

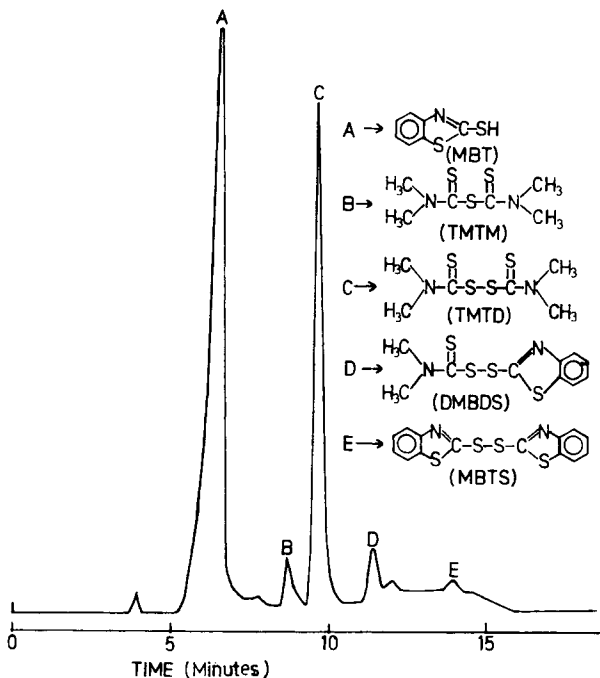


Figure 1 High-performance liquid chromatogram of undercured vulcanizate obtained at 140°C for 2 min. Stock composition: NR 100 g; zinc oxide 5 phr; stearic acid 2 phr; sulfur 0.5 phr; ZDMC 4.5 mmol; MBTS 4.5 mmol.

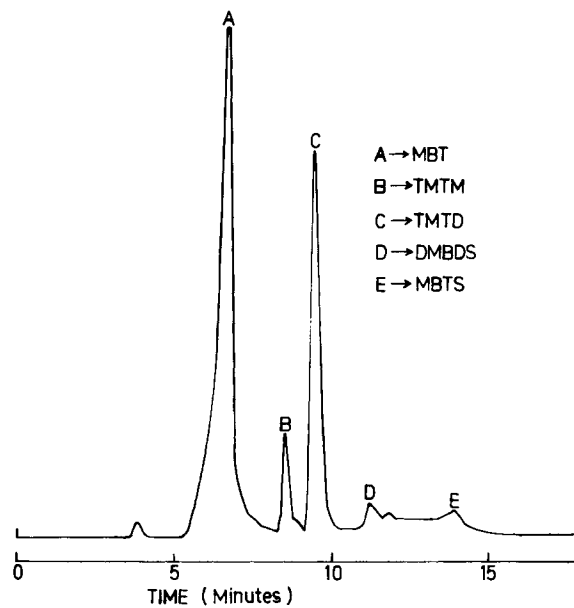


Figure 2 High-performance liquid chromatogram of undercured vulcanizate obtained at 140°C for 2 min. Stock composition: NR 100 g; zinc oxide 5 phr; stearic acid 2 phr; sulfur 0.5 phr; ZDMC 4.5 mmol; CBS 4.5 mmol.

act upon ZDC and liberate TMTD depending upon the reaction conditions. Actually, this has been observed (Figs. 1 and 2). The effect of MBT upon ZDC has been clearly shown through the formation

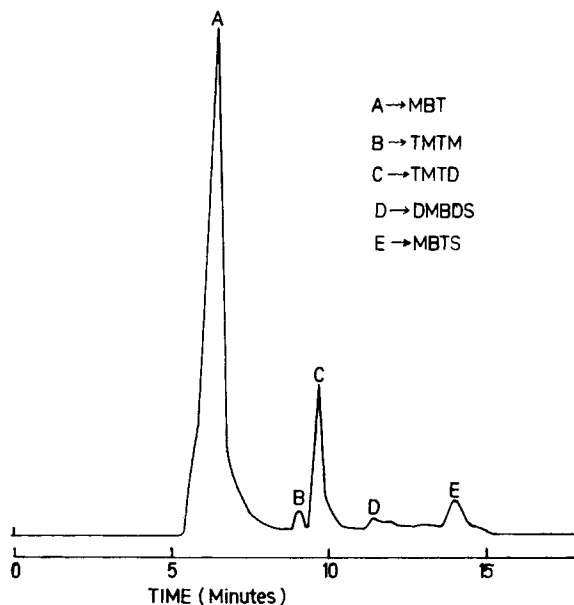
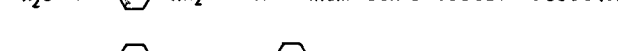
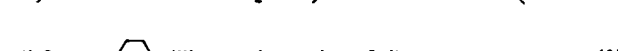
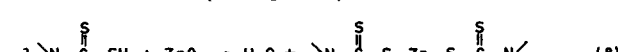
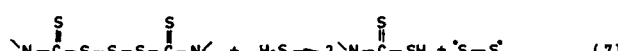
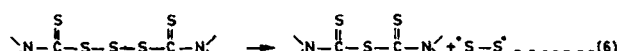
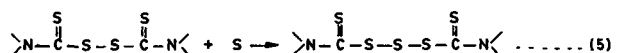
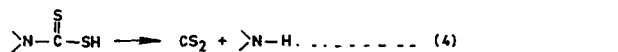
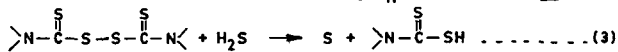
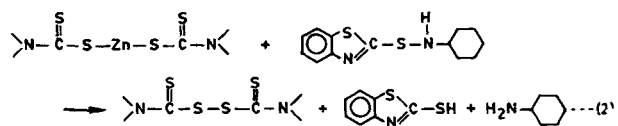
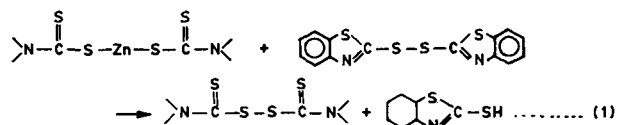


Figure 3 High-performance liquid chromatogram of undercured vulcanizate obtained at 140°C for 2 min. Stock composition: NR 100 g; zinc oxide 5 phr; stearic acid 2 phr; sulfur 0.5 phr; ZDMC 4.5 mmol; MBT 9.0 mmol.

of TMTD in the chromatogram (Fig. 3). It has been shown by previous workers^{3,10} that the MBT-TMTD system provides mutual activity. The synergistic effect observed in the MBTS-ZDC and CBS-ZDC systems thus arises from the generation of MBT and TMTD (Figs. 1 and 2). These observations explain the synergistic effect of the MBT-ZDC system (Table II), mixes 1, 10-13) discussed in an earlier section.

The results obtained from the HPLC study point out, beyond doubt, the formation of MBT and TMTD from both ZDC-MBTS and ZDC-CBS systems. The foregoing results also indicate some differences in the mutual activity of these systems. Apparently, this is not expected since both MBT and TMTD are generated simultaneously in these systems and are highly active accelerators. To understand clearly the difference in the mutual activity between MBTS-ZDC and CBS-ZDC systems, the following reaction scheme is presented:

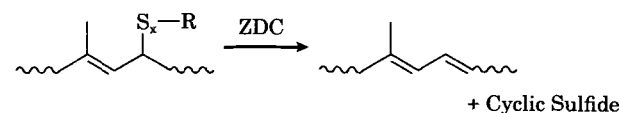


The scheme depicts the probable paths (steps 1-8) for the transformation of ZDC under the influence of MBTS and CBS in the presence of the H₂S that is formed¹¹ during the process of vulcanization. Steps 3, 6, and 7 lead to cross-linking⁹ of rubber, whereas step 8 indicates the regenerative path for ZDC. The cyclohexylamine generated from CBS (path 2) is likely to form the effective sulfurating complex¹² 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 not observed. This phenomenon may be explained by the reaction of cyclohexylamine with H₂S (path 9) and CS₂ (path 10).¹³ The capture of H₂S by cyclohexylamine not only prevents cyclohexylamine from complex formation but also severely affects the paths⁹ 3, 5, 6, and 7. As a result, there occurs a fall in the concentration of sulfur cross-links. 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 cross-links in the case of ZDC-CBS-accelerated vulcanizates. Dimethylamine is generated from TMTD during vulcanization. Like cyclohexylamine, it is also expected to react with H₂S. But it may be assumed that the effect is nearly the same in both MBTS-ZDC and CBS-ZDC 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-ZDC system, a comparatively higher amount of cross-links are likely to be generated in this system, which evidently exhibits higher synergistic activity as compared to that observed in the CBS-ZDC system.

It needs mentioning here that the chromatogram (Fig. 3) exhibiting the reaction between ZDMC and MBT indicates the formation of TMTD at a much lower level than that expected even with the use of a considerably greater amount (9 mmol) of MBT as compared to that obtained with either MBTS (4.5 mmol) under otherwise identical conditions. It seems that nascent MBT in the latter case brings about this difference.

So far, the action of ZDCs in building cross-links has been discussed. But there is the other side also, where ZDCs do take part in the destruction of sulfidic cross-links. In this process, polysulfidic linkages are broken and cyclic sulfides are formed as suggested by the previous workers¹⁴:



It has also been observed that the presence of zinc dithiocarbamates in the vulcanization of NR accelerated by the thiocarbamyl sulfenamide-MBTS system greatly influence¹⁵ the torque of the system, where, after an optimum dose of ZDC, the physical property deteriorates quickly. So, the process of vulcanization accelerated by the dithiocarbamates is confronted with two opposing factors: One involves the creation of sulfur cross-links between the hy-

drocarbon chains and the other brings about destruction of some of the linkages along with main-chain modification. The net result is the compromise between the two and is manifested in the cure and physical data obtained in the present investigation.

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