

Thiuram-Accelerated Sulfur Vulcanization. IV. Zinc Dimethyldithiocarbamate-Accelerated Sulfur Vulcanization

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SYNOPSIS

2,3-Dimethyl-2-butene (TME) was used as a model for polyisoprene in a study of zinc dimethyldithiocarbamate ($Zn_2(dmtc)_4$)-accelerated sulfur vulcanization. Mixtures of TME and curatives were heated in sealed tubes to 130°C for various times and the contents analyzed by HPLC. $Zn_2(dmtc)_4$, in the presence of sulfur, reacts with TME to form pendent groups of high sulfur rank. This reaction proceeds via a concerted mechanism without the formation of zinc perthiomercaptide as a true intermediate. Crosslinking is slow but there is no induction period, the reaction between thiuram pendent groups of high sulfur rank being catalyzed by $Zn_2(dmtc)_4$. Tetramethylthiourea is not formed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Zinc perthiomercaptides are generally regarded as the active sulfurating agent in zinc dimethyldithiocarbamate ($Zn_2(dmtc)_4$)-accelerated vulcanization,¹ though the presence of zinc perthiomercaptides is largely based on circumstantial evidence. Kawaoka² claimed the synthesis of a polysulfidic homologue of $Zn_2(dmtc)_4$ by fusion of sulfur with $Zn_2(dmtc)_4$ at 140–150°C. It was further inferred that an unstable addition compound of the type zinc diethyldithiocarbamate ($Zn_2(detc)_4$).S₈ formed between sulfur and $Zn_2(detc)_4$ in benzene at 30°C.³ Fackler et al.^{4,5} indicated that chelate ring expansion occurred with the insertion of sulfur atoms into the complex zinc *p*-dithiocumate ($Zn(p-dtc)_2$), forming $Zn(p-dtc)_2S_2$. It was suggested that related zinc dithiolates such as $Zn_2(dmtc)_4$ would activate sulfur in a similar way. Furthermore, exchange between $Zn_2(dmtc)_4$ and radioactive sulfur is observed in xylene at 130°C.^{6–8}

Coleman et al.,⁹ however, performed Raman studies on a heated $Zn_2(dmtc)_4$ /sulfur mixture, but did not detect the formation of new S—S bonds. Craig et al.⁷ found no indication of reaction between

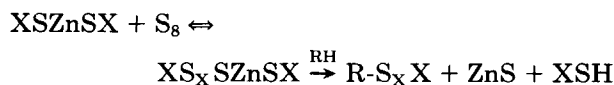
$Zn_2(dmtc)_4$ and sulfur up to 150°C in the absence of solvent, nor was radioactive $Zn_2(dmtc)_4$ found when a $Zn_2(dmtc)_4$ /sulfur–35/palmitic acid mixture was heated. This indicated that sulfur had not exchanged.

The (transient) existence of zinc perthiomercaptides remains a point of contention. However, based on NMR studies by Fackler et al.,^{4,5} it is believed that zinc perthiomercaptides are formed rapidly between $Zn_2(dmtc)_4$ and elemental sulfur prior to the formation of pendent groups in $Zn_2(dmtc)_4$ -accelerated sulfur vulcanization.

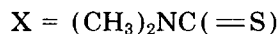
The active sulfurating agent interacts with the rubber hydrocarbon to form network-bound accelerator fragments (pendent groups), which are precursors to crosslinking. Kruger and McGill¹⁰ performed HPLC and TG analyses on the IR/ $Zn_2(dmtc)_4$ /sulfur system in the early stages of cure, and could not account for all the $Zn_2(dmtc)_4$ present initially. It was inferred that the rest of the $Zn_2(dmtc)_4$ molecules were bound to the IR chain as pendent groups.

The studies of Kruger and McGill,¹⁰ Wolfe,¹¹ and Shelton et al.¹² indicated that the participation of thiuram sulfenyl and thiuram persulfenyl radicals cannot be totally ignored in the formation of pendent groups and crosslinks, although a predominantly polar mechanism is suggested.^{1,10}

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where



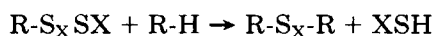
RH = rubber chain

XSH = dimethyldithiocarbamic acid (Hdmtc)

Versloot¹³ studied $\text{Zn}_2(\text{dmtc})_4$ -accelerated sulfur vulcanization of 2,3-dimethyl-2-butene (TME). No intermediate products (pendent groups) were detected, and this suggests that the reaction of pendent groups to form crosslinks is very fast and is catalyzed by $\text{Zn}_2(\text{dmtc})_4$.

Both free radical¹⁴ and polar crosslinking mechanisms have been proposed.^{1,9,11,15-17}

Crosslinks in thiuram-accelerated vulcanization are formed via the disproportionation of two pendent groups on neighboring rubber chains and/or via an interaction between a pendent groups and a neighboring rubber chain.



The latter reaction only occurs in the presence of $\text{Zn}_2(\text{dmtc})_4$, while in the absence of zinc, crosslinks result exclusively from the disproportionation of pendent groups.¹³

$\text{Zn}_2(\text{dmtc})_4$ decomposition during the vulcanization process has been mentioned in literature.^{1,11,16} Kruger and McGill¹⁰ analyzed the NR/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur/ ZnO system and calculated high *F*-values (the number of sulfide ions per chemical crosslink formed)¹⁸ in the early stages of cure. The values decreased with cure time due to the increase in crosslink density. This implies that ZnS is formed more readily than crosslinks and was rationalized in terms of the faster formation of pendent groups than the generation of crosslinks. IR/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur compounds vulcanized with the decomposition of $\text{Zn}_2(\text{dmtc})_4$ and formation of ZnS .^{10,19} The concentration of $\text{Zn}_2(\text{dmtc})_4$ decreased at a much slower rate in IR/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur/ ZnO than in IR/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur vulcanization.¹⁰ The mass loss in the former system was also much lower.

Hdmtc is produced during the formation of pendent groups and crosslinking, and may react rapidly with ZnO to form $\text{Zn}_2(\text{dmtc})_4$ and H_2O . Zinc originally involved in the $\text{Zn}_2(\text{dmtc})_4$ molecules did not

appear to trap Hdmtc in IR/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur cures.¹⁰ It was postulated that $\text{Zn}_2(\text{dmtc})_4$ formed ZnS on decomposition, which would be unreactive towards Hdmtc.

This article reports on the $\text{Zn}_2(\text{dmtc})_4$ accelerated sulfur vulcanization of TME.

EXPERIMENTAL

Materials

Tetramethylthiuram disulfide (TMTD) (Orac TMTD, chemical purity 97%, Orchem, SA), tetramethylthiuram monosulfide (TMTM) (vulkacit Thiuram MS, chemical purity 97.9%, Bayer, Germany), tetramethylthiourea (TMTU) (chemical purity 98%, Aldrich Chemical Co., Milwaukee, WI), $\text{Zn}_2(\text{dmtc})_4$ (vulkacit L, active ingredient 95%, Bayer, Germany), and TME (chemical purity 99+%, Aldrich Chemical Co.).

The compositions of mixes used in model compound vulcanization are shown in Table I (1 mL TME = 0.709 g). The procedures for model compound vulcanization and product analysis have been described.^{20,21}

The concentrations of reactants, intermediates, and products are expressed in terms of the initial mol concentration of reactant, i.e., as the mol % reactant remaining, or mol % intermediate/product formed from that reactant.

RESULTS AND DISCUSSION

The Role of Sulfur in $\text{Zn}_2(\text{dmtc})_4$ Reactions

$\text{Zn}_2(\text{dmtc})_4$ is not a vulcanizing agent, i.e., it cannot crosslink unsaturated elastomers on its own, but the introduction of sulfur into a $\text{Zn}_2(\text{dmtc})_4$ formulation

Table I Compositions of Mixtures Reacted

| Composition | Mass (g) | Mol Ratio |
|--|----------|-----------|
| a) TME/ $\text{Zn}_2(\text{dmtc})_4$ /Sulfur | | |
| TME | 0.71 | 34 |
| $\text{Zn}_2(\text{dmtc})_4$ | 0.08 | 1 |
| Sulfur | 0.06 | 1 |
| b) TME/ $\text{Zn}_2(\text{dmtc})_4$ /Sulfur/ ZnO | | |
| TME | 0.71 | 34 |
| $\text{Zn}_2(\text{dmtc})_4$ | 0.08 | 1 |
| Sulfur | 0.06 | 1 |
| ZnO | 0.02 | 1 |

leads to the formation of a crosslinked network. $Zn_2(dmtc)_4$ is unreactive on heating in the presence of the model compound, but monosulfidic pendent groups and Hdmtc are detected when mixtures of TME/ $Zn_2(dmtc)_4$ /sulfur are heated at 130°C for preset time periods (Figs. 1 and 2).

No reaction was observed on heating $Zn_2(dmtc)_4$ (approx. 1 g) with dimethylamine (Me_2NH ; approx. 0.5 mL) in a sealed tube at 150°C for 15 min. Reaction occurred when a $Zn_2(dmtc)_4$ /sulfur mixture (1:1 mol ratio, approx. 1 g) was heated with Me_2NH , and Hdmtc and TMTD were formed as major products. TMTD was a minor product.

Clearly, the presence of sulfur facilitates interaction between $Zn_2(dmtc)_4$ and labile hydrogens, including the hydrogens on the rubber chain or model olefin. We have reported²² previously that there was no indication of an interaction between $Zn_2(dmtc)_4$ and sulfur in the absence of model compounds or compounds containing a labile hydrogen, and it was concluded that zinc perthiomercaptides are not formed from the reaction of $Zn_2(dmtc)_4$ with sulfur prior to vulcanization.

Pendent Group Formation

Monosulfidic pendent groups are detected in low concentrations in the early stages of vulcanization of TME with $Zn_2(dmtc)_4$ and sulfur (Fig. 2). No higher sulfur rank pendent groups are detected. The formation of monosulfidic pendent groups is accompanied by the simultaneous formation of Hdmtc. The presence of the two species indicates that crosslinking may be preceded by the formation of pendent groups.

In the reaction of TMTD with sulfur, sulfur atoms are added sequentially to TMTD to form tetra-

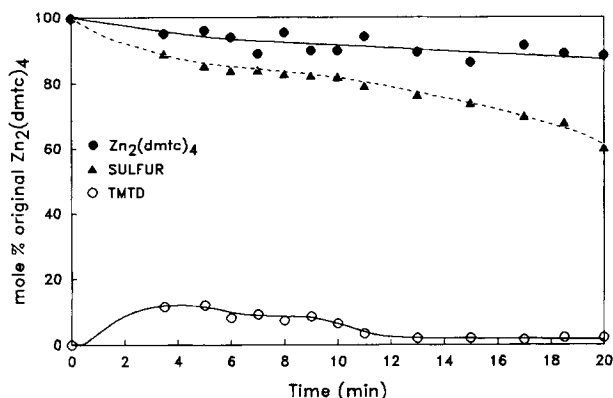


Figure 1 HPLC analyses of reactants and products in TME/ $Zn_2(dmtc)_4$ /sulfur vulcanization.

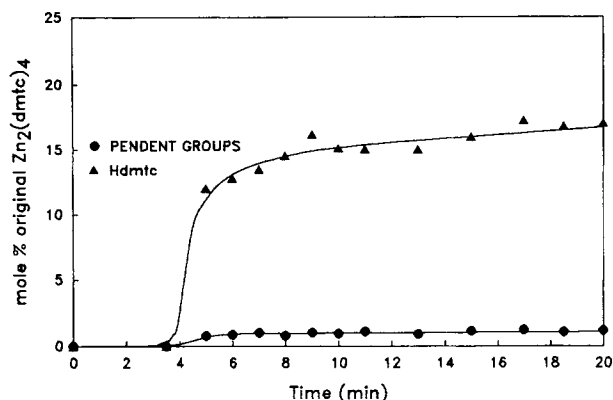


Figure 2 HPLC analyses of Hdmtc and pendent groups in TME/ $Zn_2(dmtc)_4$ /sulfur vulcanization.

methylthiuram polysulfides (TMTP).²¹ This gives rise to mainly low sulfur rank TMTP. TMTP react with the model olefin or rubber chain and, consequently, pendent groups of low sulfur rank are formed in TME/TMTD/sulfur vulcanization.²⁰ The concentrations of TMTP and pendent groups that have a high sulfur rank are very low. Crosslinks are formed exclusively via reaction between pendent groups on neighboring chains (pendent group-pendent group reactions), facilitating the formation of crosslinked products of higher sulfur rank.²³

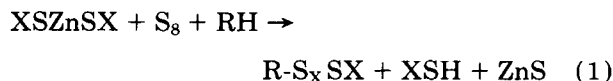
As will be shown below, crosslinking in $Zn_2(dmtc)_4$ -based vulcanization of TME occurs predominantly via reactions between pendent groups and free olefin (pendent group-chain reactions). Despite this, high sulfur rank crosslinked products are formed in TME/ $Zn_2(dmtc)_4$ /sulfur vulcanization. Calculations performed by Kruger^{10,19} on IR/TMTD/sulfur and IR/ $Zn_2(dmtc)_4$ /sulfur compounds, too, indicate that the sulfur rank of pendent groups are higher in $Zn_2(dmtc)_4$ -based vulcanizates.

The preceding remarks imply that pendent groups are formed via a different route than the sequential addition of sulfur atoms to the sulfurating agent.

It is proposed that pendent groups are formed in a concerted reaction involving a $Zn_2(dmtc)_4$ particle ($Zn_2(dmtc)_4$ has a low solubility in rubber),^{24,25} S_8 , and a model compound molecule, with the resultant formation of ZnS and Hdmtc. No true intermediates, including zinc perthiomercaptides, are formed in the reaction. Interaction will not occur in the absence of sulfur and no reaction between $Zn_2(dmtc)_4$ and sulfur, resulting in the formation of a sulfurated $Zn_2(dmtc)_4$ homolog (zinc perthiomercaptide), will occur without the presence of compounds containing a labile hydrogen, e.g., Me_2NH and TME.

Interaction of the octagonal S_8 ring with $Zn_2(dmtc)_4$ will result in a weakening of the Zn—

S bond. The presence of a model compound molecule will facilitate breaking of the bond, and removal or exchange of thiuram persulfenyl or thiuram sulfenyl groups will occur.



The sulfur rank of pendent groups will be high compared to pendent groups formed in TME/TMTD/sulfur vulcanization, because sequential addition of sulfur atoms does not occur. Pendent groups of high sulfur rank have been shown²³ to be much more reactive than groups of low sulfur rank, and crosslink formation occurs even in the early stages of $\text{Zn}_2(\text{dmtc})_4$ -based vulcanization (Fig. 3). Pendent groups of high sulfur rank will react immediately on formation and will participate in either crosslinking or exchange reactions with Hdmtc.

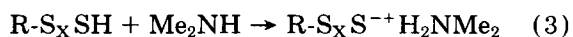
ZnS formation is characteristic of $\text{Zn}_2(\text{dmtc})_4$ -accelerated vulcanization.^{1,10,11,16,19} ZnS is reported to form rapidly in the early stages of cure due to $\text{Zn}_2(\text{dmtc})_4$ decomposition in the formation of pendent groups (reaction 1).

The Reactions of Hdmtc

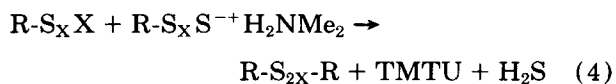
We have ascribed the delayed onset of crosslinking in TMTD-based cures in the absence of ZnO to the following reaction sequence.^{20,23} Hdmtc, liberated on pendent group formation, is stable under vulcanization conditions and participates in an exchange reaction wherein unreactive hydrogen terminated (thiol) pendent groups are formed.



Me_2NH , which forms via XS radicals once the TMTD concentration decreases, will reactivate thiol groups.



Crosslinks are formed via reaction between thiuram and dimethylammonium pendent groups, with the resultant formation of TMTU.



Hdmtc is produced early in the TME/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur vulcanization reaction, presumably during pendent group formation, and its con-

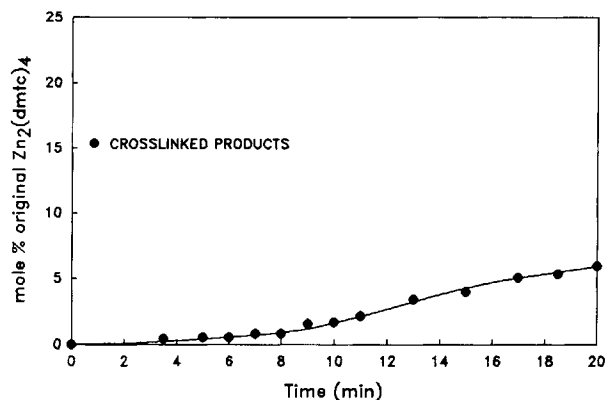


Figure 3 HPLC analyses of crosslinked products in TME/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur vulcanization.

centration subsequently remains constant for the duration of the reaction (Fig. 2). An exchange reaction, similar to that in the TME/TMTD/sulfur system, would lead to pendent groups being deactivated by the formation of thiol pendent groups and TMTD (reaction 2). TMTD is rapidly produced in the initial stages before Hdmtc is detected in the reaction mixture (Fig. 1). The exchange is very rapid and could be related to the high sulfur rank of pendent groups that would facilitate rapid exchange.

The formation of TMTD in the TME/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur vulcanization is limited (Fig. 1). These small amounts of TMTD would react with sulfur to form undetectably small concentrations of TMTP, which would, in turn, form pendent groups. While the pendent group-Hdmtc exchange would regenerate TMTD, its overall concentration decreases as the reaction progresses. Because of the low TMTD and TMTP concentrations, the concentration of thiuram radicals will be low and the formation of Me_2NH from the decomposition of sulfenyl radicals²³ will be negligible. Reactivation of thiol groups through reaction with Me_2NH (reaction 3) will not occur, and there is no apparent increase in the pendent group concentration due to the formation of dimethylammonium pendent groups (cf. Fig. 2 with reference 23). No TMTU is produced upon crosslinking.

A mixture of TME/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur was heated at 130°C. The reaction was stopped after 8 min and Me_2NH was added to the products in the reaction vessel. The mixture was allowed to stand for 1 h. A control experiment was prepared in a similar manner, with the exception that no Me_2NH was added to the contents of the reaction vessel. Thiol pendent groups are unreactive, but the addition of Me_2NH will result in the formation of dimethylammonium pendent groups²³ that are reactive and will

participate in crosslink formation (reactions 3 and 4). Comparison of the product analyses showed a marked increase in the number of crosslinks formed upon the addition of amine, indicating the existence of crosslinkable pendent groups on the model compound.

Neither TMTD nor Hdmtc is detected in TME/ $Zn_2(dmtc)_4$ /sulfur/ZnO vulcanization (Figs. 4 and 5). Hdmtc will rapidly react with ZnO to reform $Zn_2(dmtc)_4$,²⁰ and no pendent group-Hdmtc exchange reaction will take place. The absence of TMTD supports the contention that it is formed in the exchange reaction between Hdmtc and thiuram pendent groups.

$Zn_2(dmtc)_4$ is rapidly produced in TME/TMTD/sulfur/ZnS vulcanization via the reaction of Hdmtc and ZnS.²⁰ Note that the $Zn_2(dmtc)_4$ concentration does not decrease significantly in the TME/ $Zn_2(dmtc)_4$ /sulfur reaction (Fig. 1). ZnS, produced in the formation of pendent groups, will react with Hdmtc to reform $Zn_2(dmtc)_4$. ZnO reacts very readily with Hdmtc to form $Zn_2(dmtc)_4$, but addition of ZnO has no marked effect on the TME/ $Zn_2(dmtc)_4$ /sulfur vulcanization reaction, though it does result in a marginal increase in the number of crosslinks formed. The amount of ZnS formed from $Zn_2(dmtc)_4$ decomposition during pendent group formation will be limited, but will, nevertheless, aid in the removal of Hdmtc and will limit the formation of unreactive thiol pendent groups via Hdmtc exchange (reaction 2). The constant, low concentration of Hdmtc can, therefore, be ascribed to its removal in pendent group exchange reactions and in reaction with ZnS.

Formation of Crosslinks

In TME/TMTD/sulfur vulcanization the pendent group concentration increases until pendent group-

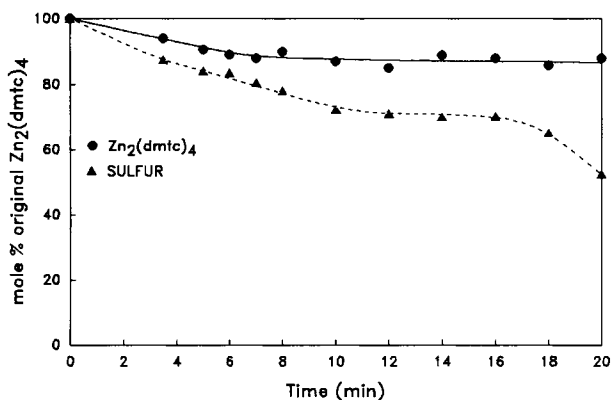


Figure 4 HPLC analyses of residual reactants in TME/ $Zn_2(dmtc)_4$ /sulfur/ZnO vulcanization.

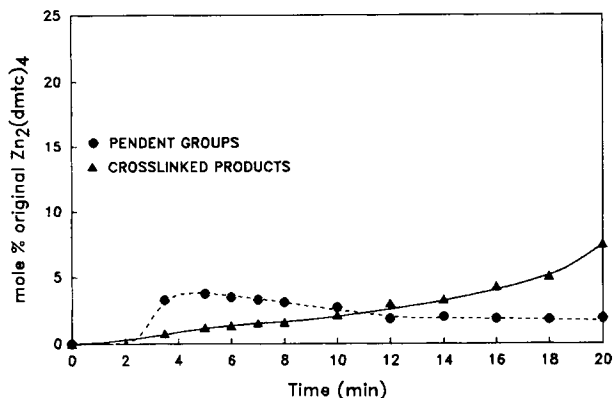
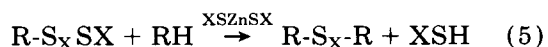


Figure 5 HPLC analyses of pendent groups and crosslinked products in TME/ $Zn_2(dmtc)_4$ /sulfur/ZnO vulcanization.

pendent group crosslinking occurs²³ (reaction 4). However, the addition of $Zn_2(dmtc)_4$ leads to an immediate decrease in the pendent group concentration,²³ suggesting that $Zn_2(dmtc)_4$ acts as a catalyst. In $Zn_2(dmtc)_4$ -accelerated vulcanization a high concentration of pendent groups is never reached and it is suggested that $Zn_2(dmtc)_4$ catalyzes crosslink formation between a pendent group and an allylic hydrogen on the model olefin (or rubber chain)



The onset of crosslinking in TME/ $Zn_2(dmtc)_4$ /sulfur vulcanization is early, but the rate of crosslinking is gradual because a high concentration of pendent groups is never reached (Fig. 3). The formation of crosslinks in the presence of such low concentrations of pendent groups is a further indication that pendent group-chain rather than pendent group-pendent group crosslinking occurs. This is consistent with earlier findings¹³ that $Zn_2(dmtc)_4$ participates directly in the crosslinking reaction by facilitating interaction between pendent groups and olefin molecules.

CONCLUSIONS

$Zn_2(dmtc)_4$ reacts with the octagonal sulfur ring and the model olefin to form thiuram pendent groups, Hdmtc and ZnS. The sulfur rank of the pendent groups formed is high compared to TMTD-based cures, where sulfur atoms are added sequentially to TMTD in the formation of the active sulfurating agent.

Exchange reactions between thiuram pendent groups and Hdmtc is limited because ZnS, produced in the formation of pendent groups, reacts with Hdmtc to reform $Zn_2(dmte)_4$. The removal of Hdmtc limits the formation of unreactive thiol pendent groups.

The onset of crosslinking is very early, and crosslink formation proceeds via a $Zn_2(dmte)_4$ -catalyzed reaction between pendent groups and free olefin. No TMTU is produced upon crosslinking, as the formation of Me_2NH from the decomposition of thiuram sulfenyl radicals is negligible and dimethylammonium pendent groups are not produced.

The reaction between ZnS and Hdmtc is less facile in rubber cures, and will lead to the increased formation of thiol pendent groups via thiuram pendent group-Hdmtc exchange. Reactivation of unreactive thiol pendent groups by Me_2NH does not occur in $Zn_2(dmte)_4$ -based vulcanization, and any pendent groups converted to thiols are lost to the crosslinking process. This will result in lower crosslink densities in the final vulcanizates.

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REFERENCES

1. L. Bateman, C. G. Moore, M. Porter, and B. Saville, *The Chemistry and Physics of Rubber-like Substances*, L. Bateman, Ed., Maclaren, London, 1963.
2. Y. Kawaoka, *Chem. Abstr.*, **44**, 2787i (1950).
3. R. E. Morris, *Ind. Eng. Chem.*, **34**, 503 (1942).
4. J. P. Fackler and J. A. Fetchin, *J. Am. Chem. Soc.*, **92**, 2912 (1970).
5. J. P. Fackler, J. A. Fetchin, and D. C. Fries, *J. Am. Chem. Soc.*, **94**, 7323 (1972).
6. H. Shizuka and T. Azami, *Chem. Abstr.*, **67**, 22666g (1967).
7. D. Craig, W. L. Davidson, A. E. Juve, and I. G. Geib, *J. Polym. Sci.*, **6**(1), 1 (1951).
8. B. Saville, *J. Polym. Sci.*, **40**, 275 (1959).
9. M. M. Coleman, J. R. Shelton, and J. L. Koenig, *Rubber Chem. Technol.*, **46**, 957 (1973).
10. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **45**, 755 (1992).
11. J. R. Wolfe, *Rubber Chem. Technol.*, **41**, 1339 (1968).
12. J. R. Shelton and E. T. McDonel, *Rubber Chem. Technol.*, **33**, 342 (1960).
13. P. Versloot, J. G. Haasnoot, J. Reedijk, M. van Duin, E. F. J. Duynstee, and J. Put, *Rubber Chem. Technol.*, **67**(2), 252 (1994).
14. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **45**, 563 (1992).
15. H. Krebs, *Rubber Chem. Technol.*, **30**, 962 (1957).
16. J. R. Wolfe, *Encycl. Polym. Sci. Technol.*, **14**, 740 (1971).
17. M. Porter, *Organic Chemistry of Sulfur*, S. Oae, Ed., Plenum Press, New York, 1977.
18. C. G. Moore and B. R. Trego, *J. Appl. Polym. Sci.*, **8**, 1957 (1964).
19. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **45**, 1545 (1992).
20. M. Geysler and W. J. McGill, *J. Appl. Polym. Sci.*, **60**, 431 (1996).
21. M. Geysler and W. J. McGill, *J. Appl. Polym. Sci.*, **55**, 215 (1995).
22. M. Geysler and W. J. McGill, *J. Appl. Polym. Sci.*, **60**, 425 (1996).
23. M. Geysler and W. J. McGill, *J. Appl. Polym. Sci.*, **60**, 439 (1996).
24. J. A. Brydson, *Rubber Chemistry*, Applied Science Publishers, London, 1978.
25. M. Porter, *The Chemistry of Sulfides*, A. V. Tobolsky, Ed., Interscience Publishers, New York, 1968, p. 165.
26. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **45**, 749 (1992).

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