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# Tetramethylthiuram Disulfide Vulcanization of Extracted Rubber. V. Low Molecular Products and the Mechanism of Zinc Oxide Activation

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The essential features of TMTD vulcanization, as revealed by compounding studies, were discussed in Paper I of this series. Thus, TMTM, a product of the TMTD vulcanization, and an active accelerator of sulfur vulcanization, was found to be an inhibitor, and ZnDMDC, a main product of TMTD vulcanization, in the presence of ZnO was found to be devoid of activating properties. As a replacement for ZnO, which is a potent activator, ZnDMDC displayed only mild activating effects. Zinc palmitate was even more potent than ZnO. Zinc sulfide was somewhat less active than ZnO. Palmitic acid and DMADC had little or no effect on the cure. The second paper reported that TMTD could be prepared in good yield by the reaction of TMTM with sulfur and also, as a result of radiosulfur techniques, that the four sulfur atoms in the TMTD molecule are chemically identical. Paper II also reported that ZnO reacted with TMTD to form sulfur and ZnDMDC in good yield. Other reactions of TMTD were discussed. Paper III, in presenting a short path distillation technique for studying vulcanizates, reported that the nearly complete removal of zinc from the TMTD vulcanizate is not accompanied by devulcanization. Paper IV reported on the behavior of rubber as an acid. This behavior results in the liberation of palmitic acid from zinc palmitate. From the comparison of the reaction of TMTD with acids and the reaction of rubber with TMTD, it was inferred that rubber is an OH-containing acid. Acids in the work reported were found to react rather slowly with TMTD to form dimethylamides and sulfur in good yield. The acidic nature of rubber did not seem to be great enough to contribute in any fundamental way to the vulcanization process.

The present paper describes further studies of the TMTD vulcanization problem.

## RADIOACTIVE TMTD PRESS VULCANIZATION

The stock used in one experiment consisted of extracted crepe 100, radioactive TMTD 4.00, and ZnO 5.00. Four sheets (wt. 15.285 g.), 2.25 × 4.25 × 0.025 in., were press cured for 45 minutes at 280 °F. Then they were subjected to short-path distillation at 0.3 mm. for 4.5 hours. The distillate which had collected during this time was separated into TMTU (0.025 g.), TMTM (0.045 g.) and ZnDMDC (0.275 g., m.p. 246–248°). A further period of distillation for 5.5 hours at 0.001 to 0.0002 mm. yielded 0.115 g. of nearly pure ZnDMDC which melted at 237–240°.

## TABLE I

| Sample | Weight, g. | Moles | Radioactivity of 5-cm.$^2$ area sample corrected to infinite thickness, c/m | Theoretical count assuming random distribution of S, c/m |
|---|---|---|---|---|
| 1. Radiosulfur............ | — | — | 22,150 | — |
| 2. Radio TMTD used in compound........... | 0.561 | 0.00234 | 6,350 | 6740 |
| 3. Stock before distillation. | 15.285 | — | 147 | — |
| 4. Stock after distillation.. | 14.765 | — | 38 | 53.7 |
| 5. Total material distilled from stock.......... | 0.520 | — | — | — |
| 6. TMTM isolated....... | 0.045 | 0.00022 | 5,700 | 5500 |
| 7. TMTU isolated........ | 0.025 | 0.0001 | 2,530 | 2880 |
| 8. ZnDMDC, m.p. 246–248° | 0.275 | — | 5,630 | 5000 |
| ZnDMDC, m.p. 237–240° | 0.115 | 0.00128 | — | — |
| 9. "ZnS" sulfur by analysis.................. | 0.0252 | 0.000786 | — | — |
| 10. Organic sulfur by analysis (total S − "ZnS" S). | 0.0414 | 0.00129 | — | — |

Table I constitutes a summary of the experiment and includes the weights and radioactivities of the starting materials and of the products. The activity of the $S^*_8$ used in making the radioactive TMTD is included in Table I. Starting with this sulfur (4 atoms) having an activity of 22,150 counts per minute and TMTM (1 mole), the calculated random activity of the TMTD equals $22{,}150 \times 4/7 \times 53.3\% = 6740$ c/m since TMTD contains 53.3% sulfur and since the reaction involves the intermingling of the three sulfur atoms in the TMTM molecule with the four starting sulfur atoms. The final two columns of the table present the radioactivity data compiled in the course of the experiment. Column 4 contains the experimental counts deduced for a sample 5 cm.$^2$ in area and of thickness greater than the maximum range of $S^{35}$ beta rays. Column 5 lists the theoretical counts that would be expected on the assumption that the four sulfur atoms in the TMTD molecule are chemically equivalent and distribute themselves equally in the resulting products.

The vulcanizate after distillation was found to contain 0.45% total sulfur. Based on the sulfur content, the calculated random activity of the distilled stock is 53.7 c/m. The found value is in fair agreement if the 60 c/m background of our counter is taken into consideration. The experimental activities of the stock and the other substances check the theoretical values sufficiently well to lead to the conclusion that the isotopic sulfur atoms of the TMTD molecules distributed themselves uniformly among the products. The organic sulfur of the distilled vulcanizate (see column 3 in Table I) amounted to 0.00129 mole or to 0.55 atom of sulfur per mole of TMTD compounded. This value is not in agreement with the usual idea that one atom of sulfur in the TMTD molecule is available for vulcanization in the presence of ZnO. If the "ZnS" sulfur is included with the organic sulfur as an essential part of the vulcanizate, then 0.89 atom of the four TMTD sulfur atoms may be considered to have become "available."

There seems to be no reason for considering the "ZnS" sulfur any more essential than the ZnDMDC sulfur which was distilled from the vulcanizate. Moreover, in the third paper, it was shown that nearly all the "ZnS" sulfur could be removed without devulcanization. Bedford and Gray[1] noted with unextracted rubber that the "ZnS" sulfur was from one-fourth to one-third the combined sulfur and they, as in the present research, used the ether–HCl method for determining this type of combined sulfur. The application of the short path distillation and zinc removal techniques were tested in a stock consisting of unextracted crepe 100.0, TMTD 4.00 and ZnO 2.00. The results shown in Table II show that ZnS is not necessary as a product of vulcanization, since in this stock it was not even formed and yet the stocks had good properties even after complete removal of "ZnS" sulfur and nearly complete removal of zinc. Had ZnS been formed it would have remained after the zinc removal treatment.

TABLE II

| Treatment | Tensile, p.s.i. | Elong., % | % Zn | "ZnS" S | Org. S |
|---|---|---|---|---|---|
| After vulc. 45 ft. at 280 °F.... | 3300 | 775 | 1.5 | — | — |
| After short-path distillation of above stock.............. | 3500 | 760 | 0.94 | 0.03 | 0.36 |
| After one Zn removal treatment............... | 3500 | 780 | 0.14 | 0.000 | 0.35 |
| After two Zn removal treatments.............. | 3600 | 760 | 0.017 | — | — |

The data in Table II seem to refute the idea held by some that the state of vulcanization of rubber is due to the presence of zinc in the vulcanizate. The favorable effects of zinc oxide and zinc salts must then be due to their reactions during vulcanization.

The combined molar quantities of ZnDMDC, TMTM, and TMTU shown in Table I account for about 67% of the TMTD compounded. No TMTD or free sulfur could be isolated from or detected in the distillate. The malodorous gaseous products, including $H_2S$ and $CS_2$, were not isolated. The small amounts of TMTU and TMTM isolated from the distillate were estimated to represent one-half and two-thirds, respectively, of the amounts of these substances actually present. With these corrections the amounts of ZnDMDC, TMTM, and TMTU account for 77% of the TMTD compounded.

The vulcanizate before and after distillation displayed a tensile of about 4000 p.s.i. and an elongation of about 750%. After short path distillation it aged rapidly, losing about half its strength during six months. This behavior is in sharp contrast to the usual good aging of the TMTD unextracted rubber compounds.

When a TMTD 4 PHR-ZNO 5 PHR stock was given a "semi-cure" of 20 minutes at 280°F. and then short path distilled, the yield of TMTM was about three times the amount reported in Table I. This result, coupled with the inhibiting effect of TMTM on TMTD vulcanization, lends support to the idea that TMTD acts by disproportionation into TMTM and a polysulfide as in reaction I.

$$2\,(CH_3)_2NC(S)SSC(S)N(CH_3)_2 \rightleftharpoons (CH_3)_2NC(S)SC(S)N(CH_3)_2 + (CH_3)_2NC(S)SSSC(S)N(CH_3)_2 \qquad (I)$$

The tetramethylthiuram tri-, tetra-, and pentasulfides could not be isolated by Levi[3] though he succeeded in separating TMTD and the hexasulfide from the reaction product of ZnDMDC and $S_2Cl_2$. He found that the reaction product of DMADC with $S_2Cl_2$ contained TMTD and sulfur ($S_8$) but was unable to isolate the hexasulfide from it. DMADC, being able to undergo interchange with various radio sulfur compounds (see Paper II), thus may catalyze more effectively than ZnDMDC the disproportionation of the thiuram sulfides and here may catalyze the disproportionation of tetrasulfide initially formed into TMTD and $S_8$. This catalytic action of the ZnDMDC appears to enable the reaction to go only as far as the hexasulfide.

The polysulfides, thus are more unstable than TMTD and $S_8$. The trisulfide, for example, should be able to dehydrogenate the rubber to re-form TMTD and liberate $H_2S$ as in reaction II if chemical reactivity and instability go hand in hand. The rubber simultaneously may become cross-linked in this operation but this type of reaction is not known to be very effective for vulcanization. Another possibility that from our viewpoint is attractive is that the polysulfide is able to form TMTM and a copolymer of rubber with diatomic sulfur fragments, $S_2$, by reaction IIa. This copolymer under appropriate conditions could liberate $H_2S$, a substance known to be reactive toward TMTD, and in this study found to be reactive toward TMTM.

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 + \text{rubber} \longrightarrow (CH_3)_2NC(S)SSC(S)N(CH_3)_2 + H_2S + \text{dehydrogenated rubber} \qquad (II)$$

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 + \text{rubber} \longrightarrow (CH_3)_2NC(S)SC(S)N(CH_3)_2 + \text{copolymer of } S_2 \text{ and rubber} \qquad (IIa)$$

## REACTION OF HYDROGEN SULFIDE WITH TMTD AND WITH TMTM

From Bedford and Gray's work it is known that TMTD and $H_2S$ form free sulfur and dimethyldithiocarbamic acid according to reaction III, the

$$\mathrm{(CH_3)_2NC(S)SSC(S)N(CH_3)_2 + H_2S \longrightarrow 2\ (CH_3)_2NC(S)SH + (S)} \qquad \text{(III)}$$

acid being unstable. Because of their reactivity toward rubber the sulfur atoms would not be expected to polymerize to $S_8$ in rubber. Rather they would be expected (*a*) to dehydrogenate the rubber (compare reaction II), (*b*) to copolymerize with rubber to form a vulcanizate (compare reaction IIa), or (*c*) to react reversibly with TMTM or TMTD to form higher sulfides. In the early stages of the process, when ample TMTM molecules are available, the re-forming of TMTD molecules should be frequent. The possibility that the abundance of TMTM in the vulcanization process is lowered by the liberation of $H_2S$ seemed to be worthy of study. A discussion of the reaction of $H_2S$ with TMTM now follows.

The decomposition of TMTM at 140° in the absence of rubber was found to be negligible, but when a slow stream of $H_2S$ was passed for one hour through the molten compound (10.4 g.) at this temperature, reaction occurred with the evolution of $CS_2$ (89%) and the sublimation of DMADC. The final product after distilling off the DMADC (1.29 g., 15.5%) was TMTU (85%). Reactions IV and V evidently are the main over-all reactions.

$$\begin{array}{llr} \mathrm{(CH_3)_2NC(S)SC(S)N(CH_3)_2 + H_2S} & \longrightarrow \mathrm{2\ (CH_3)_2NC(S)SH} & \\ & \qquad\qquad\qquad\quad \downarrow & \\ & \mathrm{CS_2 + (CH_3)_2NC(S)SNH_2(CH_3)_2} & \text{(IV)} \\ \mathrm{(CH_3)_2NC(S)SC(S)N(CH_3)_2} & \longrightarrow \mathrm{CS_2 + (CH_3)_2NC(S)N(CH_3)_2} & \text{(V)} \end{array}$$

The mechanism by which $H_2S$ might cause reaction V was found to be through the reaction of TMTM with DMADC produced by reaction IV. Thus, 9.35 g. (0.045 mole) of TMTM and 1.66 g. (0.01 mole) of DMADC were heated in a distilling flask to 140° in an oil bath for one hour. During this time a slow stream of $N_2$ was passed through the mixture and thence into a Dry Ice trap. The Dry Ice trap was found to contain 3.02 g. (88%) of $CS_2$. The distilling flask was rinsed out with benzene to give a slurry which was then filtered. Solid DMADC amounting to 1.49 g. (90% recovery) was thus obtained. The filtrate was distilled to supply 5.95 g. (100%) of TMTU. Since Delépine[6] found that TMTM and dimethylamine react to form TMTU and DMADC, the action of the salt on TMTM may be ascribed to its decomposition into $CS_2$ and dimethylamine. This action is expressed by equations Va and Vb.

$$\mathrm{(CH_3)_2NC(S)SC(S)N(CH_3)_2 + 2\ HN(CH_3)_2} \longrightarrow$$

$$\mathrm{(CH_3)_2NC(S)N(CH_3)_2 + (CH_3)_2NC(S)SNH_2)CH_3)_2} \qquad \text{(Va)}$$

$$\mathrm{(CH_3)_2NC(S)SNH_2(CH_3)_2 \rightleftharpoons CS_2 + 2\ HN(CH_3)_2} \qquad \text{(Vb)}$$

As von Braun reported, DMADC may be distilled at reduced pressure. It may be assumed, however, that the vapor over the distilling salt contains only $CS_2$ and $(CH_3)_2NH$ molecules. Pure DMADC may be quickly heated to about 140° without melting, at which temperature violent decomposition into $CS_2$ and $(CH_3)_2NH$ ensues. Impurities in small amount lower the "melting point." The heating of dithiocarbamates of primary amines produces thioureas and hydrogen sulfide in good yield but we have found in the case of the secondary amine salt DMADC that this type of reaction at 140° is not appreciable even in the presence of sulfur or of $H_2S$.

In a further examination of the behavior of DMADC it was heated at 140° in a sealed tube with $CS_2$ for one hour. The experiment yielded free sulfur in 74% yield and dimethylthioformamide in 89% yield, based on reaction XII. This was an unexpected reaction and immediately DMADC

$$(CH_3)_2NC(S)SH \longrightarrow (S) + (CH_3)_2NC(S)H \qquad \text{(XII)}$$

(4 PHR) was milled into extracted rubber and the mixture heated with $CS_2$ in the press at 318°F. There was no evidence of vulcanization and no odor of dimethylthioformamide. Therefore, it may be presumed that sulfur and the thioformamide were not liberated in the rubber.

Obviously, just because a reaction liberates sulfur in the absence of rubber, it does not follow that the reactants when heated with rubber will cause vulcanization or liberate sulfur. In this connection, though palmitic acid, zinc oxide, and zinc palmitate all liberate sulfur from TMTD, the reaction is too slow to account for vulcanization when these reagents and TMTD are heated with rubber. Actually, as stated in Paper I, palmitic acid has little effect on TMTD vulcanization, whereas the zinc compounds are vigorous activators.

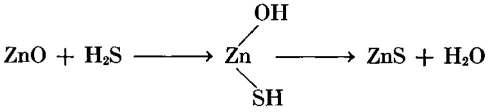
Dimethylthiocarbamyl dimethylsulfeneamide $(CH_3)_2NC(S)SN(CH_3)_2$ and dimethyl aminosulfide $(CH_3)_2NSN(CH_3)_2$ which are reaction products of TMTD (compare Paper II) were found to be mild vulcanizing agents when heated with rubber in a concentration of 4 PHR for 45 minutes at 287°F. The vulcanizates were transparent and similar in properties to rubber cured with peroxides. The sulfeneamide was also tested in the presence of 5 PHR of ZnO, but then it failed to cause vulcanization. This result seems to eliminate the sulfeneamide as a possible intermediate in TMTD vulcanization but it is worthy of further study.

## THE ACTIVATING EFFECT OF ZINC COMPOUNDS

An explanation of the beneficial effects of zinc compounds in TMTD vulcanization may now be examined. This explanation involves the action of hydrogen sulfide. Thus, it is to be noted at once that the reaction of dimethyldithiocarbamic acid produced by reactions III and IV with ZnO would form ZnDMDC, a stable end-product. This reaction is important because TMTM is used up by reactions IV and V and, to the extent that these occur, TMTM is not available for reversing reaction I or for the prevention of higher thiuram polysulfide formation. $H_2S$ is used up in IV but not in V. Bedford and Gray[1] found the complete removal of $H_2S$ from the system to be unfavorable because TMTD vulcanization occurs by way of reaction III, but as shown by Booth and Beaver[2,4] the retarding or inhibiting action of $H_2S$ in rather high concentration is quite general.

The pronounced tendency of $H_2S$ to react superficially with ZnO was also mentioned by Bedford and Gray.[1] Their report that the reaction to form water is rapid, though incomplete, is confirmed by our experiments. When 16.30 g. (0.2 mole) of ZnO were treated with a slow stream of $H_2S$ there was an almost immediate rise in temperature of about 10°. Water was evolved and the increase in weight after 40 minutes amounted to 0.39 g. During air drying for 48 hours 0.06 g. of this increase was lost. As shown by the x-ray diffraction technique, the product contained a small amount of ZnS and an electron diffraction study showed the surface to be ZnS. Calculated on the equation $ZnO + H_2S \rightarrow ZnS + H_2O$, the net increase in weight amounts to the formation of 0.02 mole (10% conversion) of ZnS. Very little reaction resulted during further treatment with $H_2S$.

That zinc compounds such as the oxide, palmitate, dithiocarbamate, and even the sulfide can contribute a buffering action on the concentration of hydrogen sulfide becomes evident by considering the distribution of zinc ions among the various anions that may be present in a TMTD-rubber mixture. The following reactions are formulated for such consideration.



$$ZnO + H_2S \longrightarrow Zn\begin{matrix}\diagup OH\\ \diagdown SH\end{matrix} \longrightarrow ZnS + H_2O \qquad (VI)$$

$$Zn[OC(O)C_{15}H_{31}]_2 + H_2S \rightleftharpoons Zn[OC(O)C_{15}H_{31}]SH + HOC(O)C_{15}H_{31} \qquad (VII)$$

$$ZnS + H_2S \rightleftharpoons Zn(SH)_2 \qquad (VIII)$$

$$Zn(SH)_2 + Zn[SC(S)N(CH_3)_2]_2 \rightleftharpoons 2\,Zn(SH)SC(S)N(CH_3)_2 \qquad (IX)$$

$$Zn[SC(S)N(CH_3)_2]_2 + H_2S \rightleftharpoons Zn(SH)SC(S)N(CH_3)_2 + HSC(S)N(CH_3)_2 \qquad (X)$$

$$HSC(S)N(CH_3)_2 + ZnS \rightleftharpoons Zn(SH)SC(S)N(CH_3)_2 \qquad (XI)$$

A further series of reactions of rubber as an acid (see Paper IV) could be considered in relation to its effect on the $H_2S$ concentration. Such an acid would enhance the behavior of the zinc compounds as buffers. Since the reactions leading to the formation of $Zn(SH)SC(S)N(CH_3)_2$ would not proceed to completion to anything like the extent of the reactions of ZnO and zinc palmitate with $H_2S$, the action of ZnS and ZnDMDC as activators would be expected to be relatively weak. This expectation was confirmed experimentally (see Paper I), *i.e.*, ZnS and ZnDMDC were found to be weak activators in comparison to ZnO and zinc palmitate.

The buffering action of the zinc compounds on the $H_2S$ concentration appears to allow the formation of cross-links containing one or two sulfur atoms as a result of reaction III, or as a result of reaction of the thiuram trisulfide with $H_2S$ to liberate sulfur atoms two at a time. This follows because, in the absence of the buffering effect, the TMTM would be largely destroyed by reactions IV and V and thiuram polysulfides containing many sulfur atoms, *e.g.*, the hexasulfide of Levi would result. These in comparison to the trisulfide should introduce more sulfur atoms per cross-link.

The availability of $H_2S$ during TMTD vulcanization, being limited by the reactions just discussed, is believed to be so slight as to result in the addition of little of it to the polyisoprene double bonds. Hence, such addition could lead to the formation at most of only a few cross-links.[9]

Because of the possible relation of zinc activation and TMTM consumption the fate of TMTM in vulcanization was examined in a stock comprising extracted rubber 100, PBNA 1.00, TMTM 2.60, ZnO 5.00, and radiosulfur 0.40. Six sheets having the dimensions 2.25 × 4.25 × 0.025 in. were cured 10 minutes at 280°F. These sheets, which were fully cured, were then short path distilled for five hours at 133°C. and at a pressure less than 0.001 mm. The products isolated from the distillate were TMTM (43% of that started with), ZnDMDC, and PBNA. The yield in moles of ZnDMDC amounted to 74% of the number of moles of unrecovered TMTM. The radioactivities of the recovered TMTM, the ZnDMDC, and the starting sulfur are presented in Table III.

## TABLE III

### RADIOACTIVITIES OF SULFUR AND PRODUCTS OF THE TMTM RADIOSULFUR VULCANIZATION

| Substance | Radioactivity, c/m Found | Radioactivity, c/m Calcd.[a] |
|---|---|---|
| Radiosulfur | 22,150 | — |
| TMTM | 1,260 | 2540 |
| ZnDMDC | 3,200 | 2320 |

[a] Assuming random distribution of the sulfur isotopes.

The radioactivity of the ZnDMDC in Table III is much too high and that of the recovered TMTM much too low for a random distribution of the isotopic sulfur atoms. In the TMTD synthesis, TMTM and $S_8$ are able to form a thiuram disulfide. The initial stage in this synthesis may be presumed to be a much higher polysulfide. It may also be presumed that this higher polysulfide could occur as an early stage in TMTM-$S_8$ vulcanization. If the reaction of the thiuram polysulfide with the rubber is irreversible and fast as compared to the interchange of TMTM with thiuram polysulfide, then, in agreement with observation, the recovered TMTM should be less active than would be the case for a random distribution of the sulfur atoms. On the other hand, since it is known that TMTM and ZnO do not react with each other at curing temperatures, the formation of ZnDMDC with an activity higher than that corresponding to a random distribution of the sulfur atoms is significant. The dithiocarbamic acid liberated by reaction IV would be radioactive in proportion to the activity of the $H_2S$ produced from the vulcanizate. This activity alone would not be sufficient to account for the high activity observed for the ZnDMDC. However, a DMADC catalyzed interchange (see Paper II) of the ZnDMDC initially formed with $S^*_8$ or with sulfur-rubber copolymer would do so. Some activity might also come from ZnDMDC formed by reaction of zinc oxide with hot thiuram polysulfides. On this basis it appears that thiuram polysulfide, $H_2S$, DMADC, and dimethyldithiocarbamic acid are essential intermediate products of the vulcanization reaction.

We have confirmed the report of Cummings and Simmons[5] that a TMTD stock may have similar stress–strain properties to one made by replacing the TMTD with a molecularly equivalent amount of TMTM and sulfur. Our TMTD stock containing 3.00 PHR and TMTD and 5 PHR of ZnO was fully cured after 40 minutes at 280°F., whereas the corresponding TMTM 2.60 PHR, sulfur 0.40 PHR, and 5 PHR of ZnO required only 10 min. at the same temperature. We found the organically combined sulfur of the short path distilled TMTM-sulfur stock to be 0.5% or nearly twice that of the TMTD stock which contained 0.28% organically combined sulfur. The "ZnS" sulfur content was not more than about 0.1%. This result is explainable on the basis that although the number of cross-links (including C to C links) in one stock may be about equal to that in the other stock, the number of sulfur atoms per cross-link is greater in the case of the TMTM-$S_8$ stock. The poor quality of the zinc free TMTD-4.00 PHR vulcanizate also may be ascribable to the presence of a plurality of sulfur atoms per cross-link formed as a result of the reaction of higher polysulfides with the rubber.

## APPLICATION TO THE THEORY OF VULCANIZATION

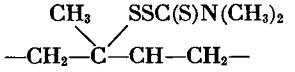
A complete theory of the structure of TMTD vulcanizates is beyond the scope of the present paper and this must, therefore, apply also to the mechanism of the vulcanization. However, a short discussion here may be warranted. The research up to this time indicates that TMTD alone is not able to fully vulcanize rubber unless a very large concentration is employed or even in the presence of ZnO if excess TMTM is present. Since TMTM should have no effect on the dissociation of TMTD into dithiocarbamate radicals it is inferred, therefore, that these radicals if formed do not account for TMTD vulcanization. This effect of TMTM, however, in reducing the higher thiuram polysulfides to the disulfide stage, where vulcanization capacity is repressed to the degree that reactions other than vulcanization become predominant, suggests that sulfur atoms, one or two at a time, may copolymerize with polyisoprene. Carbon to carbon bonds (suggested by Farmer[7]) could also be established. The source of the sulfur atoms may be by reaction III or the dissociation fragments of the thiuram trisulfide as indicated by reactions XIII and XIV (for pairs of sulfur atoms). Reaction XIV also accounts for the formation of TMTM.

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 \rightleftharpoons \underset{\text{I}}{(CH_3)_2NC(S)SS\cdot} + \underset{\text{II}}{\cdot SC(S)N(CH_3)_2} \qquad \text{(XIII)}$$

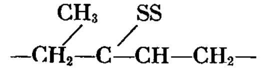
$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 \rightleftharpoons \cdot SS\cdot + (CH_3)_2NC(S)SC(S)N(CH_3)_2 \qquad \text{(XIV)}$$

The thiuram trisulfide, understandably, has not been isolated, presumably because of its instability.[3] This compound would not be capable of resonance stabilization to anything like the degree that obtains in the case of the thiuram disulfide (compare Paper II). It is presumed that a main reaction of radical II is dimerization to form TMTD which seems to be a relatively ineffective vulcanizing agent. Radical I could initiate polymerization by reacting with polyisoprene to form radical III. This radical

III



$$-CH_2-\overset{CH_3\ \ SSC(S)N(CH_3)_2}{C}-CH-CH_2-$$



$$-CH_2-\overset{CH_3\ \ SS}{C}-CH-CH_2-$$

IV

could dimerize to form a cross-link or it could react with II to produce IV and TMTM. The polymerization of IV would form a chain of cross-links. Radicals III and IV also are presumed to be active enough to initiate polymerization of polyisoprene segments thus forming C to C bonds. In this way a multiplicity of cross-link chains could be formed. It is to these polymer and copolymer chains, more or less normal to the rubber chains, that the characteristic properties of TMTD vulcanizates are believed due. These chains and the dimer of III would thus end in the grouping —SSC(S)N($CH_3$)$_2$. This grouping suggests a reason for the usual good aging properties of TMTD vulcanizates and for the poor aging observed for the short path distilled TMTD vulcanizates. Thus by a decomposition, appropriately slow, TMTD and sulfur fragments could be formed in the undistilled stock. These products by breaking peroxidation chains or by continued vulcanization would have the effect of preserving the rubber. During short path distillation the dimethyldithiocarbamyl sulfide end groups would be replaced by double bonds with the formation of ZnDMDC, ZnS, etc. In the distilled vulcanizate, where the TMTD molecules and sulfur fragments would not be available, peroxidation and degradation of the rubber would occur uninhibited. Furthermore, the newly formed double bonds would be of a different type than the polyisoprene type and would, therefore, serve as active centers for degradative oxidation.

The buffering effects of zinc compounds thus seem to account for activation of TMTD vulcanization and to be closely related to the exceptional aging properties of TMTD vulcanizates. This circumstance supports the concept that vulcanization including that with elementary sulfur is a type of polymerization, since it is well known that sulfhydryl compounds may exert both initiating and inhibiting effects, *i.e.*, "modifying" action, on polymerization. Such effects appear clearly analogous to the activating and inhibiting effects on vulcanization of sulfhydryl compounds such as $H_2S$, dodecyl mercaptan, and presumably, dimethyldithiocarbamic acid. Whether or not this analogy can be sustained by further work, it seems likely that vulcanization is a radical reaction which can be influenced by the buffering action of zinc compounds.

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**English Synopsis, see Summaries, page S16, Vol. V, 1950.**

## Résumé

(*1*) Le mécanisme d'activation par le zinc a été étudiée en utilisant le soufre radioactif et l'emploi de techniques de distillation à courte distance. (2) L'effet activateur des composés zinciques dans la vulcanisation TMTD est attribuée à l'action-tampon sur la concentration des acides $H_2S$, diméthyldithiocarbamiques, et des autres acides qui peuvent être présents dans le vulcanisat. (*3*) Les composés zinciques semblent prolonger la durée de vie du TMTM dans le vulcanisat en limitant la concentration de $H_2S$ et rendent ainsi possible une utilisation efficace du soufre disponible pour le pontage des molécules de caoutchouc par un procédé, qui semble progresser par radicaux. (*4*) La réaction du DMADC avec le $CS_2$ fournit la diméthylthioformamide et du soufre en absence, mais non en présence de caoutchouc. (*5*) L'application de ces résultats à la théorie de la vulcanisation est brièvement discutée.

## Zusammenfassung

(*1*) Der Mechanismus der Zinkaktivierung wurde unter Benutzung der radioaktiven Schwefel- und der Kurzweg-Destillierungs-technik untersucht. (2) Die aktivierende Wirkung von Zinkverbindungen der TMTD Vulkanisierung wird einer Pufferaktion auf die Konzentration von $H_2S$, Dimethyldithiocarbaminsäuren, und von anderen Säuren, die in der vulkanisierenden Kautschukverbindung vorhanden sein können, zugeschrieben. (*3*) Zinkverbindungen scheinen das Bestehen von TMTM im Vulkanisat zu verlängern, indem sie die Konzentration von $H_2S$ begrenzen und so eine wirksame Benutzung des vorhandenen Schwefels für Querbindungen in den Kautschukmolekülen ermöglichen. Dieser Prozess scheint vom Radikaltypus zu sein. (*4*) Es wurde gefunden, dass die Reaktion von DMADC mit $CS_2$ Dimethylthioformamid und Schwefel ergibt, aber nur in Abwesenheit und nicht in Gegenwart von Kautschuk. (*5*) Die Anwendung der erhaltenen Resultate auf die Theorie der Vulkanisierung wird kurz diskutiert.

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