

# Study of Curative Interactions in *cis*-1,4-Polyisoprene. VI. Interaction of Some Combinations of Sulfur, Tetramethylthiuram Disulfide, and ZnO

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## SYNOPSIS

The interaction of curatives in the systems *cis*-1,4-polyisoprene (IR)-sulfur, IR-sulfur-ZnO, IR-tetramethylthiuram disulphide (TMTD), and IR-sulfur-TMTD were studied. Thermal events observed in the differential scanning calorimetry curing curves characteristic of these systems were explained in terms of the melting/liquefaction of compounds, the evaporation of gases, and the vulcanization process itself. The similarity of the IR-sulfur and IR-sulfur-ZnO curing curves suggested that sulfur and ZnO were unreactive during vulcanization. On heating the IR-TMTD and IR-sulfur-TMTD systems, gases such as Me<sub>2</sub>NH and CS<sub>2</sub> formed easily. Although the maximum crosslink densities in the latter systems were low, the crosslink formation was found to be strongly exothermic. The sulfur efficiency parameter  $E$  was estimated for the IR-sulfur-TMTD system and decreased steeply from 37.5 (at 143.2°C) to 16.6 (at 151.0°C). This was taken as evidence that much of the bound sulfur was initially combined in pendent groups. Then  $E$  increased dramatically toward the advanced stages of cure, emphasizing the extraordinary inefficient manner in which sulfur was utilized to form crosslinks.

## INTRODUCTION

Previous studies on the structural characterization of vulcanizates revealed the networks obtained from natural rubber (NR)-sulfur vulcanization systems to be extremely complex. Moore et al.<sup>1</sup> defined a parameter  $E$  as the number of sulfur atoms combined in the network for each chemical crosslink formed. An exceedingly high  $E$  value of 53 was found on curing a NR (100)-sulfur (10) system for 2 h at 140°C, and was attributed to the incorporation of sulfur in the forms of (i) long polysulfidic crosslinks, (ii) cyclic monosulfides, and (iii) vicinal sulfidic crosslinks.<sup>1</sup>

The parameter  $E'$  measures the crosslink efficiency after partial desulfuration of the network with triphenyl phosphine, which converts sulfidic crosslinks such as RS<sub>*x*</sub>R (R = polyisoprenyl,  $x \geq 2$ ) to either mono- or disulfidic links, depending on the

detailed structure of the alkenyl or alkyl groups.<sup>2</sup> The term  $E' - 1$  or  $2$  thus provides a measure of the combined sulfur not in crosslinks, which may, for example, be involved in intrachain cyclic sulfides (and pendent groups in case of accelerated sulfur vulcanization). The expression  $\bar{x} = E - (E' - 1$  or  $2)$  is an estimate only of the average number of sulfur atoms per crosslink—these calculations will be in error if polysulfidic cyclic sulfides (and polysulfidic pendent groups in case of accelerated sulfur vulcanization) and/or vicinal crosslinks are present.<sup>2,3</sup>

The preceding approach was applied to the NR (100)-sulfur (10) system vulcanized at 140°C.<sup>2</sup> The results showed that (i) polysulfidic crosslinks with  $\bar{x} = 12 - 13$  are formed in the early stages of cure, (ii) on further heating these decrease in length to give shorter crosslinks with  $\bar{x} = 2 - 3$ , and (iii) more than 75% of the network combined sulfur was present as cyclic monosulfides.

Other unwanted features of NR-sulfur vulcanizates concerns the *cis-trans* isomerization<sup>4</sup> and scission<sup>1</sup> of the main polymer chain.

It is commonly accepted that ZnO is desirable for

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the development of good physical properties in thiuram-related vulcanization systems.<sup>5-7</sup> As such, only a few reports appeared in connection with the interactions of diene-tetramethylthiuram disulfide (TMTD) systems in the absence of ZnO. Dogadkin et al.<sup>5</sup> observed no  $\text{Me}_2\text{NH}$  on heating TMTD in mineral oil for 5 h. However, on heating a NR (100)-TMTD (3.0) mixture at  $\sim 140^\circ\text{C}$ , dimethyldithiocarbamic acid (DMDCA) was formed via the abstraction of hydrogen atoms from  $\alpha$ -methylene carbons by, e.g., thiuram sulfenyl radicals. The serious reversion that was found for the NR-TMTD mixture, was attributed to oxidative decomposition of the network, accelerated by  $\text{Me}_2\text{NH}$  and  $\text{CS}_2$  formed on the decomposition of DMDCA.<sup>5,8,9</sup> Moore et al.<sup>10</sup> reported a strong smell of  $\text{Me}_2\text{NH}$  on heating a synthetic *cis*-1,4-polyisoprene (IR) (100)-TMTD (4.0) compound at  $140^\circ\text{C}$  for 15 min. The unvulcanized material was extracted and  $\sim 4.5$  mol % of the original TMTD was found to have combined in pendent groups. The extracted IR-TMTD adduct was reheated in the presence of ZnO, and a low crosslink density ( $0.29 \times 10^{-5}$  mol/cm<sup>3</sup> rubber) resulted. It was concluded that the actual precursors to crosslinking,  $\text{RS}_x\text{SX}$  [ $\text{R}$  = polyisoprenyl,  $x \geq 1$ ,  $\text{X} = \text{Me}_2\text{NC}(\text{S})$ ], were not formed by the simple interaction of IR and TMTD. This study comments on the experimental data that were obtained on analyzing some combinations of IR with sulfur, TMTD and ZnO, with reference to the mechanism of vulcanization.

## EXPERIMENTAL

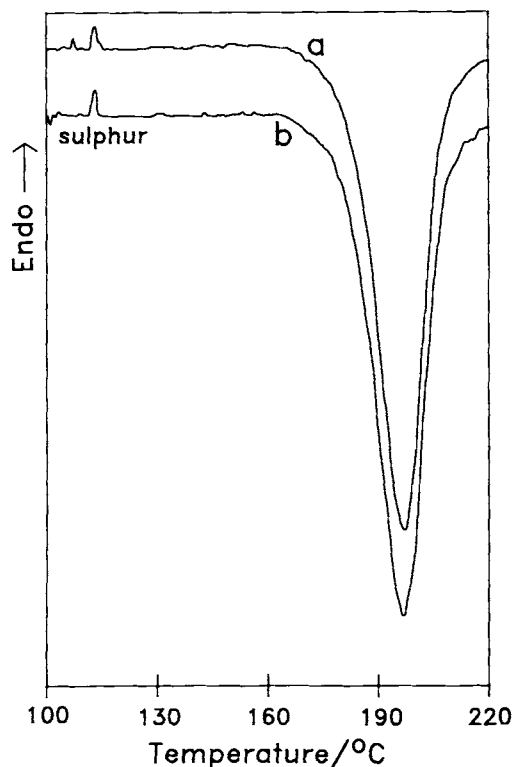
Experimental details were given in previous studies<sup>11,12</sup> of this series. Samples were vulcanized in a differential scanning calorimetry (DSC), and the network as well as the extractables analyzed. Thin-layer chromatography (TLC) and high-pressure liquid chromatography (HPLC) played a substantial role in the latter analysis.

## RESULTS AND DISCUSSION

### Unaccelerated Sulfur Vulcanization

#### IR-Sulfur

The DSC curve of the IR (100)-sulfur (9.46) compound revealed sulfur melting at  $112^\circ\text{C}$ , followed by a large vulcanization exotherm with a trough temperature at  $196.9^\circ\text{C}$  [Fig. 1(a)]. The exotherm



**Figure 1** DSC spectra. Scan rate  $2.5^\circ\text{C}/\text{min}$ . (a) IR (100)-sulfur (9.46),  $\text{Mi} = 17.121$  mg. (b) IR (100)-sulfur (9.46)-ZnO (3.00) (1.0 : 1.0 mol ratio),  $\text{Mi} = 14.920$  mg. The vulcanizate in (a) appeared maroon/transparent and that in (b) brown-beige/opaque on swelling in benzene.

originated from the crosslinking reactions as well as subsequent network maturing reactions. The TLC analysis revealed that part of the elemental sulfur was still uncombined at  $190^\circ\text{C}$ , implying that the energy dissipated was still to be connected with crosslink formation. All of the sulfur had combined with the rubber network at  $220^\circ\text{C}$  (Table I). The decrease of 48% in the crosslink density in proceeding from  $190$  to  $220^\circ\text{C}$  was interpreted in terms of reversion reactions wherein decomposition was more important than desulfuration.

It was interesting that the differential thermal analysis (DTA) thermographs of Bhaumik et al.<sup>13</sup> on the NR (68)-sulfur (32) compound showed the mainly exothermic hard rubber reaction overlapping with a smaller endotherm starting at  $\sim 200^\circ\text{C}$ . The latter peak was accompanied by the evolution of  $\text{H}_2\text{S}$  and was interpreted to a dehydrogenation reaction of ebonite by sulfur at high temperatures. (Dehydrogenation of an alkene is an endothermic reaction,  $\Delta H^\circ \cong 125.5$  kJ/mol.<sup>14</sup>) However, evaporation of  $\text{H}_2\text{S}$ , from whatever source, would also be endothermic ( $\Delta H_{\text{evap}} = 18.7$  kJ/mol.<sup>15</sup>)

**Table I** Analysis of the Compounds Shown, at Various Temperatures along the DSC Curing Curve

Compound (Parts per Hundred)	Temp (°C)	Compounds Extracted/Mol % of Initial Reagent, by HPLC or Detected by TLC				Mass Loss (%)	Degree of Crosslinking/mol cm <sup>2</sup> Rubber Network × 10 <sup>6</sup>			Polysulfides (%)
		S <sub>8</sub>	TMTD	TMTM	TMTU		1/2Mc	1/2Mc <sup>a</sup>	1/2Mc <sup>b</sup>	
IR (100) sulfur (9.46) [Fig. 1(a)]	190.0	<sup>c</sup>				0.07	4.02			
	220.0	0				0.28	2.08			
	220.0	0				0.51	2.00			
ZnO (3.00) [Fig. 1(b)]										
	IR (100) TMTD (8.86) [Fig. 2(a)]	150.2				0.19	0.00			
	154.8					0.47	0.06			
	159.1	0.0	4.9	0.0	31.9	1.45	3.07	1.62		47.2
190.0	0	<sup>d</sup>	0		7.03	0.91				
IR (100) sulfur (9.46) TMTD (8.86) [Fig. 3(a)]	135.4					0.13	0.00			
	143.2	94.3	27.1	0.0	34.6	0.62	0.41		0.02	95.7
	151.0	69.2	9.8	0.0	60.1	3.90	4.97		1.42	71.5
	164.1	9.1	11.4	0.0	67.1	6.53	6.31		2.23	64.5
	190.3	0.0	4.3	0.0	57.7	8.05	3.24		1.95	39.9

<sup>a</sup> Crosslink density after 2 h propane-2-thiol/piperidine treatment.

<sup>b</sup> Crosslink density after 4 h propane-2-thiol/piperidine treatment.

<sup>c</sup> Compound easy to detect with TLC.

<sup>d</sup> Compound barely detected with TLC.

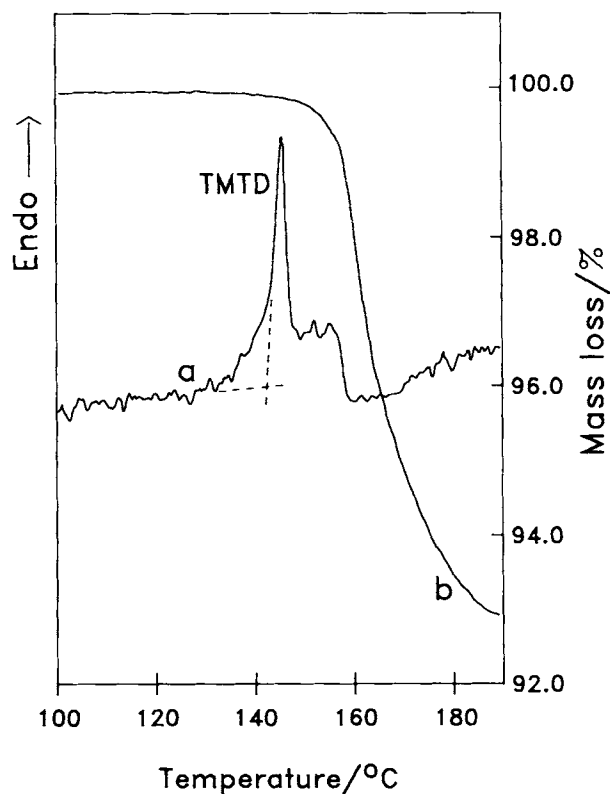
### IR/Sulfur/ZnO

Morrell<sup>16</sup> remarked that the addition of ZnO halved the vulcanization time of the NR (100)-sulfur (8) curing system, but physical properties such as the tensile strength were unaffected. There is, however, consensus in the literature that ZnO is a very mild accelerator for the sulfur vulcanization of the polyisoprenes<sup>17-20</sup> and has a negligible effect on the properties of NR (acetone-extracted)-sulfur vulcanizates.<sup>17</sup> The vulcanization exotherm obtained on heating an IR (100)-sulfur (9.46)-ZnO (3.00) (1.0:1.0 mol ratio) system [Fig. 1(b)] was virtually the same as that obtained in the absence of ZnO [Fig. 1(a)]. The trough temperature remained at 196.9°C, indicating that ZnO had not performed as an accelerator in the IR-sulfur compound. The crosslink densities were the same for the IR-sulfur and IR-sulfur-ZnO mixtures at 220°C (Table I), which could imply that the physical properties were similar. These results tied in with the fact that sulfur and ZnO were inert toward each other in the absence of IR.<sup>21</sup>

### Accelerated Sulfur Vulcanization

#### IR-TMTD

TMTD liquified at 142.7°C on scanning an IR (100)-TMTD (8.86) mixture to 190°C (Fig. 2), whose temperature was slightly higher than the fu-



**Figure 2** DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)-TMTD (8.86), *M<sub>i</sub>* = 19.864 mg. The sample quenched at 190°C appeared light brown/transparent on swelling in benzene. (b) TGA spectrum.

sion temperature of TMTD powder at 138.9°C.<sup>22</sup> The ensuing endotherm between 148 and 158°C was associated with the evaporation of gases, since the TGA revealed that a mass loss had initiated at 145.5°C. These volatiles were not analyzed but, based on literature evidence, were attributed mainly to Me<sub>2</sub>NH and CS<sub>2</sub>.

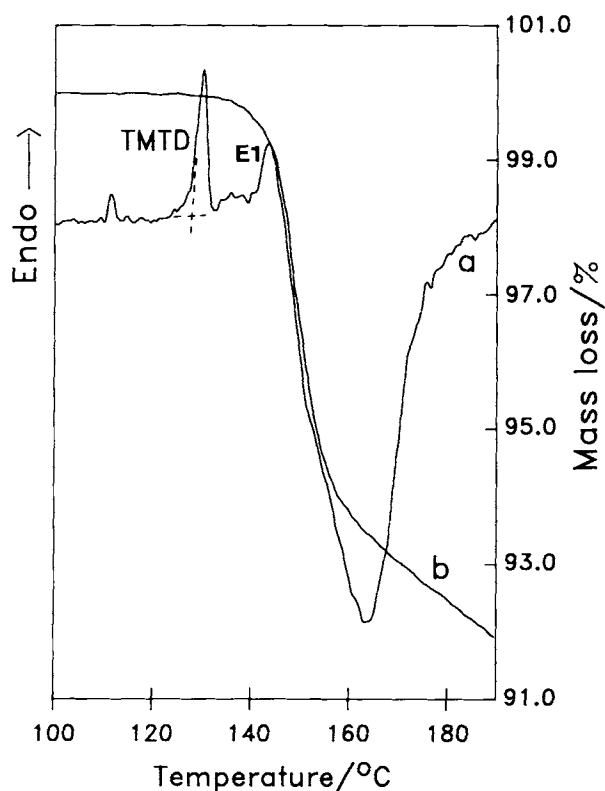
With reference to the IR (100)-TMTD (8.86) system under discussion (Fig. 2), the sum of the energies suddenly became exothermic at ~ 158°C, which was unexpected as the differential TGA (DTGA) curve showed the maximum rate of evaporation (1.29%/min) to be at 160.4°C. There was, however, a sharp increase in the crosslink density in going from 154.8 to 159.1°C (Table I), implying that a considerable amount of energy was released in crosslinking. The maximum crosslink density at 159.1°C ( $3.07 \times 10^{-5}$  mol/cm<sup>3</sup> rubber) was low, in agreement with literature evidence. Of importance was the fact that a rather large number of these crosslinks (47.2%) was polysulfidic at 159.1°C, i.e., R-S<sub>x</sub>-R ( $x > 2$ ). Reversion reactions occurred toward 190°C, as was perceived by the drop in the crosslink density value.

#### IR-Sulfur-TMTD

Sulfur melted at 110.8°C on scanning an IR (100)-sulfur (9.46)-TMTD (8.86) (1.0 : 1.0 mol ratio) mixture (Fig. 3). The liquefaction of TMTD at 128.0°C was ~ 15°C lower than that of TMTD alone in IR (cf. Fig. 2). A similar phenomenon was also observed with a mixture of these curatives in the absence of IR.<sup>22</sup>

The endotherm E1, starting at 140.8°C, was ascribed to the evaporation of gases since the DTGA revealed a mass loss commencing at 142.7°C. In proceeding from 143.2 to 151.0°C in the DSC analysis of the IR-sulfur-TMTD mixture, the net energy dissipated changed from endo- to exothermic. It was clear from TGA studies, which showed the maximum rate of gas evaporation (1.48%/min) to be at 149.0°C, that a strongly exothermic event had occurred concurrently. The net exotherm in this temperature range was inter alia associated with the formation of crosslinks, and the magnitude of the energy liberated was partially masked by the overlapping volatilization endotherm.

*The Existence and Nature of the Pendent Groups.* The HPLC analysis on the extra-network material revealed that TMTD had reacted very fast, since only 27.1 mol % TMTD was present at 143.2°C. By taking into account the concentrations of TMTD, tetramethylthiuram monosulfide (TMTM), and

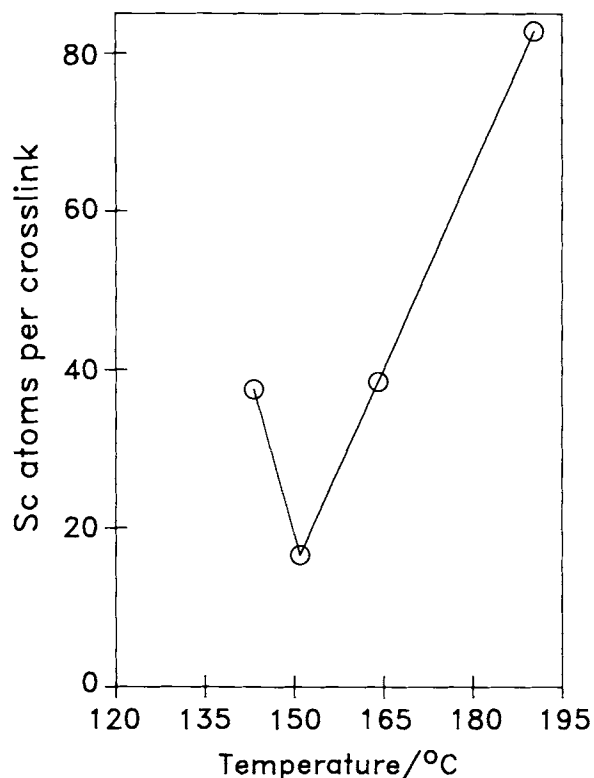


**Figure 3** DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)-sulfur (9.46)-TMTD (8.86) (1.0 : 1.0 mol ratio),  $M_i = 19.997$  mg. The vulcanizate quenched at 190°C appeared brown/transparent and had voids on swelling in benzene. (b) TGA spectrum.

tetramethylthiourea (TMTU), as well as the mass loss measured by TGA, it was possible to account for 69.9 mol % of the original TMTD at 143.2°C. It was inferred that the rest of the TMTD was bound to the network as pendent groups, a phenomenon that has been observed for the IR-TMTD-ZnO system.<sup>10</sup>

The crosslink efficiency  $E$  was estimated by calculating the number of sulfur atoms combined in the network for each crosslink formed—the calculations did not take into account the sulfur atoms of network-bound SX groups, and no correction was made for physical entanglements in applying the Flory-Rehner<sup>23</sup> equation. The calculated  $E$  values displayed a definite trend as the cure proceeded in the IR-sulfur-TMTD compound (Fig. 4). The steep decline in  $E$  from 37.5 Sc atoms/crosslink (at 143.2°C) to 16.6 Sc atoms/crosslink (at 151.0°C), was taken as evidence that much of the bound sulfur was not initially involved in crosslinks but was combined in pendent groups.

It was interesting to estimate the number of sulfur atoms per pendent group for several of the com-



**Figure 4** The variation of the Sc atoms/crosslink ratio as curing proceeded for the IR (100)-sulfur (9.46)-TMTD (8.86) vulcanization system. The calculations did not take the sulfur atoms of the network-bound S(S)CN(CH<sub>3</sub>)<sub>2</sub> groups into account. The data points were connected merely to illustrate the general trend in *E*.

pounds that were studied in this investigation. These calculations were based on the assumption that the mass loss at a particular temperature was solely due to accelerator fragments. The calculation for the IR-sulfur-TMTD system, in particular, was warranted at the initial cure stages only, due to the fact that a considerable amount of chemical species other than accelerator fragments, had evaporated at later cure stages (cf. Table I). The method of calculation will be explained for the IR-sulfur-TMTD system, on the basis of Tables I and II. Since 69.9 mol % of the initial TMTD could be accounted for at 143.2°C, then 30.1 mol % of the TMTD was network bound. Consequently ( $33.5 \times 10^{-5}$  mol TMTD/cm<sup>3</sup> rubber) (0.301) (2) =  $20.2 \times 10^{-5}$  mol/cm<sup>3</sup> pendent groups were present. Because 94.3 mol % of the elemental sulfur was extracted at 143.2°C, it implied that ( $33.5 \times 10^{-5}$  mol sulfur/cm<sup>3</sup> rubber) (0.057) (8) =  $15.3 \times 10^{-5}$  mol/cm<sup>3</sup> sulfur atoms were combined. The polysulfide determination showed that 95.7% of the crosslinks were polysulfidic. Assuming that only trisulfidic and disulfidic crosslinks prevailed, then (0.41

$\times 10^{-5}$  mol crosslinks/cm<sup>3</sup> rubber) [(3) (0.957) + (1) (0.043)] =  $1.2 \times 10^{-5}$  mol/cm<sup>3</sup> sulfur atoms were combined in the network as sulfidic crosslinks. The number of atoms from elemental sulfur to be associated with pendent groups was therefore ( $15.3 \times 10^{-5} - 1.2 \times 10^{-5}$ ) =  $14.1 \times 10^{-5}$  mol/cm<sup>3</sup>. Thus ( $14.1 \times 10^{-5} / 20.2 \times 10^{-5} + 1$ ) = 1.70 sulfur atoms were combined per pendent group.

**Formation and Destruction of Crosslinks.** There was a definite delay in the formation of crosslinks after the sulfur-TMTD liquefaction since the crosslink density was zero at 135.4°C and low at 143.2°C (Table I). The crosslink density of  $4.97 \times 10^{-5}$  mol/cm<sup>3</sup> at 151.0°C reconfirmed that TMTD did accelerate sulfur vulcanization since the vulcanization exotherm had not even started under similar conditions in the IR (100)-sulfur (9.46) compound (cf. Figs. 1 and 3). It was remarkable that 30.8 mol % of the original elemental sulfur had been used to form  $4.97 \times 10^{-5}$  mol/cm<sup>3</sup> crosslinks (up to 151.0°C), but that another 60.1% of the sulfur was necessary to increase the crosslink density to  $6.31 \times 10^{-5}$  mol/cm<sup>3</sup> (up to 164.1°C). The extremely inefficient way in which sulfur was utilized in the formation of crosslinks can also be appreciated by the steep increase in *E* from 151.0°C (*E* = 16.6) to 164.1°C (*E* = 38.5) to 190.3°C (*E* = 82.8), Figure 4. The low concentration of 9.1 mol % elemental sulfur at the trough temperature of 164.1°C in the IR-sulfur-TMTD vulcanization curve (Fig. 3) implied that the remaining part of the exotherm was largely due to network maturing reactions. These were mainly crosslink destruction reactions since the polysulfidic crosslinks decreased from 4.07

**Table II** Calculation of Number of Sulfur Atoms per Pendent Group at 143.2°C, in the DSC Scan of the IR-Sulfur-TMTD Vulcanization Compound from Table I

Quantity Calculated	mol/cm <sup>3</sup> Rubber Network
Crosslink density	$0.41 \times 10^{-5}$
Number of pendent groups	$20.2 \times 10^{-5}$
Network-bound sulfur atoms <sup>a</sup>	$15.3 \times 10^{-5}$
Sulfur atoms in crosslinks <sup>b</sup>	$1.2 \times 10^{-5}$
Sulfur atoms in pendent groups <sup>c</sup>	$14.1 \times 10^{-5}$
Sulfur atoms per pendent group	1.70 <sup>d</sup>

<sup>a</sup> Refers to sulfur other than in the SX moieties of pendent groups.

<sup>b</sup> Assume trisulfidic and disulfidic crosslinks.

<sup>c</sup> Neglecting sulfur in the SX moieties of pendent groups.

<sup>d</sup> Refers to the indice x in RS<sub>x</sub>X (R = polyisoprenyl).

**Table III Variation of the Polysulfidic, Mono- and/or Disulfidic Crosslinks at Various Temperatures along the DSC Curve, for the IR-Sulfur-TMTD System from Table I**

Temperature (°C)	143.2	151.0	164.1	190.3
Polysulfides (mol/cm <sup>3</sup> rubber network × 10 <sup>6</sup> )	0.39	3.55	4.07	1.29
Mono- and/or disulfides (mol/cm <sup>3</sup> rubber network × 10 <sup>6</sup> )	0.02	1.42	2.24	1.95

× 10<sup>-5</sup> (at 164.1°C) to 1.29 × 10<sup>-5</sup> mol/cm<sup>3</sup> (at 190.3°C), and the monosulfidic crosslinks from 2.24 × 10<sup>-5</sup> (at 164.1°C) to 1.95 × 10<sup>-5</sup> mol/cm<sup>3</sup> (at 190.3°C) (Table III).

## CONCLUSIONS

Since only 69.9 mol % of the original TMTD could be accounted for at 143.2°C on heating the IR (100)-sulfur (9.46)-TMTD (8.86) compound (Table I), it was inferred that the rest of the TMTD was bound as pendent groups. The indice  $x$  in RS <sub>$x$</sub> X (R = polyisoprenyl) was estimated to be 1.70, implying that ~ 70% of these pendent groups were disulfidic and the rest monosulfidic. Model compound studies with 2-methylpent-2-ene suggested that rubber-bound intermediates of type RS <sub>$x$</sub> X ( $x \geq 2$ ) are precursors to crosslinking<sup>24,25</sup> and, contrary to speculations in the literature,<sup>10</sup> the results indicate that these can be formed in the absence of ZnO. This argues against the involvement of ZnO in the formation of the active sulfurating agent, which was believed to form prior to crosslinking in thiuram-related vulcanization systems. A similar conclusion was reached in studies where it was attempted to form zinc dimethyldithiocarbamate by the interaction of TMTD and ZnO in the absence of rubber.<sup>22</sup>

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