

## **Structural Characterization of Vulcanizates. Part IV. Use of Triphenylphosphine and Sodium Di-*n*-butyl Phosphite to Determine the Structures of Sulfur Linkages in Natural Rubber, *cis*-1,4-Polyisoprene, and Ethylene-Propylene Rubber Vulcanizate Networks**

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### **Synopsis**

Determinations of the degree of chemical crosslinking and crosslinking efficiency values  $E$  (i.e., the number of sulfur atoms combined in the network per chemical crosslink present) have been used in conjunction with the chemical probes triphenylphosphine and sodium di-*n*-butyl phosphite to establish the structural features of sulfur links in vulcanizate networks derived from a variety of accelerated natural rubber-sulfur systems, from a *cis*-1,4-polyisoprene-TMTD-zinc oxide system, and from natural rubber and ethylene-propylene rubber crosslinked with a dicumyl peroxide-sulfur system. The triphenylphosphine converts polysulfide links into monosulfide and, to a lesser extent, disulfide links. The values of  $E'$ , i.e., the number of sulfur atoms combined in the network per chemical crosslink present after triphenylphosphine treatment are, therefore, a measure of the extent of main-chain modification in the network by cyclic monosulfide groups and/or pendant groups of the type:  $-S_x-\text{Accel.}$  (where  $x \geq 1$  and Accel. is an accelerator fragment). Sodium di-*n*-butyl phosphite cleaves di- and polysulfide crosslinks but leaves monosulfide and carbon-carbon crosslinks intact, and thus determination of the degree of chemical crosslinking before and after treatment with this reagent yields estimates of these two different classes of crosslinks. The combined results indicate that the efficiency of utilizing sulfur for crosslinking and, therefore, the structural complexity of the derived networks are very sensitive to the nature of the vulcanizing system (type and relative concentrations of crosslinking agent, accelerator, and activator) and vulcanizing conditions (time and temperature of cure). In general, the proportion of crosslinks which are di- and/or polysulfidic decreases with increasing cure time, and for the accelerated sulfur systems the structural complexity of the network increases with cure time, especially at higher vulcanizing temperatures and with low concentrations of fatty acid activator.

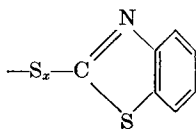
### **I. INTRODUCTION**

In Part I<sup>1</sup> of this series the crosslinking efficiency of sulfur  $E$ , defined as the number of sulfur atoms combined in the network per chemical crosslink present, was determined for unaccelerated natural rubber (NR)-sulfur vulcanizates which had been cured for various times at 140°C. When

allowance was made for main-chain scission which accompanied crosslinking,  $E$  values in the range 40–55 were obtained, these high values reflecting the marked inefficiency of sulfur as a crosslinking agent in the unaccelerated system and revealing the considerable structural complexity of the network. The inefficient use of sulfur is attributed to its wasteful combination: (a) in crosslinks containing long polysulfide chains ( $RS_xR$ ; R = rubber hydrocarbon chain,  $x \geq 2$ ); (b) in cyclic monosulfide groups along the main chain; (c) in vicinal sulfidic crosslinks which act physically as a single crosslink; and presumably (d) in long intramolecular sulfidic links ( $\overline{RS_x}$ ), although no unequivocal evidence exists for this structural feature. In Part II<sup>2</sup> triphenylphosphine was used as a chemical probe in the vulcanizate networks described in Part I to give semiquantitative descriptions of: (1) the average number of sulfur atoms in the crosslink, i.e., the value of  $x$  in  $RS_xR$ ; (2) the change in  $x$  with cure time; and (3) the proportion of combined sulfur which is present in isolated cyclic monosulfide groups. More rigorous quantitative description of the features (1)–(3) was prevented by our inability to determine in an actual network the number of vicinal crosslinks (c) and intramolecular sulfidic links (d).

The utility of triphenylphosphine depends on its reaction with polysulfide links (as in  $RS_xR$ ) to give monosulfide links (RSR) or disulfide links ( $RS_2R$ ), the limiting extent of desulfurization depending on the detailed structures of the alkenyl or alkyl groups R—. <sup>3</sup> Thus, determination of the amount of the combined sulfur in the network which is removed by the triphenylphosphine treatment, coupled with the  $E$  values of the original networks, yield data on the structural features (1)–(3) within the limitations already discussed.

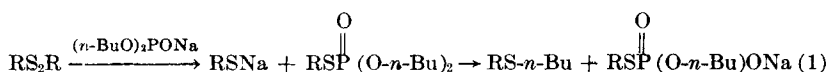
The present paper describes the use of triphenylphosphine to resolve the structural features of sulfur linkages in several types of accelerated NR-sulfur vulcanizate networks, in networks derived from the *cis*-1,4-polyisoprene-tetramethylthiuram disulfide (TMTD)-zinc oxide system (Part III<sup>4</sup> of this series), and in networks obtained from NR and ethylene-propylene rubber (EPR) by means of a dicumyl peroxide (DCP)-sulfur system. Provided that the NR networks derived from the above systems possess solely the same structural features as the unaccelerated NR-sulfur networks, then triphenylphosphine treatment together with determination of  $E$  values will yield information on the features (1)–(3) for these networks. However, it must be anticipated that a main-chain modification additional to cyclic monosulfides may exist in these networks, viz., groups pendent to the main rubber chain consisting of sulfidic links terminated by an accelerator residue or fragment from the TMTD or DCP (e.g.,



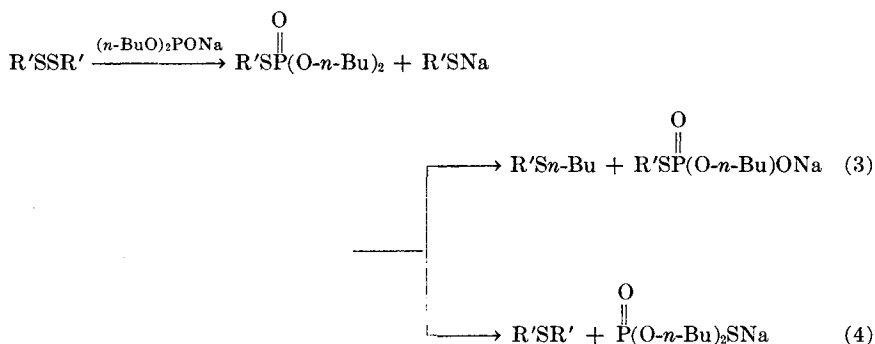
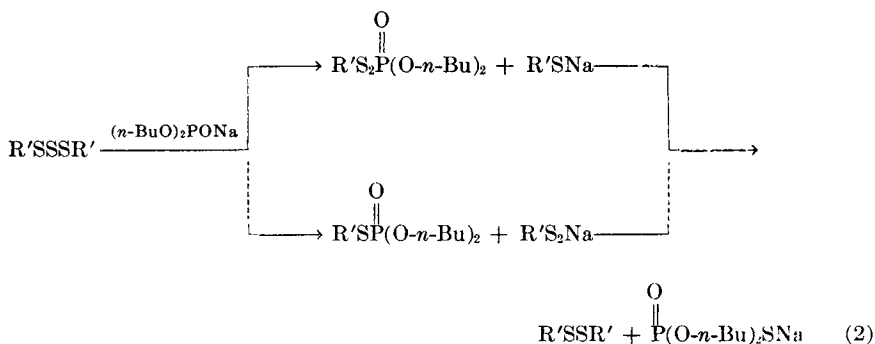
where  $x \geq 1$  in the case of 2-mercaptobenzothiazole (MBT)-accelerated systems). The presence of these groups prevents definitive information about (1)–(3) being obtained from  $E$  values and from the results of triphenylphosphine treatment since some of the combined sulfur in the network which is removed as triphenylphosphine sulfide could have originated from pendent polysulfide links (e.g., as present in  $-\text{S}_x-\overset{\text{O}}{\text{C}}=\text{N}-\text{C}_6\text{H}_4-\text{S}$  or  $-\text{S}_x-\text{C}=\text{S}$  ( $\text{NMe}_2$ ), where  $x \geq 2$ ) which are known<sup>5</sup> to react with triphenylphosphine to give corresponding pendent groups with  $x = 1$ . In this event, however, the difference in crosslinking efficiency values before and after triphenylphosphine treatment, i.e.,  $E - E'$  (where  $E'$  is the number of sulfur atoms combined in the network after triphenylphosphine treatment per chemical crosslink present in the original network) will be some measure of polysulfidic links in the original network, and the value of  $E'$  will be a measure of the extent of main-chain modification by cyclic monosulfide groups and/or pendent groups of the type specified above. For example, a value of  $E'$  of 1–2 in a network known to be crosslinked solely by sulfur signifies that the original network has negligible sulfidic main-chain modifications, and when it is associated with a high  $E$  value it indicates that the original network contains polysulfidic crosslinks. In contrast, a high value of  $E'$  indicates extensive main-chain modification by sulfidic groups.

Examples will be given in this paper of the structural details of sulfidic linkages in networks which are derivable from the use of triphenylphosphine, coupled with  $E$  values of the original network, especially when the results so obtained are considered in conjunction with data from model olefin sulfurations and from the application of alternative chemical probes.

One such probe now being developed is a benzene solution of sodium di-*n*-butyl phosphite [(*n*-BuO)<sub>2</sub>PONa] and preliminary results showing the present utility and limitations of this probe with sulfur vulcanizates are reported here. Sodium di-*n*-butyl phosphite is used to distinguish carbon-carbon and monosulfide crosslinks from di- and polysulfide crosslinks. Its application in this respect depends on the fact that in benzene solution at 25–80°C. it is unreactive toward carbon-carbon bonds such as are present in peroxide vulcanizates of NR and towards carbon-sulfur bonds in monosulfides, RSR (where R is alkyl or alkenyl).<sup>6</sup> It does, however, react readily with dialkyl disulfides at 25°C. according to the scheme<sup>6–8</sup> shown in eq. (1) (see also comparable reaction of sodium diethyl phosphite in tetrahydrofuran<sup>9</sup>):



(where R is alkyl) and with dialkenyl trisulfides and disulfides at 25°C. as shown in eqs. (2)–(4),<sup>6</sup> where R' is alkenyl:



Alkenyl alkyl disulfides also react according to eqs. (3) and (4).<sup>5</sup> Thus, if di- and polysulfide crosslinks react via eq. (2) followed by eq. (3), then determination of the proportion of the original chemical crosslinks in a network which are destroyed by the sodium di-*n*-butyl phosphite treatment will give a direct measure of the proportion of the chemical crosslinks which are di- and/or polysulfidic; the crosslinks remaining after the treatment will be carbon-carbon and/or monosulfidic. If it is known from independent evidence (e.g., model olefin sulfuration studies) that the network contains only sulfidic crosslinks, then use of the probe will permit determinations of the concentrations of monosulfide crosslinks and of di- and/or polysulfide crosslinks. The occurrence of reaction (4), which involves the conversion of disulfide crosslinks (R'SSR') into monosulfide crosslinks (R'SR'), would lead to an overestimate of monosulfide crosslinks and an underestimate of di- and/or polysulfide crosslinks. It is known that in the case of model dialkenyl disulfides, reaction (4) competes with reaction (3), their relative importance depending on the structure of the alkenyl (R') group.<sup>6</sup> However, in the case of actual networks, reaction (4) is regarded as of negligible importance, firstly, because the mobility of the intermediate R'SP(O)(O-*n*-Bu)<sub>2</sub> and R'SNa groups when they are part of the rubber chain may be sufficiently restricted to prevent their subsequent reaction; and secondly—and more pertinently—many vulcanizate networks are, as is reported here, completely solubilized on treatment with the probe, indicating a virtually complete and permanent cleavage of all the crosslinks.

## II. MATERIALS AND EXPERIMENTAL METHODS

### Materials

Triphenylphosphine, recrystallized from absolute ethanol, had a melting point of 80.0°C. AnalaR benzene was distilled from sodium. Sodium di-*n*-butyl phosphite (ca. 0.13 or 0.4M in benzene) was prepared by adding sodium to redistilled di-*n*-butyl phosphite (b.p. 117.5–118°C./9 mm.) in dry benzene under reflux.<sup>10</sup> The NR(RSS1, yellow circle) was the same as used in Part I,<sup>1</sup> and the synthetic *cis*-1,4-polyisoprene was the same as used in Part III.<sup>4</sup> Ethylene-propylene rubber (EPR) was a sample of an experimental grade of material (designated EPR 59) kindly supplied by Hercules Powder Company Ltd., Wilmington, Delaware, U. S. A. Rubbers were compounded by standard procedures, and the molecular weight of the rubber hydrocarbon component of the mix was determined as in Parts I<sup>1</sup> and III.<sup>4</sup> Vulcanization was effected at 140 ± 0.25°C. or at 100 ± 1°C. to produce sheets either 1 mm. or 2 mm. in thickness.

### Experimental Methods

#### *Treatment of Networks with Triphenylphosphine*

Vulcanizates were extracted with organic solvents under the conditions specified in the tables, and those containing zinc sulfide were subsequently treated with ether-hydrochloric acid. This involved swelling the extracted dried vulcanizate (ca. 10 g.) in ether (ca. 200 ml.) overnight and then adding concentrated hydrochloric acid (ca. 20 ml.) and refluxing for 2–3 hr. in nitrogen. The vulcanizates were then washed with water, dried, and extracted with hot acetone for 24 hr. in nitrogen and subsequently dried to constant weight. Removal of zinc sulfide by this means is essential, since it is found that zinc sulfide when present in the vulcanizate prevents the triphenylphosphine from removing all of the potentially removable sulfur combined in the network. The ether-hydrochloric acid treatment does not cause any substantial change in the crosslink density of networks (see equilibrium  $v_r$  values before and after treatment, Tables V and VI) nor does it alter the amount of combined sulfur in the network which is removable by triphenylphosphine, as judged by the identity of sulfur removed by triphenylphosphine from a hot acetone-extracted vulcanizate from NR(100)-sulfur (10) cured for 4 hr. at 140°C. and from the same network after the acid treatment.

Three methods of triphenylphosphine treatment were used, the second and third being developments of the first which is the original method used in Part II.<sup>2</sup> In all cases  $\geq 1$  g.-mole of triphenylphosphine/g. atom of sulfur combined in the vulcanizate network was used.

**Method A.** Weighed amounts of the vulcanizate networks and triphenylphosphine were evacuated in glass tubes and dry benzene (once degassed) was distilled into the tubes which were then sealed *in vacuo*, kept overnight, and heated at 80°C. for the specified times.<sup>2</sup>

TABLE I  
Treatment with Sodium Di-*n*-butyl Phosphite of Vulcanizate Networks Derived from NR-Dicumyl Peroxide (DCP) Systems

Expt. no.	Treatment of network <sup>a</sup>	Equilibrium $v_r$ (swelling in <i>n</i> -decane 48 hr. at 25°C.)	$1/2 M_c^N$ , chem., (g.-mole chemical crosslinks/g. rubber network) $\times 10^5$	Loss of original chemical crosslinks, %
Network from NR(100)-DCP(3); cured 90 min. at 140°C.; $[\eta]$ of rubber hydrocarbon component of mix in benzene = 2.64 dl./g. at 25°C.				
1	Original network	0.307	5.90	0
2	Extracted with hot benzene for 24 hr. under nitrogen	0.303	5.6 <sub>s</sub>	4
3	Treated with 0.4M solution of ( <i>n</i> -BuO) <sub>2</sub> PONa <sup>b</sup> for 24 hr. at 25°C. <i>in vacuo</i> and extracted as in expt. 2	0.301	5.5 <sub>s</sub>	6
4	Treated with 0.13M solution of ( <i>n</i> -BuO) <sub>2</sub> PONa for 24 hr. at 25°C. and 5 hr. at 80°C. <i>in vacuo</i> and then extracted as in expt. 2	0.303	5.6 <sub>s</sub>	4
Network from NR(100)-DCP(1.35); cured 130 min. at 150°C.; $[\eta]$ of rubber hydrocarbon component of mix in benzene = 3.43 dl./g. at 25°C.				

6	Treated with 0.4M solution of ( <i>n</i> -BuO) <sub>2</sub> PONa plus phenyl-β-naphthylamine <sup>c</sup> for 24 hr. at 25°C. and 5 hr. at 80°C. <i>in vacuo</i> after one degassing, then extracted as in expt. 2	0.266	3.34	16
7	Treated with 0.4M solution of ( <i>n</i> -BuO) <sub>2</sub> PONa for 24 hr. at 25°C. and 5 hr. at 80°C. <i>in vacuo</i> and then extracted as in expt. 2	0.258	3.12	22
Network from NR(100)-DCP(1.35); cured 125 min. at 130°C.; [η] of rubber hydrocarbon component of mix in benzene = 3.43 dl./g. at 25°C.				
8	Original network	0.217	1.75	0
9	Swollen in predegassed benzene for 20 hr. at room temperature <i>in vacuo</i> , then frozen for 4 hr. in liquid N <sub>2</sub>	0.216	1.72 <sub>s</sub>	1.4
10	Benzene added to network, N <sub>2</sub> passed through benzene for 3 min., benzene then frozen and sample swollen <i>in vacuo</i> for 20 hr. at room temperature.	0.214	1.67	4.6
11	Treated as in expt. 10 plus additional heating for 3 hr. at 80°C. <i>in vacuo</i>	0.215	1.7	3.1
12	Heated in benzene for 24 hr. at 25°C. and 5 hr. at 80°C. <i>in vacuo</i> and then extracted as in expt. 2	0.212	1.64	6.3
13	Treated with 0.4M solution of ( <i>n</i> -BuO) <sub>2</sub> PONa plus phenyl-β-naphthylamine <sup>c</sup> for 24 hr. at 25°C. and 5 hr. at 80°C. <i>in vacuo</i> after one degassing; then extracted as in expt. 2	0.198	1.30	26

<sup>a</sup> Vulcanizates were extracted with hot acetone for 24 hr. under nitrogen and then dried *in vacuo* at room temperature. All networks, after the specified treatment, were finally dried *in vacuo* at room temperature.

<sup>b</sup> In this and other experiments ca. 33 ml. of sodium di-*n*-butyl phosphite solution/g. rubber network was used.

<sup>c</sup> Ca. 0.25 g./g. rubber network.

**Method B.** This was identical with method A, except that acetone was used instead of benzene.

**Method C.** Weighed amounts of the networks were allowed to swell overnight in a solution of triphenylphosphine (ca. 1 g. of triphenylphosphine in 20 ml. of dry benzene) under nitrogen, the benzene was then removed *in vacuo* at room temperature and the dried networks containing the triphenylphosphine heated *in vacuo* at 80°C. for the specified times. The treated networks were freed from triphenylphosphine and triphenylphosphine sulfide by continuous cold benzene extraction for 24 hr. in nitrogen in the dark. The amount of sulfur removed from the network by the triphenylphosphine treatment was determined either (a) by the difference between the amount of sulfur combined in the original network ( $S_c$ ) and that in the treated network ( $S_c'$ ); or (b) by determination of the sulfur present in the benzene extract as triphenylphosphine sulfide. Values of  $S_c$ ,  $S_c'$ , and sulfur as triphenylphosphine sulfide were determined on ca. 100 mg. samples by the method of Part I.<sup>1</sup>

#### *Treatment of Networks with Sodium Di-n-butyl Phosphite*

Vulcanizate networks were placed into benzene solutions of sodium di-*n*-butyl phosphite (ca. 1 g. of network in 20 ml. of either 0.13*M* or 0.4*M* solution of the phosphite, this being a 3- to 30-fold excess of the reagent over that required assuming 1 g.-mole of phosphite reacts with 1 g.-atom of sulfur combined in the network). Nitrogen was passed through the solution for several minutes and the mixture sealed *in vacuo*. The reactants were heated for 24 hr. at 25°C. and then in most cases for 3–5.5 hr. at 80°C., conditions shown by independent experiments to be sufficient to cleave all the di- and polysulfide crosslinks in the network (see Tables II and V). The treated networks were freed from unreacted sodium di-*n*-butyl phosphite and most other phosphorus compounds present as extra-network material by continuous extraction with hot benzene for 24 hr. in nitrogen, and the networks were then dried *in vacuo* to constant weight at room temperature. The extracted dried networks usually contained ca. 5 wt.-% of insoluble nonrubber material of unknown composition.

In control experiments, the above treatment was applied to acetone-extracted vulcanizates derived from a NR-dicumyl peroxide system, i.e., to networks containing carbon-carbon crosslinks. The results (Table I) show that for the most highly crosslinked network ( $1/2 M_{c, \text{chem}}^N = 5.9 \times 10^{-5}$  g.-mole chemical crosslinks/g. rubber network) the above treatment leads to only slight loss of chemical crosslinks ( $\pm 6\%$ ; expts. 3 and 4), but the percentage loss of original crosslinks becomes more pronounced in less highly crosslinked networks (cf. expts. 6, 7, 13 with expts. 3 and 4). This loss in crosslinks can be minimized, but not completely obviated, by taking special precautions to prevent oxidative degradation of the network by trace amounts of oxygen present during the treatment (cf. expts. 6 and 7). Supplementary experiments (expts. 2, 9–12) show that treatment of the networks in various ways in the absence of sodium di-*n*-butyl phosphite



causes only a slight loss in crosslinks, indicating that the major part of the loss observed in expts. 6, 7, and 13 must be due to the sodium di-*n*-butyl phosphite. The nature of the chemical groups in the network which are cleaved by the treatments described is not known, but it is likely that they are at least in part peroxide groups ( $\text{---O---O---}$ ) which would certainly be cleaved by the sodium di-*n*-butyl phosphite. Such peroxide groups may be present in the original NR or could have been introduced into the polyisoprene main chains or as crosslinks during the mastication process or during the post-cure handling of the vulcanizates. Insofar as these phosphite-labile groups are also present in the sulfur-NR networks described here then the estimated values of crosslinks cleaved by the sodium di-*n*-butyl phosphite will include di- and polysulfide crosslinks plus other phosphite-labile crosslinks, but the estimates of monosulfide crosslinks (i.e., crosslinks not cleaved by the reagent) will not be affected.

*Determination of the Degree of Chemical Cross-linking ( $1/2 M_{c, \text{chem.}}^N$ ) of Vulcanizate Networks*

For the untreated vulcanizate networks values of  $1/2 M_{c, \text{chem.}}^N$ , where  $M_{c, \text{chem.}}^N$  is the number-average molecular weight of the chain segments between crosslinks in the network, were usually determined from stress-strain evaluations of the elastic constant  $C_1$  obtained on dry or partially swollen strips of the vulcanizates. The method used to determine  $C_1$  values and to convert them into  $1/2 M_{c, \text{chem.}}^N$  values is described in Part I<sup>1</sup> and Part III.<sup>4</sup> For the determination of  $C_1$  values in the swollen state the vulcanizates were swollen in Sebacate 79 (A. Boake Roberts and Co. Ltd.) to a  $v_r$  value of 0.5–0.7, where  $v_r$  is the volume fraction of rubber in the swollen sample; no correction to  $C_{1, \text{swollen}}$  values was made for the filler contribution since the effect of filler on  $C_1$  in the swollen state will be negligible.

For a few of the untreated vulcanizate networks (viz., those of Tables IV and VII), values of  $1/2 M_{c, \text{chem.}}^N$  were derived from equilibrium values of  $v_r$ , the volume fraction of rubber network in the swollen rubber at equilibrium swelling, the swellings being conducted in *n*-decane for 48 hr. at 25°C. in the dark. The  $v_r$  values were related to the corresponding  $C_1$  values by the equation:

$$-\ln(1 - v_r) + v_r + \mu v_r^2 = 2C_1 V_0 v_r^{1/3} / RT \quad (5)$$

where  $\mu$  is a polymer-solvent interaction coefficient characteristic of the rubber network and swelling liquid,  $V_0$  is the molar volume of the swelling liquid,  $R$  is the gas constant and  $T$  is the absolute temperature. In applying eq. (5) a value of  $\mu = 0.41$  is taken for the networks obtained by using the "efficient" MBT-accelerated NR-sulfur system (Table IV), this value being derived from the equilibrium  $v_r$  and  $C_{1, \text{dry}}$  values of representative extracted and hydrochloric acid-treated samples of these vulcanizates as will be described in detail elsewhere,<sup>11</sup> and a value of  $\mu = 0.44$  is used for the vulcanizate networks obtained from the *cis*-1,4-polyisoprene-TMTD-zinc

TABLE II  
Structural Characteristics of a Vulcanizate Network from an Efficient MBT-Accelerated NR-Sulfur System Before and After Treatment with Sodium Di-*n*-butyl Phosphite<sup>a,b</sup>

Original network		Equilibrium		Equilibrium		Loss in original chemical crosslinks, %	
Equilibrium $\nu_r$ (swelling in $n$ -decane at 25°C.)	$C_{1, \text{swollen}}$ at 25°C., dynes./cm. <sup>2</sup> $\times 10^{-6}$	$\mu$	$C_{1, \text{swollen}}$ at 25°C., (swelling in $n$ -decane at 25°C.)	$\nu_r$	$C_{1, \text{swollen}}$ at 25°C., dynes./cm. <sup>2</sup> $\times 10^{-6}$	Based on $\mu$ determined for the treated networks	Based on $\nu_r$ and $\mu$ determined for treated networks $\mu = 0.42$
		$1/2 M_c^{N, \text{chem.}}$ g.-mole chemical crosslinks/g. rubber network $\times 10^5$					$1/2 M_c^{N, \text{chem.}}$ g.-mole chemical crosslinks/g. rubber network $\times 10^5$
0.276	1.44 <sub>3</sub>	0.42	0.223 <sup>c</sup>	0.223 <sup>c</sup>	0.78 <sup>c</sup>	1.70	48
0.276	1.43 <sub>5</sub>		0.224 <sup>f</sup>	0.224 <sup>f</sup>	0.74 <sup>f</sup>	1.75	41
			0.234 <sup>d</sup>	0.234 <sup>d</sup>	0.78 <sup>d</sup>		

<sup>a</sup> Mix: NR(100)-sulfur(0.5)-MBT(1.5)-zinc oxide (5.0)-lauric acid(10.0); cured 144 hr. at 100°C.  $[\eta]$  of rubber hydrocarbon component of mix in benzene = 2.43 dl./g. at 25°C.

<sup>b</sup> Vulcanizate was hot extracted for 48 hr. with azeotropic mixture of methanol-acetone-chloroform and then treated with hydrochloric acid-ether; 16.3 wt.-% of the vulcanizate was removed by this treatment; the network contained  $S_c = 0.31$  wt.-% and had  $E = 2.4_s$  atoms of sulfur combined in the network per chemical crosslink present.

<sup>c</sup> Network treated with 0.4M solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. and 4 hr. at 80°C.

<sup>d</sup> Network treated with 0.4M solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. and 19 hr. at 80°C.

oxide system (Table VII), this value being derived from the equilibrium  $v_r$  and  $C_{1, \text{dry}}$  data of the unextracted vulcanizates described in Part III.<sup>4</sup>

The loss in chemical crosslinks effected by sodium di-*n*-butyl phosphite was usually assessed from equilibrium values of  $v_r$  of the networks in *n*-decane after treatment with the chemical probe together with values of  $1/2 M_{c, \text{chem.}}^N$  of the original networks as described above. The  $v_r$  values of the sodium di-*n*-butyl phosphite-treated networks were calculated by assuming that the extranetwork material present acted as a filler. In using these values of  $v_r$  to obtain estimates of  $1/2 M_{c, \text{chem.}}^N$  of the treated networks it is assumed that  $\mu$  is the same for the networks before and after treatment with the sodium di-*n*-butyl phosphite and it is evaluated by means of eq. (5) from the measured values of  $C_1$  and  $v_r$  of the untreated vulcanizate networks. This procedure and the assumed constancy of  $\mu$  are not unequivocal, but were accepted in these initial studies because of the difficulty frequently experienced in determining  $C_1$  values from stress-strain measurements on the treated networks which had been considerably degraded by the sodium di-*n*-butyl phosphite. The extent to which the procedure is reliable was tested on vulcanizate networks obtained from the system: NR(100)-sulfur(0.5)-MBT(1.5)-zinc oxide(5)-lauric acid(10) cured for 144 hr. at 100°C. Values of  $v_r$  and  $C_{1, \text{swollen}}$  were determined on the networks before and after treatment with sodium di-*n*-butyl phosphite and were used to obtain  $\mu$  and  $1/2 M_{c, \text{chem.}}^N$  values of the respective networks (Table II). The results show an increase in  $\mu$  after treatment and indicate that use of the  $\mu$  value of the untreated network to estimate the number of crosslinks broken by the sodium di-*n*-butyl phosphite leads to an appreciable error in this estimate for the networks examined.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### Accelerated NR-Sulfur Vulcanizing Systems

Tables III and IV give the data for the structural characteristics of vulcanizate networks formed at various cure times with MBT-accelerated systems which lead, respectively, to inefficient and efficient use of sulfur for crosslinking purposes.<sup>11,12</sup>

For the system of Table III, containing only 1 phr of lauric acid, the inefficient use of sulfur is revealed by the values of  $E$  which increase progressively with reaction time from 15.8 to 19.8. Throughout the cure range studied, a significant proportion of the combined sulfur is removed by triphenylphosphine treatment, indicating the presence of polysulfide links ( $-\text{S}_x-$ ;  $x \geq 2$ ) in the network, but the proportion of the total combined sulfur which is polysulfidic decreases with cure time. As indicated earlier, these polysulfidic links may be present in the network either as actual crosslinks or in pendent groups of the type

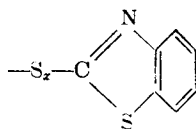


TABLE III  
Structural Characteristics of Vulcanizate Networks Derived from an Inefficient MBT-Accelerated NR-Sulfur System<sup>a</sup>

Cure time, min.	$C_1$ of original vulcanizate at 25°C., dynes/cm. <sup>2</sup> × 10 <sup>-4</sup>	$1/2 M_c$ , chem., g.-moles chemical crosslinks/g. rubber network × 10 <sup>8</sup> (based on $C_1$ values of original vulcanizate)	Vulcanizate removed by extraction <sup>b</sup> and acid treatment, wt.-%	Sulfur as zinc sulfide ( $S^{2-}$ ), wt.-% of rubber network		Sulfur combined in network ( $S_b$ ), wt.-% of rubber network		Number $E$ of sulfur atoms combined in network		$S_c$ removed by treatment of network with $(C_6H_5)_3P$ , % <sup>c</sup>	Number $E'$ of sulfur atoms combined in network per chemical crosslink present after treatment with $(C_6H_5)_3P$		Equilibrium $\nu_r$ (swelling in $n$ -decane at 25°C.)	% of chemical crosslinks which are di- and/or polysulfidic
				wt.-% of rubber network	wt.-% of rubber network	per chemical crosslink present	per chemical crosslink present	Extracted ether-HCl-treated vulcanizate	Network after treatment with $(n-BuO)_2PONa^d$					
10	0.98	2.33	5.5	0.10	1.18	15.8	47	8.4	0.282	—	—	—	—	~100
30	1.01	2.42	5.7	0.20	1.46	18.8	35	12.2	—	—	—	—	—	—
120	0.94	2.20	5.9	0.25	1.40	19.8	30	13.8	0.265	0.127	0.127	0.127	0.127	71 <sup>f</sup>

<sup>a</sup> NR(100)-sulfur (1.5)-MBT (1.5)-zinc oxide (5.0)-lauric acid (1.0); cured at 140°C.  $[\eta]$  of rubber hydrocarbon component of mix in benzene = 2.51 dl./g. at 25°C.

<sup>b</sup> Samples extracted for 24 hr. in hot acetone under nitrogen.

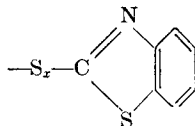
<sup>c</sup> Vulcanizate networks heated with triphenylphosphine by method C for 72 hr. at 80°C.

<sup>d</sup> Network treated with 0.4M solution of  $(n-BuO)_2PONa$  for 24 hr. at 25°C. and 4.5 hr. at 80°C.

<sup>e</sup> Too swollen to measure.

<sup>f</sup> Determined from equilibrium  $\nu_r$  values of the networks before and after treatment with  $(n-BuO)_2PONa$ , for a value of  $\mu = 0.46$  derived from the  $C_1$  and equilibrium  $\nu_r$  values of the unextracted vulcanizate.

where  $x \geq 2$ . The present data do not permit quantitative determination of the relative amounts of these two types of polysulfidic links, but the results from the treatment of the network with sodium di-*n*-butyl phosphite clearly show that throughout the cure range studied a substantial proportion of the crosslinks contain  $-S_x-$  links with  $x \geq 2$ . At the earliest cure time studied, which is close to optimum crosslinking, virtually all the crosslinks are of this form and even when vulcanization is extended well into the region of modulus reversion (120 min. at 140°C.) over 70% of the crosslinks are di- or polysulfidic. Analyses of the products derived from the reaction of 2-methylpent-2-ene with the accelerator-sulfur and TMTD-zinc oxide systems analogous to the rubber systems described in this paper show the virtual absence of carbon-carbon crosslinks,<sup>13,14</sup> and thus for the vulcanizates derived from these systems those crosslinks which resist cleavage by sodium di-*n*-butyl phosphite must be monosulfidic. The values of  $E'$  given in Table III are high, indicating that there is extensive modification of the original networks by cyclic monosulfide groups or by pendent groups of the type:



where  $x \geq 1$ . This form of main-chain modification increases substantially relative to crosslinking as vulcanization proceeds and as the average length of  $-S_x-$  in the crosslinks decreases, as evidenced by the increase in  $E'$  from 8.4 at 10 min. cure to 13.8 at 120 min. cure.

As will be discussed more fully elsewhere,<sup>11</sup> use of a temperature of 100°C. instead of 140°C. with the vulcanizing system of Table III leads to some improved use of sulfur for crosslinking, as reflected in  $E$  values ranging from 11 at early cure times to 14 at optimum crosslinking. However, the combined use of 100°C. and a high fatty acid level (10 phr of lauric acid) as in the system of Table IV, leads to markedly more efficient use of sulfur for crosslinking\* and a consequent marked change in the pattern of sulfur combination in the network. This is revealed by the much higher crosslink density attained with the available sulfur (1.5 phr in both systems) and by the much lower  $E$  values, which range from ca. 7 at early cure time to 2.6 at maximum crosslinking. A high proportion of the combined sulfur in the initially formed network is polysulfidic (cf.  $E = 6.9$  and  $E' = 2.7$  for the 3 hr. network) and nearly all of the crosslinks are of the type  $RS_xR$  ( $x \geq 2$ ). With increasing cure time up to 144 hr. crosslinking increases progressively, while the proportion of total combined sulfur which is polysulfidic decreases (cf.  $E = 2.6$  and  $E' = 2.1$  for the 144 hr. network), and the proportion of monosulfide crosslinks increases so that at maximum crosslinking about 55% of the crosslinks are monosulfidic. The  $E'$  values are low throughout

\* This effect was demonstrated earlier by Barton and Hart,<sup>15</sup> but they did not attempt a more detailed structural resolution of the networks as is reported here.

TABI  
 Structural Characteristics of Vulcanizate Networks Deriv

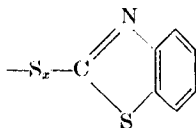
Cure time, hr.	Sol. content of vulcanizate wt.-% <sup>b</sup>	$1/2 M_c^N$ , chem., g.-moles chemical crosslinks/g. rubber network $\times 10^6$ (based on equilibrium $v_r$ of extracted and acid-treated networks and use of $\mu = 0.41$ )	Sulfur as zinc sulfide ( $S^=$ ), wt.-% of rubber network	Sulfur combined in network ( $S_0$ ), wt.-% of rubber network	Number $E'$ sulfur atoms combined in network per chemical crosslink present
3	17.6	1.26	0.019	0.28	6.9
24	15.0	7.54	0.35	0.84	3.5
144	14.6	11.7	0.61	0.99	2.6

<sup>a</sup> NR (100)-sulfur (1.5)-MBT (1.5)-zinc oxide (5.0)-lauric acid (10.0); cured 100°C.  $[\eta]$  of rubber hydrocarbon component of mix in benzene = 3.1 dl./g. at 25°C

<sup>b</sup> Amount of extranetwork material removed by 24 hr. hot acetone extraction followed by ether-hydrochloric acid treatment.

<sup>c</sup> Vulcanizate networks heated with triphenylphosphine by method A as follows: 3 hr. cure heated for 115 hr. at 80°C.; 24 hr. cure heated for 144 hr. at 80°C.; 144 hr. cure heated for 96 hr. and for 192 hr. at 80°C., both treatments giving the same percentage of removable sulfur.

the whole cure range and tend to decrease slightly with increased cure time (cf.  $E' = 2.7$  at 3 hr., decreasing to  $E' = 2.1$  at 144 hr.) These values imply that in these networks, in contrast with those described above (Table III), there must be very little structural modification of the main chains by cyclic monosulfides or pendent groups



where  $x \geq 1$ , since each crosslink must contain between one and two of the sulfur atoms combined in the triphenylphosphine-treated networks. Comparison of the data of Tables III and IV shows the marked simplification in network structure which results from the combined action of reduced reaction temperature and increased fatty acid levels in MBT-accelerated NR-sulfur vulcanizing systems; as indicated earlier this simplification is due principally to the change in fatty acid level.

Table V details the structural characteristics of vulcanizate networks derived from an "efficient" *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS)-accelerated system<sup>16</sup> identical with the "efficient" MBT-accelerated system of Table IV, except for replacement of the MBT by a molar equivalent of CBS. Differences exist in the rates of crosslinking of NR with the two systems, but the structural characteristics of the derived vulcanizate networks are broadly similar and show the same trends with increasing cure

**m an Efficient MBT-Accelerated NR-Sulfur System\***

S <sub>c</sub> moved by treatment network with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, %	Number E' of sulfur atoms combined in network per chemical crosslink present after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Equilibrium $v_r$ of vulcanizate networks (swelling in <i>n</i> -decane at 25°C.)			Chemical crosslinks which are di- and/or polysulfidic, %
		Extracted, ether-HCl- treated vulcanizate	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P- treated network	( <i>n</i> -BuO) <sub>2</sub> PONa- treated network	
61	2.7	0.188	0.132	d,e	~100 <sup>d</sup>
31	2.4	0.327	0.300	—	—
19	2.1	0.374	0.346	0.312 <sup>f</sup>	45 <sup>f</sup>

Network treated with 0.13*M* solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C.

<sup>d</sup> Too swollen to measure.

<sup>e</sup> Network treated with 0.13*M* solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. and 5 hr. at 30°C.

times. Special features of the data of Table V are: firstly, the close identity in the equilibrium  $v_r$  values of the extracted vulcanizates before and after treatment with the hydrochloric acid-ether reagent, indicating the absence of any zinc thiolate or zinc perthiolate crosslinks ( $RS_xZnS_xR$ ;  $x \geq 1$ ) in the networks throughout the cure range studied; secondly, the small loss in crosslinks resulting from the treatment of the triphenylphosphine-treated networks with sodium di-*n*-butyl phosphite, indicating that any di- and polysulfide crosslinks in the original networks are reduced almost completely to monosulfide crosslinks by the triphenylphosphine treatment as is consistent with studies with model sulfides; and thirdly, comparison of the equilibrium  $v_r$  values of the networks before and after treatment with triphenylphosphine indicates some loss in crosslinks after the treatment, and this is most pronounced when the original networks contain a high proportion of polysulfide crosslinks (this effect is also shown in Table IV). The most probable cause of this last effect is the intermolecular and intramolecular interchange of S—S bonds in the swollen network prior to or during the desulfurizing reaction of the triphenylphosphine. This leads to a "supercoiled" network<sup>17</sup> in which the network chains are permanently "locked in" to their new configurations characteristic of the swollen state, since the crosslinks, by being reduced to monosulfides which are thermally stable, can no longer rearrange after removal of the swelling agent to the configuration of the original underformed network. The supercoiled network will have an apparently lower crosslink density relative to the original network;<sup>17</sup> there may also be some real loss of crosslinks insofar as intermolecular polysulfide links are converted into intramolecular monosulfide links by the occurrence of the interchange and desulfurization processes in the swollen network. A possible contributory cause of the loss

TAB I  
 Structural Characteristics of Vulcanizate Networks Deriv

Cure time, hr.	Sol. content of vulcanizate, wt.-% <sup>b</sup>	1/2 $M_c^N$ , chem., g.-moles chemical crosslinks/g. rubber network $\times 10^3$ (based on $C_1$ values of azeotrope-extracted and ether-HCl-treated dry vulcanizates)			Sulfur as zinc sulfide (S <sup>2-</sup> ), wt.-% of rubber network	Sulfur combined in network (S <sub>c</sub> ), wt.-% of rubber network	Number $E'$ of sulfur atoms combined in network per chemical crosslink present	S <sub>c</sub> removed by treatment of network with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, % <sup>c</sup>	Number $E'$ sulfur atoms combined in network per chemic crosslink present after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P <sup>d</sup>
3.5	16.1	5.2	0.23	1.24	7.5	65	2.6		
20	16.1	8.6	0.43	1.20	4.4	50	2.2		
144	14.9	10.4	0.65	1.03	3.1	19	2.5		

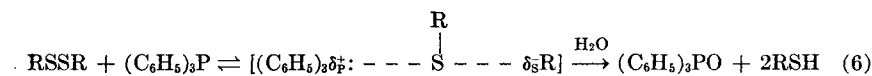
<sup>a</sup> NR (100)-sulfur (1.5)-CBS (2.37)-zinc oxide (5.0)-lauric acid (10.0); cured 100°C.  $[\eta]$  of rubber hydrocarbon component of mix in benzene at 2.32 dl./g = 25'

<sup>b</sup> Amount of extranetwork material removed by 48 hr.'s hot extraction with an azeotropic mixture of methanol-acetone-chloroform followed by ether-hydrochloric acid treatment.

<sup>c</sup> Vulcanizate networks heated with triphenylphosphine by method C for 72 hr. 80°C.

<sup>d</sup> Vulcanizate networks heated with triphenylphosphine as above and then with 0.13 *M.* solution of (*n*-BuO)<sub>2</sub> PONA for 24 hr. at 25°C. and 5.5 hr. at 80°C.

in crosslinks is the actual cleavage of S—S bonds by the combined action of triphenylphosphine and trace amounts of water present in the NR vulcanizate, e.g.:



Reaction (6) is known to occur when diphenyl disulfide is caused to react with triphenylphosphine in boiling aqueous benzene, whereas the disulfide is completely stable under anhydrous reaction conditions.<sup>18,19</sup>

The structural characteristics of networks derived from zinc dimethyldithiocarbamate (ZD<sub>N</sub>C)—accelerated NR-sulfur systems at 100°C. are detailed in Table VI. The data relating to the system with 2 phr of sulfur shows that at early cure times (0.25 hr.) most of the combined sulfur is in polysulfidic links, and the low  $E'$  value of 1.2 for this network implies that very little of the sulfur is wasted in the form of cyclic monosulfide groups or pendent groups of the type —S<sub>x</sub>C(:S)NMe<sub>2</sub>, where  $x \geq 1$ . The crosslinks for the 0.25 hr. network are entirely di- and/or polysulfidic, and with increasing cure times the crosslinks remain predominantly of this type, so that even at 20 hr. cure when a significant amount of modulus reversion has occurred, ca. 80% of the crosslinks are of the type RS<sub>x</sub>R, where  $x \geq 2$ ,



m an Efficient CBS-Accelerated NR-Sulfur System<sup>a</sup>

Equilibrium  $v_r$  values of vulcanizate networks  
(swelling in *n*-decane at 25°C.)

Azeotrope- extracted vulcanizate	Azeotrope- extracted and acid- treated vulcanizate	Azeotrope- extracted and acid- treated vulcanizate after ( <i>n</i> -BuO) <sub>2</sub> PONa treatment	Azeotrope- extracted and acid- treated vulcanizate after (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P treatment <sup>c</sup>	Azeotrope- extracted and acid- treated vulcanizate after (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P and then ( <i>n</i> -BuO) <sub>2</sub> PONa treatment <sup>d</sup>	Chemical crosslinks which are di- and/or polysulfidic, %	
					In original vulcanizate	In (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P- treated vulcanizate
0.306	0.306	e, f	0.232	0.221	~100	10 <sup>g</sup>
0.352	0.352	0.168 <sup>h</sup>	0.312	0.293	88 <sup>g</sup>	19 <sup>g</sup>
0.372	0.378	{ 0.320 <sup>e</sup> 0.324 <sup>j</sup> 0.318 <sup>h</sup>	0.346	0.334	{ 45 <sup>i</sup> 43 <sup>i</sup> 46 <sup>i</sup>	14 <sup>i</sup>

Vulcanizate network treated with 0.4*M* solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. Too swollen to measure.

Based on  $\mu = 0.43$  found for the azeotrope-extracted and acid-treated original network.

Vulcanizate network treated with 0.4*M* solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. 3.5 hr. at 80°C.

Based on  $\mu = 0.44$  found for the azeotrope-extracted and acid-treated original network.

Vulcanizate network treated with 0.13*M* solution of (*n*-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. and 5 hr. at 80°C.

although the average number of sulfur atoms in the crosslink decreases progressively as vulcanization proceeds. Concurrently with this crosslink shortening there occurs a progressively increasing degree of main-chain modification by sulfurated groups (probably mainly cyclic monosulfide and possibly some pendent groups:  $-\text{S}_x\text{C}(\text{:S})\text{NMe}_2$ ,  $x \geq 1$ ) as is evidenced by the change in  $E'$  from 1.2 at 0.25 hr. cure to 13.7 at 20 hr. cure. This increase in the structural complexity of the network with increasing cure time parallels that found in the inefficient MBT-accelerated system (Table III), but contrasts with progressive simplification as cure proceeds of the networks derived from the efficient MBT- and CBS-accelerated systems (Tables IV and V) and especially from the "sulfurless" TMTD-zinc oxide-*cis*-1,4-polyisoprene system referred to below (Table VII).

### The *cis*-1,4-Polyisoprene-TMTD-Zinc Oxide System

The structural features of the networks derived from this system depend markedly on cure time (Table VII). As described in detail in Part III<sup>4</sup> of this series, the networks formed in the initial stages of vulcanization are structurally complex, as is reflected by  $E = 15.7$  for the 0.25 hr. cure, and thereafter become structurally more simple as crosslinking proceeds up to

TABLE I  
 Structural Characteristics of Vulcanizate Networks Derived from 1

Cure time, hr.	Sol. content of vulcanizate, wt.-% <sup>b</sup>	$1/2 M_{c, \text{chem.}}^N$ (g. moles chemical crosslinks/g. rubber network) (based on $C_1$ values of dry unextracted vulcanizates) <sup>c</sup>	Sulfur as zinc sulfide ( $S^{2-}$ ), wt.-% of rubber network	Sulfur combined in network ( $S_c$ ), wt.-% of rubber network	Number of sulfur atoms combined in network per chemical crosslink present
System containing 2.0 parts sulfur					
0.25	7.5	1.50	0.17	0.34 <sub>5</sub>	7.2
2.0	4.0	4.03	0.32	1.61	12.5
20.0	3.6	3.12	0.28	1.82	18.2
System containing 3.0 parts sulfur					
0.25	10	1.64	0.039	0.41	7.8
0.50	8.7	3.12	0.087	0.77 <sub>5</sub>	7.7 <sub>5</sub>
2.0	6.9	6.25	0.24	2.29	11.4
48.0	4.9	4.90	0.38	2.61	16.6
120.0	4.9	4.76	0.43 <sub>5</sub>	2.59	16.9

<sup>a</sup> NR(100)-sulfur(2.0 or 3.0)-ZD<sub>M</sub>C(2.0)-zinc oxide(2.0); cured at 100°C.  $[\eta]$  rubber hydrocarbon component of the mixes in benzene = 2.95 dl./g. at 25°C. for containing 2.0 phr sulfur, and 2.80 dl./g. for mix containing 3.0 phr sulfur.

<sup>b</sup> Amount of vulcanizate removed by extraction with cold chloroform for 24 hr., t hot acetone for 24 hr. and treatment with ether-hydrochloric acid.

<sup>c</sup> No correction applied for the filler and other extranetwork material, since this rection will be comparable with the experimental error involved in the determination of  $C_1$ .

maximum crosslinking at 10 hr. when  $E = 3.3$ . This conclusion is now confirmed and amplified by the present data (Table VII). Thus, the trend in  $E'$  values of 9.1<sub>5</sub> at 0.25 hr. decreasing to  $E' = 3.2-3.3$  at 10 hr. indicates that main-chain modification by sulfurated groups, which we now know to mainly R-S<sub>x</sub>C(:S)NMe<sub>2</sub> ( $x \geq 1$ , R = polyisoprenyl) with lesser amounts of R-SC(:O)NMe<sub>2</sub> and R-C(:S)NMe<sub>2</sub> groups but inappreciable cyclic monosulfides,<sup>4</sup> decreases appreciably relative to crosslinks as cure proceeds. Further, the differences in the  $E$  and  $E'$  values at any given cure time show that at early cure times much of the combined sulfur is di- and polysulfidic (e.g.,  $E - E' = 6.5_5$  at 0.25 hr.) but this type of sulfur becomes less important as cure proceeds and becomes negligible at full cure (e.g.,  $E - E' \simeq 0$  at 10 hr.) The data from the sodium di-*n*-butyl phosphite treatment indicate that initially the crosslinks are entirely di- and/or polysulfidic but shorten as cure proceeds so that at full cure over 80% of the crosslinks are monosulfidic. As discussed fully in Part III<sup>4</sup> the intermediate compounds,

Ac Dimethyldithiocarbamate (ZD<sub>M</sub>C)-Accelerated NR-Sulfur Systems<sup>a</sup>

Removed treatment of network with C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, % <sup>d</sup>	Number E' of sulfur atoms combined in network per chemical crosslink present after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Equilibrium $v_r$ of vulcanizate networks (swelling in <i>n</i> -decane at 25°C.)			Chemical crosslinks which are di- and/or polysulfidic, %
		Extracted vulcanizate	Extracted and ether-HCl-treated vulcanizate	Vulcanizate network after treatment with (n-BuO) <sub>2</sub> PONa	
(83)	1.2	0.188	0.180	Network dissolved <sup>e</sup>	~100
(50)	6.3	0.286	0.278	Network almost completely dissolved <sup>e</sup>	~100
51	6.1				
(25)	13.7	0.276	0.270	0.098 <sup>f</sup>	79 <sup>g</sup>
71	2.3	—	—	Network dissolved <sup>e</sup>	~100
62	2.9	—	—	Network almost completely dissolved <sup>e</sup>	~100
47	6.1	—	—	Network almost completely dissolved <sup>e</sup>	~100
—	—	—	—	—	—
19	13.7	—	—	—	—

Vulcanizate networks heated with triphenylphosphine by method C for 96 hr. at C., except for values in parentheses where vulcanizates (ca. 3 g.) were heated with triphenylphosphine (ca. 1.2 g.) in acetone (23 ml.) for 96 hr. at 80°C. (method B).

Vulcanizate networks treated with 0.4M solution of (n-BuO)<sub>2</sub>PONa at 25°C.

Vulcanizate network treated with 0.4M solution of (n-BuO)<sub>2</sub>PONa for 24 hr. at C. and 4.5 hr. at 80°C.

Based on  $v_r$  of 0.270 for original acid-treated network and  $v_r$  of 0.098 of treated network and for  $\mu = 0.45$  derived from  $v_r$  and  $C_1$  values of original network.

RS<sub>x</sub>C(:S)NMe<sub>2</sub> ( $x \geq 2$ ) are formed rapidly in the early stages of the reaction and undergo a slower subsequent reaction in the presence of zinc oxide (or zinc sulfide) to give sulfur crosslinks and ZD<sub>M</sub>C. Confirmatory evidence for this is as follows. A vulcanizate network formed at an early stage of cure was freed from all extranetwork material except residual zinc oxide and traces of zinc sulfide by cold dichloromethane extraction for 48 hr. and then had  $1/2 M_{c, \text{chem.}}^N = 1.43 \times 10^{-5}$  g.-moles chemical crosslinks/g. rubber network.\* On heating this network *in vacuo* for 5 hr. at 140°C. considerable further crosslinking occurred, and the resulting network had  $1/2 M_{c, \text{chem.}}^N = 3.57 \times 10^{-5}$ . On treatment of the original network with triphenylphosphine (by method C) for 72 hr. at 80°C. the original  $1/2 M_{c, \text{chem.}}^N = 1.43 \times 10^{-5}$  was unchanged, but this treatment would convert all RS<sub>x</sub>C(:S)NMe<sub>2</sub> ( $x \geq 2$ ) groups into RSC(:S)NMe<sub>2</sub> groups<sup>5</sup> which are

\* Values of  $1/2 M_{c, \text{chem.}}^N$  described here and below were obtained from equilibrium  $v_r$  values in *n*-decane at 25°C. and use of  $\mu = 0.44$  for the networks.

TAB.  
 Structural Characteristics of Vulcanizate Networks Derived from a *cis*-1

Cure time, hr.	$1/2 M_{c, \text{chem.}}^N$ , g.-moles chemical crosslinks/g. rubber network based on equilibrium $v_r$ of network and $\mu = 0.44$ ) $\times 10^5$	Vulcanizate removed by extraction, wt.-% <sup>b</sup>	Sulfur as zinc sulfide (S <sup>2-</sup> ), wt.-% of rubber network	Sulfur combined in network (S <sub>c</sub> ), wt.-% of rubber network	Nitrogen combined in network (N <sub>c</sub> ), wt.-% of rubber network	Number of sulfur atoms combined in network per chemical crosslink present
0.25	1.19	6.9	0	0.60	0.073	15.7
1.0	1.56	5.7	0.02	0.55 <sub>s</sub>	0.072	11.1
10.0	2.84	7.0	0.06	0.30	0.015	3.3

<sup>a</sup>  $[\eta]$  of rubber hydrocarbon component of the mix in benzene at 25°C. = 1.31 dl./g.

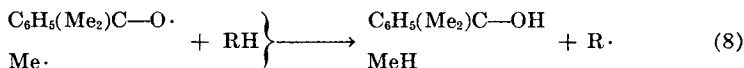
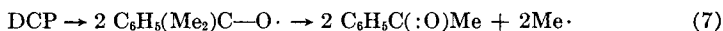
<sup>b</sup> Sample extracted with cold dichloromethane for 48 hr. under nitrogen.

<sup>c</sup> Extracted vulcanizates heated with triphenylphosphine by method C for 96 hr at 80°C., except for value in parentheses where the extracted and ether-hydrochloric acid treated vulcanizate was heated with triphenylphosphine by method B for 96 hr. at 80

incapable of subsequent reaction to give sulfur crosslinks.<sup>4,20</sup> Consistent with this, on heating the triphenylphosphine-treated network *in vacuo* for 5 hr. at 140°C. the crosslink density was virtually unchanged ( $1/2 M_{c, \text{chem.}}^N = 1.39 \times 10^{-5}$ ).

### NR- and Ethylene-Propylene Rubber (EPR)-Dicumyl Peroxide (DCP)-Sulfur Vulcanizing Systems

Only limited structural characterization has been made of the networks derived from these systems (Tables VIII and IX), but the data are sufficient to indicate the important role of sulfur in modifying the crosslinks formed when it is introduced into a peroxide vulcanizing system. Thus for the NR system (Table VIII), the carbon-carbon crosslinks which would be formed in the absence of sulfur are largely replaced by  $RS_xR$  ( $R = \text{polyisoprenyl}$ ;  $x \geq 2$ ) when sulfur is present. The polysulfide crosslinks are presumably formed by the sequence:



(where  $\text{RH} = \text{cis-1,4-polyisoprene}$  and  $\text{H}$  is an  $\alpha$ -methylene or  $\alpha$ -methyl hydrogen atom).

I  
 Iyisoprene (100)-TMTD(4)-Zinc Oxide (4) System Cured at 140°C.<sup>a</sup>

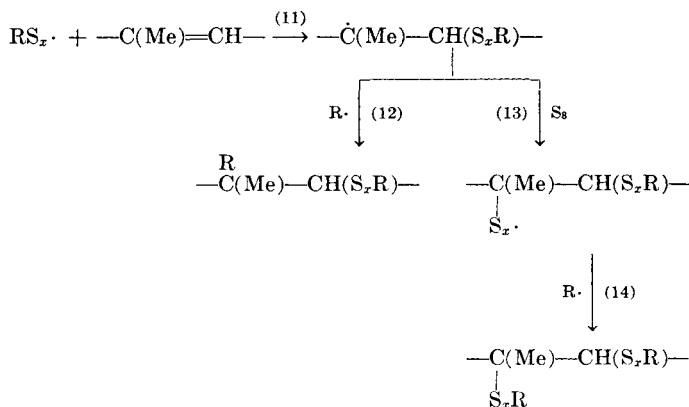
S <sub>0</sub> owed by treatment of network with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, % <sup>e</sup>	Number E' of sulfur atoms combined in network per chemical crosslink present after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Equilibrium v <sub>r</sub> of vulcanizate networks (swelling in n-decane at 25°C.)			Chemical crosslinks which are di- and/or poly- sulfidic, %	Nitrogen combined in network after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P (N <sub>c</sub> '), wt.-% of rubber network
		Original network	Network after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Network after treatment with (n-BuO) <sub>2</sub> PONa <sup>d</sup>		
42	9.1 <sub>5</sub>	0.127	0.135	<sup>e</sup>	100	0.050
30	7.8	0.175	0.176	0.116	27 <sup>f</sup>	0.059
{ 0 {(3)	{ 3.3 { 3.2	0.242	0.241	0.223	17.5 <sup>f</sup>	0.017

Vulcanizate networks treated with 0.4M solution of (n-BuO)<sub>2</sub>PONa for 24 hr. at C. and 3 hr. at 80°C.

Too swollen to measure.

Determine from v<sub>r</sub> values before and after treatment with (n-BuO)<sub>2</sub>PONa and using μ = 0.44.

Alternative routes to di- and polysulfidic crosslinks are possible: viz. (1) thermal reaction of sulfur with NR as occurs in unaccelerated sulfur vulcanization of NR; and (2) intermolecular addition of the persulfenyl radical RS<sub>x</sub>· to the double bond:



Clarification of the relative importance of these various routes to sulfidic crosslinks is not possible from the methods described here, and would be best achieved by use of appropriate model olefins. The approximately 30% of original crosslinks which are not cleaved by sodium di-n-butyl phosphite (Table VIII) are presumably carbon-carbon and/or monosulfide.

The E' values of 3.2-3.8 suggest that some of the combined sulfur must be wasted as sulfurated main-chain modifications (e.g., cyclic monosulfides or pendent groups such as R-S<sub>x</sub>Me, x ≥ 1), but the possibility cannot be dis-

TABLE VIII  
Structural Characteristics of Vulcanizate Networks Derived from a NR(100)-Dicumyl Peroxide(4)-Sulfur(1.4) System  
Cured at 140°C.<sup>a</sup>

Cure time min.	$1/2 M_c^{\text{chem.}}$ g.-moles chemical crosslinks/g. rubber network $\times 10^8$ (based on $C_1$ of dry extracted vulcanizate) <sup>b</sup>	Sulfur combined in network (S <sub>c</sub> ), wt.-% of rubber network	Number $E$ of sulfur atoms combined in network	$S_c$ removed by treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, % <sup>c</sup>	Number $E'$ of sulfur atoms combined in network per chemical crosslink present after treatment with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P		Equilibrizate networks of vulcanizate networks (swelling in <i>n</i> -decane at 25°C.)		Chemical crosslinks which are di- and/or polysulfidic, %
					per chemical crosslink present	removed by treatment of network with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, % <sup>c</sup>	Extracted network	Network after treatment with (n-BuO) <sub>2</sub> PONa <sup>d</sup>	
35	2.63	0.57	6.8	53	3.2	0.254	0.162	70 <sup>e</sup>	
80	4.03	0.95	7.4	48.5	3.8	0.293	0.202	73 <sup>f</sup>	

<sup>a</sup>  $[\eta]$  of rubber hydrocarbon component of mix in benzene at 25°C. = 3.24 dl./g.

<sup>b</sup> Vulcanizates extracted with hot acetone for 24 hr. under nitrogen.

<sup>c</sup> Vulcanizate networks heated with triphenylphosphine by method C for 96 hr. at 80°C.

<sup>d</sup> Vulcanizate networks treated with 0.4M solution of (n-BuO)<sub>2</sub>PONa for 24 hr. at 25°C. and 4.5 hr. at 80°C.

<sup>e</sup> Determined from  $\nu_r$  values of networks before and after treatment with (n-BuO)<sub>2</sub>PONa and use of  $\mu = 0.42$  derived from the  $C_1$  and  $\nu_r$  values of the original network.

<sup>f</sup> Determined from  $\nu_r$  values of networks before and after treatment with (n-BuO)<sub>2</sub>PONa and use of  $\mu = 0.435$

TABLE IX  
Structural Characteristics of Vulcanizate Networks Derived from Ethylene-Propylene Rubber(EPR)-Dicumyl Peroxide-Sulfur Systems

Mix <sup>a</sup>	Cure time, min.	Cure temp., °C.	Vulcanizate removed by extraction with hot acetone for 24 hr., wt.-%	Sulfur combined in network (S <sub>c</sub> ), (wt.-% of extracted vulcanizate network)	S <sub>c</sub> removed by treatment of network with (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P, % <sup>b</sup>	Equilibrium $\nu$ , of vulcanizate networks (swelling in benzene at 25°C.)	
						Extracted vulcanizate network	Network after treatment with (n-BuO) <sub>2</sub> PONa <sup>c</sup>
Mix I	240	140	13.0	0.45	—	—	—
	40	165	13.3	0.41	0	0.34	0.35
Mix II	240	165	13.0	0.41	—	—	—
	40	165	16.0	2.04	51	0.35	0.19
240	165	15.0	2.03	—	—	—	—

<sup>a</sup> Mix I: EPR(100), dicumyl peroxide(4.0), sulfur(0.4); Mix II: EPR(100), dicumyl peroxide(8.0), sulfur(4.0).

<sup>b</sup> Extracted vulcanizates heated with triphenylphosphine by method C for 90 hr. at 80°C.

<sup>c</sup> Extracted vulcanizates treated with 0.4M solution of (n-BuO)<sub>2</sub>PONa for 24 hr. at 25°C.

counted that these  $E'$  values reflect the existence of vicinal crosslinks as formed in the reaction sequence (9)  $\rightarrow$  (11)  $\rightarrow$  (13)  $\rightarrow$  (14).

The inclusion of sulfur in an EPR-DCP vulcanizing system is known to improve the physical properties (especially strength) of the resulting vulcanizates.<sup>21-23</sup> All or part of the sulfur in the mix becomes combined in the network but the extent of combination and the form in which it is combined depend upon the ratio of sulfur:peroxide when vulcanization is conducted under conditions leading to complete decomposition of peroxide (Table IX). When this ratio is low, all the incident sulfur is combined in the network after 40 min. at 165°C. (mix I, Table IX) but none of it is present in di- or polysulfidic links as shown by the inability of triphenylphosphine to remove any combined sulfur or of sodium di-*n*-butyl phosphite to cause cleavage of any crosslinks. However, at a much higher sulfur: peroxide ratio (mix II, Table IX) the crosslinking efficiency of the peroxide and the proportion of the initial sulfur which is combined in the network are reduced, much of the combined sulfur is now di- and polysulfidic, and a significant proportion of the crosslinks is di- and/or polysulfidic.

#### IV. CONCLUDING REMARKS

The present work shows how the structural features of sulfur vulcanizate networks can be greatly clarified by measurements of chemical crosslinks ( $1/2 M_{c, \text{chem.}}^N$ ) and combined sulfur coupled with the application of the chemical probes: triphenylphosphine and sodium di-*n*-butyl phosphite. In the light of the experience gained here it is apparent that some refinement in the methods used in these structural characterizations is both necessary and possible. Thus, it is recommended that triphenylphosphine treatment be done on unswollen networks (method C), since this is the most efficient way of reducing di- and polysulfide links to monosulfide links. With regard to the use of sodium di-*n*-butyl phosphite it is recommended: (a) that one studies NR vulcanizates with as high degrees of crosslinking as possible (equilibrium  $\nu_r$  values in *n*-decane at 25°C.  $\geq 0.3$ ) to obviate the imprecision in the estimates of di- and polysulfide crosslinks which occurs in less crosslinked networks due to the reagent cleaving the small number of other (presumably peroxide) links which are either present in the original rubber or are introduced during the mastication process (see Table I); (b) that estimates of  $1/2 M_{c, \text{chem.}}^N$  both before and after treatment with the reagent should be based on stress-strain ( $C_1$ ) measurements since, as shown by the data of Table II, the networks resulting from the sodium di-*n*-butyl phosphite-treatment have appreciably higher  $\mu$  values than the untreated networks, presumably due to the presence of bound phosphorus-containing groups. The determination of  $1/2 M_{c, \text{chem.}}^N$  from stress-strain ( $C_1$ ) rather than swelling ( $\nu_r$ ) measurements is recommended for all NR-vulcanizate networks since, as is clearly shown here, the value of  $\mu$  (as derived from  $C_1$  and equilibrium  $\nu_r$  measurements as described above) for networks from a given rubber and with a given swelling liquid is not independent of the vul-



canizing system or of the cure time. In fact,  $\mu$  increases significantly as the sulfur content of the network increases, especially when this sulfur is present in cyclic monosulfide main-chain modifications. This feature of variable  $\mu$  values is exemplified by  $\mu = 0.42$  for NR-peroxide vulcanizates swollen in *n*-decane at 25°C.;<sup>24</sup>  $\mu = 0.46$  for the 120 min. cured MBT-accelerated vulcanizate network (Table III) which contains 1.4% combined sulfur most of which is in sulfurated main-chain modifications; and  $\mu = 0.50$  for an unaccelerated NR-sulfur vulcanizate network which contains 5.2% combined sulfur,<sup>6</sup> most of which (ca. 80%) is present in cyclic monosulfide groups.<sup>2</sup>

The present results show that the pattern of sulfur combination in vulcanizate networks is very dependent on the vulcanizing system used (i.e., type and relative concentration of crosslinking agent, accelerator, and fatty acid activator) and on the vulcanizing conditions (time and temperature of cure). By controlled variation of these reaction variables one can produce NR networks which range from those which are structurally very simple and which contain mainly monosulfide crosslinks and negligible modification of the original rubber chains (Tables IV, V, and VII) to those which approach the structural complexity of unaccelerated NR-sulfur networks<sup>1,2</sup> and have much of the combined sulfur present in di- and polysulfidic crosslinks and wastefully combined in sulfurated main-chain modifications (Tables III and VI). These variations in the structural features of networks derived from a given rubber will be reflected in differences in the physical properties and aging characteristics of the vulcanizates, as is discussed in detail elsewhere.<sup>25,26</sup>

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### Résumé

On a employé les déterminations du degré de pontage chimique et les valeurs de l'efficacité de pontage ( $E$ ; c.à.d. le nombre d'atomes de soufre combinés dans le réseau par pont chimique présent) en connection a-vec les essais chimiques: la triphénylphosphine et le di-*n*-butyl phosphite de sodium pour établir la nature des liens à base de soufre dans les réseaux vulcanisés dérivés d'une variété de système caoutchouc naturel accéléré-soufre, à partir du système *cis*-1,4-poly-isoprène-TMTD oxyde de zinc, et à partir de caoutchouc naturel et de caoutchouc éthylène-propylène reticulé au moyen d'un système peroxyde de dicumyle soufre. La triphénylphosphine convertit le lien polysulfure en monosulfure et en importance moindre en liens disulfure. Les valeurs de  $E'$ , c.à.d. le nombre d'atomes de soufre combinés dans le réseau par pontage chimique présent après traitement à la triphénylphosphine sont, par conséquent, une mesure de l'étendeur des modifications de la chaîne principale dans le réseau par les groupes monosulfures cycliques et/ou groupes latéraux du type  $-S_x-$ Accel (ou  $x \geq 1$  et Accel est un fragment accélérateur). Le di-*n*-butyl phosphite de sodium se scinde en di- et polysulfure ponté mais laisse le monosulfure et les ponts carbone-carbone intacts, et donne la détermination du degré de pontage chimique avant et après traitement avec ce réactif et fournit ainsi une estimation relative de ces deux types différents de pontage. Les résultats combinés indiquent que l'efficacité du soufre utilisé pour le pontage et, par conséquent, la complexité structurale des réseaux dérivés, sont très sensibles à la nature du système vulcanisant (type et concentration relative de l'agent de pontage, accélérateur et activateur) et les conditions de vulcanisation (temps et température de traitement). En général, la proportion de pontage di- et/ou polysulfures diminue avec l'augmentation du temps de traitement, et pour les systèmes accélérés au soufre, la complexité structurale du réseau augmente avec le temps de traitement, spécialement à température plus élevée de vulcanisation et aux faibles concentrations d'acide gras activateur.

### Zusammenfassung

Die Bestimmung des chemischen Vernetzungsgrades und der Werte für die Vernetzungsausbeute ( $E$ ; d.h. die Anzahl der pro Vernetzung im Netzwerk gebundenen Schwefelatome) wurde zusammen mit chemischen Methoden (Triphenylphosphin und Natriumdi-*n*-butylphosphit) zur Ermittlung der Struktur der Schwefelbrücken in Vulkanisaten einer Reihe von Naturkautschuk-Schwefel-Beschleunigersystemen, eines *cis*-1,4-Polyisopren-TMTD-Zinksystems und von Dicumylperoxyd-Schwefel-vernetzten Naturkautschuk- und Äthylpropylenkautschuk-Systemen benützt. Triphenylphosphin wandelt Polysulfidbrücken in Monosulfid-, und zu einem geringeren Ausmass, in Disulfidbrücken um. Die  $E$ -Werte, d.h. die Zahl der im Netzwerk pro chemische

Vernetzung nach Behandlung mit Triphenylphosphin gebundenen Schwefelatome, sind daher ein Mass für den Grad der Modifizierung der Hauptkette im Netzwerk durch cyclische Monosulfidgruppen oder Seitengruppen vom Typ  $-S_x-$ Accel. (wo  $x \geq 1$  und Accel. ein Beschleunigerbruchstück ist). Natrium-di-*n*-butylphosphit spaltet Di- und Polysulfidvernetzungen, lässt aber Monosulfid- und Kohlenstoff-Kohlenstoffvernetzungen intakt; die Bestimmung des chemischen Vernetzungsgrades vor und nach Behandlung mit diesem Reagens liefert daher ein Mass für diese beiden verschiedenen Vernetzungsarten. Die Ergebnisse lassen in ihrer Gesamtheit erkennen, dass die Wirksamkeit der Ausnützung des Schwefels für die Vernetzung und daher die strukturelle Kompliziertheit des abgeleiteten Netzwerks sehr empfindlich gegen die Natur des Vulkanisationsystems (Typus und relative Konzentration von Vernetzer, Beschleuniger, und Aktivator) und die Vulkanisationsbedingungen (Temperatur und Dauer) ist. Im allgemeinen nimmt der Anteil an Di- und Poly-sulfidvernetzungen mit zunehmender Vulkanisationsdauer ab. Bei Schwefel-Beschleunigersystemen steigt die strukturelle Kompliziertheit des Netzwerks mit der Vulkanisationsdauer, besonders bei höherer Vulkanisationsdauer und niedriger Konzentration des Fettsäureaktivators, an.

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