

Structural Characterization of Vulcanizates. Part III. The *cis*-1,4-Polyisoprene Tetramethylthiuram Disulfide-Zinc Oxide System

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Synopsis

The vulcanization of a purified synthetic *cis*-1,4-polyisoprene (100 parts) with tetramethylthiuram disulfide (TMTD; 4 parts) and zinc oxide (4 parts) at 140°C. yields a network which at short cure time (15 min.) is structurally complex, containing 13.5 atoms of sulfur and 4.3 atoms of nitrogen per chemical crosslink present. The network becomes progressively simpler in structure as crosslinking proceeds, and at full cure (10 hr.) contains 3.2 atoms of sulfur and 0.7 atoms of nitrogen per chemical crosslink present. The initial network complexity is due mainly to the presence of rubber-bound intermediate compounds, $R \cdot S_x C(:S)N(CH_3)_2$ ($R =$ polyisoprenyl; $x \geq 2$), which yield sulfidic crosslinks and zinc dimethyldithiocarbamate (ZDMC) on heating with zinc oxide or zinc sulfide as revealed by the efficient crosslinking on further heating at 140°C. of extracted undercured vulcanizates. Evidence is presented that the intermediate compounds result from interaction of the polyisoprene with a sulfurating species formed by a prior reaction of TMTD with zinc oxide, and not, as previously supposed by others, by direct reaction of the polyisoprene with TMTD. Our knowledge of the detailed structure of the network obtained at full cure is presented, together with estimates of the principal extra-network compounds (ZDMC, tetramethylthiourea, and zinc sulfide) formed at full cure; these compounds together with the sulfur and nitrogen combined in the network account for ca. 90% of sulfur and nitrogen originally present as TMTD.

I. INTRODUCTION

This paper describes the structural characterization of vulcanizates derived from the synthetic *cis*-1,4-polyisoprene-tetramethylthiuram disulfide (TMTD)-zinc oxide system at 140°C. and at various cure times. The structural features studied include the network *per se*, i.e., the nature of the crosslinks and of modifications of the polyisoprene chain at points distant from the crosslink, and the extra-network material which represents both reactants and products derived from these which are not an integral part of the network. The work described here, coupled with complementary studies (both published and unpublished) referred to in the text, reveal the time-dependent nature of the vulcanizate structure and clarify the chemical processes involved in the vulcanization of olefinic elastomers with the TMTD-zinc oxide system.

Synthetic *cis*-1,4-polyisoprene was used in preference to natural rubber (NR) in order to facilitate the accurate analysis of nitrogen bound in the

rubber network and to assess the influence of the nonrubber constituents of NR on its cure characteristics and vulcanizate structure. The latter aspect is dealt with briefly here, but will be expanded in a subsequent part of this series.

II. MATERIALS AND EXPERIMENTAL METHODS

Materials

cis-1,4-Polyisoprene (Ameripol SN, kindly supplied by Goodrich-Gulf Chemicals, Inc.) after 24 hr. hot acetone extraction in nitrogen and drying *in vacuo* at room temperature, contained S, 0.01%; N, 0.010%; ash, 0.2%. TMTD (Vulcafor TMT of Imperial Chemical Industries Ltd.) was recrystallized from chloroform-ethanol to give a sample having m.p. 155–156°C. (Calc. for $C_8H_{12}N_2S_4$: C, 30.0; H, 5.0; N, 11.7; S, 53.3%. Found: C, 30.0; H, 4.9; N, 11.8; S, 52.9%.) Zinc oxide was No. 3 Normal French Process grade, kindly supplied by Amalgamated Oxides (1939) Ltd. NR was Yellow Circle RSS1.

Preparation of Vulcanizates

Mix I. Mix I consisted of *cis*-1,4-polyisoprene (100 parts by weight); TMTD (4.0); ZnO (4.0). The TMTD and zinc oxide were masterbatched separately with part of the rubber on a mill at 40–50°C. and then blended rapidly with the remaining rubber at the same temperature to minimize atmospheric oxidation of the rubber. Mixes were stored in nitrogen prior to vulcanization which was effected in $12 \times 10 \times 0.1$ cm. molds at $140 \pm 0.5^\circ\text{C}$. Molds were rapidly cooled before opening the press.

Mix II. This consisted of *cis*-1,4-polyisoprene (100); TMTD (4.0). This was prepared and cured as for mix I above.

Determination of Number-Average Molecular Weights (\bar{m}_n) of the Polyisoprene Prior to Vulcanization

From limiting viscosity numbers, $[\eta]$, of the rubber hydrocarbon component (>99.4% sol) of the mixes, determined as in Part I,¹ estimates of \bar{m}_n were obtained using the empirical relation:² $[\eta]$ (dl./g.) = $2.29 \times 10^{-7} \bar{m}_n^{1.33}$. In one case an independent osmometric determination of \bar{m}_n agreed within 1.4% of the value derived from the above calibration.

Determination of Degrees of Chemical Crosslinking of Vulcanizate Networks

(a) From Stress-Strain Measurements

Equilibrium stress-strain measurements were made at 25°C. on samples of both unextracted vulcanizates and vulcanizates subjected to continuous cold extraction with dichloromethane for 24 hr. in nitrogen in the dark and were used as described in Part I¹ to obtain values of the elastic constant.

C_1 , and of λ^* , the extension ratio at which the experimental stress-strain curve departs from the linear portion by 2.5% of C_1 . The measured C_1 values were converted to C_1^N values, i.e. values of the elastic constant C_1 appropriate to the network, by assuming that all extra-network material acts as inert filler and by applying the equation:

$$C_{1, \text{ measured}} = C_1^N (1 + 2.5 x + 14.1 x^2) \quad (1)$$

where x is the volume fraction of extra-network material in the unextracted or extracted vulcanizate. Values of C_1^N and λ^* were then used independently as described in Part I¹ to obtain values of the physically effective chemical degree of crosslinking ($1/2 M_{c, \text{ chem.}}^N$) (gram-moles of chemical crosslinks per gram of rubber network), where $M_{c, \text{ chem.}}^N$ is the number-average molecular weight of the chain segments between crosslinks in the network. Near-identical values of $M_{c, \text{ chem.}}^N$ were obtained from the C_1^N data for the unextracted and extracted vulcanizates obtained at a given cure time, and therefore only the data for the unextracted samples are quoted below.

(b) From Swelling Measurements

Equilibrium values of v_r^N , the volume fraction of rubber network in the swollen rubber, were obtained for both unextracted and extracted vulcanizates by immersing them in *n*-decane for 48 hr. at 25°C. (cf. Moore and Watson³). The percentage gel (i.e., the weight per cent of the vulcanizate insoluble in the swelling agent under the given conditions) was also determined. Values of v_r^N were determined assuming the density of the rubber network to be 0.910 g./ml. and that of *n*-decane to be 0.726 g./ml. at 25°C. and by making appropriate corrections for the extra-network material in the swollen vulcanizates. Values of v_r^N were then converted into values of C_1^N by means of the empirical relationship between C_1 and $v_{r(n\text{-decane})}$ obtained for peroxide vulcanizate networks of natural rubber;⁴ it is assumed that a value of μ , the polymer-solvent interaction coefficient of the Flory-Huggins swelling equation, of 0.42 found for NR-peroxide vulcanizate networks also applies for the present vulcanizate networks throughout the crosslinking range studied. The C_1^N values were then used to obtain values of $1/2 M_{c, \text{ chem.}}^N$ as described above.

Extraction of Vulcanizates

Extraction conditions were chosen to effect rapid and complete removal from the network of all organic extra-network compounds without causing decomposition or further reaction of the latter (particularly unreacted TMTD) or changes in the rubber network during the extraction process. Of several methods tried, the preferred one involved continuous cold extraction with dichloromethane for 24 hr. under nitrogen in the dark. This method is experimentally more convenient than a discontinuous cold ethyl acetate-extraction procedure.⁵ Continuous extraction with either

cold ethyl acetate or acetone resulted in appreciable decomposition of unreacted TMTD in the boiling solvent, and continuous extraction with hot solvents caused further crosslinking of undercured vulcanizates.

Chemical Analysis of Vulcanizates

(a) *Determination of Combined Sulfur (S_c) and Combined Nitrogen (N_c) in the Vulcanizate Network and Inorganic Sulfide Sulfur ($S^=$) in the Extra-Network Material*

The sum of ($S_c + S^=$) in the extracted vulcanizates was determined on ca. 300 mg. samples by the methods described in Part I.¹ Replicate analyses agreed well within the experimental error for the methods of $\pm 0.02\%$ S. Inorganic sulfide sulfur ($S^=$) was determined independently on 1 g. samples milled to a fine crumb.⁶ Values of S_c were then derived by difference.

Combined nitrogen in the network (N_c) was determined on 500 mg. samples by a micro-Kjeldahl method⁷ modified to accommodate the macro samples by using 6 ml. sulfuric acid for the digestion. The experimental error was $\pm 0.003\%$ N. Allowance was made for nitrogen present in the original rubber.

(b) *Determination of Organic Extra-Network Compounds*

(1) **Unreacted Tetramethylthiuram Disulfide (TMTD).** The TMTD present in dichloromethane extracts was determined by reacting it with excess of thiosulfate ion in the presence of zinc ions.⁸ The dichloromethane extract from a known weight of vulcanizate (ca. 7 g.) was made up to 500 ml. with the same solvent. A portion (400 ml.) of the solution was reduced to about 10 ml. by removal of solvent, diluted with methanol (50 ml.) and then treated with 0.1*N* aqueous zinc acetate (5.0 ml.) and 0.2*N* aqueous sodium thiosulfate (5.00 ml.) and the mixture allowed to stand for 1 hr., during which time zinc dimethyldithiocarbamate (ZDMC) precipitated. The dichloromethane and most of the methanol were removed at room temperature under reduced pressure and the aqueous residue was extracted with dichloromethane (2 \times 30 ml.) to remove all organic material. The aqueous solution was titrated with 0.1*N* iodine solution to determine unreacted thiosulfate ion and hence the amount of TMTD originally present. In control experiments, determinations of standard solutions of TMTD (40–100 mg.) in the presence of ZDMC (50–250 mg.) and tetramethylthiourea (TMTU) (20–80 mg.), thereby covering the concentration ranges of these compounds expected in vulcanizate extracts, were accurate to within $\pm 1\%$.

(2) **Zinc Dimethyldithiocarbamate (ZDMC).** *Method A.* This is based on the determination of zinc in the dichloromethane extracts of the vulcanizates and the assumption that zinc in the extract is present solely as ZDMC. The solvent was removed from an aliquot (50.0 ml.) of the original extract obtained as in (1) above and the residue digested with 2:1

(v/v) mixture of glacial acetic acid/concentrated hydrochloric acid (1 ml.) for 4 hr. followed by boiling the product with water for 1 hr. to obtain an aqueous solution of zinc ions derived from the ZDMC. The latter was adjusted to pH 9 with dilute ammonium hydroxide and the zinc ions were determined by titration with a 0.01*N* solution of the disodium salt of diaminoethanetetraacetic acid using Solochrome Black indicator.

Method B. This is essentially the same as method A except that zinc ion determined on the dichloromethane extracts obtained after determination of TMTD as in (1) above. For the acid digestion 5 ml. of the mixed acids were used. In this determination of ZDMC allowance was made for the ZDMC produced during the determination of TMTD.

Method C. This colorimetric method was used to determine small amounts of ZDMC. The basis of the method is the conversion of ZDMC into the highly yellow-colored cupric dimethyldithiocarbamate (CuDMC) and colorimetric determination of the latter by comparison with standard solutions of CuDMC. Aliquots of the dichloromethane extracts were dried down, redissolved in chloroform, and the ZDMC then converted into CuDMC by treatment with a 1% solution of cupric nitrate in 1*N* ammonium hydroxide, the visible light absorption of the resulting solution then being measured with a Spekker photoelectric absorptiometer fitted with violet filters. Standard solutions of CuDMC were determined within an accuracy of $\pm 1.5\%$. It was established that neither TMTD (\leq the concentration of ZDMC present in the extract) nor TMTU (\leq one-third of the ZDMC concentration) interfered with the determination of the ZDMC.

These methods were compared with reference to an undercured (0.5 hr. at 140°C.) and to a fully-cured (10 hr. at 140°C.) vulcanizate (Table I). They were all in good agreement for the 10 hr.-cured sample, as were methods A and C for the 0.5 hr.-cured sample. Method B gives low estimates for the latter sample, due, probably to rubber which is soluble in the dichloromethane being coagulated on addition of aqueous reagents and thus occluding some of the TMTD and ZDMC during their estimations.

(3) **Tetramethylthiourea (TMTU).** Estimates of TMTU were made only on vulcanizates devoid of unreacted TMTD. Weighed portions of the vulcanizates were sealed *in vacuo* within 15 min. of removal from the mold and then heated at 60°C. for 108 hr. and the sublimed TMTU, to-

TABLE I
Comparison of Methods for Determining Zinc Dimethyldithiocarbamate (ZDMC)
in Dichloromethane Extracts of Vulcanizates

| Vulcanizate (cure time, hr., at 140°C.) | ZDMC, mole-% of original TMTD | | |
|---|-------------------------------|----------|----------|
| | Method A | Method B | Method C |
| 0.5 | 36.0 | 31.6 | 37.2 |
| 10.0 | 71.9 | 71.0 | 72.6 |

gether with other volatile material, collected in a side tube cooled in liquid nitrogen. The volatile material was dissolved in water and the TMTU determined by formation of a molecular complex with mercuric nitrate.⁹ An accuracy of $\pm 1\%$ was achieved using 5 mg. samples of TMTU and 0.01*N* aqueous mercuric nitrate.

Ultraviolet spectrometric determination of TMTU in the dichloromethane extracts, using the well-defined maximum, $\epsilon = 18,400, 261 \text{ m}\mu$ present in the spectrum of dichloromethane solutions of pure TMTU, was abandoned because of interference by other compounds in the extracts.

Thermal Treatment of Extracted Vulcanizates

Extracted vulcanizates were sealed *in vacuo* after degassing for 5 hr. at $<10^{-5}$ mm. Hg pressure and were then heated at $140 \pm 0.1^\circ\text{C}$. for the times specified below. The vulcanizates were then extracted for 24 hr. with hot chloroform in nitrogen in the dark and dried *in vacuo* to constant weight; this extraction procedure did not alter the network structure as assessed by the equivalence of ν , values before and after extraction.

III. EXPERIMENTAL RESULTS

Structural Characterization of Vulcanizates Derived from the *cis*-1,4-Polyisoprene-TMTD-Zinc Oxide System (Mix I: Cured at 140°C .)

(a) *The Vulcanizate Network*

Table II records the data relating to the physical characterization of the unextracted and extracted vulcanizates produced at different cure times. Disparity exists between the values of $1/2 M_{c, \text{chem.}}^N$ obtained from stress-strain and volume swelling measurements, and this becomes more marked with increasing degree of crosslinking. The reason for the disparity is not clear, but it may possibly be due to the value of μ appropriate to these networks being different from that ($\mu = 0.42$) which obtains for peroxide-NR vulcanizate networks.⁴ Since any chemical modification of the main chains of the rubber is more likely to affect the swelling characteristics (by causing a change in μ for a given swelling agent) rather than the elastic behavior of the network, we have chosen to use the values of $1/2 M_{c, \text{chem.}}^N$ derived from C_1^N data (from stress-strain measurements) in the further structural characterization of the network.

Table III details the analyses for sulfur and nitrogen combined in the network (S_c and N_c) together with sulfur (S^-) present as zinc sulfide in the extra-network material. The values of S_c and N_c , taken in conjunction with the derived values of $1/2 M_{c, \text{chem.}}^N$, yield values of the number of atoms of sulfur and nitrogen, respectively, combined in the network per chemical crosslink present at various stages of cure (Table III).

TABLE III
 Determination of Nitrogen (N_c) and Sulfur (S_c) Combined in Vulcanizate Networks, and of Sulfur (S^-) present as Zinc Sulfide in Vulcanizates Derived from the *cis*-1,4-Polyisoprene-TMTD-Zinc Oxide System (Mix I) at 140°C.

| Cure time, hr. | Material extracted by dichloro-methane, wt.-% of unextracted vulcanizate | Ash, wt.-% of extracted vulcanizate | Combined nitrogen (N_c), wt.-% of extracted vulcanizate | Sulfide sulfur (S^-), wt.-% of extracted vulcanizate | Combined sulfur (S_c), wt.-% of extracted vulcanizate | N_c , g. atoms N/g. rubber network $\times 10^5$ | S_c , g. atoms S/g. rubber network $\times 10^5$ | Atoms of | |
|----------------|--|-------------------------------------|---|--|---|--|--|---|---|
| | | | | | | | | nitrogen combined in network per chemical crosslink present | sulfur combined in network per chemical crosslink present |
| 0.25 | 6.88 | 3.65 | 0.083 | 0 | 0.59 | 6.2 | 19.4 | 4.3 | 13.5 |
| 0.5 | 6.28 | 3.55 | 0.083 | 0 | 0.58 | 6.2 | 19.0 | 3.8 | 11.7 |
| 1.0 | 5.68 | 3.3 | 0.083 | 0.02 | 0.55 | 6.2 | 18.0 | 3.4 | 10.0 |
| 2.0 | 5.15 | 3.0 | 0.075 | 0.03 | 0.51 | 5.55 | 16.6 | 2.7 | 8.2 |
| 6.0 | 4.86 | 3.0 | 0.040 | 0.05 | 0.35 | 2.95 | 11.3 | 1.0 | 3.8 |
| 10.0 | 4.98 | 3.0 | 0.030 | 0.06 | 0.30 | 2.2 | 9.7 | 0.7 | 3.2 |

TABLE IV
 Determination of Organic Extra-Network Material (TMTD;
 ZDMC; TMTU) in Vulcanizates from the *cis*-1,4-Polyisoprene-TMTD-Zinc
 Oxide System (Mix I) at 140°C.

| Cure time, hr. | TMTD, % of original TMTD | ZDMC, mole-% of original TMTD | | TMTU, mole-% of original TMTD |
|----------------------|-----------------------------------|----------------------------------|----------|--|
| | | Method A | Method B | |
| 0.25 | 15.0 | — | 19.3 | — |
| 0.5 | 11.0 | 35.8 | 31.6 | — |
| 1.0 | 5.9 | 46.8 | 43.9 | — |
| 2.0 | 2.4 | — | 52.2 | — |
| 6.0 | 0 | 69.2 | 68.7 | 11.2 |
| 10.0 | 0 | 71.8 | 71.0 | 11.1 |

(b) *Organic Extra-Network Material*

Analyses of these (unreacted TMTD, ZDMC, and TMTU) at various cure times are given in Table IV. The presence of the above compounds in the vulcanizates was confirmed by their isolation and identification by elemental analyses, melting points, and mixed melting points with the authentic compounds. The estimates for TMTD and for ZDMC by method B may be low for the reason already given. Estimation of TMTU was restricted to the fully-cured vulcanizates (6 and 10 hr. cure) which were devoid of unreacted TMTD; the presence of the latter in the undercured vulcanizates would have led to unreliable estimates of TMTU in these vulcanizates since some of the TMTU estimated may have resulted from the thermal decomposition of TMTD during the distillation procedure used to isolate the TMTU.

Table V details the distribution of the sulfur and nitrogen in the various components of the vulcanizates, obtained after 6 and 10 hr. cure at 140°C., the results being expressed as percentages of the sulfur and nitrogen originally present in the TMTD. Under these conditions all the original TMTD had reacted (cf. Table IV). Attempts were made to trace the sulfur and nitrogen not accounted for in Table V. It was established that some sulfur could be lost as volatile sulfurated compounds (e.g., carbon disulfide) during the press cure or immediately upon opening the molds, as evidenced by the results of Table VI which relate to elemental analyses on vulcanizates, the analyses being done within a few minutes of removal of the samples from the cold molds. The data of Table VI also indicate that nitrogenous compounds are not lost from the vulcanizates in this way. The presence of carbon disulfide in the vulcanizates, which was detected by smell, is consistent with its identification in NR-TMTD-zinc oxide vulcanizates,¹⁰ and in the products of the reaction of monoolefins with TMTD and zinc oxide at 140°C.^{11,12} Tetramethylthiuram monosulfide (TMTM), which was found by Craig *et al.*¹⁰ in NR vulcanizates, could not be detected in the present fully-cured vulcanizates.

TABLE V
Distribution of Reacted Sulfur and Nitrogen in Various Components of
Vulcanizates Derived from Mix I (6 and 10 Hr. Cure at 140°C.)

| Element | Location of the reacted sulfur or nitrogen | % of sulfur or nitrogen present originally in TMTD | |
|----------|---|--|-------------|
| | | 6 hr. cure | 10 hr. cure |
| Sulfur | Sulfur combined in network (S_c) | 16.9 | 14.5 |
| | Sulfide sulfur (S^-), i.e., as ZnS | 2.5 | 2.8 |
| | Zinc dimethyldithiocarbamate | 69.0 | 71.8 |
| | Tetramethylthiourea | 2.8 | 2.8 |
| | Total | 91.2 | 91.9 |
| Nitrogen | Nitrogen combined in network (N_c) | 8.8 | 6.7 |
| | Zinc dimethyldithiocarbamate | 69.0 | 71.8 |
| | Tetramethylthiourea | 11.2 | 11.1 |
| | Total | 89.0 | 89.6 |

**Thermal Treatment of Extracted Vulcanizates Derived from the
cis-1,4-Polyisoprene-TMTD-Zinc Oxide System (Mix I: Cured at 140°C.)**

Table VII details the measured C_1^N values and analytical data (N_c , S^- , S_c) for the reheated extracted vulcanizates which had subsequently been hot chloroform-extracted. The C_1^N values were used to obtain estimates of $1/2 M_{c, \text{chem}}^N$ and the latter were used in conjunction with the N_c and S_c values to obtain values of the number of atoms of nitrogen and sulfur combined in the reheated vulcanizate networks per chemical crosslink present.

Table VIII details the amounts of ZDMC formed during the reheating periods and their relation with the amounts of N_c and S_c which are lost from the initial vulcanizate networks and with the additional crosslinks which are formed during the reheating period.

TABLE VI
Determination of Sulfur and Nitrogen Content of Vulcanizates Immediately
Following Their Removal from the Molds (Mix I: Cured at 140°C.)

| Sample | Total sulfur, % | Total nitrogen, % | Loss of | Loss of |
|---------------------------------|-----------------------|-------------------------|---|--|
| | | | sulfur, % relative to sulfur content of mix | nitrogen, % relative to nitrogen con- tent of mix |
| Mix I, unvulcanized | 2.05 | 0.445 | — | — |
| Mix I, 0.5 hr. cure | 1.98 | 0.456 | 3.4 | (2.5% gain) |
| Mix I, 10.0 hr. cure | 1.90 | 0.453 | 7.3 | (1.8% gain) |
| Calcd. for 4 pts. TMTD in mix I | 1.97 | 0.443 | — | — |

TABLE VII
Structural Characterization of Initial Extracted Vulcanizates from Mix I after Subsequent Reheating at 140°C. and Extraction with Hot Chloroform

| Initial cure time, hr. | Re-heating period at 140°C., hr. | $C_1N \times 10^{-6}$ at 25°C. of reheated extracted vulcanizate, dynes./cm. ² | $1/2M^N \times 10^5$, g. moles chemical cross-links/g. rubber network | Ash, wt.-% of extracted vulcanizate | Combined Nitrogen (N _c), wt.-% of extracted vulcanizate | Sulfide sulfur (S ⁻), wt.-% of extracted vulcanizate | Combined sulfur (S _c), wt.-% of extracted vulcanizate | N _c , g. atoms of N/g. rubber network $\times 10^5$ | S _c , g. atoms of S/g. rubber network $\times 10^5$ | Atoms of nitrogen combined in net-work per chemical crosslink present | Atoms of sulfur combined in net-work per chemical crosslink present |
|------------------------|----------------------------------|---|--|-------------------------------------|---|--|---|--|--|---|---|
| 0.25 | 7.75 | 1.06 | 3.03 | 3.52 | 0.018 | 0 | 0.30 | 1.35 | 9.8 | 0.4 | 3.2 |
| 0.5 | 7.5 | 1.11 | 3.20 | 3.35 | 0.019 | 0 | 0.30 | 1.4 | 9.8 | 0.4 | 3.1 |
| 1.0 | 3.0 | 1.16 | 3.38 | — | — | — | — | — | — | — | — |
| 1.0 | 7.0 | 1.11 | 3.20 | 3.21 | 0.030 | 0.02 | 0.31 | 2.2 | 10.0 | 0.7 | 3.1 |
| 2.0 | 6.0 | 1.11 | 3.20 | 3.07 | 0.030 | 0.03 | 0.30 | 2.2 | 9.7 | 0.7 | 3.0 |
| 6.0 | 2.0 | 1.06 | 3.03 | 3.04 | 0.030 | 0.05 | 0.32 | 2.2 | 10.4 | 0.7 | 3.4 |
| 10.0 | 2.0 | 1.03 | 2.98 | 2.90 | 0.030 | 0.06 | 0.29 | 2.2 | 9.4 | 0.7 | 3.2 |

TABLE VIII
 Formation of Zinc Dimethyldithiocarbamate (ZDMC) During the Reheating at 140°C. of the Initial Extracted Vulcanizates,
 and the Relationship of ZDMC Formed to the Loss of N_c and S_c from the Initial Vulcanizates and to the Additional Crosslinks Formed

| Initial cure time, hr. | Reheating period at 140°C., hr. | ZDMC formed, g./g. rubber network $\times 10^3$ (method C) | Loss in N_c on reheating initial extracted vulcanizate, g. atoms/g. rubber network $\times 10^5$ | | Loss in S_c on reheating initial extracted vulcanizate, g. atoms/g. rubber network $\times 10^5$ | | Proportions of removed N_c and S_c found as ZDMC | | Increase in $1/2M_c^N$, chem. during reheating period, g.-moles chemical crosslinks/g. rubber network $\times 10^5$ | No. of molecules of ZDMC formed per additional crosslink |
|---------------------------------|--|---|--|---------------|--|-----------|--|------|---|---|
| | | | $\times 10^5$ | $\times 10^5$ | N_c , % | S_c , % | | | | |
| 0.25 | 7.75 | 6.11 | 4.9 | 9.6 | 82 | 84 | 1.60 | 1.25 | | |
| 0.5 | 7.5 | 5.90 | 4.8 | 9.2 | 83 | 86 | 1.58 | 1.22 | | |
| 1.0 | 3.0 | 5.26 | — | — | — | — | 1.57 | 1.10 | | |
| 1.0 | 7.0 | 5.53 | 4.0 | 8.0 | 91 | 91 | 1.39 | 1.30 | | |
| 2.0 | 6.0 | 4.22 | 3.35 | 6.9 | 83 | 81 | 1.17 | 1.18 | | |
| 6.0 | 2.0 | 0.57 | 0.75 | 0.9 | (50) | 82 | 0.04 | 1.10 | | |
| 10.0 | 2.0 | 0.17 | 0 | 0.3 | — | 73 | (-0.05) | — | | |

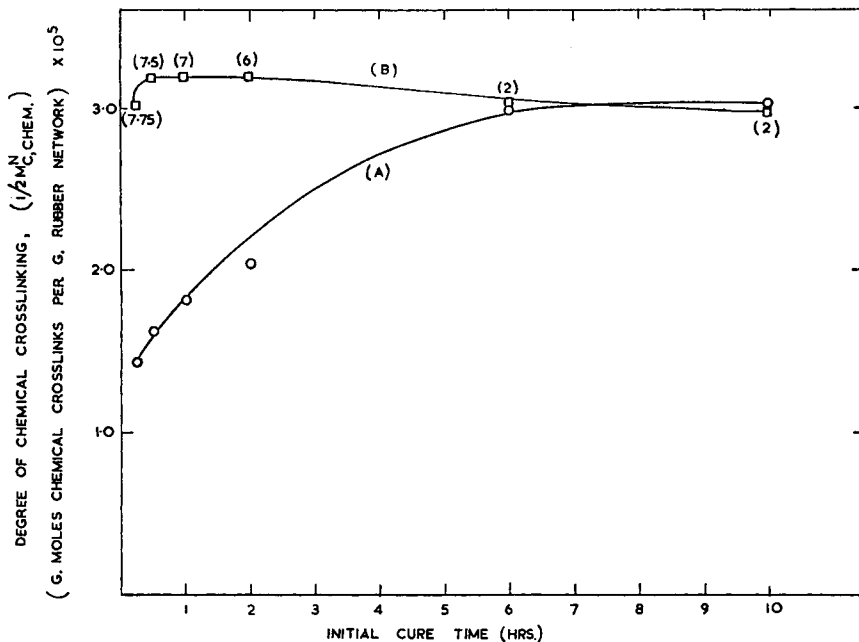


Fig. 1. Variation of degree of chemical crosslinking with cure time in extracted *cis*-1,4-polyisoprene-TMTD-zinc oxide vulcanizates (mix I) cured at 140°C. and the crosslink densities of these vulcanizates after extraction and reheating *in vacuo* at 140°C. for the times (in hours) denoted in parentheses in curve B. (O), initial vulcanizates; (□), reheated vulcanizates.

In order to facilitate comparison of the results for the initial vulcanization process with those for the secondary vulcanization process which occurs during the reheating of the initial extracted vulcanizates, certain of the tabulated data, together with other relevant data, are presented in graphical form. Figure 1 shows the degree of chemical crosslinking ($1/2 M_{c, \text{chem.}}^N$) as a function of initial cure time and of the reheating period for the two systems. Figure 2 shows the proportions of sulfur and nitrogen originally present in the TMTD which become combined in the network at different cure times, and Figure 3 gives the number of nitrogen and sulfur atoms combined in the network per chemical crosslink present at different stages of cure.

Experiments with the *cis*-1,4-Polyisoprene-TMTD System (Mix II)

The product obtained from heating *cis*-1,4-polyisoprene with TMTD in the absence of zinc oxide (mix II) in a press at 140°C. for 0.25 hr. was a plastic, unvulcanized material which was almost completely soluble in *n*-decane at 25°C. and which smelled strongly of dimethylamine. The product, after extraction for 8 days with cold ethyl acetate followed by drying *in vacuo* at room temperature, contained 2.94×10^{-5} g.-atoms *N*/g. rubber

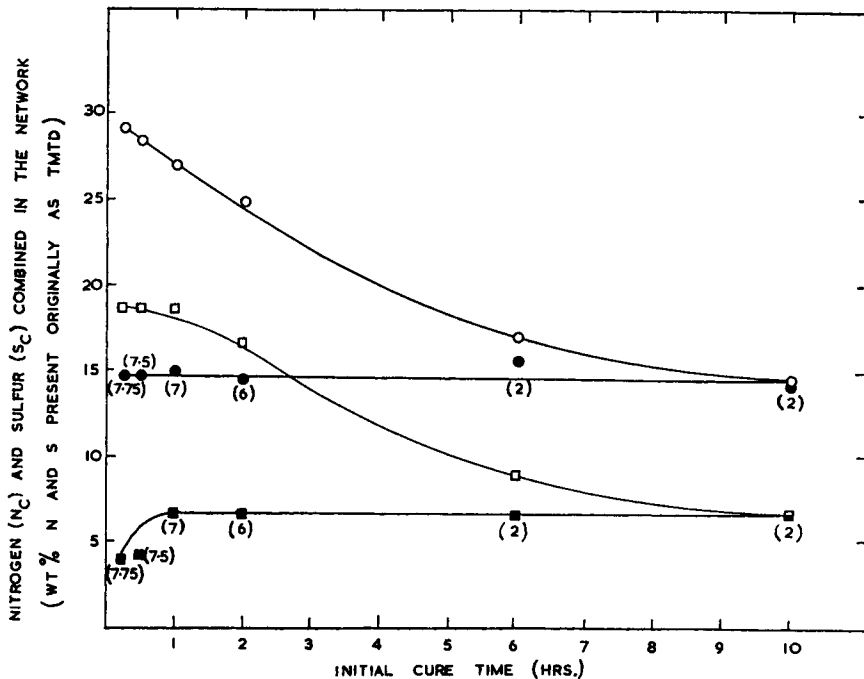


Fig. 2. Relationship between cure time and proportions of nitrogen (\square) and sulfur (\circ) present originally in mix I as TMTD, combined in the networks of extracted *cis*-1,4-polyisoprene-TMTD-zinc oxide vulcanizates cured at 140°C. and between the proportions of nitrogen (\blacksquare) and sulfur (\bullet) combined in the networks after reheating the initial extracted vulcanizates at 140°C. *in vacuo* for the times (in hours) stated in parentheses.

and 6.59×10^{-5} g.-atoms S/g. rubber, i.e., 9% of the nitrogen and 10% of the sulfur originally present in the TMTD.

This extracted rubber-TMTD adduct was milled with zinc oxide (4 g. zinc oxide/100 g. rubber-TMTD adduct) and the mix (mix III) heated in a press for either 2 or 7.75 hr. at 140°C. The resulting vulcanizates, which were very soft and sticky, were extracted for 24 hr. with hot dichloromethane and dried *in vacuo*. The ZDMC in the extracts was determined (method C) and the nitrogen and sulfur contents and equilibrium v_r values of the extracted vulcanizates were measured (Table IX).

IV. DISCUSSION

The crosslinking of extracted synthetic *cis*-1,4-polyisoprene by the TMTD-zinc oxide system at 140°C. is slower and less efficient than that of NR (RSS1, yellow circle). This is shown by the data of Figure 4 and by the facts that when the degree of chemical crosslinking of the two rubbers at full cure is assessed on a comparable basis (*viz.*, by estimates from equilibrium swelling measurements) the *cis*-1,4-polyisoprene utilizes 5.0 molecules of TMTD per crosslink, whereas NR requires only 3.6 molecules of

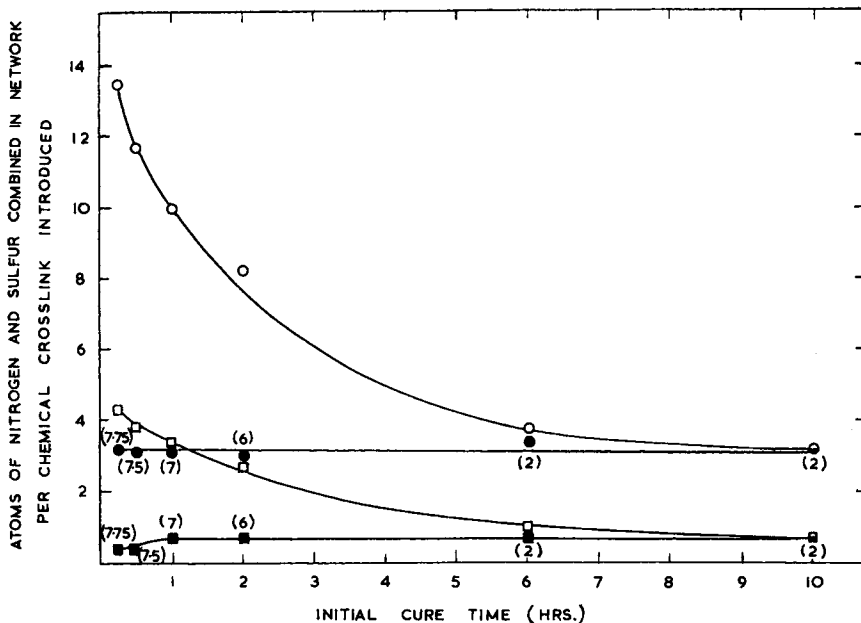


Fig. 3. Variation of structural complexity of networks of *cis*-1,4-polyisoprene-TMTD-zinc oxide vulcanizates (mix I) cured at 140°C. and of the networks after reheating the extracted vulcanizates for the times (in hours) stated in parentheses: (□) atoms of nitrogen in initial vulcanizate; (O) atoms of sulfur in initial vulcanizate; (■) atoms of nitrogen after reheating; (●) atoms of sulfur after reheating.

TMTD per crosslink.¹³ This difference in crosslinking is probably associated with the absence from the synthetic polyisoprene of the nitrogenous bases and fatty acids present in the NR which act as activators and which lead to more efficient use of the TMTD for crosslinking purposes. This view is supported by the cure characteristics (Fig. 4) of an extracted low nitrogen content NR and by the fact that the addition of a nitrogen base or a fatty

TABLE IX

Physical and Chemical Characterization of Vulcanizates Derived from the Interaction at 140°C. of Zinc Oxide with the Extracted Product (Mix III) Obtained from Heating *cis*-1,4-Polyisoprene with TMTD for 0.52 hr. at 140°C.^a

| Cure time, hr. | Gel, wt.-% (insoluble in <i>n</i> -decane) | v_r of gel (in <i>n</i> -decane at 25°C.) | C_1^N of gel based on v_r , dynes/cm. ² $\times 10^{-6}$ ^b | Vulcanizate soluble in CH ₂ Cl ₂ , wt.-% | N_e of vulcanizate, g.-atom N/g. rubber network $\times 10^6$ | S_e of vulcanizate, g.-atom S/g. rubber network $\times 10^6$ | ZDMC formed, g.-mole/g. rubber network $\times 10^6$ |
|----------------|--|---|--|--|---|---|--|
| 2.0 | 88.7 | 0.061 | 0.05 | 13 | 2.0 | 3.6 | 0.24 |
| 7.75 | 90.4 | 0.064 | 0.06 | 14.5 | 1.8 | 2.95 | 0.37 |

^a The rubber-TMTD adduct of mix III had $[\eta]_{\text{benzene, 25}^\circ\text{C.}} = 1.64$ dl./g., equivalent to $\bar{M}_n = 1.4 \times 10^6$.

^b C_1^N values derived from v_r values by use of the Flory-Huggins equation using $\mu = 0.42$.

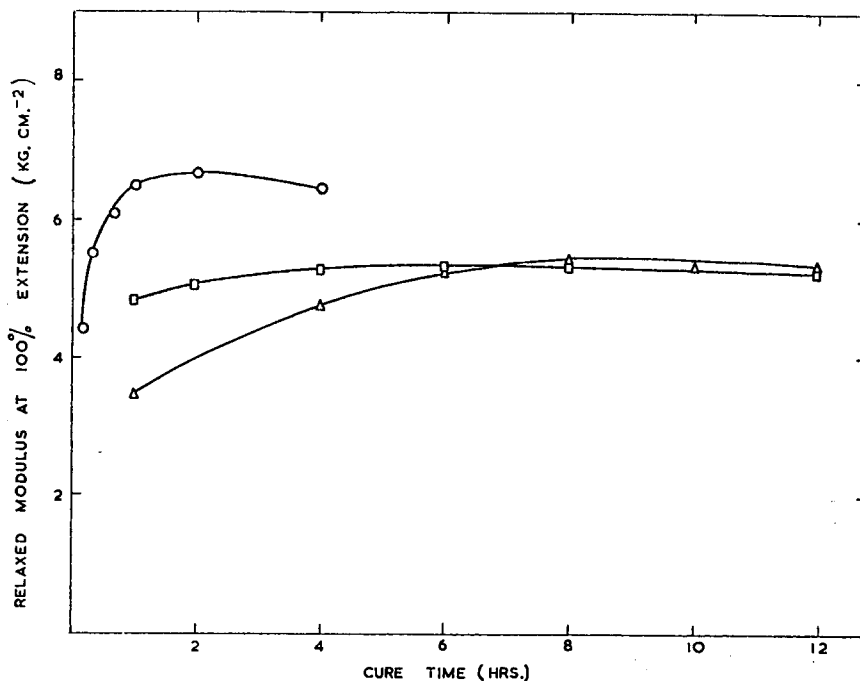


Fig. 4. Comparative rates and extents of cure of (O) NR (RSS1, yellow circle); (□) purified NR (acetone-extracted highly purified rubber, U.S. Rubber Co., nitrogen content, 0.04%); (Δ) *cis*-1,4-polyisoprene (acetone-extracted Ameripol-SN, Goodrich-Gulf Chemicals, Inc., using the system: rubber (100)-TMTD (4)-zinc oxide (4) at 140°C. $\bar{M}_n \times 10^{-5}$ for RSS1 in the mix, 1.86; purified NR in the mix, 1.94; *cis*-1,4-polyisoprene in the mix, 1.41).

acid to the *cis*-1,4-polyisoprene-TMTD-zinc oxide system or to a comparable monoolefin sulfuration system leads to more efficient use of the TMTD.¹⁴

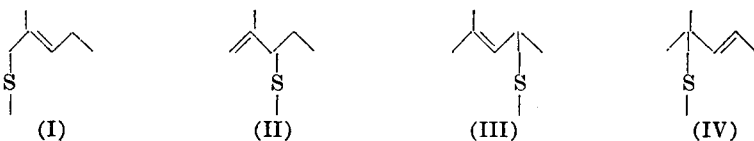
Structural Features of Fully-Cured *cis*-1,4-Polyisoprene-TMTD-Zinc Oxide Vulcanizates

Despite the above differences in the curing behavior of NR- and synthetic *cis*-1,4-polyisoprene-TMTD-zinc oxide systems, both systems lead to vulcanizate networks which at full cure are structurally very simple. It is a characteristic of the NR system that there is no appreciable network reversion on extended cure; this applies also to the synthetic *cis*-1,4-polyisoprene system (Table II). The near parity in crosslinking densities for a given cure derived from C_1^N and λ^* data for vulcanizates throughout the cure range (Table II) is consistent with the absence of any appreciable scission of the polyisoprene chains during the vulcanization process, which contrasts with the extensive main-chain scission of NR during its vulcanization with sulfur in the absence of accelerators.¹

The structural simplicity of the synthetic *cis*-1,4-polyisoprene network

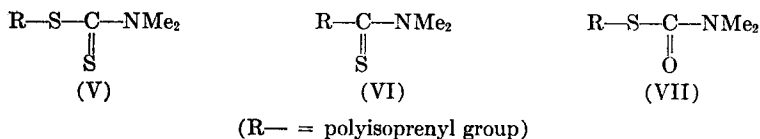
obtained at full cure with the present system is revealed by the fact that only 3.2 atoms of sulfur and 0.7 atoms of nitrogen are combined in the network for each chemical crosslink present, as assessed from stress-strain (C_1^N) estimates of the crosslink density. When the combined sulfur is related to the number of crosslinks derived from equilibrium swelling measurements it is found that about 2.8 atoms of sulfur are combined in the network per chemical crosslink present, which compares well with the value of 3.0 sulfur atoms combined per crosslink obtained similarly for a fully-cured NR vulcanizate.¹³ The very efficient use of sulfur for crosslinking in the present system contrasts with its very inefficient use in an unaccelerated NR-sulfur system at 140°C., where, when allowance is made for main-chain scission during cure, between 40 and 55 sulfur atoms are combined in the network per crosslink present, figures which reflect the considerable structural complexity of the network with much of the sulfur being present in cyclic sulfide modifications of the polyisoprene chains.^{1,15}

It is now known with certainty, both from studies with vulcanizates¹³ and with model olefins¹² that the crosslinks in polyisoprene-TMTD-zinc oxide vulcanizates are almost entirely (> 97.7%) sulfidic, there being a negligible number of carbon-carbon crosslinks present, contrary to previous contentions.¹⁶⁻¹⁸ It must not be inferred from the present results that the crosslinks in a fully cured vulcanizate contain on average about 3 sulfur atoms, since some of the sulfur is associated with the combined nitrogen in residues from the TMTD combined as pendent groups along the polyisoprene chains. The present work does not resolve the detailed structures of the crosslinks (i.e., the number of sulfur atoms in the crosslinks and the pattern of the hydrocarbon units at the crosslink termini) or of the main chain modifications. However, complementary studies using chemical probes with actual vulcanizates and others involving the characterization of the products of the sulfuration of model olefins with TMTD and zinc oxide have gone far to resolve these features. The crosslinks are predominantly monosulfidic as judged by the use of the probes: lithium aluminium hydride,¹⁹ triphenylphosphine, and sodium di-*n*-butyl phosphite.²⁰ Consistent with this, the sulfidic products derived from the reaction of 2-methylpent-2-ene with TMTD and zinc oxide at 140°C. under conditions simulating full cure in the polyisoprene system are dialkenyl sulfides, comprising 86 mole-% monosulfide and 14 mole-% disulfide and containing the alkenethio groups (I-IV) in the order of relative abundance (I > III > II > IV).¹⁴



With regard to the main-chain modifications, the present studies with actual vulcanizates show that there must be present along the polyisoprene chains pendent groups which contain both nitrogen and sulfur. Examina-

tion of the noncrosslinked material obtained from the sulfuration of 2-methylpent-2-ene and the diisoprene, 2,6-dimethylocta-2,6-diene, indicates that very few cyclic monosulfides are formed, and that the principal main-chain modifications are (V-VII) in the relative order: (V > VI > VII).¹⁴ Since the present fully-cured vulcanizate network contains



only 0.7 atoms of nitrogen and 3.2 atoms of sulfur per crosslink (Table III) then the above pendent groups must be collectively fewer than the crosslinks and thus it is concluded that the TMTD-zinc oxide system yields a structurally very simple network at full cure, containing mainly monosulfide crosslinks with lesser amounts of disulfide crosslinks and having only limited modification of the polyisoprene chains.

The principal extra-network materials at full cure are unreacted zinc oxide, ZDMC, TMTU, and zinc sulfide (Table V). The limiting yield of ZDMC observed in the present system is about 72 mole-% of the incident TMTD, a value significantly higher than the limiting yield of 66.7 mole-% of ZDMC claimed by Scheele et al.^{5,21-28} to apply irrespective of the structure of the rubber, the reaction temperature, and the concentrations of thiuram disulfide, rubber hydrocarbon, and zinc oxide, providing the latter is present in excess.

Structural Features of *cis*-1,4-Polyisoprene-TMTD-Zinc Oxide Vulcanizates as a Function of Cure Time

The structures of the vulcanizate networks are time-dependent throughout the cure range up to full cure. At early cure times the networks are structurally complex, as revealed by the large numbers of sulfur and nitrogen atoms combined in the network per crosslink present (Table III), but as crosslinking proceeds the networks become structurally more simple²⁹⁻³¹ (Table III, Figs. 2 and 3). The present data do not reveal further details of the time-dependent nature of network structure, but studies with chemical probes and model olefins show (1) that the crosslinks are initially polysulfidic and decrease in sulfur chain length as cure proceeds;^{14,20} and (2) that additional to the pendent groups (V-VII) and a few cyclic monosulfide groups, the main chains are modified by substantial amounts of R-S_xC-(S)NMe₂ groups (VIII, R = polyisoprenyl, $x \geq 2$).¹⁴ The latter are now identified as the rubber-bound intermediate compounds which act as the immediate precursors to the crosslinks which are formed simultaneously with part of the ZDMC as cure proceeds. This conclusion as to the structure of the intermediate compound contradicts the earlier proposal of Bevilacqua^{32,33} that it is R-SC(S)NMe₂ (R = polyisoprenyl), formed by prior interaction of the rubber with the TMTD. The compound R-SC-

(:S)NMe₂ is now seen to be a relatively unreactive species under the vulcanization conditions used and it thus survives as the most important main chain modification in the fully-cured network (see above). The release of Me₂NC(:S)S—groups as ZDMC from the intermediate compound (VIII) explains the observed decrease in combined nitrogen and sulfur in the network with increasing cure time (Fig. 2) and crosslinking (Fig. 3). The presence of an intermediate compound which yields crosslinks on further cure has been inferred previously: firstly, from the observations of Scheele et al.^{15,23,25,30} that the thiuram disulfide reacts much faster (2–4-fold) than zinc dialkyldithiocarbamate and crosslinks are formed (cf. also the data of Table IV and Fig. 1) and thus the ZDMC must, in part, be formed from some compound other than TMTD, but containing Me₂NC(:S)S—groups; secondly, since more sulfur is combined in the network at early stages of cure than at long cure time,^{30,31} an observation confirmed in the present work (Table III, Figs. 2 and 3); and thirdly, by the qualitative observation that an acetone-extracted undercured vulcanizate crosslinked further on heating and yielded an antioxidant, presumed to be ZDMC.³⁴ This third line of evidence is confirmed and amplified here, and this, in conjunction with the actual isolation and identification of the compound (VIII, R = alkenyl, $x = 2$) from a model olefin reaction with TMTD and zinc oxide,¹⁴ provides the most convincing evidence for the existence of a rubber-bound intermediate compound. The present evidence is that when undercured vulcanizates, which have been extracted and thus freed from all extra-network compounds apart from zinc oxide and zinc sulfide, are reheated at 140°C. they are crosslinked further (Fig. 1), lose a substantial part of the combined nitrogen and sulfur (Table VII; Figs. 2 and 3), and yield ZDMC which accounts for a substantial proportion (80–90%) of the nitrogen and sulfur lost from the network (Table VIII). The secondary crosslinking occurring on reheating the extracted undercured vulcanizates (0.25–2 hr. original cure time) is more efficient than the primary crosslinking process carried to full cure, since in the former case a higher degree of crosslinking is obtained (Fig. 1) despite the fact that some of the incident TMTD was unreacted in the original curing (Table IV) and was thus extracted from the vulcanizates prior to their reheating. Further, the networks resulting from the reheating treatment are structurally as simple as or simpler than the network obtained at full cure in the original system (cf. the atoms of nitrogen and sulfur combined per crosslink present for the two systems, Fig. 3, Tables III and VII). The present data relating to the structural features of the vulcanizate network obtained after 0.25 hr. cure at 140°C. and its subsequent history on reheating (Tables III and VII) suggest that the rubber-bound intermediate compound is formed rapidly in the early stages of cure and then undergoes a slower reaction leading to crosslinks. In the latter process about 1.2 molecules of ZDMC are formed for each additional crosslink (Table VIII), suggesting that the main crosslinking reaction involves the destruction of two molecules of the intermediate compound (VIII) for each crosslink formed, which therefore amends our earlier sup-

position³⁵ that the final crosslinking process involves one molecule of (VIII) interacting with an olefinic unit and yielding half a molecule of ZDMC.

It is inappropriate here to discuss the precise mechanism of formation of the intermediate compound (VIII) and of its subsequent reaction to give sulfidic crosslinks. We still regard (VIII) as being formed by the prior interaction of TMTD with zinc oxide to give a sulfurating species which then reacts with the polyisoprene to yield the intermediate compound,³⁵ which contrasts with the proposals of Bevilacqua^{32,33} and others^{31,36} that the initial reaction is between TMTD and the polyisoprene. Bevilacqua proposed that this reaction yields $R-SC(:S)NMe_2$ groups V and $Me_2N.C(:S)SH$, and that zinc oxide plays the secondary role of hydrolyzing $R-SC(:S)NMe_2$ groups and neutralizing $Me_2N.C(:S)SH$. Support for the rejection of the Bevilacqua mechanism is provided: (a) by the isolation of the compound (VIII, $R = \text{alkenyl}$, $x = 2$) from a model-olefin sulfuration; (b) by the observation that the extracted undercured vulcanizates provide crosslinks on reheating in the absence of TMTD, which compound is required according to Bevilacqua to oxidize the hydrolyzed intermediate (RS^-) to disulfide crosslinks; and (c) by the demonstration that although *cis*-1,4-polyisoprene and TMTD react together in the absence of zinc oxide, the adduct formed is virtually incapable of yielding crosslinks on subsequent heating with zinc oxide (Table IX), which shows that the intermediate (VIII, $R = \text{polyisoprenyl}$, $x \geq 2$) which is the actual precursor to the crosslinks is not formed simply by reaction of TMTD and the polyisoprene.

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Résumé

La vulcanisation d'un *cis*-1,4-polyisoprène synthétique purifié (100 pts) au moyen de disulfure de tétraméthylthiurame (TMTD; 4 pts) et d'oxyde de zinc (4 pts) à 140°C fournit un réseau qui, après 15 min. de traitement, possède une structure complexe, 13,5 atomes de soufre et 4,3 atomes d'azote étant présents pour une liaison chimique transverse. Le réseau acquiert progressivement une structure plus simple quand le pontage se poursuit et après traitement complet (10 h.), il contient 3,2 atomes de soufre et 0,7 atomes d'azote par pont chimique. La complexité du réseau initial est due principalement à la présence de composés intermédiaires "rubber-bound," $R \cdot S_x C(:S)N(CH_3)_2$ ($R =$ polyisoprényle; $x \geq 2$) qui donnent naissance à des ponts sulfurés et à du diméthyl-dithiocarbamate de zinc (ZMDC) en chauffant avec de l'oxyde de zinc ou du sulfure de zinc, comme le montre le pontage efficace réalisé par un chauffage ultérieur à 140°C des vulcanisats extraits avant la fin du traitement. On montre que les composés intermédiaires proviennent de l'interaction du polyisoprène avec un produit sulfurant, formé par une réaction antérieure du TMTD avec l'oxyde de zinc et non, comme d'autres auteurs le supposaient précédemment par réaction directe du polyisoprène avec le TMTD. Nos connaissances concernant la structure détaillée du réseau obtenu après traitement complet est présentée ici, en même temps que nos suppositions à propos des principaux produits extérieurs à réseau (ZDMC), tétraméthylthiourée et sulfure de zinc) formés à la fin de ce traitement. Dans ces composés ainsi que dans le soufre et l'azote insérés dans le réseau, on retrouve environ 90% du soufre et de l'azote présents initialement sous forme de TMTD.

Zusammenfassung

Die Vulkanisation eines gereinigten synthetischen *cis*-1,4-Polyisoprenes (100 Teile) mit Tetramethylthiuramdisulfid (TMTD; 4 Teile) und Zinkoxyd (4 Teile) bei 140°C liefert ein Netzwerk, das bei kurzer Vulkanisationsdauer (15 Min.) eine komplexe Struktur mit 13,5 Schwefelatomen und 4,3 Stickstoffatomen pro chemischer Vernetzung

besitzt. Mit fortschreitender Vernetzung wird die Netzwerkstruktur zunehmend einfacher und bei voller Vulkanisation (10 Stdn.) enthält sie 3,2 Schwefelatome und 0,7 Stickstoffatome pro vorhandener chemischer Vernetzung. Der anfängliche komplexe Charakter des Netzwerkes wird hauptsächlich durch die Anwesenheit kautschukgebundener Zwischenprodukte, $R \cdot S_x C(:S)N(CH_3)_2$ ($R =$ Polyisoprenyl; $x \geq 2$) verursacht, welche beim Erhitzen mit Zinkoxyd oder Zinksulfid sulfidische Vernetzungen und Zinkdimethyldithiocarbamat (ZDMC) liefern, wie die wirksame Vernetzung extrahierter, nicht ausvulkanisierter Proben beim weiteren Erhitzen auf 140°C zeigt. Es wird gezeigt, dass die Zwischenprodukte aus der Reaktion von Polyisopren mit einer vorher aus TMTD und Zinkoxyd gebildeten sulfurierend wirkenden Verbindung stammen und nicht, wie früher von anderen Autoren angenommen wurde, aus der direkten Reaktion von Polyisopren mit TMTD. Angaben über die detaillierte Struktur des bei voller Vulkanisation erhaltenen Netzwerkes werden gemacht, sowie über die hauptsächlichlichen, neben dem Netzwerk entstehenden Verbindungen (ZDMC), Tetramethylthioharnstoff und Zinksulfid); diese Verbindungen enthalten zusammen mit dem im Netzwerk gebundenen Schwefel und Stickstoff etwa 90% des ursprünglich als TMTD vorhandenen Schwefels und Stickstoffs.

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