# Structural Characterization of Vulcanizates. Part VII.   The N-Cyclohexylbenzothiazole-2-sulfenamide-Accelerated Natural Rubber–Sulfur System

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## Synopsis

The crosslinking efficiency of sulfur in the vulcanization system comprising (in parts by weight) natural rubber (100), sulfur (1.5), N-cyclohexylbenzothiazole-2-sulfenamide (2.37), zinc oxide (5), and lauric acid (1–10) is relatively insensitive to the lauric acid concentration and to the temperature of vulcanization (between 100 and 140°C.). The networks formed contain initially 8–11 combined sulfur atoms per chemical crosslink present, but this number falls progressively to about 4 as the reaction proceeds. The results are consistent with the intermediate formation of a rubber-soluble complex of cyclohexylamine with zinc benzothiazolyl mercaptide. This complex is believed to be responsible also for the further slow crosslinking which the vulcanizates undergo on standing at room temperature.

## INTRODUCTION

In Part VI of the series[1] the influence of fatty acid concentration, vulcanization temperature, and vulcanization time on the efficiency $E$ of crosslinking of natural rubber (NR) with sulfur in the presence of 2-mercaptobenzothiazole (MBT) and zinc oxide was described. It was shown that very efficient utilization of sulfur for crosslinking is attained by using a combination of high fatty acid concentration, low temperature, and long vulcanization time, and that it results in vulcanizate networks of simple structure. In this paper the effect of cure time and the combined effects of varying fatty acid concentration and temperature on crosslinking efficiency in NR–sulfur vulcanization accelerated by a typical delayed-action accelerator, N-cyclohexylbenzothiazole-2-sulfenamide (CBS), are examined. For comparative purposes the molar concentration of accelerator has been kept at the level used in Part VI,[1] but only two combinations, high fatty acid concentration with low temperature (100°C.) and low fatty acid concentration with high temperature (140°C.), have been studied since preliminary work by Mr. P. McL. Swift showed that changes in these variables lead to much smaller changes in vulcanizate modulus with CBS as accelerator than had been observed with MBT. The efficiency of sulfur vulcaniza-

tion of NR with the use of a concentration of CBS more in keeping with technological practice is described in Part VIII.[2]

## MATERIALS AND EXPERIMENTAL METHODS

### Materials

The NR was the homogenized sample of RSS1 (Yellow Circle), which is described as sample 2 in Part VI of this series.[1] CBS was a sample of Santocure (Monsanto Chemicals Ltd.) purified by twofold recrystallization from light petroleum (b.p. 80–100°C.) shortly before use. (The low stability of CBS at room temperature gives rise to rubber mixes showing shorter scorch times and slower rates of cure, if the unrecrystallized material is used for their preparation.) Other vulcanizing ingredients were those previously described.[1]

### Preparation of Vulcanizates

Mixing and curing (Table I) were carried out as described previously,[1] except that all vulcanizates were prepared in the form of sheets 18 × 18 × 0.1 cm.

TABLE I
Mix Formulations and Cure Temperatures Used in the
Preparation of CBS-Accelerated NR–Sulfur Vulcanizates

| | Mix no. | |
| --- | --- | --- |
| | A | B |
| Parts, wt. | | |
| NR | 100 | 100 |
| Sulfur | 1.5 | 1.5 |
| CBS | 2.37 | 2.37 |
| Zinc oxide | 5.0 | 5.0 |
| Lauric acid | 10.0 | 1.0 |
| Cure temp., °C. | 100 | 140 |

Viscosity measurements were made on centrifuged toluene solutions of the rubber mixes, and values of the limiting viscosity number of the rubber hydrocarbon component, relative to benzene, $[\eta]_{benzene}$, were obtained by using the relationship established by Bristow and Westall.[3] The initial number-average molecular weights $(\bar{M}_n)$ of the rubber hydrocarbon were then derived by means of the expression[4]

$$[\eta]_{benzene} \; (dl./g.) = 2.29 \times 10^{-7} \bar{M}_n^{1.33} \tag{1}$$

### Chemical Analysis of Vulcanizates

All analyses were made on samples cut from the central 14 cm. squares of the vulcanized sheets.

Determinations of sulfur combined in the vulcanizate networks, $S_c$, and of inorganic sulfide sulfur, $S^{2-}$ were made as described in Part VI,[1] the acetic acid–hydrochloric acid mixture [footnote (g), Table IX, Part VI] being used to decompose the zinc sulfide in the vulcanizates. Extraction with hot acetone for 96 hr. under nitrogen in the dark was less efficient than extraction with a hot azeotropic mixture[1] of acetone, chloroform, and methanol under the same conditions in removing extra-network material other than zinc oxide and zinc sulfide from the vulcanizates; this was demonstrated by lower percentages of extracted material and higher sulfur contents after extraction when acetone alone was used. Only the results obtained on vulcanizates extracted with the azeotrope are given below.

### Physical Characterization of Vulcanizates and Determination of Degree of Chemical Crosslinking of Rubber Hydrocarbon Component of Vulcanizate Networks

Values of relaxed modulus at 100% extension, MR 100, and tensile strength were determined as in Part VI.[1]

Stress–strain measurements were made at 22°C. on strips cut from the central 14 cm. square of the molded sheets, with the instrument designed by Greensmith and O'Dwyer and described briefly in Part VI.[1] For the vulcanizates from mix B (Table I) the values of $C_1$ and $C_2$, the elastic parameters of the Mooney-Rivlin equation

$$f[2A_0(\lambda - \lambda^{-2})]^{-1} = C_1 + \lambda^{-1}C_2 \qquad (2)$$

(in which $f$ is the force required to maintain a sample of unstrained cross-sectional area $A_0$ at an extension ratio $\lambda$) were obtained from plots of $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ versus $\lambda^{-1}$ in the region of low and moderate extension. The $C_1$ values pertaining to the raw vulcanizates, $C_{1,RV}$, were converted by the methods of Part V of this series[5] to values of $C_{1,ERM}$ (the $C_1$ pertaining to the partially collapsed vulcanizate network devoid of filler and rubber-soluble diluent) and $C_{1,RH}$ (the $C_1$ of the rubber hydrocarbon component of the network). Values of $C_{1,RH}$ were then used to obtain values of $(2M_{c,\,chem}^{RH})^{-1}$ (gram-mole chemical crosslinks per gram rubber hydrocarbon in the network) by means of the expression[6]

$$C_{1,RH} = [\rho RT(2M_{c,\,chem}^{RH})^{-1} + 0.78 \times 10^6][1 - 2.3M_{c,\,chem}^{RH} \bar{M}_n^{-1}]$$

$$\text{dynes/cm.}^2 \quad (3)$$

where $\rho$ is the density of the rubber hydrocarbon (0.915 g./ml. at 25°C.), $M_{c,\,chem}^{RH}$ is the number-average molecular weight of the rubber hydrocarbon chain segments between adjacent chemical crosslinks, $R$ is the gas constant, and $T$ is the absolute temperature.

As in the case of the MBT-accelerated NR vulcanizates described in Part VI,[1] which contained high loadings of zinc laurate and zinc laurate–zinc benzothiazol-2-yl mercaptide (ZMBT) complexes, the raw vulcanizates from mix A (Table I) gave plots of $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ versus $\lambda^{-1}$ which

TABLE II

Values of $\chi$ for Representative Vulcanizate Networks Derived from Mix A, Table I

| Cure time at 100°C., hr. | Wt. loss on extraction, % | Elastic constants at 25°C., dynes/cm.$^2 \times 10^{-6}$ | | | Equil. $v_r$ of network in $n$-decane at 25°C. | $\chi$ |
|---|---|---|---|---|---|---|
| | | $C_{1,\mathrm{ERV}}$ | $C_{2,\mathrm{ERV}}$ | $C_{1,\mathrm{ERM}}$ | | |
| 6 | 12.4 | 1.34 | 1.28 | 1.33 | 0.266 | 0.422 |
| 20 | 12.0 | 2.59 | 1.69 | 2.56 | 0.337, 0.340 | 0.405, 0.410 |
| 144 | 11.0 | 2.99 | 2.03 | 2.95 | 0.357, 0.356 | 0.400, 0.402 |

TABLE III

Modulus (MR 100) and Tensile Strength Data for Vulcanizates Derived from the CBS-Accelerated NR–Sulfur System (Mixes A and B, Table I)[a]

| Cure time | MR 100, kg./cm.$^2$ | Tensile strength, kg./cm.$^2$ |
|---|---|---|
| Mix A: | | |
| hr. at 100°C. | | |
| 3 | 8.55 | 389 |
| 6 | 11.8 | 389 |
| 12 | 12.6 | 380 |
| 20 | 14.0 | 358 |
| 50 | 14.6 | 297 |
| 144 | 14.7 | 237 |
| Mix B: | | |
| min. at 140°C. | | |
| 20 | 8.45 | 350 |
| 30 | 9.9 | 344 |
| 45 | 10.2 | 300 |
| 120 | 10.25 | 273 |
| 240 | 9.95 | 261 |

[a] Figures for MR 100 are means of two results; those for tensile strength are medians of three results.

were curved throughout the whole extension range and which were dependent on the history of the sample. (In this case the situation was complicated still further by additional crosslinking of the sample on standing at room temperature; see p. 2263ff.) These features are again believed to be due to slow solidification of zinc laurate or its ZMBT complexes in the vulcanizate. Values of $C_1$ and $C_2$ for these vulcanizates were obtained by making stress–strain measurements on samples from which the extra-network materials had been removed by extraction with the acetone–chloroform–methanol azeotrope described above. These values ($C_{1,ERV}$) were then used to compute values of $C_{1,ERM}$ which, in conjunction with values of $v_r$, the volume fraction of rubber network in the swollen rubber network after swelling to equilibrium in $n$-decane for 48 hr. at 25°C. in the dark, gave estimates of $\chi$, the rubber network–swelling liquid interaction parameter of the Flory-Rehner equation (see Part V[5]). Errors in $\chi$ due to further crosslinking of the vulcanizates during extraction (see Section III) were avoided by treating samples for $C_1$ and $v_r$ measurements in precisely the same way. The values of $\chi$ so obtained for representative networks derived from mix A were nearly constant over the whole cure range (Table II). (The apparent small decrease in $\chi$ with increasing cure time may be due to some overestimation of $C_1$ at the higher degrees of crosslinking because of the intrusion of finite extensibility effects at low elongations in highly crosslinked networks.) The average value of $\chi$ for these networks (0.408) is very similar to that observed for analogous MBT-accelerated sulfur vulcanizates[1] and to the values obtained for the vulcanizates from mix B (see Table IV). A $\chi$ value of 0.41 has therefore been used to derive esti-

## TABLE IV

Physical Characterization of Vulcanizate Networks Derived from the CBS-Accelerated NR–Sulfur System (Mix B, Table I) and Estimates of the Degrees of Chemical Crosslinking of the Rubber Hydrocarbon Component of the Networks

| Cure time at 140°C., min. | $[\eta]_{benz.}$ rubb. hydrocarb. compon. of mix at 25°C., dl./g. | $\bar{M}_n$ of rubb. hydrocarb. compon. of mix, $\times 10^{-5}$ | Elastic constants, dynes/cm.² $\times 10^{-6}$ | | | Equil. $v_r$ of network in $n$-decane at 25°C. | $\chi$ | $C_{1,RH}$ dyne/cm.² $\times 10^{-6}$ | Deg. crosslink.[a] ($\times 10^4$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | $C_{1,RV}$ | $C_{2,RV}$ | $C_{1,ERM}$ at 25°C. | | | | |
| 20 | 3.49 | 2.51 | 1.72 | 1.06 | 1.97 | 0.306 | 0.410 | 1.82 | 0.54 |
| | | 2.16 | 1.94 | 1.09 | | | | | |
| 30 | 3.49 | 2.51 | 2.11 | 1.16 | 2.10 | 0.313 | 0.408 | 2.24 | 0.71$_5$ |
| | | 2.16 | 2.07 | 1.10 | | | | | |
| 45 | 3.49 | 2.51 | 2.19 | 1.20 | 2.20 | 0.315$_5$ | 0.402 | 2.32 | 0.75 |
| | | 2.16 | 2.17 | 1.10 | | | | | |
| 120 | 3.49 | 2.51 | 2.22 | 1.21 | 2.12$_5$ | 0.314$_5$ | 0.409 | 2.35$_5$ | 0.77 |
| | | 2.16 | 2.09 | 1.25 | | | | | |
| 240 | 3.49 | 2.51 | 2.01$_5$ | 1.23 | 2.03$_5$ | 0.313 | 0.416 | 2.14 | 0.67 |
| | | 2.16 | 2.00 | 1.12 | | | | | |

[a] Gram-mole chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_{c,\,chem}^{RH})^{-1}$.
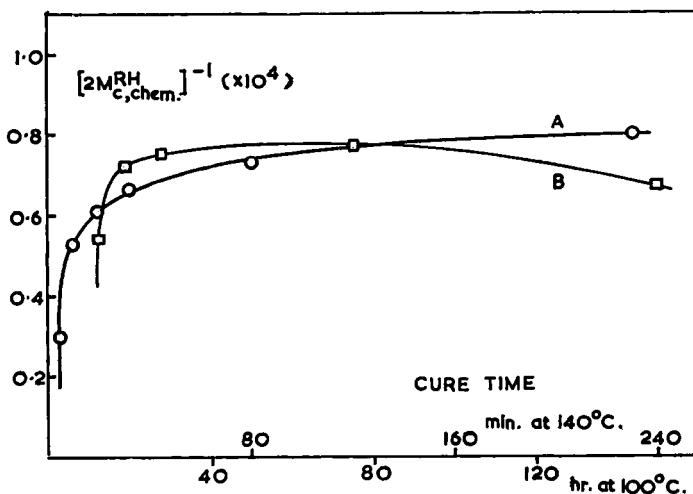
Fig. 1. Relation between degree of chemical crosslinking, $(2M^{RH}_{c,\,chem.})^{-1}$, and vulcanization time of mixes A and B (Table I).
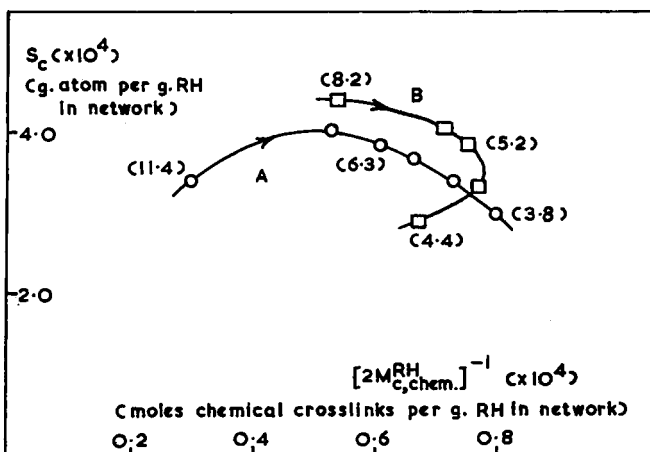


Fig. 2. Relation between sulfur combined in the network, $[S_c]$, and the degree of chemical crosslinking, $(2M^{RH}_{c,\,chem.})^{-1}$, of mixes A and B (Table I). Arrows on the curves indicate the direction of increasing vulcanization time. Values of the sulfur crosslinking efficiency $E$ are given in parentheses on the curves.

mates of $(2M^{RH}_{c,chem})^{-1}$ indirectly from $v_r$ measurements[1] for all the vulcanizates from mix A described here.

Values of $E$ and $F$ for the vulcanizates were determined according to the definitions:

$$E = [S_c]/(2M^{RH}_{c,\,chem})^{-1} = \text{no. of sulfur atoms combined in network per chemical crosslink present}$$

$$F = [S^{2-}]/(2M^{RH}_{c,\,chem})^{-1} = \text{no. of sulfide ions formed per chemical crosslink present in network}$$

TABLE V
Chemical Characterization of Vulcanizate Networks Derived from CBS-Accelerated NR-Sulfur System (Mix B, Table I)

| Cure time at 140°C, min. | $[S_c + S^{2-}]$ extr. vulc., wt.-% | Wt. loss on extrn. raw vulc., % | $[S_c + S^{2-}]^a$ of RV, wt.-% | $[S^{2-}]$ of RV, wt.-% | $[S_c]$ ($\times 10^4$)[b] | $[S^{2-}]$ ($\times 10^4$)[c] | Deg. crosslink.[d] ($\times 10^4$) | $E$[e] | $F$[f] |
|---|---|---|---|---|---|---|---|---|---|
| 20 | 1.45 | 6.36 | 1.33 | 0.085 | 4.42 | 0.30 | 0.54 | 8.2 | 0.6 |
| 30 | 1.47₅ | 5.13 | 1.37 | 0.222 | 4.08 | 0.79 | 0.71₅ | 5.7 | 1.1 |
| 45 | 1.51 | 5.12 | 1.40 | 0.314 | 3.87 | 1.11 | 0.75 | 5.2 | 1.5 |
| 120 | 1.51 | 5.15 | 1.40 | 0.447 | 3.37 | 1.59 | 0.77 | 4.4 | 2.1 |
| 240 | 1.47₅ | 4.95 | 1.37₅ | 0.552 | 2.93 | 1.96 | 0.67 | 4.4 | 2.9 |

[a] Corrected for the sulfur content of the raw rubber; RV, raw vulcanizate.
[b] Gram-atom of sulfur per gram of rubber hydrocarbon in the network.
[c] Gram-ion of sulfide per gram of rubber hydrocarbon in the network.
[d] Gram-mole chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_{c,\,chem}^{RH})^{-1}$.
[e] Number of sulfur atoms combined in the network per chemical crosslink present.
[f] Number of sulfide ions formed per chemical crosslink present in the network.

## EXPERIMENTAL RESULTS AND DISCUSSION

The results are given in Figures 1 and 2 and Tables III–VII.

The differences between the values for $(2M_{c,\,chem}^{RH})^{-1}$, $E$, and $F$ quoted for mix A and those published previously (Bateman,[7] Fig. 15.17) are due to the fact that the present $(2M_{c,\,chem}^{RH})^{-1}$ values have been derived from equilibrium $v_r$ measurements with the use of a $\chi$ value determined independently on extracted vulcanizates, whereas the earlier results were obtained from stress–strain ($C_1$) measurements by a procedure devised in these laboratories. We now believe that the procedure adopted did not entirely take into account either the contribution made by the considerable quantity of extra-network material present to the stress–strain properties of the vulcanizates or the further crosslinking of the vulcanizates on standing at room temperature (see below). Small changes in the results for both mixes are due to application of the methods of Part V.[5]

Both the CBS-accelerated systems described here show the induction periods in crosslinking (Fig. 1) which are characteristic of sulfenamide acceleration. It is believed that during this period the CBS is converted into a cyclohexylamine complex of ZMBT, which then reacts with sulfur to give a complex which effects sulfuration of the rubber.[7] The formation, during this induction period, of a chemical species which is very active in causing crosslinking of NR is indicated by two facts: that a sample of mix B heated to 140°C. but removed from the press and cooled rapidly after 17 min. was uncured but reached a good degree of cure on subsequent storage for three months at room temperature, and that vulcanizates of mixes A and B which have been cured for short times undergo further crosslinking on standing at room temperature (see below). Further evidence of the nature of this species will be given in a forthcoming publication.

The two vulcanization systems undergo only a limited loss of crosslinks on extended cure (Fig. 1), and this is reflected by the absence of modulus reversion (Table III). Optimum tensile strength was attained in the first two vulcanizates of each system, and the magnitude was observed to be sensitive to the purity of the CBS: an unpurified commercial sample of the accelerator gave vulcanizates with optimum tensile strengths only 70% of those in Table III.

With MBT as accelerator a mix containing 10 parts of lauric acid per 100 rubber and cured at 100°C. attains a degree of chemical crosslinking about five times that reached by a mix containing only 1 part of lauric acid per 100 rubber and cured at 140°C.[1] Replacement of MBT by an equimolar quantity of CBS gives rise to a vulcanizing system which is strikingly less dependent on fatty acid concentration and on temperature of cure; thus, very similar degrees of chemical crosslinking are attained by mix A cured at 100°C. and by mix B cured at 140°C. (Fig. 1). This similarity in efficiency of use of a given quantity of sulfur for crosslinking is reflected in the $E$ values for the two systems (Fig. 2). For mix A cured at 100°C. the combination of 11 sulfur atoms in the rubber network is initially required to

TABLE VI

Physical Characterization of Vulcanizate Networks Derived from CBS-Accelerated NR–Sulfur System (Mix A, Table I) and Estimates of Degrees of Chemical Crosslinking of the Rubber Hydrocarbon Component of the Networks

| Cure time at 100°C., hr. | $[\eta]_{benz.}$ rubb. hydrocarb. compon. of mix at 25°C., dl./g. | $\bar{M}_n$ rubb. hydrocarb. compon. of mix, $\times 10^{-5}$ | Equil. $v_r$ of network in $n$-decane at 25°C. | Elastic constants at 25°C., dynes/cm.$^2$ $\times 10^{-6}$ | | Deg. crosslink.[b] |
|---|---|---|---|---|---|---|
| | | | | $C_{1,\mathrm{ERM}}$[a] | $C_{1,\mathrm{RH}}$ | |
| 3 | 2.76 | 2.1$^c$ | 0.238 | 1.08 | 1.19 | 0.30 |
| 6 | 2.42 | 1.9 | 0.281 | 1.59$_5$ | 1.75$_5$ | 0.53 |
| 12 | 2.66 | 2.1 | 0.294 | 1.78 | 1.96 | 0.61 |
| 20 | 2.76 | 2.1 | 0.302 | 1.90 | 2.09 | 0.66$_5$ |
| 50 | 2.42 | 1.9 | 0.311 | 2.04 | 2.24 | 0.73 |
| 144 | 2.30 | 1.8 | 0.318 | 2.16 | 2.38 | 0.80 |

[a] Derived from $v_r$ values.
[b] Gram-mole of chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_{c,\mathrm{chem}}^{\mathrm{RH}})^{-1}$.

TABLE VII

Chemical Characterization of Vulcanizate Networks Derived from the CBS-Accelerated NR–Sulfur System (Mix A, Table I)

| Cure time at 100°C, hr. | $[S_c + S^{2-}]$ extr. vulc., wt.-% | Wt. loss on extrn. raw vulc., % | $[S_c + S^{2-}]^a$ of RV, wt.-% | $[S^{2-}]$ of RV, wt.-% | $[S_c]^b$ $(\times 10^4)$ | $[S^{2-}]^c$ $(\times 10^4)$ | Deg. crosslink.$^d$ $(\times 10^4)$ | $E^e$ | $F^f$ |
|---|---|---|---|---|---|---|---|---|---|
| 3 | 1.19 | 13.6 | 1.00 | 0.112 | 3.41 | 0.43 | 0.30 | 11.4 | 1.4 |
| 6 | 1.53 | 13.3 | 1.30 | 0.248 | 4.04 | 0.95 | 0.53 | 7.6 | 1.8 |
| 12 | 1.55 | 13.0 | 1.32 | 0.314 | 3.86 | 1.21 | 0.61 | 6.3 | 2.0 |
| 20 | 1.54 | 12.6 | 1.32 | 0.357 | 3.70 | 1.37 | $0.66_5$ | 5.6 | $2.0_5$ |
| 50 | 1.61 | 12.8 | 1.37 | 0.477 | 3.43 | 1.83 | 0.73 | 4.7 | 2.5 |
| 144 | 1.58 | 12.6 | 1.35 | 0.562 | 3.02 | 2.16 | 0.80 | 3.8 | 2.7 |

$^a$ Corrected for the sulfur content of the raw rubber; RV, raw vulcanizate.
$^b$ Gram-atom of sulfur per gram of rubber hydrocarbon in the network.
$^c$ Gram-ion of sulfide per gram of rubber hydrocarbon in the network.
$^d$ Gram-mole of chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_{c,\text{chem}}^{RH})^{-1}$.
$^e$ Number of sulfur atoms combined in the network per chemical crosslink present.
$^f$ Number of sulfide ions formed per chemical crosslink present in the network.

form one chemical crosslink, but this number falls continuously to 3.8 at long reaction times; this feature was also observed in the case of the comparable MBT-accelerated system (where $E$ changed from 6 to 2.4) and implies that, for these two systems, a progressive simplification of the network structure takes place as vulcanization proceeds. Similarly, vulcanization of mix B at 140°C. gives $E$ values ranging from 8 to 4.4 with increasing cure time. This contrasts sharply with the corresponding MBT system (mix D, Fig. 4, Part VI[1]), where E *increased* with cure time from 14 to 19.

The final $E$ values of about 4 achieved by the two CBS-accelerated systems are higher than the ultimate efficiency (2.4) of the most efficient MBT-accelerated system. That most of this difference in $E$ values is an accurate reflection of differences in sulfur utilization is shown by the relative optimum crosslinking levels reached by the systems (ca. $0.8 \times 10^{-4}$ moles for the CBS systems, compared with $1.2 \times 10^{-4}$ for the most efficient MBT system, per gram rubber hydrocarbon in the network). However, a contributing factor to the higher final $E$ values of the CBS-accelerated systems is the combination of larger amounts of sulfur in the network. Some of this sulfur evidently does not arise from the molecular sulfur added in the mix, since values of $[S_{c2} + S^{2-}]$ after extended cure exceed $4.84 \times 10^{-4}$ g.-atom per gram of rubber hydrocarbon ($\equiv 1.5$ g. of sulfur per 100 g. of NR); see Tables V and VII. Independent evidence of the combination with the rubber of sulfur-containing accelerator moieties in the form of "pendent" groupings and of the role of these groupings in the formation of sulfur crosslinks has already been presented in the case of tetramethylthiuram disulfide–zinc oxide ("sulfurless") vulcanization[8,9]; evidence of their presence in thiazole-accelerated sulfur vulcanization systems has recently been obtained.[10]

The relatively high $E$ values (14–19) observed for the "inefficient" MBT-accelerated system described previously[1] imply that much of the sulfur is wastefully combined in cyclic monosulfide modifications of the main rubber chains. The final $E$ values of about 4 combined sulfur atoms per crosslink in the present systems imply that this type of modification can occur to only a very limited extent at any stage of the cure, since at least one of these sulfur atoms is actually in the crosslink and an unknown proportion of the remainder is present in pendent groups terminated by accelerator residues. Furthermore, since cyclic monosulfide groups are essentially stable to heat or further sulfuration, only minor amounts can be present at any stage of vulcanization in these two systems. These conclusions are confirmed by the results of treating the vulcanizates with triphenylphosphine, which removes all the sulfur atoms but one from polysulfide chains in crosslinks and pendent groups.[11] Vulcanizates derived from mix A, after treatment with triphenylphosphine, contained a constant number $E' = 2.5$ of sulfur atoms combined in the network per chemical crosslink present, irrespective of cure time, reflecting the simplicity of the network throughout cure. Broadly similar results have been obtained

from vulcanizates derived from mix B, but values of $E'$ increase slightly as cure proceeds, implying some increase in network complexity in this case.[12]

The essential lack of dependence of the CBS-accelerated systems on lauric acid concentration, shown by their overall similarity in crosslinking efficiency, is explicable in terms of the necessity of forming a soluble ZMBT complex from the accelerator.[7] Barton and Hart[13] were the first to demonstrate that the maximum crosslinking potential of sulfur is not realized unless an excess of such a complex is present in the vulcanizing system. The production of an adequate quantity of a soluble ZMBT complex from the ZMBT formed in an MBT-accelerated system requires the presence of excess of a zinc carboxylate[1,13] or of a nitrogen base.[7] With CBS such added ligands are unnecessary, since in the thermal, hydrolytic, or reductive breakdown of the accelerator in the presence of zinc oxide the formation of ZMBT is accompanied by the release of cyclohexylamine,[14] which forms a 2:1 complex with ZMBT, which is very soluble in hydrocarbons[15] and is an active catalyst for the crosslinking of NR by sulfur.[16,17] Mix B already has the capacity to form a considerable quantity of this complex, and hence the addition of zinc laurate in the form of lauric acid, as in mix A, leads to only a small further improvement in the efficiency of crosslinking.

The formation of zinc sulfide (denoted by $F$ values in Tables V and VII) conforms to the stoichiometry of crosslink formation:

$$2RH + S_{x+1} + ZnO \xrightarrow{\text{CBS}} R\text{---}S_x\text{---}R + H_2O + ZnS$$
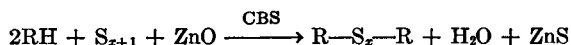
over only a limited range of reaction, irrespective of the amount of zinc laurate present and of cure temperature. The additional zinc sulfide appearing in the later stages of vulcanization is associated, at least in part, with crosslink degradation, as in the corresponding MBT systems,[1] but a proportion may have arisen from hydrogen sulfide produced in side reactions of the sulfenamide or cyclohexylamine with sulfur. This extra source may also account for the suprastoichiometry of zinc sulfide formation in the vulcanizates from mix A, in which no crosslink degradation is physically evident.

### Post-Vulcanization Crosslinking in CBS-Accelerated Sulfur Vulcanizates

While this work was in progress, other work in these laboratories[18] showed that sulfur vulcanizates of NR and of cis-1,4-polybutadiene prepared with CBS as accelerator are prone to undergo further crosslinking on standing at room temperature. This post-vulcanization crosslinking was found to be independent of the presence of oxygen and to be especially marked in the case of undercured vulcanizates. It could be stopped by storing the vulcanizates at $-26°C$.

The occurrence of this slow crosslinking reaction in some of the vulcanizates described here was confirmed by following changes in the relaxed modulus (MR 100) of freshly prepared vulcanizates on standing at 22°C.

Except for the first vulcanizate of each series (20 min. from mix B, 3 hr. from mix A), increases over a period of 56 days were confined to 0–4% of the original moduli. The 20 min. cure from mix B showed an increase in MR 100 of 7% during this time, whereas the 3 hr. cure from mix A showed an increase of 31%. Evidently, post-vulcanization crosslinking is only substantial in this latter vulcanizate, suggesting that the presence of uncombined sulfur (cf. Table VII) is necessary for the effect to occur. The prominence of the reaction in the case of CBS-accelerated vulcanization is ascribed to the formation of a particularly active, rubber-soluble zinc–accelerator complex, which is able to cause crosslinking of the rubber by sulfur at room temperature.

The possible intrusion of low-temperature crosslinking on the results of Tables III–VII requires consideration. Measurements of $C_1$ and $v_r$ were generally made within seven days of the preparation of the vulcanizates, so that the derived values of $(2M_{c,\text{chem}}^{\text{RH}})^{-1}$ should be closely representative of their chemical crosslink densities at the time of leaving the press. Less certainty attaches to the $[S_c]$ values, since these were measured on samples extracted with the azeotropic mixture at 57.5°C.; since the presence of free sulfur appears to be necessary for substantial further crosslinking the extent of the latter will depend upon the (unknown) rate at which sulfur is extracted by the azeotrope. This leads to some uncertainty in the derived values of the crosslinking efficiency $E$, but this uncertainty is likely to be serious only in the case of the 3 hr. cure from mix A.

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## Résumé

L'efficacité de pontage du soufre dans le système soumis à la vulcanisation (caoutchouc naturel 100, soufre 1.5; N-cyclohexylbenzothiazole-2-sulfenamide 2.37, oxyde de zinc 5, acide laurique 1 à 10 parts en poids) est relativement peu sensible à la concentration en acide laurique et à la température de vulcanisation (entre 100 et 140°C).   Les réseaux formés contiennent initialement 8 à 11 atomes de soufre combinés par pont chimique présent mais ce chiffre tombe progressivement à environ 4 à mesure que la réaction progresse.   Les résultats sont en accord avec la formation intermédiaire d'un complexe, soluble dans le caoutchouc constitué de cyclohexylamine et de benzothiazolyl–mercaptide de zinc.   Ce complexe est vraisemblablement responsable du pontage lent ultérieur que subissent les vulcanisats abandonnés à température de chambre.

## Zusammenfassung

Die Vernetzungsausbeute von Schwefel im Vulkanisationssystem:   Naturkautschuk 100, Schwefel 1,5, N-Cyclohexylbenzothiazol-2-sulfenamide 2,37, Zinkoxyd 5, Laurinsäure 1–10 Gewichtsteile, ist gegen die Laurinsäurekonzentration und die Vulkanisationstemperatur verhältnismässig unempfindlich.   Die gebildeten Netzwerke enthalten anfänglich 8–11 gebundene Schwefelatome pro vorhandener chemischer Vernetzung und diese Zahl nimmt mit fortschreitender Reaktion stetig auf etwa 4 ab.   Die Ergebnisse sind konsistent mit der intermediären Bildung eines kautschuklöslichen Cyclohexylamin-Zinkbenzothiazolylmerkaptid-Komplexes.   Dieser Komplex wird auch für die weitere langsame Vernetzung der Vulkanisate beim Stehen bei Raumtemperatur verantwortlich gemacht.