

Studies on Thiazole-accelerated Sulphur Vulcanisation of Rubber

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Sulphur vulcanisation of natural and non-pigmented styrene-butadiene rubbers accelerated by 2-mercaptobenzothiazole in the presence of zinc oxide and stearic acid has been studied. Free sulphur decreases, obeying a first order law in regard to time. With respect to thiazole concentration, the orders of reaction are 0.8 for free sulphur decrease and 0.6 for cross-link formation. The amount of zinc sulphide formed increases with increasing proportion of thiazole employed and with time of cure until the sulphur is almost consumed. The cross-link density and mechanical properties of the vulcanisates indicate an optimum thiazole concentration. Inclusion of stearic acid increases the efficiency of vulcanisation and improves the properties of the vulcanisates. It has been suggested that 2-mercaptobenzothiazole, zinc oxide and stearic acid form a soluble complex zinc salt of the accelerator $\left\{ (C_6H_4S_2) \begin{array}{c} \nearrow \\ \searrow \end{array} CS_2 \right\}_2 Zn(C_{18}H_{35}O_2)_2$ which reacts with sulphur causing it to react with the rubber.

The mechanism of vulcanisation has been a challenging problem to rubber scientists, of as great a magnitude as the process of vulcanisation has been of importance to the industrialists. A vast amount of literature has accumulated on the subject but the investigators often differ in their findings and little work has been presented on the order of reaction with respect to the concentration of accelerator.

Comprehensive work has been carried out in this laboratory on sulphur vulcanisation accelerated by 2-mercaptobenzothiazole (MSH), its zinc salt (MSZnSM) and N-cyclohexyl benzothiazole-2-sulphenamide in the absence and presence of zinc oxide, and with inclusion of stearic acid. Part of the results has already been reported (BHATNAGAR AND BANERJEE, 1966 and 1967). In this paper, sulphur vulcanisation accelerated with MSH in the presence of zinc oxide and stearic acid is described.

It is well-known that the addition of fatty acids in sulphur vulcanisation of rubber in the presence of MSH and zinc oxide markedly improves the physical properties of the vulcanisates. Although much valuable information has been reported earlier, the mechanism of reaction, however, still remains a subject of

speculation. The experimental results and the theoretical interpretations advanced by earlier workers (BENISKA AND DOGADKIN, 1959; CORAN 1964; LORENZ AND ECHE, 1957) are not in harmony and this work has, therefore, been undertaken in this laboratory. In this investigation, the concentration of MSH has been varied over a wide range and, on the basis of the results obtained from the measurements of cross-linking, free sulphur decrease, change in MSH concentration, zinc sulphide formation, tensile strength and modulus, a suitable mechanism has been suggested.

EXPERIMENTAL

Table 1 lists the compound formulations studied in the present investigation.

Procedures for mixing, vulcanisation and the determination of free sulphur, chemical cross-links, tensile strength, modulus, etc., have been described earlier (BHATNAGAR AND BANERJEE, 1966 and 1967). 2-mercaptobenzothiazole and its zinc salt were determined iodometrically after extraction with alcohol and glacial acetic acid, respectively. Zinc sulphide was estimated by the method described by ADAM AND JOHNSON (1953).

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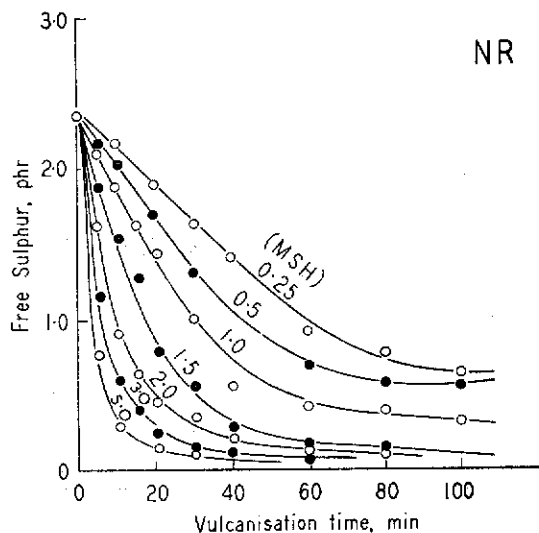


Figure 1. Decrease of free sulphur with time of vulcanisation at different MSH concentrations for NR.

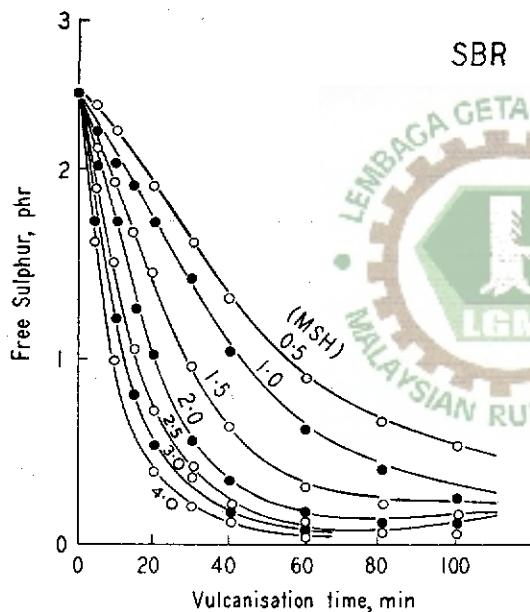


Figure 2. Decrease of free sulphur with time of vulcanisation at different MSH concentrations for SBR.

TABLE 1. FORMULATIONS

Stock	Parts by weight
Pale crepe (IX) or styrene-butadiene rubber (1502)	100
Zinc oxide	3.0
Stearic acid	3.0
Sulphur	2.5
2-mercaptobenzothiazole	0.25, 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00

RESULTS

Decrease of Free Sulphur

The decrease of free sulphur after the induction period follows a first order law with respect to the time of cure and the order is 0.8 with respect to MSH concentration for both natural rubber (NR) and styrene-butadiene rubber (SBR), respectively. The data are represented in Figures 1 and 2 and the reaction orders are computed from Figure 3.

Change in MSH Concentration

Data on total free MSH concentration (from glacial acetic acid extract), MSH concentration

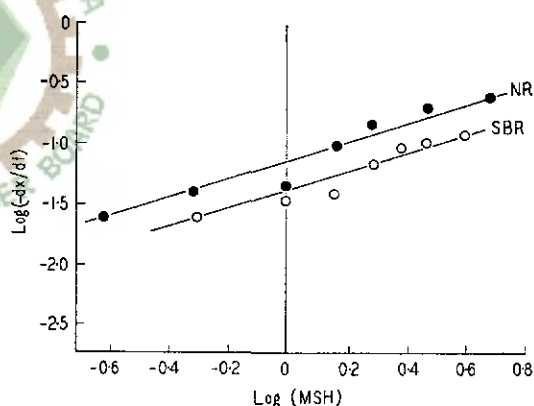


Figure 3. Log-log plot of velocity of free sulphur decrease and MSH concentration for NR and SBR.

TABLE 2. DATA ON ZINC SULPHIDE SULPHUR AND MSH CONCENTRATIONS

Parameter studied	Vulcanisation time (min)	MSH (p.p.h.r.)						
		0.25	0.50	1.00	1.50	2.00	3.00	5.00
Zinc sulphide sulphur (p.p.h.r.)	5	—	—	—	—	0.261	0.331	0.494
	10	0.050	0.132	0.156	0.235	0.333	0.468	0.695
	20	0.120	0.263	0.322	0.466	0.580	0.462	0.802
	30	0.302	0.335	0.478	0.601	0.711	0.623	0.961
	40	0.364	0.518	0.685	0.681	0.797	0.900	1.080
	60	0.430	0.576	0.792	0.791	0.885	0.968	1.063
	80	0.482	0.620	0.840	0.860	0.965	0.965	—
	100	0.482	0.641	0.912	—	—	—	—
Total free MSH (p.p.h.r.)	0	—	0.455	0.926	1.451	1.932	2.890	4.750
	10	—	0.450	0.872	1.288	1.654	2.552	4.264
	20	—	0.398	0.789	1.126	1.522	2.386	4.003
	40	—	0.308	0.789	1.115	1.500	2.386	3.985
	60	—	0.300	0.666	1.180	1.500	2.312	3.197
	80	—	0.308	0.606	1.077	1.536	2.328	3.985
	100	—	0.318	0.655	1.077	1.458	2.321	3.833
Free MSH (p.p.h.r.)	0	—	0.455	0.921	0.462	1.930	2.726	—
	10	—	0.299	0.595	0.888	1.232	1.798	—
	20	—	0.136	0.478	0.750	1.006	1.496	—
	40	—	0.108	0.402	0.726	0.908	1.250	—
	60	—	0.115	0.432	0.755	0.993	1.258	—
	80	—	0.123	0.452	0.755	0.916	1.275	—

Recipe: NR 100
 Sulphur 2.5
 Zinc oxide 3.0
 Stearic acid 3.0
 MSH variable

Vulcanisation temperature at $(140 \pm 0.5)^{\circ}\text{C}$

(from alcohol extract) are recorded in *Tables 2* and *3* for both the rubbers. Total MSH decreases at a rapid rate in the initial stages and attains a limiting value when most of sulphur has been consumed. Nearly twenty and thirty per cent of MSH (originally added) are consumed for NR and SBR, respectively. Free MSH (as estimated in the alcohol extract) is always found to be less than total free MSH indicative of the formation of the zinc salt of MSH.

Increase in Chemical Cross-links

The increase in chemical cross-links with time of cure and MSH concentration is shown in *Figures 4* and *5* for the two rubbers. The reaction orders, computed from $\log(dx/dt)$ versus $\log(\text{MSH})$ plots, shown in *Figure 6*,

are found to be 0.6 for both the rubbers. The rates of cross-link formation, i.e., dx/dt are recorded in *Table 4*. Compared to the systems without stearic acid (BHATNAGAR AND BANERJEE, 1967), there is a substantial increase in both the rate of formation and the total number of cross-links formed.

Formation of Zinc Sulphide

The data on sulphur present as zinc sulphide are recorded in *Tables 2* and *3* for the two rubbers. The sulphide sulphur increases with increase in MSH concentration and time of cure, but almost attains a limiting value when most of the sulphur is used. Sulphide formation is considerably increased compared to the system without stearic acid.

Tensile Strength and Modulus

The values of tensile strength and modulus are found to increase with MSH concentration and attain limiting values. These are graphically shown in Figure 7 and it may be seen that the curves level off at about 2.0 p.p.h.r. MSH which may be taken as the optimum level of MSH to be used in such a system. Another noteworthy feature is the absence of tensile strength and modulus reversion which is quite prominent in the absence of stearic acid. The optimum cure times determined from the plots of these properties against cure time (not shown) are closely similar to those found for minimum free sulphur and maximum cross-linking.

DISCUSSION

The rate of sulphur decrease is more rapid in

NR than in SBR stocks and the process is found to be activated by the presence of both zinc oxide and stearic acid. SHEPPARD AND SUTHERLAND (1946) demonstrated by infrared spectroscopy that zinc stearate is formed even at room temperature in uncured stocks containing zinc oxide, stearic acid and accelerator. It is obvious, therefore, that at vulcanisation temperatures, this reaction will occur. However, as the vulcanisation progresses, the presence of stearic acid is invariably observed and zinc stearate is found to decrease (SHEPPARD AND SUTHERLAND, 1946). These findings suggest that stearic acid is formed from zinc stearate, presumably by the attack of H_2S , generated during vulcanisation.

In the present study 3.0 p.p.h.r. zinc oxide and 3.0 p.p.h.r. stearic acid were used, and

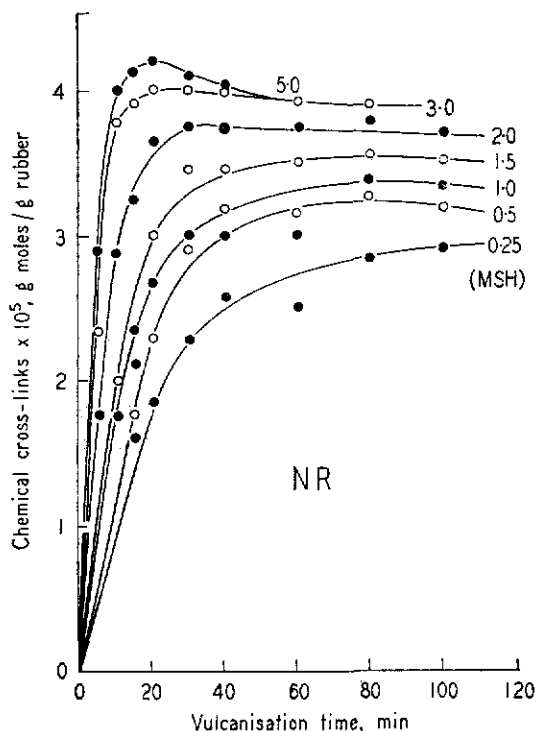


Figure 4. Variation of chemical cross-links with time of vulcanisation at different MSH concentrations for NR.

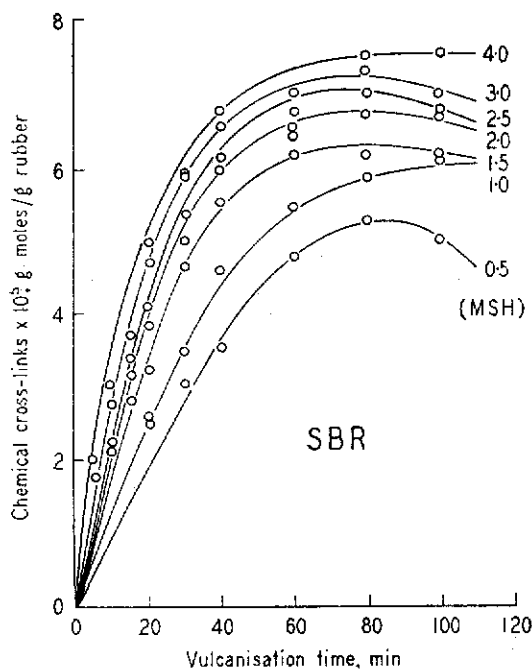


Figure 5. Variation of chemical cross-links with time of vulcanisation at different MSH concentrations for SBR.

assuming complete transformation to zinc stearate, the amount formed is about 3.33 p.p.h.r. and excess of zinc oxide remains as such.

It may be seen from Figure 8 that when the rates of sulphur decrease and cross-link formation are plotted against MSH concentration, almost no change is noticed after 3.0 to 3.4 p.p.h.r. of MSH. At this region, the molar ratio of MSH: zinc stearate in the formulation corresponds to 4:1. It is believed that an active complex between MSH, zinc oxide and zinc stearate is formed. Such ideas have been also put forward by earlier investigators (CORAN, 1964 and 1965; SCHEELE, 1961), but the chemical nature of the complex was not presented.

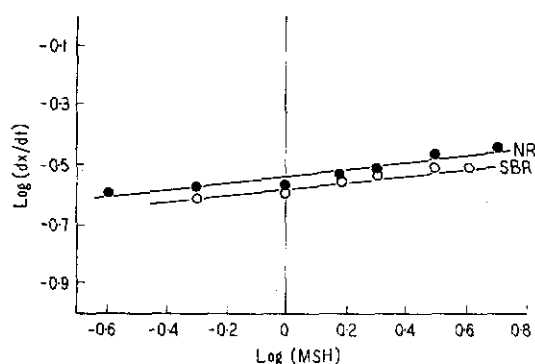


Figure 6. Log-log plot of velocity of cross-link increase and MSH concentration.

TABLE 3. DATA ON ZINC SULPHIDE SULPHUR AND MSH CONCENTRATION

Parameter studied	Vulcanisation time (min)	MSH (p.p.h.r.)						
		0.50	1.00	1.50	2.00	2.50	3.00	4.00
Zinc sulphide sulphur (p.p.h.r.)	5	—	—	—	—	—	0.017	0.118
	10	—	0.058	0.050	0.089	0.140	0.140	0.159
	20	0.020	0.099	0.133	0.202	0.259	0.272	0.360
	30	0.045	0.152	0.192	0.258	0.300	0.339	0.399
	40	0.076	0.169	0.192	0.258	0.376	0.450	0.472
	60	0.076	0.140	0.215	0.360	0.448	0.465	0.510
	80	0.099	0.169	0.250	0.315	0.412	0.450	0.492
	100	0.153	0.169	0.248	0.355	0.389	0.450	0.492
Total free MSH (p.p.h.r.)	0	0.502	0.963	1.448	1.940	2.426	2.920	3.192
	5	—	—	—	—	—	2.556	3.138
	10	—	0.956	1.289	1.695	2.132	2.500	3.202
	20	0.468	0.898	1.238	1.596	1.988	2.365	3.186
	40	0.458	0.898	1.175	1.526	1.930	2.231	3.136
	60	0.419	0.850	1.100	1.366	1.826	2.325	3.102
	80	0.339	0.786	1.175	1.440	1.932	2.325	3.102
	100	0.406	0.786	1.175	1.458	1.930	2.280	3.055
Free MSH (p.p.h.r.)	0	—	0.958	1.463	1.880	2.455	2.896	—
	10	—	0.322	0.673	0.820	1.425	2.689	—
	20	—	0.275	0.526	0.706	1.227	2.006	—
	40	—	0.200	0.593	0.669	1.074	1.575	—
	60	—	0.225	0.518	0.656	1.003	1.510	—
	80	—	0.208	0.523	0.670	1.052	1.523	—

Récipe: SBR 100
Sulphur 2.5
Zinc oxide 3.0
Stearic acid 3.0
MSH variable

Vulcanisation temperature at $(140 \pm 0.5)^{\circ}\text{C}$

TABLE 4. VALUES OF RATES OF SULPHUR DECREASE AND CROSS-LINK FORMATION FOR NR AND SBR

MSH conc. (p.p.h.r.)	Natural rubber		Styrene-butadiene rubber	
	From FS* (dx/dt) × 10 ²	From CL† (dx/dt) × 10 ⁶	From FS (dx/dt) × 10 ²	From CL (dx/dt) × 10 ⁶
0.25	- 2.50	1.00	-	-
0.50	- 3.91	1.20	- 2.80	0.90
1.00	- 4.52	1.20	3.60	1.10
1.50	-10.00	2.00	- 4.05	1.50
2.00	-16.10	2.50	- 6.62	2.00
2.50	-	-	- 9.11	2.20
3.00	-21.40	4.00	-10.10	2.60
4.00	-	-	-11.30	2.80
5.00	-22.00	4.50	-	-

*FS = Free sulphur

†CL = Cross-linking

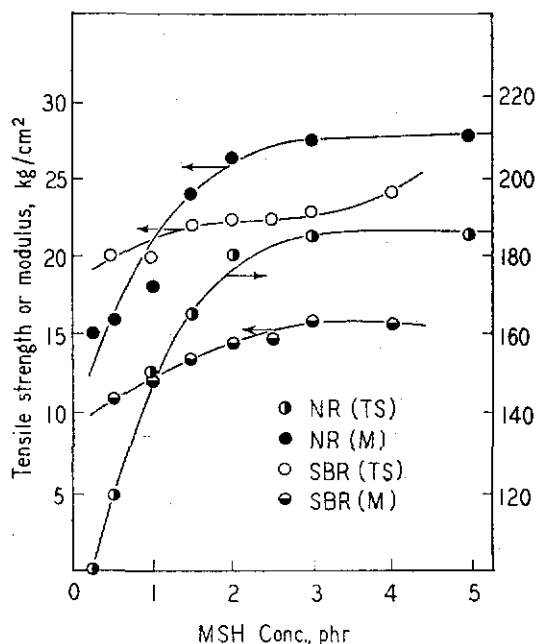
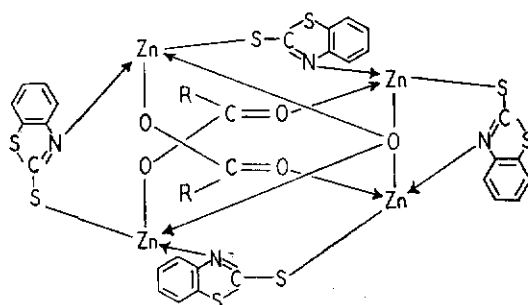


Figure 7. Plot of maximum tensile strength or modulus attained, against MSH concentration.

Recently CORAN (1964) suggested the formation of the complex having the empirical formula $\{[\text{MSZnSM}]_2 [\text{Zn stearate}]\}$ ZnO and the structural formula depicted here:

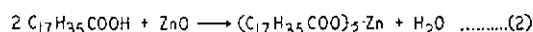
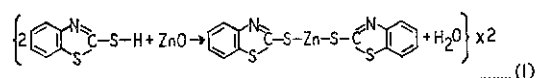


The authors gave evidence in support of the structure by showing that on heating MSH: ZnO: stearic acid in the molar ratio of 4:4:2, three moles of water are lost and a residue having a melting point of 108°–109.5°C is obtained. The molecular weight also was reported to be similar to that required by the proposed structure.

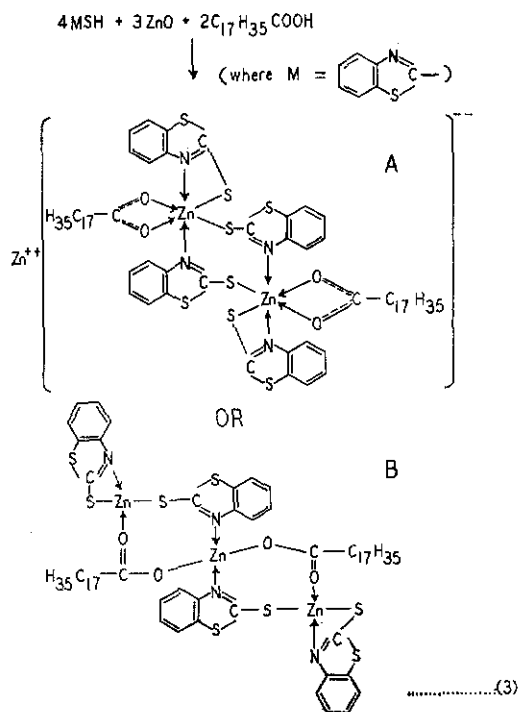
CORAN (1965) also showed that the first step in such a system is the formation of MSZnSM, which does not exist in the above structure. Also, osmometric molecular weight measurements are not highly accurate for such low molecular weights. The manner in which the complex takes part in vulcanisation was not explained.

The authors believe that stearic acid is completely converted to zinc stearate and that the complex formation occurs between MSH: ZnO: stearic acid in the molar ratio of 4:3:2. When these materials in this ratio were heated in a flask, three moles of water were lost and the residue, recrystallised from benzene, melted at 107°–109°C. Therefore it is believed that the structure given by CORAN (1964) may not be correct. More probable structures of the complex formed are suggested below.

The following reactions are proposed:



Zinc oxide, present in excess, rapidly combines with MSH giving MSZnSM at vulcanisation temperature [reaction (1)]. However, reaction (2) also occurs and is much faster.



The structures are given on a hypothetical basis. Internal chelation has already been demonstrated (CORAN, 1964; BATEMAN *et al.*, 1963), and spectroscopic and X-ray evidence (CORAN, 1964; CARR AND RAFTER, 1940) are also reported for chelation of zinc by amine or carboxylate ligands.

It is found that, in the initial stages of vulcanisation, the difference between MSH estimated by acetic acid and alcohol extractions is quite large indicative of the formation of MSZnSM.

Since in the early stages zinc oxide reacts with fatty acid to form zinc stearate and excess of ZnO reacts with MSH giving MSZnSM, the latter is immediately solubilised by the former leading to the formation of complex (A) or (B). This is believed to be very reactive and

capable of opening the S₈ ring. In its insoluble form, the zinc salt of MSH is not an active accelerator as reported in an earlier communication (BHATNAGAR AND BANERJEE, 1967). During the process of vulcanisation all the H₂S (if any) generated by the reaction between MSH, sulphur and rubber reacts with the zinc stearate.

In complex (A) or (B), the sulphur atoms attached to the zinc atom have nucleophilic properties and bear negative charges. Further, the occupation of vacant zinc orbitals by external ligands, like carboxylate ions, weakens the -Zn-S- bonding and thus increases the nucleophilicities of the mercaptide sulphur atoms (BATEMAN *et al.*, 1963). Since nucleophiles can split open the S₈ ring, the complex (C) or (D) is probably formed with sulphur [reaction (4)].

Since the bond -S_x-Zn- is rendered weaker due to co-ordination by external ligands, the complex (C) or (D) reacts with rubber with cleavage at this bond according to reaction (5). H₂S and zinc stearate formed in reaction (5)

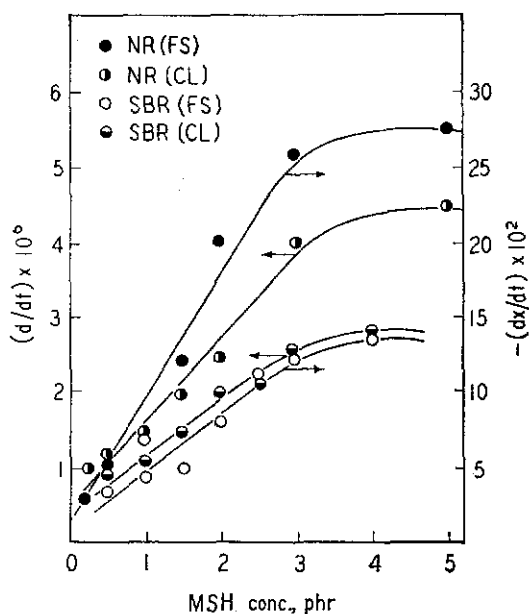
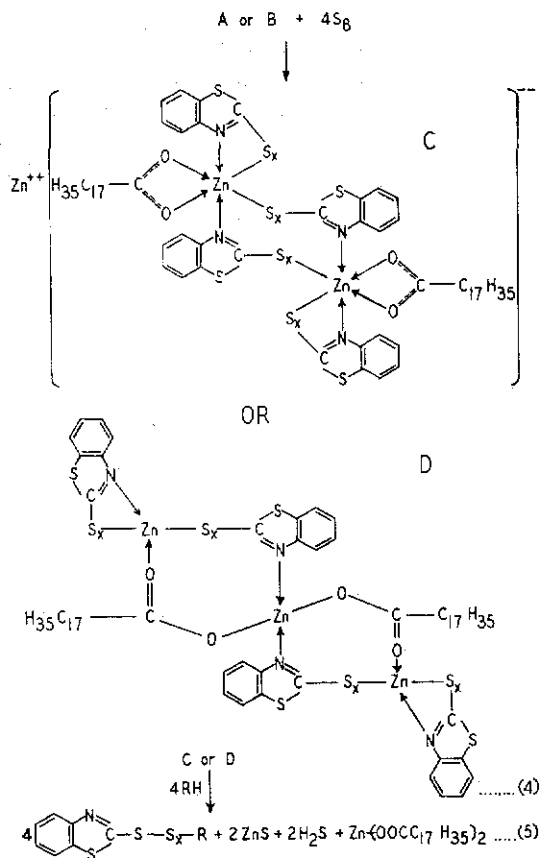
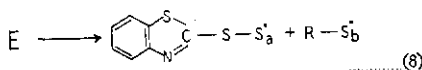
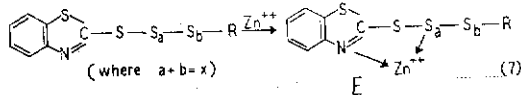


Figure 8. Plot of rates of free sulphur decrease and cross-link formation against MSH concentration. (FS—free sulphur; CL—cross-linking)



react to produce zinc sulphide and stearic acid [reaction (6)]. This reaction is rapid, even at room temperature (DOGADKIN AND BENISKA, 1958). Stearic acid is again converted to zinc stearate with excess of zinc oxide present in the mix.

Since a sufficient quantity of soluble zinc ions is available due to zinc stearate, the following reactions suggested by CORAN (1964) probably take place.



Zinc ions give rise to an internally chelated complex of the type (E). In this case, the normally weakest -S-S- bond adjacent to the thiazole group would be stabilised and the cleavage would have to occur at an -S-S- bond nearer to the rubber chain. This reaction is believed to be fast at vulcanising temperatures. The radicals R-Sb[•] can form cross-links by mutual combination and possibly also MSS_a[•] can react with rubber molecules to produce rubber radicals which can, in turn, combine with RS_b[•] to form cross-links.

The above mechanistic scheme is consistent with the formation of greater numbers of cross-links, faster consumption of sulphur and increased sulphide formation in the presence of stearic acid than in its absence. This is attributed to the presence of soluble zinc ions. Higher sulphur up-take can be explained due to the formation of the more active complex (C) or (D) due to solubilisation of the zinc salt of MSH by carboxylate ligands. The increase in cross-links and zinc sulphide can also, to some extent, be due to the attack of zinc oxide or zinc ions on the initially-formed polysulphidic cross-links.

The plots between zinc sulphide sulphur and organically combined sulphur (Figure 9) indicate a linear relation at the early stages of

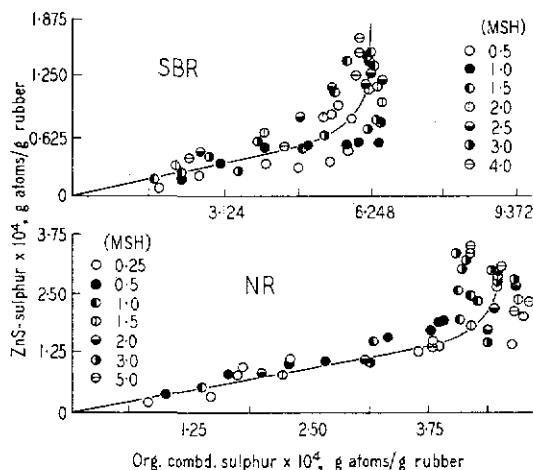
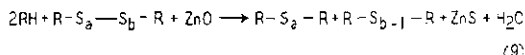
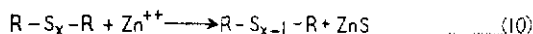


Figure 9. Variation of zinc sulphide sulphur with organically combined sulphur.

vulcanisation. After most of the sulphur has been used up, the sulphide sulphur continues to increase indicating likely involvement of polysulphide cross-links [reaction (9)].



Similar types of curves are obtained when sulphide sulphur is plotted against chemical cross-links, as shown in *Figure 10*. No reversion is apparent as was observed in the absence of stearic acid. However, the sulphide sulphur is found to increase at a slightly faster rate near the end indicating that the polysulphidic cross-links are involved in the formation of sulphide sulphur in the later stages. Since zinc ions are available in sufficient quantity, reaction (10) is probably more prominent and there is, therefore, no increase in total number of chemical cross-links.



Plots of sulphide sulphur against modulus were found to obey a linear relationship, confirming the observations of BARTON AND HART (1953). From the slopes of the linear portions in *Figures 9 and 10*, g atoms of sulphur consumed

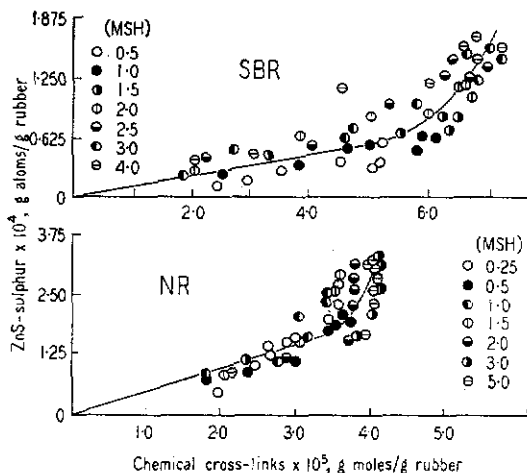


Figure 10. Variation of zinc sulphide sulphur with chemical cross-links.

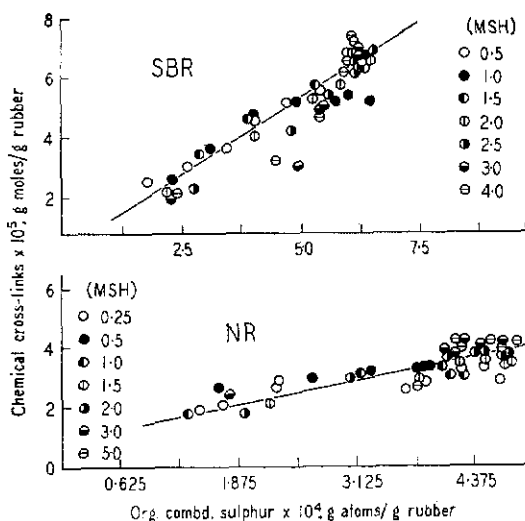


Figure 11. Variation of chemical cross-links with organically combined sulphur.

as sulphide sulphur per g atom of organically combined sulphur or sulphur combined per chemical cross-link formed, are determined and are given in *Table 5*. Similar values showing distribution of sulphur in the vulcanisates formed without stearic acid or zinc oxide or both are also shown in *Table 5*. The plots between organically combined sulphur and chemical cross-links are shown in *Figure 11* for the two rubbers. A linear relation is again indicated between the two. The values computed from the slopes are recorded in *Table 5*. It is apparent that cross-linking efficiency is considerably improved and the utilisation of sulphur becomes more efficient when zinc oxide and stearic acid are used in accelerated gum stocks.

An interesting relation is exhibited by the plots between organically combined sulphur and combined MSH. S-shaped curves are obtained (not shown) and the linear portions for all the curves in both the cases possess the same slope. A similar relation was noticed in stocks containing no zinc oxide and stearic acid. The values computed from the slope show the number of g atoms of organically combined sulphur per g mole of MSH combined with the rubber. The values are recorded in *Table 5* for both the rubbers. Compared to stocks where

TABLE 5. RESULTS OF SOME PARAMETERS CHARACTERISING VULCANISATES

Accelerator system	S _c /CL		C _A /CL		S _z /CL		S _c /C _A		S _z /S _c	
	NR	SBR	NR	SBR	NR	SBR	NR	SBR	NR	SBR
MSH	46	22	7.0	3.4	—	—	28	21	—	—
MSH + ZnO	22	16	2.5	2.0	6.0	1.0	40	30	0.25	0.06
MSH + ZnO + Stearic acid	15	12.5	—	—	3.0	1.0	41	35	0.46	0.11

Recipe: Rubber 100
Sulphur 2.5
Zinc oxide 3.0
Stearic acid 3.0
MSH variable

S_c = Combined sulphur (g atoms/g of rubber)
CL = Cross-linking (g mole/g of rubber)
C_A = Combined MSH (g mole/g of rubber)
S_z = Zinc sulphide sulphur (g atom/g of rubber)

TABLE 6. DATA ON FREE SULPHUR AND CROSS-LINKING FOR MSH AND MSZnSM ACCELERATED STOCKS

Parameter studied	Vulc. time (min)	MSZnSM (1.19% p.p.h.r.)		MSH (1.0 p.p.h.r.)	
		NR	SBR	NR	SBR
Free sulphur (p.p.h.r.)	0	2.385	2.406	2.360	2.406
	5	2.128	2.128	2.122	2.206
	10	1.903	2.015	1.886	2.052
	20	1.378	1.653	1.451	1.702
	30	0.957	1.398	1.000	1.410
	40	0.553	1.119	0.548	1.046
	60	0.395	0.555	0.408	0.605
	80	0.354	0.406	0.372	0.413
	100	0.288	0.326	0.298	0.250
Chemical cross-links × 10 ⁵ (g mole/g of rubber)	20	2.28	2.32	2.68	2.53
	30	2.79	2.80	3.00	3.48
	40	3.28	3.98	3.01	4.62
	60	3.32	5.62	3.05	5.48
	80	3.28	6.02	2.95	5.93
	100	3.20	6.04	3.19	6.18

Recipe: NR/SBR 100
Sulphur 2.5
Zinc oxide 3.0
Stearic acid 3.0
MSH 1.0 or
MSZnSM 1.19
Vulcanisation temperature at (140 ± 0.5)°C

zinc oxide is absent, the activation of sulphur by each mole of MSH is considerably improved and finally results in increased cross-linking efficiency.

It is noteworthy that in the presence of zinc oxide, stearic acid and MSZnSM, the rate of sulphur decrease and rate of cross-link formation are almost the same (*Table 6*). A very slight increase in overall rate of reaction is noticed in MSZnSM accelerated stocks due, probably, to the fact that MSZnSM is directly solubilised to give the complex (A) and (B), while in MSH accelerated stocks, MSZnSM must first be formed from MSH and zinc oxide. In the absence of stearic acid, MSZnSM is not very active as reported earlier. Thus the mechanism is the same for MSH and MSZnSM accelerated sulphur vulcanisation when both zinc oxide and stearic acids are present.

Although accurate and quantitative agreement is lacking due to complexities in the system, yet the mechanism presented explains most of the findings.

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DISCUSSION

Chairman: Dr. W. L. Resing

Dr. P. Thirion queried the validity of using the same polymer solvent interaction coefficient to calculate cross-link density for both vulcanisates cured with sulphur and with dicumyl peroxide. This might lead to an error as much as a factor of 2.