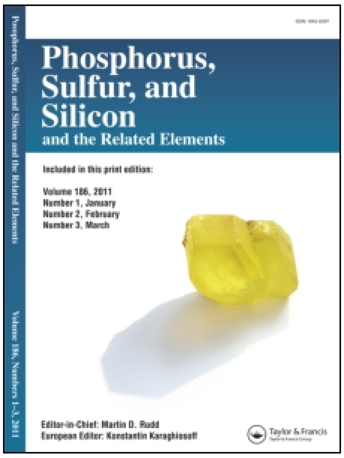

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THE INFLUENCE OF EXCESS ZINC STEARATE ON THE CHEMISTRY OF SULPHUR VULCANIZATION OF NATURAL RUBBER

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THE INFLUENCE OF EXCESS ZINC STEARATE ON THE CHEMISTRY OF SULPHUR VULCANIZATION OF NATURAL RUBBER

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Abstract In sulphur vulcanization of natural rubber excess zinc stearate enhances the yield of crosslinks, reduces their average length, and inhibits their destruction.

Sulphur vulcanization of natural rubber[1] is normally carried out at 140-180°C with the aid of zinc oxide, a fatty acid or its zinc salt, and an organic accelerator - such as a derivative of benzothiazole-2-thiol or of a dithiocarbamic acid. During vulcanization crosslinks of from one to as many as nine sulphur atoms connect the allylic carbons of the polyisoprene chains to produce a three-dimensional network. The crosslinks are formed via intermediates, which consist of accelerator groups bound through two or more sulphur atoms to the polyisoprene. The crosslinks are initially mainly polysulphidic; these then

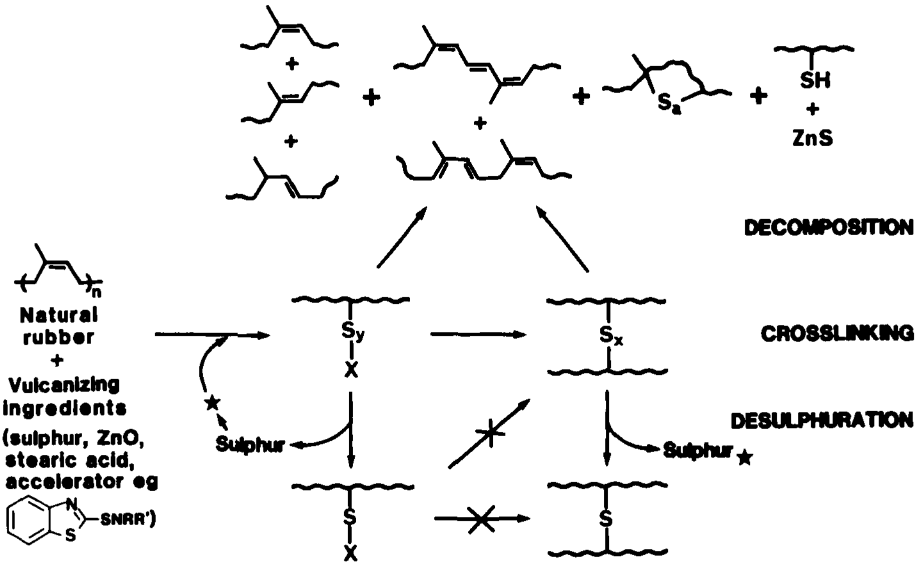


FIGURE 1 Reactions of intermediates and crosslinks.

experience several competing reactions, notably crosslink shortening with additional crosslinking, and crosslink destruction with main-chain modification (rearrangement of double bonds, increased unsaturation and cyclic sulphide formation). The intermediates, as well as being precursors to crosslinks, can undergo similar reactions. The main competing pathways are shown in Figure 1.

Two approaches were employed to investigate the effect on the course of vulcanization of using excess zinc stearate in otherwise typical sulphur vulcanization formulations. In the first of these the structures of rubber vulcanizates were characterized by a combination of selective cleavage of crosslinks through treatment with chemical probe reagents and determination of crosslink concentrations through stress-strain measurements.[2] This enabled the evolution of the crosslink structures to be determined either during vulcanization or after vulcanization at typical service temperatures. Results obtained from vulcanizations at 150°C are depicted in Figure 2, which compares a conventional formulation (thin lines), containing 2% (w/w) stearic acid, with a corresponding formulation (thick lines) with excess zinc stearate (6.6 %, w/w). The excess stearate increases both the yield and the retention of crosslinks. The additional crosslinking is mainly monosulphidic indicating that desulphuration of crosslinks is promoted.

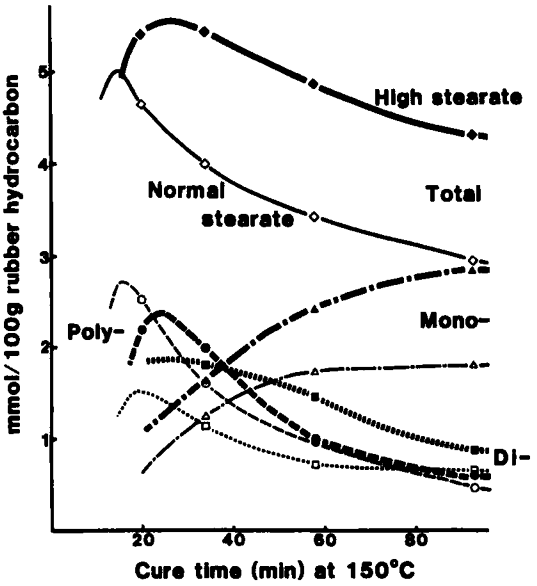
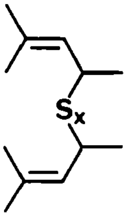


FIGURE 2 Effect of cure time on sulphidic crosslink distribution.

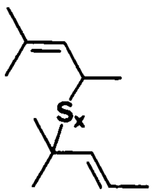
More detailed information regarding the changes in chemistry was gained by the second approach, in which the reactions of low-molecular-weight 'model crosslinks' (2 and 3) and a 'model intermediate' (8) were investigated using the 'model polyisoprenes' (9 and 10) as solvents. Some results from reactions of the disulphide (2) are summarized in Table 1. The complex (14) was included in some reactions, as such compounds are believed to be active species in vulcanizations employing the commonly used benzothiazolesulphenamides as accelerators.[1] The results confirm that the stearate promotes desulphuration. Formation of products associated with destruction of crosslinks, the alkenes (10-13), is also inhibited. However, here there is a distinction in that while crosslink cleavage leading to the monoenes (10 and 11) is strongly inhibited, cleavage leading to the dienes is unaffected.

TABLE 1 Products from a model crosslink (2) with diene (9) as solvent (100°C/6 days) (mol %).

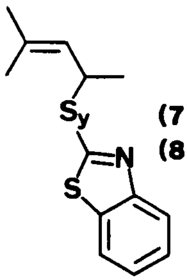
14 present? Zinc stearate present?	No No	Yes No	Yes Yes
Unreacted 2	82	25	34
Shorter crosslinks: 1 + 4	3	12	30
Longer crosslinks: 3 + 6	1.5	2.0	2.5
New crosslinks: $C_{10}H_{17}SC_6H_{11}$	0	20	19
Rearranged crosslink: 5	2.5	0.4	0.8
Broken crosslinks: monoenes 10 + 11	20	67	1.8
dienes 12 + 13	29	15	16
Accelerator derivative: 7	-	0.1	6



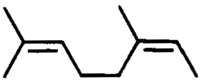
(1) x=1
(2) x=2
(3) x=3

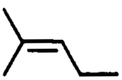


(4) x=1
(5) x=2
(6) x=3



(7) y=1
(8) y=2


(9)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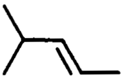
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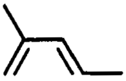
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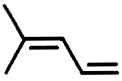
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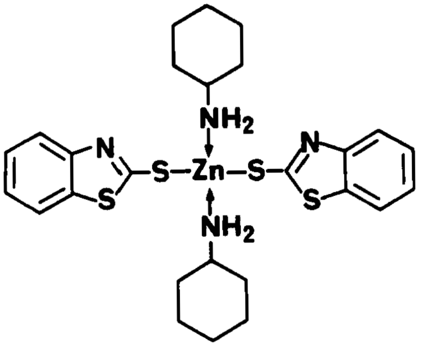
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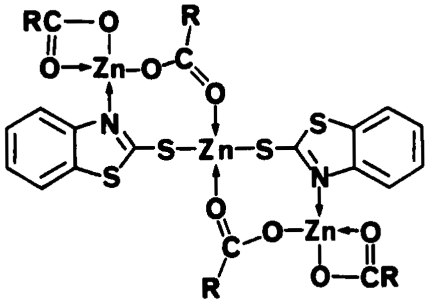
(15)

It is believed that addition of stearate leads to replacement of amine ligands in the zinc-accelerator complex (e.g. 14) by carboxylate ligands, eventually giving the complex (15).[3] The carboxylate complexes are thought to be more soluble in rubber; for instance addition of zinc stearate to a suspension of the complex (14) in pentane renders it soluble. This may improve the efficiency of vulcanization causing the increased formation and desulphuration of crosslinks. The carboxylate ligands would also alter the reactivity of the complex; presumably this leads to the reduced destruction of crosslinks.

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