VULCANISATION OF RUBBERS IN THE PRESENCE OF ORGANIC ACCELERATORS

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I. INTRODUCTION

Craig's extensive review[1] on the vulcanisation of rubber with sulphur, published in 1957, took no account of Soviet, German, and Japanese work published in the last decade. The present review aims to make up in some part this deficiency in Craig's review in respect of the chemistry of vulcanisation of rubber in the presence of accelerators.

In recent years workers on vulcanisation have mainly concentrated their attention on the elementary chemical reactions of the process, the mechanism of action of the accelerators, and on establishing the nature of the vulcanisation structures and their influence on the physico-mechanical properties of the vulcanisate. For these purposes, in addition to purely chemical methods, physical methods of analysis have come to the fore (optical and electron spectroscopy, isotope exchange, and kinetic studies with radioactive sulphur). Substantial results have been obtained in the study of the reactions of sulphur with model low-molecular-weight compounds. Two tendencies are observed in the treatment of the general character of the chemical reactions of sulphur with rubber: in some investigations of the structural changes of rubber on vulcanisation a substantial role has been ascribed to radical processes, whilst in others the elementary reactions are considered as taking place by a polar (ionic) mechanism. The different views on the mechanism of vulcanisation apparently arise not so much from different interpretations of the experimental facts, but rather because a unified approach cannot be applied to the complex phenomenon of vulcanisation. The reaction mechanism depends on the thermodynamic conditions of the reaction, the type of rubber, and, particularly, on the type of accelerators and activators used. These were the conclusions to which Shelton and McDonel came[2]. For this reason the present review, in addition to considering some general features of vulcanisation, contains material relating to various types of vulcanisation systems.

II. VULCANISATION WITH DI- AND POLY-SULPHIDES

1. Vulcanisation with Di-2-benzothiazyl Disulphide (DBTD) and *N*,*N*-Dithiomorpholine (DTM)

It has been shown[3,4] that DBTD vulcanises sodium butadiene and butadiene–styrene rubber on heating to 143° in the absence of sulphur. The DBTD is partially reduced to the mercaptan and partially combines with the rubber: the extracted vulcanisate contains sulphur and nitrogen (Fig. 1). Of the 60% reacted DBTD ~30% is reduced to mercaptobenzothiazole (MBT) and ~20% is attached to the rubber as the benzothiazyl sulphide radical. The presence of the latter in the rubber is confirmed by the ability of the vulcanisate to undergo isotopic exchange with DBTD containing ^{35}S in the disulphide group. The MBT is apparently formed by the splitting out of hydrogen from the α-methylene groups and from the tertiary carbon atom of the DBTD radicals formed by its thermal dissociation. The possibility of this decomposition into free radicals at vulcanisation temperatures is confirmed by the initiation of isoprene polymerisation by DBTD.

Determination of the molecular weight by light scattering and calculation of the number of cross-linkages in the vulcanisate indicate that each act of addition of a benzothiazyl sulphide radical to the rubber is accompanied by

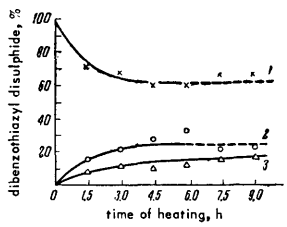
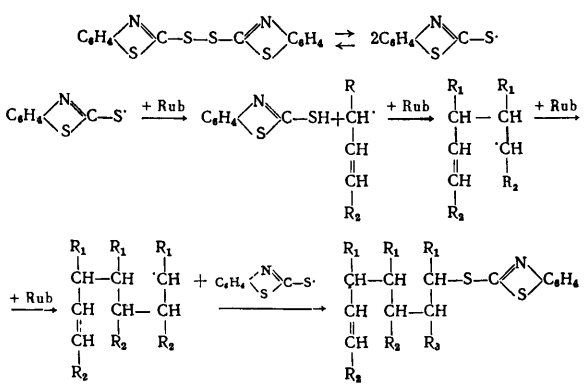


Fig. 1. Change of 1) DBTD, 2) MBT, and 3) sulphur content on heating solutions of butadiene rubber (in percentages of the initial DBTD content).

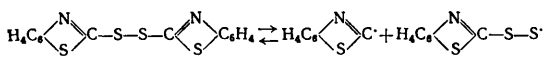
~2.7 elementary additions of rubber molecules; this corresponds to the following scheme for the reaction of DBTD with the rubber:



where Rub = rubber.

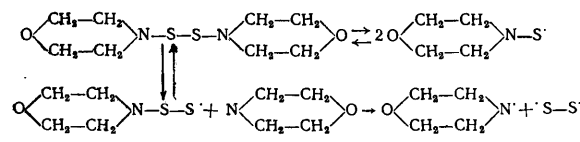
This scheme does not exhaust all possible reactions. It does not cover direct reaction between the benzothiazyl sulphide radicals and the double bonds of the rubber. Cross-linkages can also be formed by reaction between two polymeric radicals formed by the elimination of hydrogen from the α-methylene groups. The formation of C–C bonds between rubber chains by the above scheme is confirmed by the thermal stability of vulcanisates obtained with DBTD without sulphur, approximating to that of vulcanisates obtained by the action of γ-rays[5].

The symmetrical decomposition of DBTD shown in the above scheme is not the only possible one. In a number of experiments using DBTD containing ^{35}S, it was shown that the sulphur activity was not identical in the vulcanisate and in the acetone extract. This observations requires the recognition of the asymmetrical decomposition



There are grounds for supposing that the benzothiazyl disulphide radical is more active in the cross-linking of rubber than the monosulphide radical[6,7].

The kinetics of vulcanisation of rubber with N,N'-dithiomorpholine and N,N'-dithiopiperidine[8] also indicate that these accelerators undergo asymmetric decomposition, since the amount of sulphur combined with the rubber is considerably greater than the amount of combined nitrogen (Fig. 2). In this case, and unlike vulcanisation with DBTD, elementary sulphur is formed on heating the mixture of rubber and accelerator. The quantity of "free" sulphur, determined by Schulte's method after extraction with acetone at various stages in the vulcanisation, passes through a maximum. These observations suggest the following scheme for the decomposition of N,N'-dithiomorpholine:



The kinetic curve *3* (Fig. 2) shows a maximum because in the initial stage of vulcanisation the rate of decomposition of N,N'-dithiomorpholine exceeds the rate of addition of sulphur to the rubber.

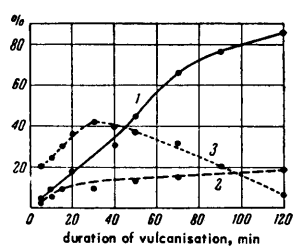
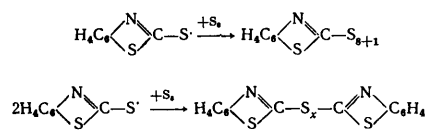


Fig. 2. Kinetics of combination of sulphur and nitrogen during vulcanisation of mixtures containing N,N'-dithiomorpholine:
1) combined sulphur; 2) combined nitrogen; 3) "true" free sulphur.

2. Vulcanisation with Sulphur in the Presence of Di-2-benzothiazyl Disulphide

This follows an equation of the first order (with respect to sulphur), the rate constant being directly proportional to the accelerator concentration[3]. In this case, as in heating a rubber–disulphide mixture, the elements of the accelerator are combined with the rubber and the disulphide is reduced to the mercaptan. The only difference is that the mercaptan formed then reacts with the components of the vulcanisation mixture and is almost completely used up by the end of the process. Thus, in addition to the reactions described above for the interaction of rubber with DBTD, the vulcanisation of rubber with sulphur in the presence of DBTD must be assumed to involve the opening of the eight-membered ring of elementary sulphur by the action of accelerator and rubber radicals. In particular, we must assume the formation of the intermediates



These intermediates are unstable and decompose with the formation of sulphur diradicals containing a variable number of sulphur atoms. These then react with rubber molecules to form cross-linkages. Bresler[9,10] has demonstrated the vulcanisation activity of sulphur diradicals in experiments on the cross-linking of rubber in a vacuum under the action of a molecular beam of elementary sulphur. Since the rate-controlling step in the vulcanisation is the decomposition of the DBTD into radicals, it becomes clear why the rate of addition of sulphur is linearly dependent on the accelerator concentration.

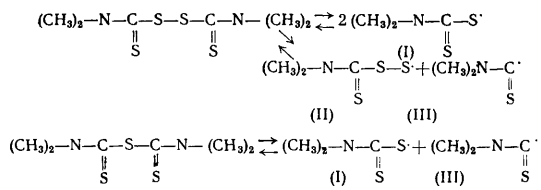
3. Vulcanisation with Thiuram Disulphides

In recent years the mechanism of the vulcanising action of thiuram disulphides has been discussed in great detail in the literature, mainly in a series of studies by Scheele

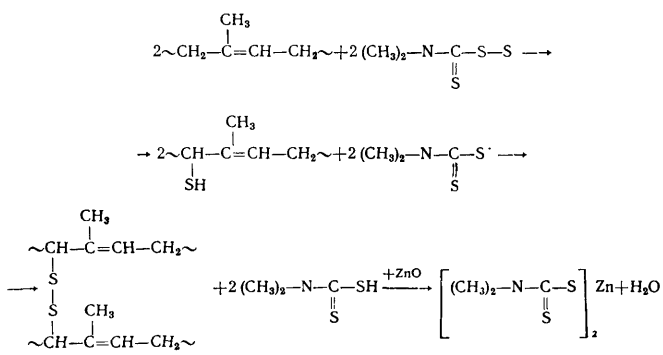
and coworkers[11]. It has been shown that when mixtures containing a tetra-alkylthiuram disulphide and zinc oxide are vulcanised in a press, by which technically valuable thiuram vulcanisates are normally obtained, the thiuram does not undergo extensive thermal decomposition. The only conversion product which is extracted from the vulcanisates is zinc dialkyldithiocarbamate (Zn DTC); the kinetics of its formation follows a first order course, and in the limit 66.6 mole % of the thiuram added to the mixture is converted[12] to Zn DTC.

The radical mechanism given by these workers for the reaction between the thiuram and the rubber with the formation of cross C–C links in the vulcanisate is in general analogous to that suggested earlier by Dogadkin and coworkers[3] for DBTD.

Bielstein and Scheele[13] later showed that the reaction of tetramethylthiuram monosulphide (TMTM) with rubber in the presence of zinc oxide also gives Zn DTC, but the rubber molecules are not cross-linked. It was therefore concluded that the decomposition of tetramethylthiuram disulphide (TMTD) can take place either at the S–S bond or at the C–S bond, while TMTM decomposes only at the C–S bond:



Cross-linkages are formed only by the reaction of the rubber molecules with the TMTD radical (II):



In accordance with this mechanism, the vulcanisate should contain combined sulphur and nitrogen from the TMTD, and this was later demonstrated by Dogadkin and Shershnev[14]. An interesting feature of the reaction of TMTD with rubber is the presence of a maximum on the kinetic curves of sulphur combination in the initial period[14–16]. After a slight decrease, the amount of TMTD sulphur combined with the rubber remains constant, but in mixtures containing zinc oxide the formation of cross-linkages continues (Fig. 3), *i.e.* the thiuram vulcanisate contains C–C bonds in addition to C–S bonds[17–19].

When TMTD reacts with rubber, it apparently decomposes into symmetrical and asymmetrical radicals in a definite ratio, and this is the reason for the limiting amounts of combined sulphur and Zn DTC formed[11,14,16,20].

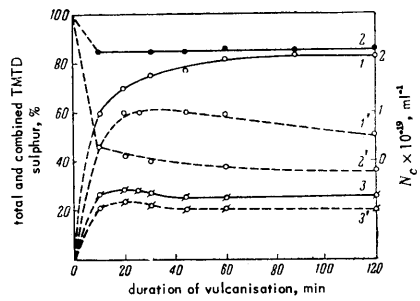
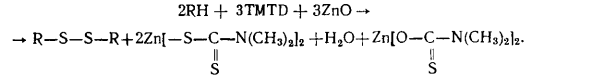


Fig. 3. Kinetics of the vulcanisation of polyisoprene rubber with TMTD:
1) and 1′) change of the number of cross-linkages in mixtures with and without zinc oxide; 2) and 2′) change of total TMTD sulphur content in mixtures with and without zinc oxide; 3) and 3′) change of combined TMTD sulphur in mixtures with and without zinc oxide.

Free-radical vulcanisation mechanisms and polymerisation mechanisms in the presence of TMTD and TMTM have been investigated in a number of studies[21–26]. Recently Bevilacqua[27] proposed a mechanism for vulcanisation with thiuram based on the symmetrical decomposition of TMTD into radicals under the vulcanisation conditions, with the formation of only disulphide cross-linkages:

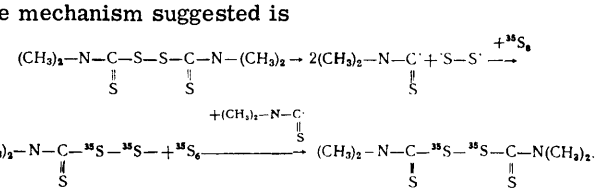


A discussion of the role of zinc oxide in this process will be given later, since this is closely related to the mechanism of action of activators and the explanation of the reversion effect in vulcanisation.

4. Vulcanisation with Sulphur in the Presence of Thiurams and Dithiocarbamates

Bresler and coworkers[9] consider that the rate-determining step in the vulcanisation of rubber with sulphur in the presence of a thiuram is the reaction of the elementary sulphur (S_8) with the accelerator. This follows from their demonstration that the velocity constant for the combination of sulphur with the rubber is identical with the isotope exchange constant for the exchange of sulphur with the thiuram. They consider that the two sulphur atoms in the disulphide bridge of the TMTD take part in the exchange with the elementary sulphur, which is not in agreement with Craig's results[28].

The mechanism suggested is

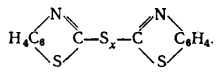


The rubber molecules are cross-linked by the ·S–S· diradical, and an activated S_8 molecule can attach itself at the points of cross-linking to form polysulphide bonds.

Scheele and Franck[29] consider that Zn DTC is also formed in vulcanisation with sulphur in the presence of TMTD and zinc oxide. Scheele and Birghan[30] showed that the vulcanisation of rubber with sulphur in the presence of zinc diethyldithiocarbamate is a zero-order reaction. Deviations are observed with a molar ratio S_8/Zn DTC > 1. The percentage of Zn DTC consumed also increases, but the quantitative relations are very complex. If zinc oxide is also present in the mixture, there is very little conversion of the Zn DTC. It was suggested that in these cases an intermediate is formed which contains a sulphur chain: this decomposes, liberating active sulphur, which then cross-links the rubber molecules.

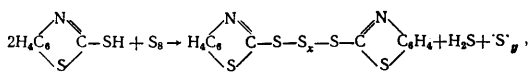
III. VULCANISATION IN THE PRESENCE OF MERCAPTOBENZOTHIAZOLE (MBT)

Sulphur reacts with MBT at vulcanisation temperatures to form hydrogen sulphide and a polysulphide of structure:



Dogadkin and Tutorskii[31] have studied the kinetics of this process. On heating a mixture of sulphur and MBT in liquid paraffin, H_2S is given off at a constant rate v (Fig. 4) which depends on the total concentration C of sulphur and MBT, but the ratio v/C increases with increasing MBT concentration and decreases with increasing sulphur concentration. The latter effect may be due to the absorption of SH radicals by the sulphur under the reaction conditions, forming compounds of type $HS-S_x-SH$. With increasing sulphur concentration the quantity of absorbed SH groups increases.

No hydrogen sulphide is detected when sulphur and MBT are heated in sealed ampoules at 140°, so that the equilibrium represented by the equation

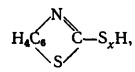


is characterised by a negligible H_2S concentration, and a marked evolution of hydrogen sulphide is only achieved if the latter is continuously removed from the reaction zone.

The energy of activation for the formation of H_2S by the reaction of sulphur with MBT is ~ 33 500 cal mole^{-1}, while the energy of activation for vulcanisation in the presence of MBT is ~ 21 000 cal mole^{-1}. These facts are in clear opposition to Fisher's theory[32], according to which the main reaction in vulcanisation is the formation of hydrogen sulphide, which then combines with the rubber to form thiol groups which are oxidised to disulphide and polysulphide bridges between the rubber chain molecules.

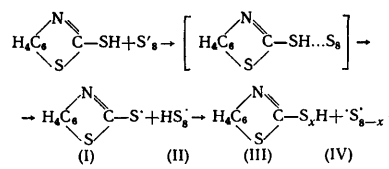
During vulcanisation there is simultaneous combination of sulphur and MBT with the rubber[33] (Fig. 5): the combination of the accelerator with the rubber virtually ceases when the free sulphur is used up; if fresh sulphur (from solution) is added to the vulcanisate, the combination of MBT with the rubber again takes place (Fig. 5, curve *3*).

The kinetics of the combination of the sulphur with the rubber follows an equation of the first order[33-35], the kinetic constants being linearly dependent on the accelerator concentration[33,34,36,37]. Fig. 5 shows that 1 mole of combined accelerator activates approximately 4 moles of sulphur. An intermediate polysulphide of structure



has been separated from the vulcanisate. This compound has an absorption maximum at 330 mμ, characteristic of linear polysulphides. Its sulphur content depends on the time of vulcanisation, passing through a maximum; this has been shown analytically and by isotope exchange with radioactive sulphur. The maximum sulphur content of the intermediate corresponds to a value of x greater than 3.

The above experimental data suggest the following mechanism for the main reaction[33]:



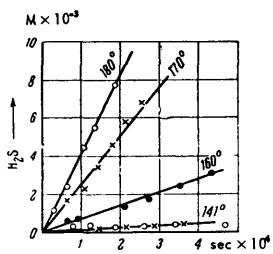


Fig. 4. Kinetics of evolution of hydrogen sulphide on heating sulphur and MBT at various temperatures in liquid paraffin.

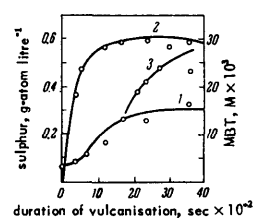


Fig. 5. Kinetics of the combination of (1) sulphur and (2) MBT during vulcanisation of butadiene rubber at 143°; (3) combination of MBT after the introduction of sulphur into the vulcanisate by swelling.

The benzothiazyl sulphide (I) and perthiol (II) radicals are stabilised by conjugation. They react to form the benzothiazyl hydropolysulphide (III) and the diradical (IV) with variable sulphur contents.

The perthiol radical $HS_x^{\cdot}$ may contain a variable number of sulphur atoms. A number of studies[1] have attributed the main role in vulcanisation to the HS· radical. If this were correct, the S–S bonds in the vulcanisate would not contain more than two sulphur atoms, but the experimental results show that the vulcanisates obtained with MBT and diphenylguanidine contain bonds with a substantially greater number of sulphur atoms. In particular, this has been shown by isotope exchange between the vulcanisates and elementary radioactive sulphur. The total quantity of sulphur which can exchange varies with the period of vulcanisation and passes through a maximum (Fig. 6). At the same time the exchange capacity per unit of combined sulphur decreases steadily. This means that polysulphide bonds are formed in the first stages of the vulcanisation, and then rearrange to form bonds with a lower sulphur content. In vulcanisation in the presence of MBT, therefore, the radicals (II) and (IV) play the major part.

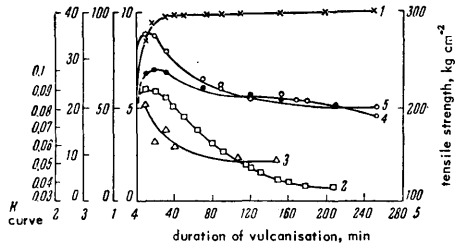


Fig. 6. Change of the physicochemical properties of natural rubber on vulcanisation:
1) combined sulphur $[(S_{comb}/S_{total}) \times 100, \%]$;
2) exchangeable sulphur (moles per litre of rubber);
3) exchange capacity $[(I_0 - I_1)/(I_0 - I_1 S_{free}) + (S_{comb}/S_{total}) \times 100\ (\%)]$ [The correctness of this formula is uncertain because of the poor print in the Russian original (Ed. of Translation).];
4) number of cross-linkages $N_c \times 10^{19}$, $mole^{-1}$;
5) strength.

Tsurugi and Fukuda[38] have studied the reaction of MBT and its zinc salt with diphenylmethane, which they consider to be a rubber model. According to them, it is the resulting MBT Zn salt which possesses accelerating activity in MBT–sulphur–zinc salt systems; this reacts with sulphur to form zinc sulphide, sulphide diradicals, and MBT radicals. The mechanism for the reaction of these radicals with diphenylmethane is analogous to that considered above and suggested by Dogadkin and coworkers[3].

IV. VULCANISATION IN THE PRESENCE OF SULPHENAMIDES

Recently extensive use has been made of sulphenamide accelerators containing the group –C–S–N=, especially *N*,*N*-diethyl-2-benzothiazylsulphenamide (Vulcacite AZ, DEBSA), *N*-cyclohexyl-2-benzothiazylsulphenamide (Vulcacite CZ, CBSA), and others. The main property of these accelerators is the presence of a definite induction period of low velocity on the kinetic curves representing the combination of sulphur and the change of the modulus[39]. This property bestows technical advantages on the sulphenamide accelerators with respect to premature vulcanisation (scorching) and better formability, and consequently they give greater stability of bond in laminated goods, particularly of synthetic rubbers[40]. The kinetics of vulcanisation and mechanism of action of sulphenamide accelerators have been studied by Dogadkin and coworkers[39,41,42].

In the vulcanisation of sodium butadiene rubber the rate of combination of sulphur in the initial period is approximately the same as in vulcanisation without an accelerator (Fig. 7). The energy of activation is ~30 kcal $mole^{-1}$; this is the energy of activation of vulcanisation without an accelerator and corresponds to the energy of opening of the eight-membered sulphur ring[43]. The energy of activation in the main period of sulphur combination is 14 kcal $mole^{-1}$, demonstrating the active part played by the accelerator, or rather its decomposition products, in the combination of the sulphur with the rubber in this period. The rate of combination of sulphur in the main period depends on the initial concentrations of sulphur and accelerator, the dependence being linear for the latter.

The formation of a three-dimensional structure in mixtures containing DEBSA is also characterised by a prolonged induction period. A single three-dimensional network with a concentration of cross-linkages of the order of $0.1-0.4 \times 10^{-4}$ mole g^{-1} of rubber is formed after 15–30 min, when the quantity of combined sulphur is ~40% of that added.

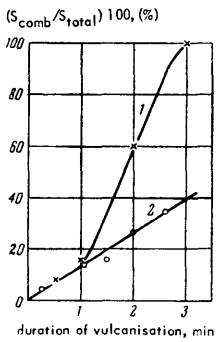
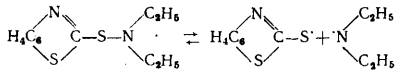


Fig. 7. Kinetics of the combination of sulphur in mixtures:
1) with DEBSA; 2) without an accelerator.

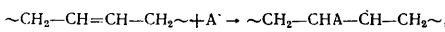
The presence in the vulcanisation system of oxygen and oxygen-containing compounds has a substantial effect on the kinetic curves. The longest induction period is observed in vulcanisation with the exclusion of oxygen (Fig. 8). In pure oxygen there is no induction period and the kinetic curve for the combination of sulphur is transformed from an S-shaped to a convex curve. The acceleration of the combination of sulphur with the rubber caused by molecular oxygen finds explanation in the oxidation of the rubber to form polymeric radicals which can react with the sulphur. Moreover, the peroxide radicals formed in the oxidation of rubber can apparently form an oxidation–reduction system with the sulphenamides[44,45], so that the formation of accelerator radicals is enhanced; indeed, cumene hydroperoxide increases the rate of combination of sulphur in the presence of DEBSA.

Heating rubber with sulphenamide accelerators (in the absence of sulphur) causes vulcanisation, with combination of the accelerator elements with the rubber and the formation, in the case of DEBSA, of 2-mercaptobenzothiazole and diethylamine (Fig. 9). The amount of cross-linking produced in the rubber in this process is proportional to the amount of DEBSA consumed. From these facts, the mechanism of decomposition of DEBSA can be represented by the equation

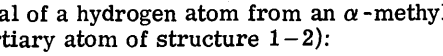


The accelerator radicals (A·) formed in the decomposition produce cross-linking in the rubber by two reactions:

(a) addition to a doubly bonded carbon atom:



(b) removal of a hydrogen atom from an α-methylene group (or tertiary atom of structure 1–2):



where AH is mercaptobenzothiazole or diethylamine. The resulting polymeric radicals react together or with the double bonds of other rubber molecules, forming the cross –C–C– links of the three-dimensional vulcanisate structure.

The conversion of DEBSA in the presence of sulphur and activators is the same as in a binary rubber–accelerator mixture.

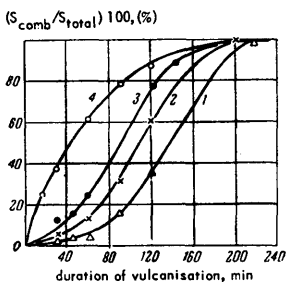


Fig. 8. Influence of oxygen on the combination of sulphur in mixtures with DEBSA: 1) 0.02; 2) 4.7; 3) 21; 4) 100 vol. % O_2.

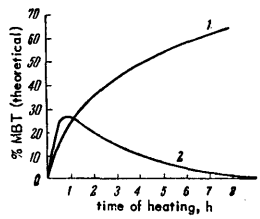
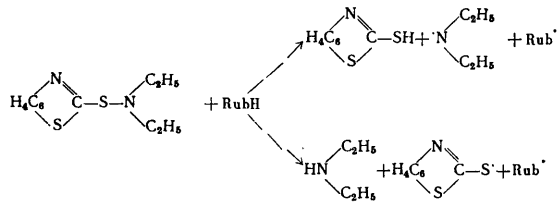


Fig. 9. 1) Combination of the mercaptobenzothiazyl radical (according to the combined-sulphur content) with rubber; 2) change of free MBT content in the system rubber + 6 wt.% DEBSA.

On the basis of the experimental results obtained, the following mechanism of action of DEBSA as a vulcanisation accelerator may be put forward. At the vulcanisation temperature, as indicated above, the accelerator dissociates into benzothiazyl and diethylamine radicals, which react with the rubber by withdrawing hydrogen from the molecular chains, forming mercaptobenzothiazole and diethylamine. The MBT reacts with sulphur by the mechanism given in section III. The curve depicting the concentration of MBT in the mixture has a maximum, which corresponds to the maximum rate of combination of sulphur with rubber. The decreased free MBT concentration beyond the maximum is due to its combination with the rubber, which continues as long as the mixture contains free sulphur[33]. Diethylamine must also be considered as having an analogous action as an accelerator, but it takes part in the vulcanisation to a lesser degree than the mercaptan, so that its content in the vulcanisation mixture gradually increases.

This theory can explain the S-shaped form of the kinetic vulcanisation curve which is typical of sulphenamide accelerators. As indicated above, the rate and energy of activation of sulphur combination in the initial period correspond with those for vulcanisation in the absence of an accelerator. It can therefore be deduced that the molecular form of *N,N*-diethyl-2-benzothiazylsulphenamide does not activate sulphur. The activation is due to the benzothiazyl and diethylamine radicals formed by the dissociation of the sulphenamide, and, in particular, to the mercaptobenzothiazole and diethylamine produced by the reaction of DEBSA with the rubber. In accordance with this mechanism,



each reaction of a DEBSA molecule with the rubber produces a molecule of active accelerator (mercaptan or amine) and two free radicals which can react with the sulphur. In other words, a DEBSA molecule is replaced by *three* active groups which can react with sulphur. This type of reaction is also responsible for the auto-acceleration of the process — the transition from the induction period to the main reaction period.

The increase in the rate of combination of sulphur in the main reaction period is also due to the following circumstance. As already stated, during the vulcanisation a considerable proportion of the DEBSA molecule is replaced by twice their number of new accelerators, the mercaptobenzothiazole and diethylamine molecules. The action of these two accelerators is not additive: in admixture they accelerate the combination of sulphur with the rubber to a greater extent than either taken separately in the same molar concentration. The reason for the increased activity of mixtures of two accelerators is discussed in section VI below.

The particular kinetics of the combination of sulphur with rubber in mixtures with sulphenamide accelerators are reflected in the dynamics of formation of the cross-linkages and of the change of plastoelastic properties of the mixture. Unlike other vulcanisation accelerators (MBT, thiuram, etc.), DEBSA leaves the vulcanisation mixture in the viscous-flow condition for a prolonged period, the plasticity of the mixture increasing in the initial stage despite combination of sulphur. This indicates that DEBSA promotes the thermal and thermal-oxidative decomposition of the molecular chains of rubber. There are grounds for supposing that this decomposition proceeds by the free-radical mechanism established by Pike and Watson[46].

V. VULCANISATION IN THE PRESENCE OF ORGANIC BASES

Organic bases are among the few vulcanisation accelerators which do not contain sulphur. The mechanism of their action has been studied in least detail.

Krebs[47] considers that amines react with sulphur and convert it into an active form soluble in rubber, the reaction being an ionic chain reaction:

$$R_3N^+ \rightarrow \overline{S}_n^- \rightarrow R_3N^+ + S^{\cdots}\!-\!S^- + S_8 \xrightarrow{+\overline{S}_n^-} R_3N^+\!-\!S\ldots S^- \rightarrow R_3N^+\!-\!S^-\ldots\overline{S}\!+\!S_8 \text{ etc.}$$

Scheele and coworkers[48] have made a kinetic study of vulcanisation in the presence of organic bases. They found that, in the presence of diphenylguanidine (DPG), the reaction between rubber and sulphur, as in the absence of accelerators, has a fractional order (0.75–0.8) with respect to the decrease in the quantity of free sulphur over the temperature range 100°–140°. The energy of activation is 29.8 kcal mole^{-1}. Initially there is a sharp decrease in the DPG concentration, reaching 55% of the original; it then becomes steady, but the free sulphur concentration still decreases. The velocity constant for the last reaction increases linearly with increase of the DPG concentration in the initial mixture up to ~2.5%, after which the constant remains practically unchanged. The initial sulphur and DPG concentrations have no influence on the order of the reaction. Based on the aforementioned work of Krebs, Scheele and coworkers assume an ionic mechanism for the vulcanisation activity of amines:

$$RNH_2 + S_8^- \rightleftarrows S_8^- + H^+$$

$$H^+ + RNH_2 \rightleftarrows RNH_3^+$$

At elevated temperature the negative ion $RNH\!-\!S_x^-$ is formed, which then gives up sulphur by the reaction

$$RNH\!-\!S_x^- + Rub \rightarrow RNH\!-\!S_y^- + Rub\!-\!S_y.$$

The base is thus a catalyst, and gives an intermediate with the sulphur. The study of various amines as accelerators showed that the velocity constant for the reaction between sulphur and rubber increases with increase of the dissociation constant of the amine, while tertiary amines do not accelerate vulcanisation. Of the amines studied (diethyl- and dimethyl-aniline, monoethyl- and monomethyl-aniline, α-naphthylamine, *o*-, *m*-, and *p*-toluidine, aniline, benzylamine) the only exception to this rule was DPG.

Aniline increases the evolution of hydrogen sulphide in the reaction of sulphur with diphenylmethane[49].

Moore and others[50] studied the reaction of sulphur with low-molecular olefines in the presence of diethylamine, and showed that the latter reacts with sulphur to form hydrogen sulphide and compounds in which sulphur has replaced hydrogen:

$$CH_3\!-\!CH_2\!-\!NHC_2H_5 + 2S \rightarrow H_2S + CH_3CS\!-\!NH\!-\!C_2H_5 \xrightarrow{+(C_2H_5)_2NH} \rightarrow C_2H_5NH_2 + CH_3CSN(C_2H_5)_2.$$

The quaternary ammonium salt $(C_2H_5)_2NH_2^+SH^-$, which reacts with double bonds, can then be formed. The reaction, according to Moore's results, proceeds by a polar mechanism, considered in more detail below.

The amine accelerator is decomposed during vulcanisation[48,51,52].

In vulcanisation in the presence of DPG, the main feature is apparently the reaction between the decomposition products of the accelerator and the sulphur, giving polysulphides. The part played by such polysulphides and their further heterolytic dissociation has been described by Bateman and coworkers[53–55], who suggested an ionic mechanism for the reactions. They showed that the reaction products of olefines with sulphur at 110°–140° are linear polysulphides and cyclic sulphides. From the kinetics of the process, Bateman suggested the following mechanism:

Initiation: (polar dissociation of the polysulphide) polysulphide $\rightarrow TS_a^+TS_b^-$ (1)

Chain growth: $TS_a^+ + RH(C=C) \rightarrow TS_aRH^+$ (satd.) (2)

$$TS_aRH^+ \text{ (satd.)} + RH(C=C) \rightarrow \begin{cases} TS_aRH_2 \text{ (satd.)} + R^+ & (3) \\ TS_aR(C=C) + RH_2^+ & (4) \end{cases}$$

$$\left.\begin{matrix} R^+ \\ RH_2^+ \end{matrix}\right\} + S_8 \rightarrow \begin{cases} RS_a^+ & (5) \\ RH_2S_a^+ & (6) \end{cases}$$

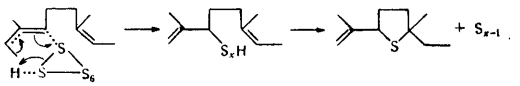
Chain breaking: $\left.\begin{matrix} R^+ \\ RH_2^+ \\ TS_aRH^+ \end{matrix}\right\} + TS_b \rightarrow$ non-chain conversion (7), (8), (9)

Here RH(C=C) is a mono-olefine; the term "(satd.)" signifies the absence of a C=C bond; H is the hydrogen of an α-methylene group; T = R or RH_2; a and $b \geq 1$.

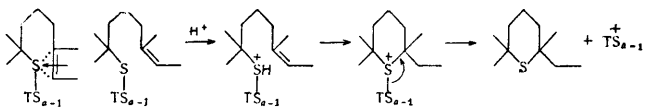
The mechanism of formation of the initial polysulphide is not clear. The fundamental step in the mechanism given above is the heterolytic dissociation of the S–S bond, which the authors consider the most probable process under vulcanisation conditions. The electron donor activity of the olefine double bond (reaction of unsaturated compounds with metal ions) will, in the authors' opinion, facilitate polarisation of the S–S bond in the S_8 and polysulphide molecules.

The large number of products obtained in the reaction of sulphur with olefines is due to the various possible directions in which the cation formed can react: combination with an associated anion or sulphur molecule, and exchange with a proton or hydride ion of the olefine molecule.

Bateman and coworkers[53] give detailed schemes for the reaction of sulphur with various low-molecular unsaturated compounds: octene-1, di- and tri-alkylethylenes, and 2,6-dimethylocta-2,6-diene, which explain the formation of complex polysulphides including those of cyclic structure. Cyclic monosulphides are formed as secondary products in the reaction of sulphur with 1,5-dienes. They are produced from the initially formed polysulphides, which react by proton transfer to give thiocarbonium ions, leading to intramolecular heterolysis of the added polysulphide bonds. Cyclic sulphides cannot therefore be formed independently of polysulphides. The reaction is:



Protonation of the double bond adjacent to the added sulphur by means of R^+ or TS_a^+RH produces a cyclic sulphide rather than a cross-linkage. The carbonium ion is converted to a polysulphide ion without combining with the sulphur, and this explains why sulphur reacts with 1,5-dienes more slowly than with mono-olefines. Ross[54] established this experimentally. With polyolefines there is irregular protonation, producing cyclic sulphides by the reaction



The TS_b^- anion formed in the dissociation of the polysulphide is thought to take part mainly in chain breaking by reacting with a carbonium or polysulphide ion, producing polysulphides.

The reaction mechanism suggested for the natural rubber model (2,6-dimethyloctadiene-2,6) can, it is thought, be applied also to reactions in rubber[56].

VI. ACTION OF SYSTEMS OF TWO VULCANISATION ACCELERATORS

Systems of two accelerators are widely used in technology, since they provide more effective vulcanisation than either material used alone. In early studies[57,58] the increased activity of two accelerators was explained by the formation of eutectic mixtures or salt-like compounds having a greater solubility in the rubber and a greater chemical activity. This explanation proved unsatisfactory, and the question received further study by Dogadkin and coworkers[59,60].

The experimental data on the kinetics of vulcanisation in the presence of various combinations of the most widely used accelerators enable the double systems to be divided into three groups: (1) systems with mutual activation of the accelerators; (2) systems with activation of one accelerator (the vulcanisation activity of such systems is no greater than that of the more active accelerator when used alone at the same molar concentration); (3) systems in which the activity of the accelerators is additive.

The first group includes systems of disulphides and mercaptans with organic bases, and disulphides and sulphenamides; the second includes combinations of sulphenamides with organic bases; and the third, combinations of sulphenamides and disulphides with monosulphides, and also combinations of accelerators of a single chemical type.

It is remarkable that vulcanisation in the presence of systems of the first and second groups shows an initial period of slow vulcanisation, in which the rate of vulcanisation is less than the rate expected on the basis of additivity of action of the accelerators (Fig. 10). In other words, in the initial stage for a certain composition, the accelerators exhibit mutual inhibition, and only in subsequent stages is there a sharp increase in the activity of the system. It may thus be concluded that in the initial stage of heating the vulcanisation mixture the accelerators react with one another, forming a less active complex,

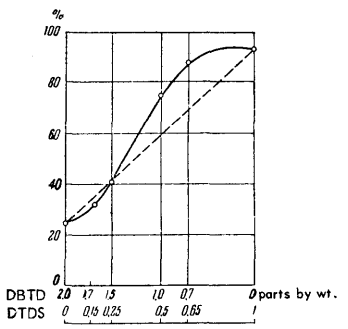


Fig. 10. Change of the amount of sulphur consumed after 5 min vulcanisation in the system DBTD + dimethylthiocarbamyl dimethylsulphenamide (DTDS).

which then dissociates into free radicals which initiate the reaction of the rubber with the sulphur and polymerisation of the molecular chains of the rubber. The active complex forms at a molar ratio of the accelerators.

The accelerators of the active systems of the first and second groups interact on heating in xylene and a xylene solution of rubber. There is marked formation of MBT when a mixture of DBTD and DPG is heated in xylene; the diphenylguanidine is here the hydrogen donor for the reduction of the disulphide. On heating DBTD with sulphenamide accelerators, *e.g.* with *N*-cyclohexyl-2-benzothiazylsulphenamide, the mercaptan is only formed when the solution contains rubber, since the benzothiazyl radicals produced by the dissociation of the intermediate complex cannot extract hydrogen from the solvent molecules, and the hydrogen donors are the α-methylene groups of the rubber.

The quantity of MBT produced by the action of an active mixture of two accelerators is many times the quantity of mercaptan formed by the action of either accelerator alone

(Fig. 11; the dotted lines show the formation of mercaptan assuming additivity of action of the accelerators). This is a convincing proof of the interaction of the accelerators and the formation of an intermediate complex which decomposes into free radicals:

$$RSSR+R'R''NH \rightarrow \left[\begin{matrix}RSSR\\R'R''NH\end{matrix}\right] \rightleftarrows RSH+RS^{\cdot}+R'R''N^{+},$$

i.e. the decomposition of the disulphide, like that of a peroxide[61], is activated by an amine.

The further development of the process when using certain accelerators may include the steps:

$$RS^{\cdot}+R'R''NH \rightarrow RSH+R'R''N^{\cdot}$$
$$R'R''N^{\cdot}+RSSR \rightarrow RSNR''R'+RS^{\cdot}.$$

These steps explain the formation of two new extremely active accelerators: MBT (RSH) and the sulphenamide (RSNR"R'), and can also be considered as the reason for the increased vulcanisation activity of the initial binary system of accelerators.

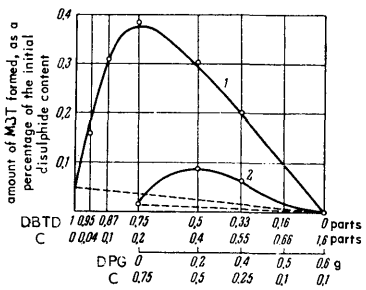
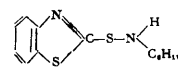
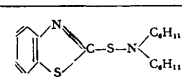
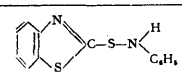
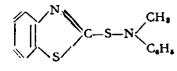
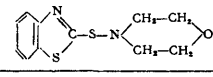
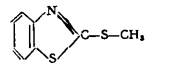
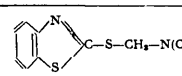
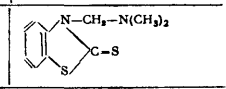
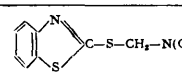
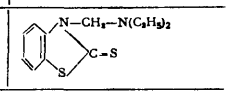
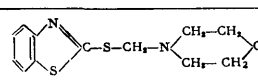
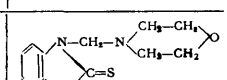
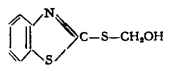
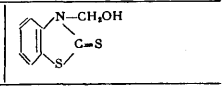
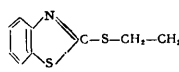
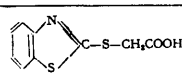


Fig. 11. Formation of MBT by the reaction of *N*-cyclohexyl-2-benzothiazylsulphenamide (C) with (1) DBTD and (2) DPG on heating in a rubber solution for 90 min at 150°.

TABLE 1. Dipole moments of MBT derivatives.

Assumed formula	Molar polarisation	Molar refraction	Dipole moment $\mu\times10^{18}$, *D*	Formula established from measurement of dipole moment
	246.0	75.6	2,87	as shown
	288.5	101.4	3.01	as shown
	190.8	74.1	2.38	as shown
	202.9	89.1	2.45	as shown
	130.3	68.3	1.73	as shown
	87,5	51.1	1.30	as shown
	463.9	64.3	4.39	
	470.8	73.5	4.38	
	533.4	73.0	4.72	
	486.4	52.6	4.58	
	169	57.3	2.33	as shown
	461.9	54.8	4.44	as shown

VII. STRUCTURE AND ACTIVITY OF VULCANISATION ACCELERATORS

The connection between chemical structure and vulcanisation activity of the accelerators has been often reviewed[62]. Attempts have been made to establish a relationship between accelerator activity and its physical properties, particularly its dipole moment. In recent years the attention of workers has been attracted towards a possible evaluation of the activity of sulphur-containing accelerators by their ability to exchange sulphur with radioactive sulphur. Blokh and coworkers[63-65] used 2-mercaptobenzothiazole derivatives to show that the rate of isotope exchange at vulcanisation temperatures runs parallel to the rate of vulcanisation in the presence of the accelerators. The thiol sulphur of MBT exchanges with elementary sulphur, and substitution of a methyl group causes loss of vulcanisation activity and precludes isotope exchange. However, more recent studies have shown that this relationship is not always observed; thus the zinc salts of mercaptobenzothiazole and dithiocarbamic acid, which are active accelerators, exchange with ^{35}S only with difficulty. In most cases isotope exchange proceeds at a lower rate than the combination of sulphur with the rubber in the presence of equal amounts of accelerators[66]. This is understandable if it is recalled that in vulcanisation reactions, as the experimental data given above show, the reaction of the accelerator with the rubber plays a substantial part.

The exchange reaction of disulphides and sulphenamides with compounds containing similar groups with labelled atoms is of undoubted interest for evaluating the activity of these accelerators. Gur'yanova[67] has shown that exchange between disulphides and mercaptans takes place by a radical mechanism:

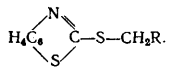
$$RSSR+R'SH \rightarrow RSSR'+RSH.$$

The degree of exchange is determined by the energy of the S–S bond, which, in its turn, depends on the nature of the radicals R and R'. This method has been used to

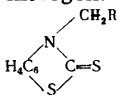
evaluate the vulcanisation activity of sulphenamide accelerators of various structure[68], using exchange with DBTD labelled in the disulphide bridge. The experimental results demonstrated a good correlation between the degree of exchange and the activity of the accelerator.

Of the sulphenamide derivatives of mercaptobenzothiazole, the unsubstituted benzothiazylsulphenamide shows the smallest activity. Substitution of the amino hydrogen by alkyl radicals increases the activity of the accelerator. The introduction of two phenyl groups causes almost complete loss of vulcanisation activity. Substitution of one hydrogen by a phenyl group produces an accelerator of similar activity to DEBSA. Of the compounds studied the most active was *N*-cyclohexyl-2-benzothiazylsulphenamide.

It was shown in section IV that a characteristic feature of sulphenamide accelerators is the existence of an induction period, both as regards taking up of sulphur and change of plasticity. This induction period is not observed with 2-methylthiobenzothiazole derivatives, which can be divided into two groups according to their dipole moment (Table 1). Some have a dipole moment of 2.38–2.87 *D*, indicating that the methyl group is attached to the thiol sulphur:



These have a low vulcanisation activity. Others have a dipole moment of 4.3–4.7 *D*, indicating that the methyl group is attached to the nitrogen:



These compounds possess high vulcanisation activity, apparently because the energy of the $-N-CH_2R$ bond is less than the energy of the $-S-CH_2R$ bond.

VIII. INFLUENCE OF THE STRUCTURE OF RUBBER ON ITS VULCANISATION CAPACITY

The ability of rubber to undergo vulcanisation with sulphur is determined first by the presence of double bonds in its molecular chains. The kinetics of the reaction with sulphur depends on the number of double bonds and the nature of the substituents present. Dogadkin and coworkers[69] used butadiene polymers to show that the position of the double bonds also plays a part. In the vulcanisation of solutions of rubbers containing various ratios of 1,4- and 1,2-structures, it was found that sulphur combines with the double bonds of the main chains at a faster rate than with the double bonds of the vinyl side chains (Fig. 12): the energy of activation for the combination of sulphur with the main chains in the presence of accelerator A-100 is 14 kcal mole^{-1}, but 19 kcal mole^{-1} in the case of combination with the vinyl side chains. The different activity of the double bonds of the 1,4- and 1,2-structures towards sulphur has been demonstrated by observing the change in the absorption bands at a frequency of 965 cm^{-1} (for 1,4-structures) and 909 cm^{-1} (for 1,2-structures) on vulcanisation.

If the vulcanisation is carried out in a press, the difference in the rates of combination of sulphur with rubbers of different structure disappears, apparently because of

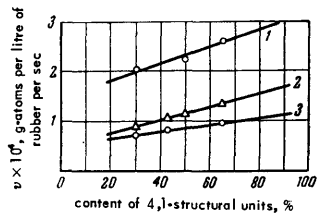


Fig. 12. Rate of combination of sulphur as a function of the structure of the rubber: 1) 155°; 2) 142°; 3) 135°.

the increased concentration of double bonds and hence of the increased absolute rates of reaction as compared with vulcanisation in solution.

According to the spectroscopic data, there is no decrease in the number of double bonds in the initial period of vulcanisation. This means that, in this stage of the vulcanisation, reactions in which the α-methylene groups of the 4,1-structure take part are predominant. Various mechanisms are possible for these reactions; the removal of hydrogen by the accelerator radicals is apparently the main process (see sections II and III). In the main vulcanisation period the decrease in unsaturation is linearly dependent on the amount of combined sulphur, but (unlike cases described in the literature for natural rubber) the decrease in unsaturation is 4–6 times that calculated on the assumption that one atom of sulphur combines with each double bond. This increase may be due to polymerisation of the molecular chains at the double bonds, or to the formation of intramolecular rings.

The degree of cross-linking $\Delta E_\infty/\Delta S$ is a linear function of the number of double bonds of 1,4-structure.

In the vulcanisation of butadiene rubbers with thiuram in the absence of sulphur, the degree of cross-linking increases with increase of their content of 1,4-structures, but the amount of combined TMTD sulphur decreases. The greater reaction of TMTD with rubbers with a higher content of 1,2-structures is apparently due to the combination of TMTD radicals with the vinyl side chains, which does not produce cross-linkages; these arise, as shown above, by reaction of the TMTD with the double bonds or α-methylene groups of 1,4-structure[14].

IX. ROLE OF VULCANISATION ACTIVATORS

Vulcanisates of better quality are obtained in the presence of activators. Some workers[70,71] suggest that the metal oxides used as activators form salt-like compounds with the accelerators which are more soluble in the rubber and therefore more active. They react with sulphur to produce unstable compounds which liberate sulphur in the active form[38]. Dogadkin and coworkers[72,73] have shown that the choice of activator depends on the type of rubber, the accelerator, and the filler.

The most widely used activator is zinc oxide. In its presence sulphur reacts with rubber by a first-order reaction, and in its absence by a reaction of fractional order[48]. The rate of combination of sulphur in mixtures without an accelerator and with MBT in the presence of

zinc oxide and stearic acid is either the same as or slightly less than the rate in mixtures without activators (Fig. 13). The activators considerably increase the number of cross-linkages in the vulcanisate[74,75].

In vulcanisation in the presence of zinc oxide, part of the sulphur is combined as zinc sulphide, which is formed to a greater extent in mixtures without an accelerator than in mixtures with accelerators (MBT, DPG). It has been shown experimentally that zinc sulphide can form by various reactions occurring in sulphur vulcanisation: the reaction of zinc oxide or stearate with hydrogen sulphide, the reaction of the zinc salt of the accelerator (MBT) with sulphur or hydrogen sulphide; and the reaction of polysulphides with zinc oxide, stearate, or mercaptide. The last reaction suggests the possible formation of zinc sulphide by the reaction of zinc oxide with the polysulphide bonds of the vulcanisate; this was confirmed by the increase in the zinc sulphide content when the vulcanisate was heated after acetone extraction. The same is observed on prolonged heating of a vulcanisate in which the sulphur is completely combined with the rubber. This reaction explains the sharp increase in the ratio ZnS/S_{comb} which is observed in the final stage of vulcanisation beyond the optimum. These reactions compete with the main reaction in which the sulphur combines with the rubber, and they must therefore be considered as one of the reasons for the retarding action of zinc oxide on the combination of sulphur with the rubber. It is interesting that zinc oxide retards the rate of exchange between ^{35}S and MBT and reduces the degree of exchange, while stearic acid activates it, *i.e.* there is an analogy with the influence of zinc oxide and stearic acid on the combination of sulphur with rubber in the presence of MBT as accelerator.

Zinc oxide alone does not accelerate the formation of cross-linkages in the vulcanisation of mixtures with MBT, but there is a sharp increase in the rate of cross-linking when both zinc oxide and stearic acid are present[76].

There is a linear relationship between the number of cross-linkages and the quantity of sulphur combined with the rubber (organically bound sulphur, *i.e.* the quantity of sulphur in the extracted vulcanisates less the sulphur present as ZnS) up to the point immediately after the vulcanisation optimum (Fig. 14). The slope of the straight lines of Fig. 14 determines the "degree of bridging". Comparison of the slopes shows that stearic acid accelerates the combination of sulphur without increasing the percentage

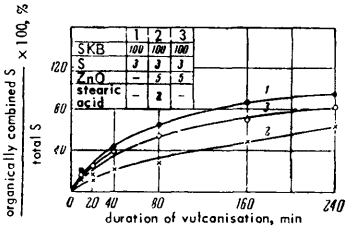


Fig. 13. Kinetics of the combination of sulphur in butadiene rubber (SKB) mixtures without an accelerator. Composition of mixtures in parts by weight.

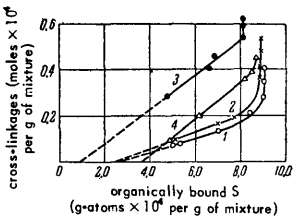


Fig. 14. Number of cross-linkages as a function of the amount of sulphur combined with the rubber during vulcanisation of mixtures of the composition (in parts by weight):

	1	2	3	4
SKB	100	100	100	100
Sulphur	3	3	3	3
ZnO	–	–	5	5
Stearic acid	–	2	2	–
MBT	1	1	1	1

of sulphur present in the cross-linkages. The "degree of bridging" increases sharply when zinc oxide is present in the mixture. The role of zinc oxide as a vulcanisation activator is therefore that of increasing the percentage of sulphur forming cross-linkages in the vulcanisate.

Dogadkin and Beniska's results[74] indicate the following possible mechanism for the role of zinc oxide in the formation of cross-linkages in the vulcanisate: (1) reaction of zinc oxide or salts with thiol polysulphides, producing zinc sulphide and sulphur diradicals which then join molecules of the rubber; (2) oxidation of the thiol groups to form cross-linkages by the reactions

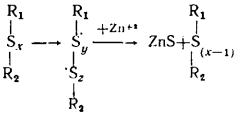
$$2RSH+ZnO+S \rightarrow R{-}S{-}S{-}R+ZnS+H_2O \text{ or}$$

$$\begin{matrix} R_1SH \\ R_2SH \end{matrix} +ZnO \rightarrow \begin{matrix} R_1{-}S \\ \\ R_2{-}S \end{matrix} Zn+H_2O;$$

(3) reaction of zinc oxide or salts with the polysulphide bonds of the vulcanised structure by the reaction:

$$R_1{-}S_x{-}R_2 \xrightarrow{+Zn^{++}} R_1{-}S_y{-}R_2+ZnS.$$

An increase in the number of cross-linkages will be observed only when part of the polysulphide sulphur is liberated as a new diradical $\cdot S_z^{\cdot}$ which can then react with rubber molecules to form a new cross-linkage. The number of cross-linkages will remain the same if the recombination of the radicals occurs at the original site:



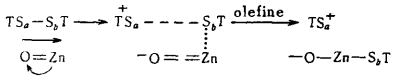
The increased number of cross-linkages and the decreased sulphide content thereof in the presence of zinc oxide is shown by the decreased degree of isotope exchange between the extracted vulcanisate (obtained with radioactive sulphur) and elementary non-radioactive sulphur after the vulcanisation optimum, and also by comparison with the vulcanisate obtained in the absence of zinc oxide. Another

illustration is the lower rate of stress relaxation, *i.e.* greater thermal stability, of the vulcanisation structures obtained in the presence of zinc oxide (see below).

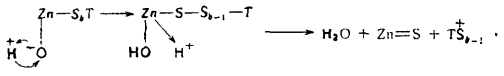
Lorenz and Echte[76] also reported a maximum on the curve of combined polysulphide sulphur against time of vulcanisation.

Bateman and coworkers[53] studied the part played by zinc oxide in the reactions of sulphur with model compounds. In the presence of zinc oxide, the rate of combination of sulphur with a 1,5-diene increases, a greater amount of cyclic sulphides is formed, and the sulphide content of the cross-linkages decreases[74]. In the presence of stearic acid, the rate of this reaction decreases, and equal quantities of cyclic and cross-linked sulphur-containing products are formed. Further addition of MBT increases the rate of reaction and decreases the number of cyclic sulphides.

Great weight is given to the catalytic activity of zinc oxide in the reactions studied. The higher rate of combination of sulphur in the presence of zinc oxide is explained by polarisation of the polysulphide[53] on the ZnO surface:



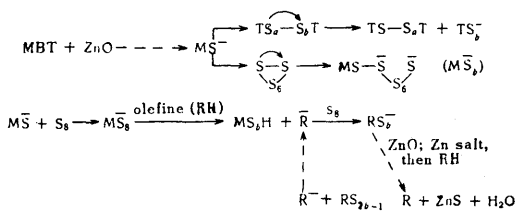
The resulting complex dissociates more easily to give the TS_b^- ion, or a proton adds on, with the formation of water, zinc sulphide, and another polysulphide ion:



The absence of any accelerating activity of zinc oxide in the combination of sulphur in a rubber medium is explained[74] in terms of the weaker adsorption and desorption of protons in a medium of high viscosity, and by the poisoning of the zinc oxide surface by the non-hydrocarbon components of the rubber. The increased number of cross-linkages and the decreased number of cyclic structures in the presence of zinc oxide and stearic acid is explained by the combination of the zinc stearate formed under these conditions with a proton which would otherwise attach itself to a double bond and so form a ring. The action of the zinc salt does not therefore involve the removal of sulphur atoms from the sulphides initially formed.

In the 1,5-diene–sulphur–zinc oxide–stearic acid–MBT system, the rate of combination of sulphur increases and the quantity of sulphur combined as cyclic sulphides noticeably decreases, by comparison with the diene–sulphur system. The actual accelerator, in Bateman's opinion, is the zinc salt of the MBT.

Bateman and coworkers consider that the benzothiazylsulphide anion facilitates the heterolysis of the S–S bond:



The reaction of MS^- or R^- with the sulphur is the rate-limiting step in the whole process, and gives a first-order reaction for the combination of sulphur[31,33-37].

These workers consider that the role of the zinc salts is to stimulate the activity of additional nucleophilic centres. In its turn, the electrophilic reactivity of the labile polysulphide determines the reaction of the sulphur with the unsaturated compounds.

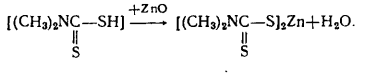
This point of view regarding the catalytic activity of zinc oxide or salts requires further confirmation. As has been reported[72,73], the choice of activator (metal oxide) depends greatly on the type of rubber, and zinc oxide is not always the best choice.

It is interesting to consider the role of activators in vulcanisation with TMTD, since Scheele *et al.*[77] explain the specific role of zinc oxide in this process by its catalytic activity and particular crystalline structure. Direct heating of tetraethylthiuramdisulphide (TETD) with zinc oxide in the range 80°–150° produces in the limit ~ 90 mole % of Zn DTC based on TETD taken. The formation of gaseous products[78] is clearly due to parallel thermal decomposition of the TETD.

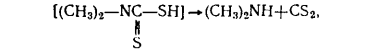
In a vulcanisation system, the limiting conversion of thiuram to Zn DTC is also independent of the initial thiuram and zinc oxide concentrations[79]; however, the rate of accumulation of Zn DTC and the rate of decrease of unchanged thiuram increase with the zinc oxide content of the mixture[78,80]. This has led to the conclusion that vulcanisation takes place on the surface of the zinc oxide crystals, since a number of other oxides do not provide satisfactory vulcanisates. In Scheele's opinion, an intermediate is formed on the surface of the zinc oxide crystals during vulcanisation. This intermediate liberates Zn DTC on decomposition and produces cross-linking in the vulcanisate[81].

Scheele and his coworkers consider that in the absence of zinc oxide the reaction of thiuram with the rubber proceeds by a completely different mechanism. Dogadkin and Shershnev[14,15,82] have shown that from a chemical point of view the reaction of TMTD with rubber is practically the same in the presence or absence of zinc oxide. Satisfactorily durable thiuram vulcanisates can be obtained without zinc oxide (*e.g.* with 10 parts by wt. of TMTD per 100 parts by wt. of rubber[83]).

The role of the zinc oxide or salts is to combine with the reaction products of the thiuram with the rubber and to suppress destructive oxidation processes in the vulcanisation system[15,82]. In the presence of zinc oxide or salts, the dimethyldithiocarbamic acid formed by the reaction of TMTD with the rubber is taken up as Zn DTC:



In the absence of metal oxides or salts, or in the presence of magnesium or calcium oxides or salts, this acid decomposes[15] into dimethylamine and carbon disulphide:



which are volatile and are removed from the vulcanisates. Under these conditions the loss of TMTD sulphur in the

vulcanisates reaches 60% of that introduced as TMTD (see Fig. 3). The number of cross-linkages formed in the vulcanisation of mixtures containing zinc oxide or salt on the one hand, and no metal oxide or with magnesium or calcium oxides or salts on the other, is greatly different[15].

In the first case reversion is not observed, but in the second it is very noticeable. The explanation of this was found in experiments on the vulcanisation of these systems in an inert atmosphere[82]; in this case the number of cross-linkages in vulcanisates containing TMTD is practically the same in the absence or presence of zinc or magnesium oxide. Chemically, the process is the same as in air; consequently the reversion of vulcanisation in the case described is due to destructive oxidation processes activated by the decomposition products of the dimethyldithiocarbamic acid. This was confirmed by thermal oxidative aging of thiuram vulcanisates with and without added Zn DTC.[84,85] Zn DTC is an antideteriorant formed during the vulcanisation.

X. CROSS-LINKING (VULCANISATION) OF RUBBER SOLUTIONS AT LOW TEMPERATURES

Vulcanisation by the Peachey process has been considered as taking place by the reaction of the rubber with nascent sulphur formed by reaction between H_2S and SO_2, but Dogadkin and Belyaeva showed[86] that this is not the case. Pure sodium butadiene rubber which has been heated at 80° in nitrogen is not vulcanised by the Peachey process, although sufficient elementary sulphur is formed. The sulphur produced by reaction between DBTD and H_2S by the process $RSSR + H_2S \rightarrow 2RSH + S$ also does not cause agglomeration of rubber solutions, although it reacts with the rubber; in this case the sulphur chemically combined with the rubber is concentrated in a small fraction of the latter (5%), which is not precipitated from solution by methanol; the fraction precipitated by the methanol (90 wt.%) is practically free of combined sulphur. Apparently the hydrogen sulphide and the sulphur formed combine intramolecularly with a small fraction of the rubber to produce cyclic structures by an ionic mechanism similar to that described by Naylor[87] in experiments with di-isoprene. Benzoyl peroxide reacts with hydrogen sulphide to produce benzoic acid and elementary sulphur; however, no agglomeration occurs when this reaction is carried out in a solution of pure rubber. These results show that nascent sulphur does not vulcanise rubber at room temperature.

The DBTD–H_2S system, which liberates sulphur, causes agglomeration (vulcanisation) of rubber when a solution of the latter containing DBTD is irradiated with scattered sunlight or ultra-violet light before being saturated with hydrogen sulphide. The rate of agglomeration depends on the time of irradiation (Fig. 15). There are definite limits to the duration of irradiation which will cause agglomeration; with too little, or after prolonged, irradiation gel formation does not occur. The composition of the gas phase over the solution affects the rate and degree of agglomeration; in nitrogen the ability to form a gel appears after a longer period of irradiation than in air, and persists for a longer period. The resulting gel contains 0.6–0.7% of combined sulphur, evenly distributed throughout its volume. According to spectrographic analysis there is a considerable loss of double bonds (27–60%). This is substantially greater than would correspond to the quantity of combined sulphur, indicating that polymerisation occurs.

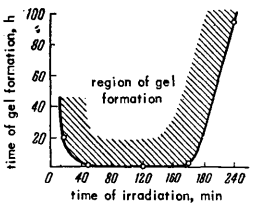


Fig. 15. Time of gel formation of rubber solutions by the action of hydrogen sulphides as a function of the duration of their preliminary ultra-violet irradiation in admixture with DBTD.

The existence of regions of gel formation is apparently due to the presence in solution of rubber radicals, produced by reaction between the rubber and the short-lived benzothiazyl radicals formed by the photochemical dissociation of the disulphide. The formation of a mercaptan can be demonstrated analytically in an irradiated rubber solution containing a disulphide, in accordance with stages 1) and 2) of the mechanism below. These observations, and the inhibiting action of small amounts of hydroquinone, phenyl β-naphthylamine, and other acceptors, suggest the following radical mechanism for the polymerisation:

1) R–S–S–R $\xrightarrow{h\nu}$ 2RS•	initiation
2) RS• + Rub → Rub• + RSH	
3) Rub• + H_2S → Rub + HS•	
4) Rub + HS• → Rub•SH	
5) Rub•SH + Rub → RubSHRub•	chain growth
6) RubSHRub• + Rub → RubSHRub–Rub• etc.	
7) Rub + Rub• → Rub–Rub•	
8) Rub–Rub• + Rub → Rub–Rub–Rub• etc.	
9) Rub• + Rub• → Rub–Rub	chain breaking

Stages 5), 6), 7), 8), and 9) in this mechanism represent the polymerisation steps.

The benzoyl peroxide–hydrogen sulphide system produces polymerisation of rubber solutions in the presence of a definite concentration of an amine, *e.g.* phenyl β-naphthylamine, and the yield of benzoic acid is higher than that expected from the bimolecular reaction:

$$[RO_2]_2 + H_2S \rightarrow 2ROOH + S.$$

These facts indicate that among the initial stage in the sequence of reactions leading to vulcanisation there is a stage in which benzoyl and amine radicals are formed[88,89]:

$$ROOR + R'R''NH \rightarrow [ROOR...R'R''NH] \leftrightarrow ROOH + RO^{\cdot} + R'R''N^{\cdot}.$$

and these radicals then react with rubber and hydrogen sulphide molecules to form, by analogy with the above mechanism, polymeric and thiol radicals, which initiate polymerisation.

XI. THE REVERSION EFFECT AND OPTIMUM VULCANISATION

Most of the physicochemical properties of rubber change irregularly during vulcanisation, and pass through a maximum or minimum. This kinetic effect gives rise to the technically important reversion effect and vulcanisation

optimum. In 1938 Dogadkin[90] suggested that the vulcanisation optimum is due to the operation of a number of factors on the properties of rubber during vulcanisation, of which some are constructive, building up the molecules, and others are destructive. The combined effect of these opposing processes is to produce kinetic curves showing a maximum or minimum, although their individual kinetics are described by smooth curves. This suggestion was later developed experimentally and theoretically[91]. The constructive processes include the action of vulcanising agents, and for some rubbers the action of heat and oxygen; thermal oxidation and thermal degradation are considered to be the destructive processes. From these general considerations, the following kinetic equation has been derived for the change of strength (π) of the vulcanisate[92,93]:

$$\pi = \pi_0 (1 + ax)(1 - by),$$
$$x = \frac{n}{n_{max}} = 1 - e^{-\alpha t},$$
$$y = \frac{m}{m_{max}} = 1 - e^{-\beta t},$$

where π is the strength of the mixture at time t, π_0 the strength of the initial mixture, n the number of polymerisation acts in time t, n_{max} the total maximum number of polymerisation acts, and m and m_{max} the corresponding values for the destructive acts.

In the simplest case, when polymerisation occurs under the action of sulphur and destruction occurs by thermal oxidative processes, the equation takes the form:

$$\pi = \pi_0 [1 + a(1 - e^{-k_1 t})][1 - b(1 - e^{k_2 t})],$$

where k_1 is the velocity constant for the combination with sulphur and k_2 the velocity constant for the combination with oxygen.

This equation has been confirmed in many studies of the vulcanisation of natural rubber. It cannot be applied to sodium butadiene or butadiene-styrene rubbers, since with these types of polymer the action of oxygen, even in the early stages, is to cause polymerisation and not degradation.

The effect of oxygen (and compounds containing active oxygen) on the rate of change of properties during vulcanisation has been demonstrated in many experiments. Thus if a natural rubber mixture (with MBT as accelerator) is prepared and vulcanised with strict exclusion of oxygen, the maximum on the strength curve disappears; there is no reduction of strength, because the destructive influence of oxygen is removed (Fig. 16). Since sodium butadiene rubber is polymerised in the same way by sulphur and by oxygen, its strength does not go through a maximum, whether vulcanisation is carried out in nitrogen or in oxygen.

Analogous results were obtained on vulcanisation in a press of mixtures containing tetramethylthiuram sulphide as the vulcanising agent: there was no reversion when the mixture was vulcanised with strict exclusion of oxygen. In this case the oxidative destruction is activated by the decomposition products of the accelerator: carbon disulphide and dimethylamine (see section IX of this review).

It has been suggested[94] that, under technical vulcanisation conditions in a press, oxidation processes do not occur, because direct contact between the vulcanisation mixture and the air is avoided; this cannot be the case, however, since during vulcanisation the rubber reacts with

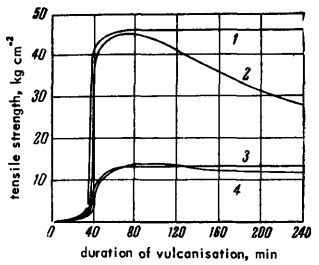


Fig. 16. Change of tensile strength during vulcanisation of mixtures of natural rubber (I) and butadiene rubber (SKB):
1) and 2) I in nitrogen and in air; 3) and 4) SKB in nitrogen and in air.

the molecular oxygen and active oxygen-containing compounds introduced into the mixture during plasticising and mixing, and in particular with the ingredients of the mixture. Direct analysis shows that the "free" oxygen content in technical filled mixtures can reach 1.2%. The infra-red spectra of a vulcanisate, recorded after prolonged heating in a press, show the characteristic absorption bands of oxygen compounds.

The influence of thermal oxidative processes on the rate of change of properties during vulcanisation clarifies the part played by certain anti-agers. Thus Tonox, which has practically no effect on the rate of combination of sulphur, markedly increases the strength of a natural rubber mixture. Vulcanisation accelerators or their reaction products have a definite influence on the thermal oxidative processes (Fig. 17).

The thermal rupture and rearrangement of S–S bonds play a very substantial part in reversion and the production of a vulcanisation optimum[95-97]. As already indicated in section IX, in the initial stage the sulphur combines with the rubber to form polysulphide groups, which are then thermally decomposed and rearrange into groups with a smaller number of sulphur atoms. The sulphide bonds can split (a) without or (b) with liberation of sulphur:

a) $RS_xR \rightleftarrows RS_{(x-y)}+R'S_y^{\cdot}$,

b) $RS_xR' \rightleftarrows RS_{(x-y-z)}R'S_y^{\cdot} + {}^{\cdot}S_z^{\cdot}$.

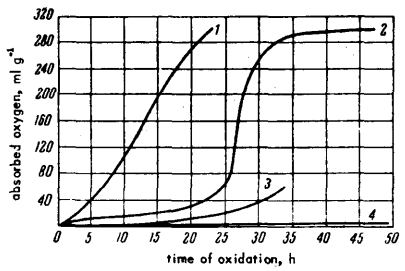


Fig. 17. Influence of accelerators on the absorption of oxygen by rubber:
1) 0.78% Captax; 2) without accelerators; 3) 0.63% diphenylguanidine; 4) 0.7% thiuram.

If the resulting radicals and sulphur can react with the rubber molecules to form new cross-linkages, this process will increase the modulus and decrease the swelling maximum. Such an effect is apparently observed in the vulcanisation of sodium butadiene rubber, which does not show reversion of vulcanisation on prolonged heating; however, the resulting polymeric radicals can be stabilised by combination with the low-molecular compounds present in the vulcanisation mixture (oxygen, accelerators, antioxidants, and their decomposition products). The sulphur formed can combine with the double bonds as thi-irane groups or form intramolecular cyclic structures by the mechanism established[87] for the reaction of sulphur with di-isoprene. The polymeric radicals of type RS_y may be stabilised because of the formation of intramolecular rings. These secondary processes following the thermal decomposition of the sulphide structures lead to a decreased number of cross-linkages or, in other words, to a decrease in the modulus and an increase in the swelling maximum; this is observed in the reversion of vulcanisation in the case of natural rubber and synthetic *cis*-isoprene rubber.

The so-called activators — metal oxides and fatty acids — play a substantial part in the rearrangement of the S–S bonds. Zinc oxide has practically no effect on the rate of combination of sulphur with rubber, but considerably increases the number of cross-linkages in the vulcanisate, by undergoing the series of reactions considered by Dogadkin and Bensika[74]. The most important reactions are those of ZnO with the thiol groups formed in the molecular chains in the reactions referred to in section IX, with sulphur and thiol and perthiol radicals, and with polysulphide linkages, the last by the reaction:

$$RS_xR' \xrightarrow{Zn} ZnS + RS_{(x-1)}R'$$

This reaction increases the ZnS content of the vulcanisate and decreases the amount of sulphur combined with the rubber; the kinetic curve for the accumulation of this sulphur in the vulcanisate (organically bound sulphur) passes through a maximum. The number of sulphur atoms per linkage also decreases, as is demonstrated by the reduced exchange capacity of vulcanisates containing ZnO, as compared with those not containing it (section IX).

An important part in the change of the vulcanisation structures is also played by the compounds produced during the vulcanisation from the accelerators. As already mentioned, during vulcanisation TMTD is reduced to dithiocarbamic acid, which with zinc oxide forms the stable zinc salt. In the absence of ZnO the dithiocarbamic acid decomposes into dimethylamine and carbon disulphide, which facilitate the thermal and particularly the thermal oxidative destruction of the rubber and its sulphur-containing compounds (see section IX).

An unequivocal index of the structural changes during vulcanisation is either the equilibrium modulus or the equilibrium degree of swelling, but not the static strength index. The direct relationship (for one type of polymer) between the strength and the number of cross-linkages holds up to a certain concentration of the latter ($\sim 4 \times \times 10^{19}$ cm^{-3} for natural rubber); further increase of the density of the vulcanisation lattice leads to a decrease in strength, apparently because of steric hindrance to the formation of the limiting orientated crystalline phase of the vulcanisate[98]. The equation given at the beginning of this section can therefore only be used for those vulcanisations in which the number of cross-linkages does not exceed this limit. For mixtures with a higher content of vulcanisation agent, the decreased strength beyond the vulcanisation optimum is due to the limiting density of cross-linking being reached, and not to destructive processes. These cases have been considered by Dogadkin and coworkers and by Gee[99-101].

XII. VULCANISATION STRUCTURES AND THEIR INFLUENCE ON THE STATIC AND DYNAMIC PROPERTIES AND ON THE FATIGUE OF VULCANISATES

As a result of vulcanisation, local chemical bonds and intermolecular (van der Waals) bonds are formed between the molecular chains. In a number of cases the configuration of the chains changes, because of cyclisation and isomerisation. For their effect on the physicochemical properties of the vulcanisates, the most significant of these changes are the chemical vulcanisation bonds — their composition, concentration, and distribution. In use, the vulcanisation structures undergo gradual changes, which is one of the causes of the aging and fatigue of the rubbers. One of the most important tasks of rubber technology is therefore to study the vulcanisation structures, to investigate the factors which affect their formation and change, to correlate the type of structure with the physicochemical properties of the vulcanisates, and to develop vulcanisation conditions which will provide the required vulcanisation structures.

It has been shown[5,75] that the chemical cross-linkages formed on vulcanisation are mainly C–C and C–S_x–C bonds with a variable sulphur content. The carbon–carbon bonds arise by reaction of the polymeric radicals among themselves and with the initial rubber molecules. The polymeric radicals, in their turn, are formed either by physical action (light, ionising radiation) or by reaction with the vulcanising agents or vulcanisation accelerators. This last case has been considered in sections II and IV for vulcanisation with disulphides and sulphenamides.

The C–S_x–C bonds are formed by reaction of the rubber with sulphur diradicals $\cdot S_x \cdot$, and thiol HS$\cdot$ and perthiol HS$_x\cdot$ radicals.

Dogadkin and Tarasova used isotope exchange between the vulcanisates and elementary sulphur or vulcanisation accelerators labelled with ^{35}S to study the nature of the vulcanisation bonds[102]. In the first case the exchange took place between plates of radioactive vulcanisate and elementary inactive ^{32}S, which was introduced in definite amounts by allowing the samples to swell in a saturated solution of sulphur in benzene. In the second case inactive vulcanisate was used, and allowed to exchange with the accelerator containing ^{35}S.

Fig. 18 shows a typical kinetic curve for isotope exchange between elementary sulphur and a vulcanisate from butadiene–styrene rubber. The change of activity passes through a maximum, which is clearly due to combination of the added elementary sulphur taking place on heating the mixture, simultaneously with the exchange (Fig. 18, curve *2*). Since in the last stages the elementary sulphur also becomes active, this combination lessens the apparent decrease of activity of the vulcanisate, so that for comparative evaluation of the exchangeable sulphur content, the activity at the maximum was used.

As Gur'yanova[103] has shown, the kinetics and degree of exchange in the case of low-molecular sulphur-containing compounds depend on the type of radical attached to the

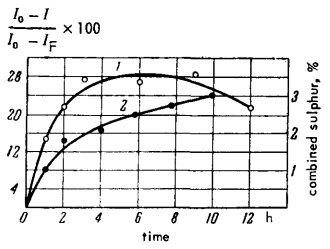


Fig. 18. 1) Kinetics of the exchange between the vulcanisate and elementary sulphur at 120°. 2) Combination of sulphur during the exchange.

sulphur atoms and on the number of sulphur atoms in the sulphide groups. Increasing the number of sulphur atoms in the sulphide group increases the rate and degree of exchange with elementary sulphur, and this has enabled the isotope exchange method to be used for determining the structure of the sulphide bonds in a vulcanisate.

The dependence of the degree of isotope exchange of vulcanisates on the number of sulphur atoms in the sulphide bonds is clearly demonstrated by comparing the rate of exchange with the rate of stress relaxation on heating the vulcanisates at 130° with strict exclusion of oxygen using Dogadkin and Tarasova's procedure[5]. It follows from the theory of high elasticity that the stress (the modulus E_∞) is a linear function of the number of chain segments between the chemical cross-linkages ($E_\infty = \gamma NKT$), so that decomposition of the molecular chains and of the chemical bonds between them leads to a decrease in the stress, which will follow a monomolecular law[104,105]. The velocity constant for the stress relaxation can be used as a measure of the stability of the chemical bonds in the vulcanisate. Fig. 19 shows the correlation between the rate of isotope exchange and the rate of stress relaxation for vulcanisates with various accelerators. The vulcanisate obtained with TMTD (but without sulphur), which due to the mechanism of the accelerator's action will contain mainly C–C and C–S–C bonds, does not exchange with sulphur and shows the lowest rate of relaxation of stress. This vulcanisate, however, exchanges with TMTD itself under the same conditions, indicating the presence in the vulcanisate of combined accelerator groups (radicals). The vulcanisate obtained with DPG and elementary sulphur shows a high rate and degree of exchange

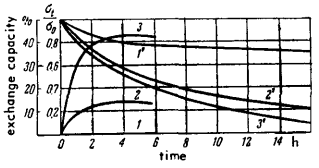


Fig. 19. Kinetics of isotope exchange (1, 2, 3) and stress relaxtion (1′, 2′, 3′) in various vulcanisates: 1) and 1′) TMTD; 2) and 2′) MBT + + S; 3 and 3′) DPG + S.

with sulphur and the greatest rate of decomposition of vulcanisation bonds under thermomechanical action, indicating that it contains the less stable polysulphide linkages C–S_x–C. This is also shown by the reaction of the vulcanisate with sodium sulphite.

Isotope exchange and stress relaxation at 130° in an inert atmosphere are good methods for investigating the nature of vulcanisation structures. The results obtained in this way have been amply confirmed by spectroscopic studies: the ultra-violet spectra between 220 and 400 mμ demonstrate the presence of polysulphide bonds at the commencement of vulcanisation, and a decrease in the number of sulphur atoms in these as vulcanisation proceeds[51].

The nature of the bonds in sulphur vulcanisates has recently been considered by Studebaker and Nabors[19], who state that the nature of the bonds can be determined by their proposed mechanism of reaction of lithium aluminium hydride with di- and poly-sulphides:

$$R{-}S{-}S{-}R \xrightarrow[\text{hydrolysis}]{LiAlH_4} 2RSH$$

$$R{-}S{-}S_x{-}S{-}R \xrightarrow[\text{hydrolysis}]{LiAlH_4} 2RSH + xS^-$$

Monosulphide bonds are shown not to react. Studebaker and Nabors consider that C–C bonds are hardly formed in vulcanisates. The number of monosulphide bonds are taken as the difference between the di- and poly-sulphide bonds, and the total number of bonds determined by the swelling limit. Thiuram vulcanisates contain predominantly monosulphide bonds, and vulcanisates with DPG and sulphur, predominantly polysulphide bonds. These results are essentially in agreement with those of Dogadkin and coworkers described above.

The type and distribution of the vulcanisation linkages have a substantial influence on the fatigue behaviour of the vulcanisates. Since the primary act of destruction of vulcanisates on thermomechanical action (we are not here concerned with the very important action of oxygen) is the mechanical decomposition of the weakest bonds, it is clear that the workability of the vulcanisate, determined by the number of deformations before destruction, will depend on the energy of the bonds and the method of deformation used. With an alternating symmetrical load with bending and rotation, the workability will increase with increase of the energy of the vulcanisation bonds. Fig. 20 shows that vulcanisates with tetramethylthiuram disulphide, which contain predominantly C–C and C–S–C bonds (energy 50–60 kcal $mole^{-1}$), have a greater workability than vulcanisates with sulphur and diphenylguanidine, which contain more C–S_x–C bonds (energy ~27 kcal $mole^{-1}$). Radiation vulcanisates, which contain the very stable C–C and C–O–C bonds, are even more stable towards repeated deformation.

Isotope exchange has provided important information on the mechanism of the fatigue of vulcanisates. Fig. 21 shows that fatigue of extracted vulcanisates from butadiene–styrene rubber by alternating bending at room temperature increases the isotope exchange, and decreases the number of cross-linkages between the rubber chains, since the swelling maximum increases. The cause of this interesting effect is not clear. Possibly at low temperatures there is mechanical rupture of the sulphur-containing cyclic structures of the vulcanisate, so increasing the number of exchanging groups. After fatigue at 120°, on the other hand, there is a sharp reduction of isotope exchange and

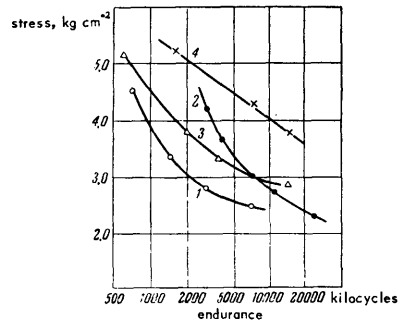


Fig. 20. Endurance of various vulcanisates to alternating symmetrical stress by bending with rotation at 120°:
1) butadiene–styrene rubber SKS–30 with DPG + sulphur; 2) SKS–30 with hexachloroethane; 3) SKS–30 with TMTD; 4) butadiene rubber SKB with DPG + sulphur.

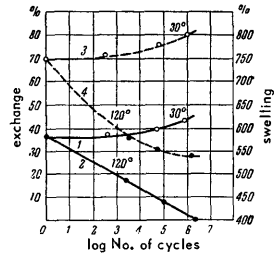
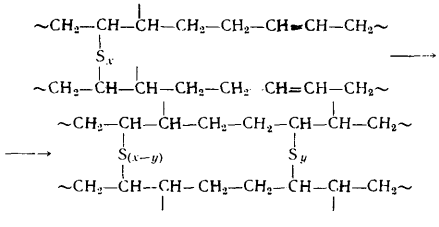


Fig. 21. Change of the degree of exchange (1, 2) and swelling limit (3, 4) during fatigue of vulcanisates at 30° and 120°.

an increase in the number of cross-linkages (the swelling maximum falls and the modulus increases). In this case, therefore, the polysulphide groups decompose to form new bonds, containing less sulphur, between the rubber molecules:



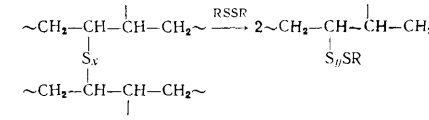
The possibility of forming polymeric radicals by mechanical stress has been demonstrated by plasticising rubber at room temperature in the presence of mercaptobenzothiazole (MBT) labelled in the thiazole ring[106].

The combination of low-molecular substances with radicals of vulcanised rubber, formed by thermomechanical action during fatigue, is observed if *p*-t-butylphenol disulphide (BPD) labelled with ^{35}S in the disulphide bridge is added to the vulcanisate. Table 2 shows that after

TABLE 2. Combination of *p*-t-butylphenol disulphide (BPD) during fatigue of butadiene–styrene rubber vulcanisates at ϵ = 50% and frequency 250 c/min.

Composition of vulcanising group	BPD added, %	Duration of fatigue, h	Temp., °C	Combined BPD as % of rubber	Combined BPD as % of BPD added
1% DPG	3.6	1.5	20	0.35	9.7
2% Sulphur	3.5	5.0	20	1.00	28.6
	3.5	2.5	100	1.55	44.3
3% Thiuram	3.6	2.5	20	0.12	3.34
	3.25	0.5	100	0.20	5.56
	3.25	5.0	100	1.62	50.0

fatigue, the rubber can combine with more than 1.5% of BPD, which is ~50% of the amount added. In this case the combination occurs mainly at the sites of the decomposed sulphide bonds:



where R = $C_6H_3OHC(CH_3)_3S$.

The reaction of the polymeric radicals, formed by thermomechanical action causing fatigue in the vulcanisate, with substances able to combine with them, opens up a new approach to the prevention of fatigue in vulcanisates. When the thermomechanical action increases the modulus (*e.g.* in the case of vulcanisates of butadiene–styrene rubber) because of decomposition and rearrangement of the radicals with the formation of new cross-linkages, the introduction of such substances (acceptors) reduces the harmful cross-linking and increases the life of the vulcanisate; this occurs when *p*-t-butylphenol disulphide or hexachloroethane is added to a vulcanisate. However, such substances cannot increase the workability of vulcanisates whose structural changes during fatigue lead to a decrease in the number of cross-linkages (when a decrease in the modulus is observed), *e.g.* vulcanisates from natural or oil-filled butadiene–styrene rubbers.

The nature of the vulcanisation bonds does not only affect the thermomechanical processes of fatigue: Kuz'minskii and coworkers[107,108] have shown that polysulphide bonds reduce the rate of oxidation of vulcanisates. A vulcanisate extracted with acetone is oxidised less rapidly than the same vulcanisate which has been treated with Na_2SO_3 to remove polysulphide sulphur. They consider that the sulphide radicals formed by the decomposition of the polysulphide bonds react with the oxidation chains and so inhibit the oxidation. It is interesting that the stabilities of various vulcanisation structures towards thermal action and radiation (ultra-violet light) are in inverse relationship[109,110].

The influence of vulcanisation structures on the static strength is demonstrated by vulcanisates of carboxylated rubbers[111]. Vulcanisation of this type of rubber with metal oxides gives products of high static strength (up to 200 kg cm^{-2} for butadiene–styrene rubber) but low thermal stability. The velocity constant for the rate of relaxation of stress in vulcanisates with salt bonds is 50–100 times that in sulphur vulcanisates of butadiene–styrene rubbers.

The number of cross-linkages, like the molecular weight of the initial polymer, is practically the same before and after relaxation; this means that thermomechanical action on these vulcanisates causes rupture and rearrangement of the salt bonds as a result of exchange reactions.

If the thermally unstable vulcanisates obtained with calcium hydroxide are irradiated with low doses (5–10 mr) of γ-radiation, they become thermally stable (the relaxation constant at 100° is[1] $\sim 6 \times 10^{-3}$ min, *i.e.* approximately the same as for sulphur vulcanisates of butadiene–styrene rubber with sulphenamide accelerators) and at the same time show a high strength of up to 400 kg cm^{-2}.

A vulcanisate has a high static strength if it contains a dense network (1 bond to about 60 monomeric units) of weak salt bonds and a sparse network (1 bond to 1000 monomeric units) of stable C–C bonds. An increase in the concentration of carbon–carbon bonds decreases the static strength (Fig. 22).

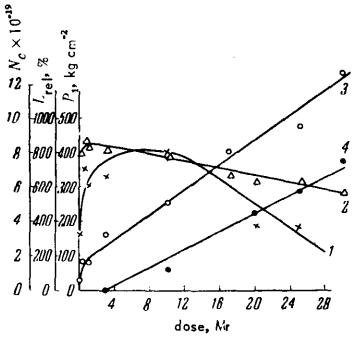


Fig. 22. Properties of a carboxyl-containing rubber (0.65% COOH) vulcanised with calcium hydroxide as a function of the γ-radiation dose: 1) tensile strength (P_1); 2) relative elongation (L_{rel}); 3) total content of cross-linkages (N_c); 4) number of cross-linkages not broken by the action of acid.

The influence of the structure of vulcanisates of carboxyl-containing rubbers on their strength is of general application, and is of undoubted interest in the formulation of the rules determining the strength of polymeric networks[112]. Polymeric networks (vulcanisates) have a high strength when in addition to a relatively sparse and uniform network of stable chemical bonds, they contain a network of less stable and easily rearranged bonds, the redistribution of which relieves the local tensions which give rise to the formation and development of centres of destruction of the polymer. This type of structure provides the conditions for the greatest development, under deformation, of orientation (crystallisation) processes, which are known to be an important factor in increasing the strength of a material.

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SPECTROSCOPIC DETERMINATION OF PEROXY COMPOUNDS DURING PHOTOCHEMICAL OXIDATION

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1. PHOTOCHEMICAL OXIDATION OF HYDROCARBONS

Many investigations of the thermal and photochemical oxidation of organic compounds indicate that the initial stages involve formation of peroxy compounds — hydroperoxides and photo-oxides — in which two oxygen atoms are linked together[1-5]. The peroxy compounds, containing the $-O-O-$ link, then decompose exothermally forming free atoms and radicals, which are the cause of the chain character of the subsequent stages of the oxidation.

Spectroscopic investigation of the peroxy compounds requires that they should be produced in greater quantities in the reaction mixture, which can be achieved mainly in photochemical oxidation reactions which take place at fairly low temperatures. Thermal oxidation involves a considerably more rapid decomposition of the intermediate reaction products, so that their concentration in the reaction mixture is insignificant. Also, a thermal process does not allow selective supply of energy to one of the reaction components. With activation by light it is possible to raise the oxidisable molecule to an excited state without affecting the intermediate and final reaction products. The photochemical oxidation is initiated by light (principally ultra-violet), which acts either directly on the oxidisable organic molecule or on a sensitiser, the latter oxidising the organic compound under the influence of visible light quanta. The path of the sensitised reaction is naturally of the greatest interest, since reaction is then effected by a small quantum, as in photosynthesis.

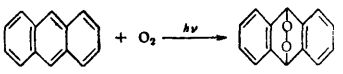
Photochemical oxidation under ultra-violet radiation has been investigated with di- and poly-olefines[6-9], alcohols[10], acetaldehyde[11,12], paraldehyde[13], propionaldehyde[12], butyraldehyde[14], benzaldehyde[15-18], acids[19], the aromatic hydrocarbons toluene[20-23], xylene[20,24], isopropylbenzene[20,25-27], and ethylbenzene[27], decalin, methylcyclohexane, 2,7-dimethyloctane, butylbenzenes and other compounds[5], dioxan[28], cyclohexene[29,30], and terpinolene (*p*-mentha-1,4(8)-diene)[31].

In all these researches the reaction kinetics and the chemical properties of those intermediate and final reaction products isolated were investigated, and on this basis mechanisms were suggested for the oxidation of organic compounds in which the initial stage is assumed to be radical formation by loss of hydrogen from the hydrocarbon. Hydroperoxides are then formed as a result of two bimolecular chain processes:

$$RH + h\nu \rightarrow R + H,$$
$$R + O_2 \rightarrow RO_2,$$
$$RO_2 + RH \rightarrow ROOH + R \text{ etc.}$$

Several organic compounds and dyes, however, absorb oxygen on prolonged or intense illumination of their solutions, peroxides — photo-oxides — being formed[32-50]. The formation of photo-oxides was first noted by Dufraisse and coworkers[32-45] in the case of the bright red hydrocarbon rubrene, solutions of which are rapidly decolorised with loss of fluorescence on exposure to sunlight or artificial light in the presence of oxygen. The colourless photo-peroxide, which is deposited on evaporation, decomposes at 180°, giving the original hydrocarbon and oxygen. Photo-oxides of other simple cyclic compounds can be obtained in a similar way. Benzene does not form a photo-oxide, but several furan and thiophen derivatives and terpenes do so, exhibiting great reactivity at the 1,4-positions. The photo-oxides of the simplest heterocyclic compounds are unstable at room temperature, and can be isolated only at low temperatures, *e.g.* the photo-oxide of 1,3-diphenylisobenzofuran.

The most stable photo-oxides are formed by polycyclic aromatic compounds — anthracene, naphthacene, pentacene, and other compounds containing an anthracene nucleus:



Other polycyclic hydrocarbons, containing the naphthalene or phenanthrene nucleus, do not yield photo-oxides. Acridine forms no photo-oxide, but dibenzacridine does, because it contains an anthracene nucleus.

The formation of photo-oxides from polycyclic aromatic compounds is associated with the higher reactivity of the *meso* positions, to which oxygen is added as a bridge lying outside the plane of the molecule (transannular peroxides), the angle between the *meso* carbon atoms and the $-O-O-$ bridge being 118°, which is somewhat larger than in peroxides (100°–105°). There is consequently some strain in transannular peroxides, but it is not very great since the heat of formation of photo-oxides is low.

The reactivity of the *meso* carbon atoms depends on the substituents, especially those in the *meso* position. Thus