Rubber Science, **28**(1): 82-121, 2015 *REVIEW ARTICLE*

CURRENT STATUS OF SULPHUR VULCANIZATION AND DEVULCANIZATION CHEMISTRY: PROCESS OF VULCANIZATION

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Received: 19 August 2014 Accepted: 21 January 2015

Joseph, A.M., George, B., Madhusoodanan, K. N. and Alex, R. (2015). Current status of sulphur vulcanization and devulcanization chemistry: Process of vulcanization. *Rubber Science,* **28**(1): 82-121.

The article presents the first part of the review on the current status of sulphur vulcanization and devulcanization chemistry. The purpose of presenting a review of the chemistry of sulphur vulcanization and devulcanization was to develop a devulcanization process and also to address the issue of very low scorch during revulcanization.

Accelerated sulphur vulcanization is a very complex chemical process. Although consensus on various reaction mechanisms are yet to reach, there is widespread agreement about three basic steps involved. These are: (i) accelerator chemistry in which the reactions of accelerator, activator and sulphur leading to the formation of an active sulphurating agent (ii) crosslinking chemistry which involves the reactions of the active sulphurating agent leading to the formation of crosslink precursors and subsequent reactions of these precursors to form polysulphidic crosslinks and (iii) postcrosslinking chemistry leading to chain shortening and degradation of the polysulphidic crosslinks and other main chain modifications. The current understanding of the chemical reactions and the underlying mechanism involved in these basic steps, both in accelerator, activator and sulphur as well as accelerator- cum- sulphur donor and activator cure systems are reviewed. Reaction mechanisms leading to scorch delay inherent to sulphenamide accelerators and those involved by the addition of prevulcanization inhibitors are also presented.

Keywords: Accelerator chemistry, Crosslinking chemistry, Postcrosslinking chemistry, Sulphur vulcanization

INTRODUCTION

The life history of natural rubber (Heideman, 2004; www.britannica.com.; Aprem, *et al.*, 2005) can be dated back to 11 June 1496, the day on which Christopher Columbus returned from his second voyage, bringing back the first rubber balls from the West Indies. The next landmark was the Spanish discovery of the use of latex for the water proofing of leather and fabrics in 1615. The rubber industry in Europe really started with Charles Macintosh in 1818, when he started exploiting the naphtha-based rubber solution as a water proofing layer between

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two fabrics. Two years later, in 1820, Thomas Hancock discovered mastication. The contributions of Sir Henry Wickham and Henry Ridley in rubber plantation also added on to the vast development and fast growth of rubber industry. The final landmark in the early history of rubber was the discovery of vulcanization by Charles Goodyear in 1839 which revolutionized the use and applications of rubber, and changed the face of the industrial world.

Understanding the chemistry of vulcanization is important to develop a devulcanization process and further vulcanization of devulcanized rubber. This review primarily focuses on the chemical aspects of vulcanization and the various devulcanization methods. The review also presents a picture of different stages of vulcanization, revulcanization of devulcanized rubber and a general outlook on the recycling and reclaiming methods. *Thus, this review remains relevant as it* handles both the vulcanization and devulcanization processes together.

VULCANIZATION

Vulcanization, named after Vulcan - Roman god of fire- is the chemical process of interlinking of rubber molecules to change the predominantly plastic/viscous properties to elastic properties. The vulcanization system is mainly a collection of additives required to transform the essentially linear polymer molecules into a three dimensional network by the insertion of crosslinks (Rodger, 1979). Sulphur vulcanization is usually carried out industrially by heating the mechanically plasticized rubber with sulphur and auxiliary vulcanizing agents such as organic accelerators, ZnO, long chain fatty acids or the zinc soaps of these acids (activators). Additional ingredients may include antioxidants, antiozonants, fillers and reinforcing agents such as carbon black. Major effects of vulcanization (Bateman *et al.*,1963; Coran,1978; 2003) on use related properties include increased tear strength, tensile strength, elastic recovery, fatigue life, toughness, low hysteresis and compression set, *etc.* The timeline of various developmental stages in the history of sulphur vulcanization is given in Figure 1.

Although the primary structural requirement for vulcanization is covalent crosslinking of the rubber chains, other modifications can occur at sites distant from the crosslinks. In addition, there is generally present extra network material such as ZnO, uncombined sulphur present in the original mix, zinc soaps, zinc sulphide, zinc salts of accelerators resulting from the vulcanization reaction etc. Structural modifications of the main chain which can occur during vulcanization process are (Bateman *et al.*, 1963).

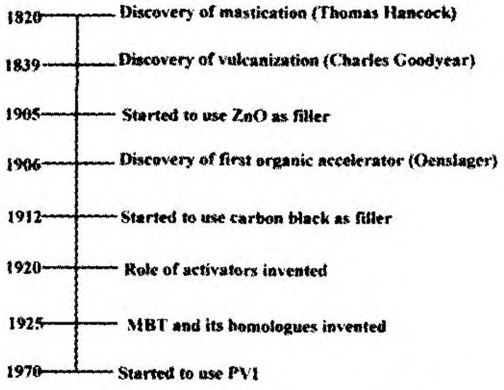


Fig. 1. Timeline of various developmental stages in the history of vulcanization of rubber

(i) Formation of pendent cyclic sulphides based on thiacyclopentane or thiacyclohexane rings

(ii) Changes in the olefinic pattern of the original rubber

(iii) Scission of main chains

Accelerators

Accelerator, in the rubber industry, is added with a curing agent or sulphur to increase the rate of vulcanization. The 8-membered ring and shorter chain structure of sulphur molecule is important in vulcanization process. The process of activation of sulphur occurs at high temperatures and can be speeded up by accelerators (Kerbs, 1957).

The most important characteristics of accelerators are scorch time, cure time and vulcanization time (Garvey *et al.*, 1953) are being illustrated in Figure 2. The scorch time is the time available at a given temperature before the stock begins to vulcanize where much of the accelerator chemistry is involved (Hoover, 1999). Cure time is the time a stock must be heated in a press at a given temperature until it reaches a technically correct cure (optimum cure time). Vulcanization time is the term that has been chosen to designate the time required after vulcanization has started until a satisfactory technical cure is reached. After attaining the maximum torque, it may increase further (marching), or decrease (reversion), or levels off. Stable cures are characterized by flat cure curves in which physical properties tend to reach a plateau as vulcanization progresses (Gehman, 1981).

The expected qualities of a good accelerator can be listed as

- It should give flat cure
- Should provide scorch safety
- Should give good storage properties for the uncured compound
- Should give good physical properties to the vulcanizates

Accelerators (Dinsmore and Vogt, 1928) generally contain sulphur and nitrogen like derivatives of benzothiazole and thiocarbanilides such as sulfenamides (Craine and Raban, 1989; Fukuda and Tsurugi, 1962; Scheele and Kerrutt, 1962), thiazoles (Lorenz and Echte, 1957; Naunton *et al.*, 1934), thiuram sulfides (Bandyopadhyay and Banerjee, 1979; Campbell, 1971; Guiliani

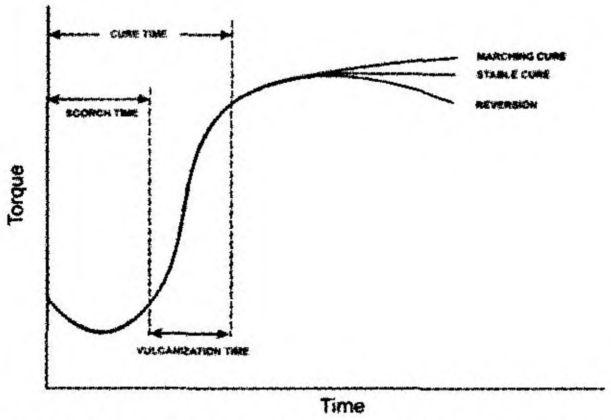


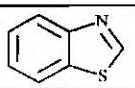
Fig. 2. A Typical rheograph showing different stages of cure

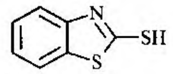
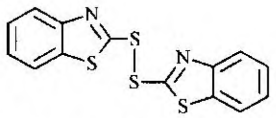
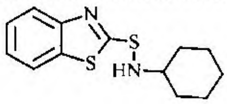
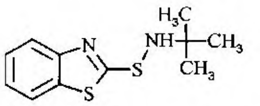
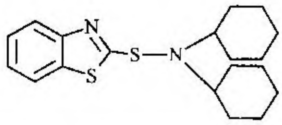
and McGill, 1995; Langenbeck and Rhlem, 1935), dithocarbamates (Cummings and Simmons, 1928) *etc.* Later various other (Dogadkin *et al.*, 1958) secondary accelerators and specific accelerators like guanidines, xanthates (Palaty and Joseph, 2000; 2004; 2011; Waddel, 2007) and morpholines also emerged.

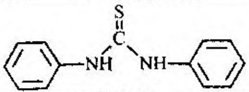
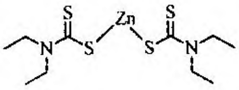
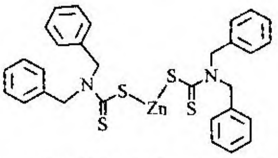
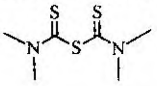
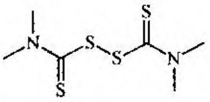
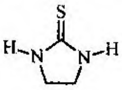
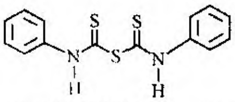
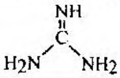
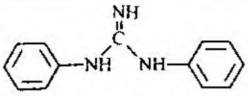
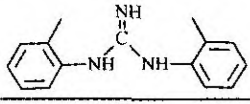
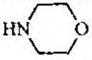
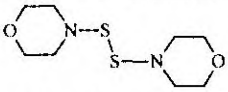
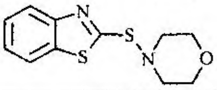
According to vulcanization rate, there are two major classes of vulcanization accelerators viz. primary accelerators or fast accelerators (semi-ultra) and secondary accelerators or ultra accelerators. Primary accelerators are characterized by very good scorch time and fast curing in the main vulcanization phase. Of the primary accelerators the major group is formed by sulfenamides and thiazole derivatives. Secondary accelerators are used as small addition to primary accelerators to boost the speed and state of cure during vulcanization. Of the secondary or ultra accelerators the main categories are the thiurams and the dithiocarbamates. Thiurams are very fast accelerators suitable also for vulcanization of low unsaturated rubbers and are used also as sulphur donors. Dithiocarbamates are ultra fast accelerators giving very fast vulcanization practically without induction period. In addition to these, guanidines form a class of slow (medium) accelerators with short induction period and broad vulcanization plateau (en.wikipedia.org; https://www.tut.fi/.htm). Classification of

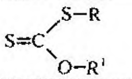
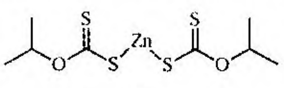
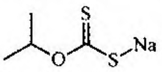
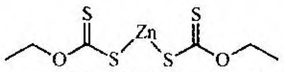
Table 1. **Classification and properties of accelerators**

BASIC GROUP : BENZOTHIAZOLE



TYPES	EXAMPLES	STRUCTURE	PROPERTIES
MERCAPTO ACCELERATORS *Used along with secondary accelerators*	**2-Mercapto Benzothiazole (MBT)**		Semi ultra accelerator, scorchy
	2-2' Dithiobenzothiazole (MBTS)		Delayed action semi ultra accelerator
SULPHENAMIDES *Widely used scorch safe accelerators*	**N-Cyclohexyl benzothiazole 2-sulphenamide (CBS)**		Semi ultra accelerator, delayed action
	N-t-butyl benzothiazole 2-sulphenamide (TBBS)		Delayed action semi ultra accelerator
	Benzothiazyl dicyclohexyl sulphenamide (DCBS)		Extremely delayed onset of cure, best scrorch resistance

BASIC GROUP : THIO CARBANILIDE			
	Zinc diethyldithio carbamate (ZDEC)		Ultra accelerator
	Zinc dibenzyldithio carbamate (ZDBC)		Nitrosamine free ulltra accelerator
	Tetramethylthiuram monosulphide (TMTM)		Ultra accelerator
	Tetramethylthiuram disulphide (TMTD)		Ultra accelerator and vulcanization accelerator
	Ethylene thiourea (ETU)		Accelerator for synthetic rubber production and as a curing agentfor epichlorohydrin elastomers
	N,N' diphenylthiourea (ETU)		Medium speed accelerator, useful as primary and secondary accelerator
BASIC GROUP : GUANIDINE			
GUANIDINES *Secondary accelerator with slow vulcanization rate*	**N,N' diphenyl guanidine (DPG)**		Medium accelerator used along with other accelerators
	N,N' di-tolyl guanidine (DOTG)		Medium accelerator
BASIC GROUP : MORPHOLINE			
MORPHOLINE ACCELERATORS *Delayed action scorch safe accelerators*	**N,N' dithiodimorpholine (DTDM)**		Sulphur donor, used along with thiurams, thiazoles, etc.
	N-oxydiethylene-2-benzothiazole sulphenamide (MBS)		Excellent delayed accelerator

	BASIC GROUP : XANTHATE	 $S{=}C(S{-}R)(O{-}R^1)$	
XANTHATES *For room temperature vulcanization of NR*	**Zinc isopropyl xanthate (ZIX)**		Ultra accelerator for low temperature curing
	Sodium isopropyl xanthate (SIX)		Water soluble ultra accelerator for latex work
	Zinc ethyl xanyhate (ZEX)		Ultra accelerator for low temperature curing

accelerators based on structure and their important features are given in Table. 1.

Activators

The ability of metal oxides in improving the efficiency of sulphur based cure systems has been discovered early in the history of vulcanization, and the most useful metal oxide applied in the "activating" role is zinc oxide. Zinc stearate, the most popular activator used today is necessarily formed *in-situ* for optimum effect. The fundamental role of vulcanization activators does not lie in their influence on the kinetics of the addition of sulphur to rubber, but rather in their influence on the nature of vulcanization structures formed and on changes in them in the course of vulcanization (Henning, 2008; Kruger and McGill, 1991; Morrison, 1984; Morrison and Porter, 1984). Vulcanization systems that contain zinc oxide (ZnO) lead to very high crosslink densities as ZnO assist the removal of pendent groups during cross-linking (Gradwell and McGill, 1996) thereby increasing the fraction of the sulphur used for crosslink formation in the vulcanizate (Chapman and Porter, 1988) influencing the heat stability and reversion effects of the vulcanizates.

ZnO has a significant effect on the number and nature of crosslinks between the molecular rubber chains (Amstrong *et al.*, 1944; Coran, 1964; 2003; Dogadkin and Beniska, 1958; Heideman *et al.*, 2004) and can there by change physical properties such as hysteresis, abrasion resistance, *etc.* and dynamic properties. Zinc oxide is claimed to benefit aged properties in certain formulations by acting as an acid scavenger (Henning, 2007; Stiehler and Wakelin, 1948). Zinc complexes such as zinc dimethyldithio carbamate (ZDMC) appeared to be homogeneous catalysts (Nieuwenhuizen *et al.*, 1998) for the processes of crosslink formation (Geyser and McGill, 1996; Layer, 1992), crosslink shortening (Bateman *et al.*, 1963; Layer, 1992; Milligan, 1966) and crosslink breaking (Mc Sweeney and Morrison, 1983; Morrison and Porter, 1984). The role of metal oxides in the process of rubber vulcanization by thiuram disulphide lies mainly in the binding of dithiocarbamic acid (DMDCA) (Craig, 1956) whose decomposition products accelerate oxidative degradation of the vulcanizate network.

Fatty acids or zinc salts of fatty acids are generally regarded as indispensible activators in conjunction with ZnO to solubilize the ZnO and the accelerator to form the actual catalyst (Dogadkin and Beniska, 1958; Feldstein *et al.*, 1958). The role of activators also depends on the type of rubber, vulcanization accelerator and active filler used (Feldstein *et al.*, 1958). ZnO has the greater influence on the degree, while stearic acid has the greater influence on the rate of the crosslinking reaction (Dogadkin and Beniska, 1958).

As shown in Figure 3, radical mechanism controls the formation of crosslinks from precursors in the absence of ZnO where as the presence of ZnO stabilizes sulphur bonds through zinc chelation thereby changing the most likely breakable bond (Ghosh *et al.*, 2003). Such bond scission leads to crosslink byproducts (accelerator polysulphides) that can further crosslink and thus enhance the rate and efficiency of vulcanization. On the other hand in the absence of zinc species the bond cleavage during the conversion of a crosslink precursor to a crosslink may result in accelerator monosulphides which cannot contribute to further crosslinking. The effect of zinc ions on the efficiency of crosslink formation is being depicted in Figure 3.

Despite the beneficial role of zinc in the chemistry of sulphur vulcanization, there are questions regarding the impact of heavy metals on human health and ecological systems when they are released into the environment. Technologies considered for reducing zinc levels include zinc oxide loading rationalization by the use of alternative zinc complexes, activators based on other metal centers, application of multifunctional additives, etc. (Heideman *et al.*, 2004; 2005; 2006; Henning, 2007; Versloot *et al.*, 1994). The practical applications of these innovations are yet to hit the scene in full swing as these strategies have not proven their merits beyond doubts.

ACCELERATED SULPHUR VULCANIZATION

Outline of basic steps

Accelerated sulphur vulcanization is a multidisciplinary field involving the aspects of radical, ionic and organosulphur

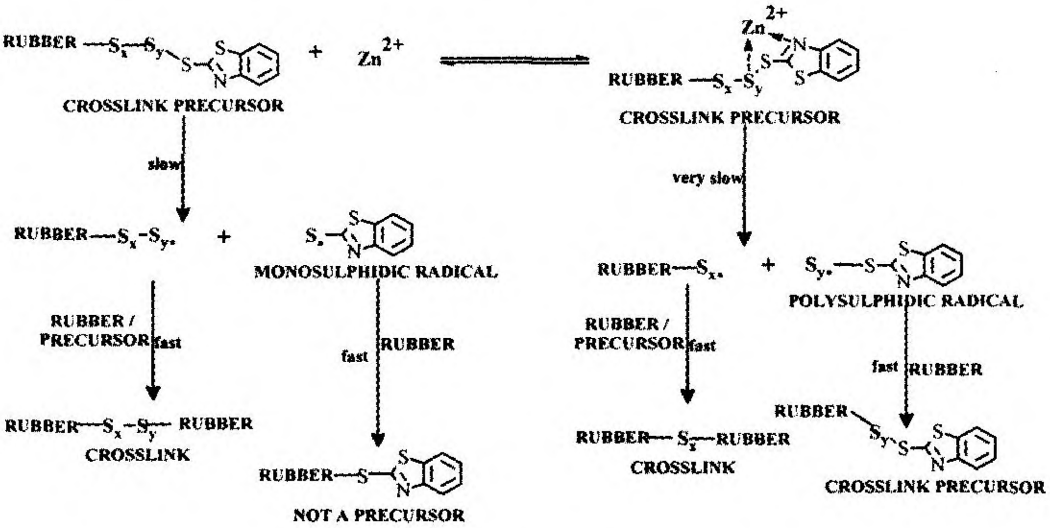


Fig. 3. Effect of zinc ions in sulphur vulcanization

Table 2. **Apparent polar or free radical character of the vulcanization reaction as observed in SBR**

Mechanism	Curing method
Polar	Unaccelerated sulphur, guanidine accelerated sulphur
Predominantly polar	Thiuram disulphide accelerated-sulphur, dithiocarbamate accelerated-sulphur, thiazole accelerated-sulphur,
Mixed polar and radical	Thiazole- disulphide accelerated-sulphur, sulphenamide accelerated-sulphur
Inconclusive	Thiuram disulphide cure
Free radical	Peroxide cure, radiation cure

chemistry, reactions in heterogeneous phase, homogeneous catalysis as well as co-ordination chemistry (Nieuwenhuizen *et al.*, 1998). There has been considerable debate concerning the mechanism of accelerated sulphur vulcanization for quite a long time. Many researchers (Bevilacqua, 1959; Coran, 1964; 2003; Scheele *et al.*, 1956; Dogadkin and Shershnev, 1960) advanced free radical mechanisms for the accelerated sulphur vulcanization of unsaturated elastomers. However, Bateman *et al.*, 1963 and Porter, 1967 suggested a polar mechanism for accelerated sulphur vulcanization. It is very difficult to generalize the discussion on accelerated sulphur vulcanization as there are many unanswered questions and many reasons to believe that both free radical and ionic reactions take place at different stages of the overall vulcanization reaction depending on the vulcanizing system (Wolfe,1968, Shelton and McDonel, 1960). The conclusions obtained by the investigations to establish the free radical or polar nature of curing reactions in styrene butadiene rubber (SBR) rubber is given in Table 2.

In addition to the decisive role it plays in the nature of crosslinking reactions the two major chemical functions of organic accelerators when used in conjunction with ZnO and fatty acids are (Bateman *et al.*, 1963)

i) to increase the rate of sulphur combination with rubber and

ii) to increase the efficiency of utilization of sulphur as a crosslinking agent by minimizing wastefully combined sulphur by decreasing length of sulphur chains in crosslinks, cyclic monosulphide formation and vicinal crosslinks.

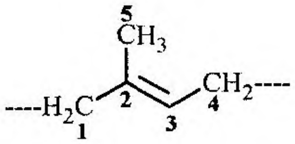


Fig. 4. The reactive allylic carbon atoms (C_4 and C_5) in NR

The reactive sites—"cure sites"—during the process of vulcanization are *allylic* hydrogen atoms lying adjacent to carbon-carbon double bonds. In natural rubber (NR), the hydrogen atoms at positions 4 and 5 are most preferred and are being shown in Figure 4.

During sulphur vulcanization, some of these C-H bonds are replaced by chains of sulphur atoms (one to eight) that link with a cure site of another polymer chain. The sulphuration of NR by accelerated sulphur systems or by sulphur donors normally occurs exclusively by α-methylenic or α-methylic substitution to give the crosslinked structures represented in Figure 5.

The initially formed crosslinks may undergo an allylic shift from the initial 4 and 5 positions and other configurations appear in the crosslinked network during

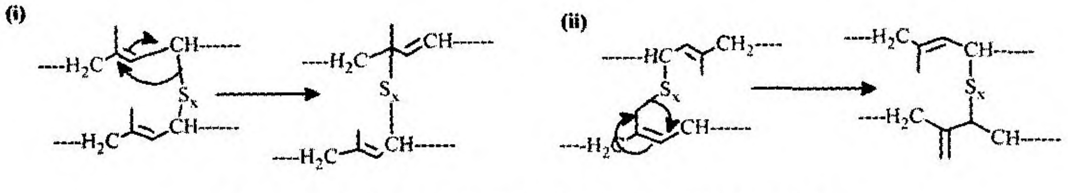


Fig. 5. Major Types of crosslinks formed at allylic sites of NR

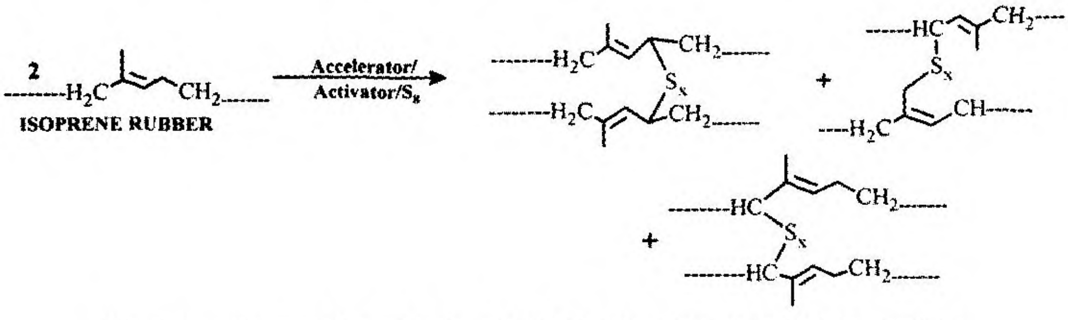


Fig. 6. New structures formed in the crosslinked network by shift of allylic crosslinks

vulcanization and post vulcanization time (Porter, 1967) which is being outlined in Figure 6.

Disappearance of the crosslinks of the disulphides and polysulphide type may occur with the formation of conjugated trienes (Blow, 1982) simultaneously as seen in Figure 7.

The crosslinks that are formed initially are usually polysulphides with high sulfur rank, which subsequently can undergo two competing reactions crosslink desulphuration, which involves rearrangement of the polysulphidic crosslinks to the more stable mono and di-sulphidic crosslinks, and crosslink decomposition/degradation where, polysulphidic crosslinks degrades to elastically ineffective cyclic sulphides, inactive pendant groups or other main-chain modifications. Thus, the main structures formed in sulphur vulcanized natural rubber are monosulphidic, disulphidic, polysulphidic and vicinal crosslinks, pendent side groups, cyclic sulphides, conjugated unsaturations, *etc.* (Porter, 1967).

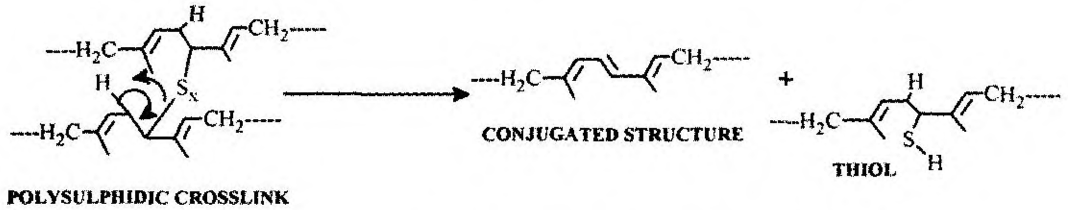


Fig. 7. Formation of conjugated structures by crosslink rearrangements

Despite the uncertainities regarding many processes taking place during the sulphur vulcanization, the widely accepted basic steps during the vulcanization reactions as outlined in Figure 8 can be divided into (i) accelerator chemistry which includes the formation of activator-accelerator complex and the active sulphurating agent, (ii) crosslinking chemistry including the formation of crosslink precursors and reactions leading to the formation of crosslinks and (iii) post crosslinking chemistry dealing with the network maturing reactions such as crosslink degradation and crosslink desulphuration.

Let us see in detail, the various steps given in the generally accepted outline of accelerated sulphur vulcanization of natural rubber as given in Figure 8.

Accelerator chemistry

Active accelerator complex

The generally accepted scheme for accelerated sulphur vulcanization (Fig. 8) suggests the formation of an active accelerator complex via a reaction between the activator and the accelerator as the first step in the vulcanization process (Heideman, 2004). But the sulphur

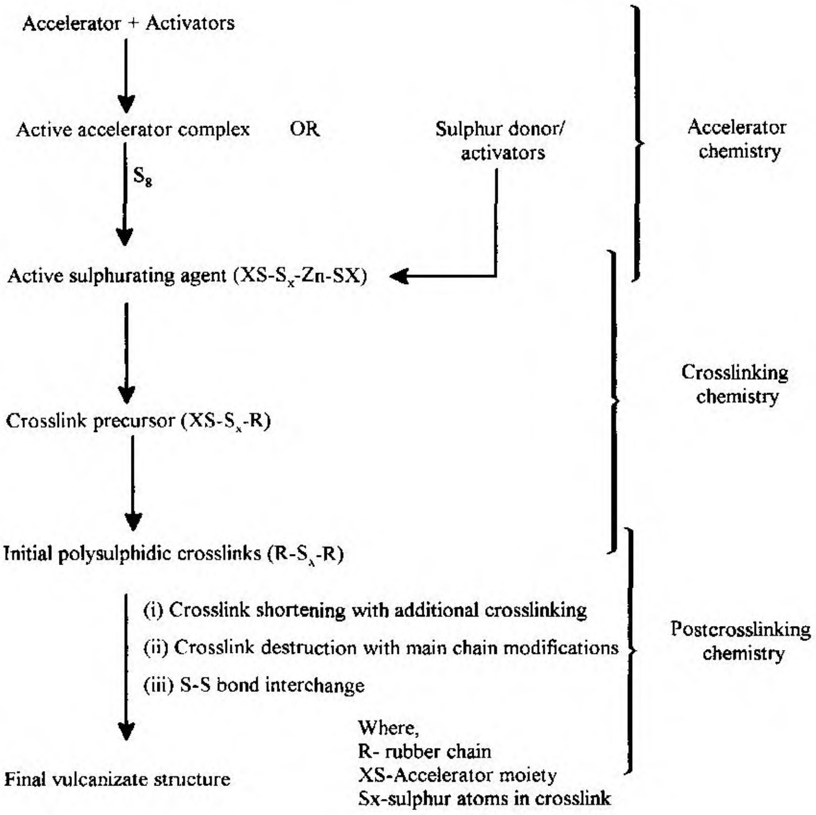


Fig. 8. Outline diagram showing different stages of vulcanization

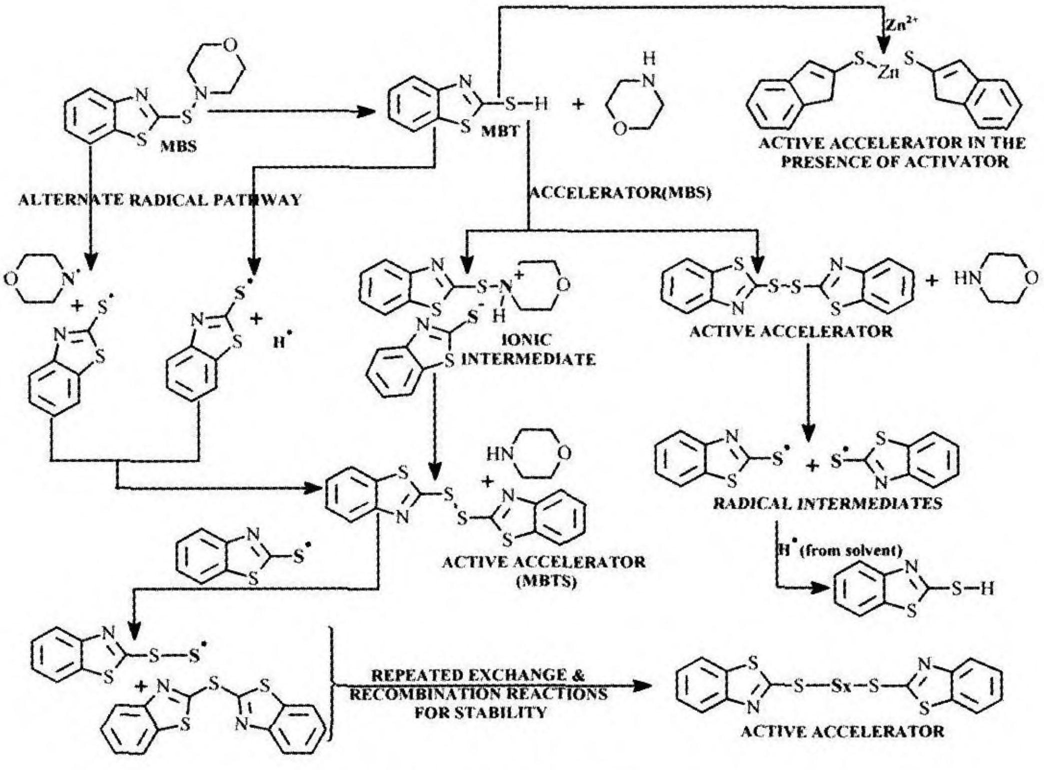


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Fig. 9. Formation of active accelerator

vulcanization literatures start with the formation of a range of active sulphurating agents which are being claimed to be produced from the active accelerator complex on reaction with molecular sulphur. Probably, the formation of active form of accelerator under the influence of the vulcanization temperature through ionic and radical path ways (Gradwell and McGill, 1994; Son *et al.*, 1972) might be regarded as the activation process as observed in benzothiazole-sulphenamide accelerated sulphur vulcanization. A variety of exchange and recombination reactions were also supposed to follow the activation process to form radicals of higher sulphur rank (Coleman *et al.*, 1973; Ghosh *et al.*, 2003; Gradwell *et al.*, 1999; Kapur *et al.*, 1974). When activators are present, the mercapto benzothiazole (MBT) part of the accelerator resulting from the thermal decomposition can form an intermediate with zinc to form the active accelerator complex (Hoover, 1999; Hoover *et al.*, 1999). The reaction steps involved in the formation of active accelerator are given in Figure 9.

The reactions described in Figure 9 shows a possibility even for the formation of accelerator polysulphides (sulphurating agents) through repeated exchange and recombination reactions. Although such reactions have been described, it might be regarded just as a possible reaction mechanism rather than a highly feasible reaction taking place during vulcanization, as in the vulcanization system in the presence of sulphur there are better ways of formation of sulphurating agents rather than this pathway.

Active sulphurating agent

Active sulphurating agents are accelerator polysulphides formed at the beginning stages of vulcanization process (Kruger and McGill, 1991) through sulphur intake of the active accelerator (Bateman *et al.*, 1963; Krebs, 1957) by various mechanisms as shown in Figure 10. These are better sulphurating species than molecular sulphur. In the absence of an activator such as ZnO these polysulphides of the type XS-S$_x$-SX (X is a group derived from accelerator) are formed by a radical pathway. When ZnO is present as an activator in the vulcanization system, it catalyses the formation of complexes, resulting in structures XS-S$_x$-Zn-SX (Ghosh *et al.*, 2003).

Even in the presence of ZnO, MBT formed initially will quickly get converted to 2, 2′-thiobisbenzothiazole (MBTS) the active accelerator, forming only small amounts of zinc accelerator complex at that stage. Additional zinc accelerator complex is formed from MBT during crosslink formation. In short, XS-S$_x$-SX is the active sulphurating agent in the absence of ZnO while both XS-S$_x$-SX and XS-Zn-S$_x$-SX may be the active sulphurating agents in the presence of ZnO. Sulphur insertion follows radical mechanism by sequential ring activation in the absence of activators where

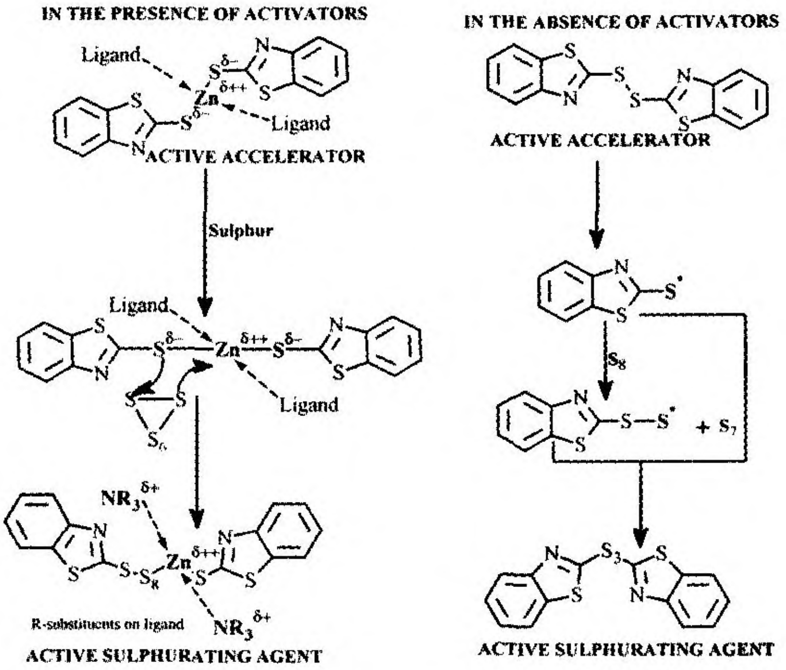

Fig. 10. Formation of active sulphurating agent

as it may follow an ionic pathway also in the presence of ZnO through sulphur ring incorporation (Bateman *et al.*, 1963; Ghosh *et al.*, 2003; Krebs, 1957).

If the zinc coordinates with an amine that is released from a sulphenamide or with carboxylate ligands which are present with stearic acid, the structure of the sulphurating agent can be represented as in Figure 11 (Ghosh *et al.*, 2003; Hoover *et al.*, 1999). This chelation is supposed to give better stability to the accelerator complex.

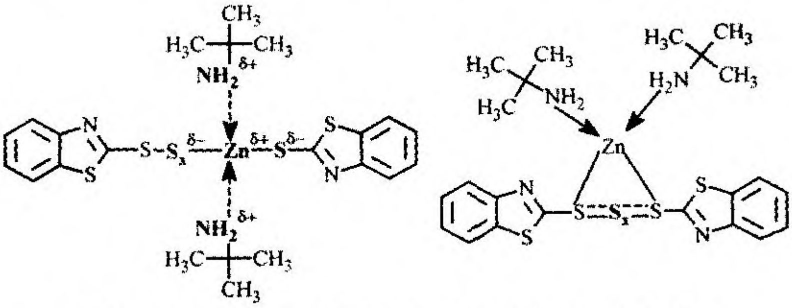
Fig. 11. Structures of sulphurating agents stabilized with ligands

Crosslinking chemistry

The crosslink precursor

Once the sulphurating agents are being formed, they react directly with the rubber molecule to give a rubber bound pendent group (Parks *et al.*, 1970) of structure R-S_x-SX (R denotes the rubber chain) which act as precursors to crosslink formation and hence the name. Desulphuration and decomposition can also be the fate of these precursors in addition to crosslink formation (Morrison, 1984). The existence of such species which was first proposed by Scheele and Franck (1959) were confirmed later by many scientists (Campbell and Wise, 1964; Moore and Watson, 1964). The crosslink precursors can be formed from both XS-S_x-SX and XS-Zn-S_x-SX species (Shelton and McDonel, 1960). Out of the radical (Coleman *et al.*, 1973) and concerted mechanisms (Coran, 1978; 2003) outlined in Figure 12 for the formation of crosslink precursors in the absence of ZnO, the latter seems more acceptable.

The concerted mechanism involves the formation of an eight membered transition state between the active sulphurating agent and rubber molecule before it gets separated into the real crosslink precursor along with MBT as a byproduct (Campbell and Wise, 1964).

In the presence of ZnO, the formation of crosslink precursors through Bateman's polar mechanism involving nucleophilic hydride displacement (Bateman *et al.*, 1963) is widely accepted even though carbanionic stepwise mechanism (Hoover *et al.*, 1999; Shelton and McDonel, 1960) and a mechanism involving a radical intermediate (Hoover *et al.*, 1999) were also proposed as given in Figure 13.

Bateman's mechanism is based on the nucleophilic character imparted to the sulphurating agent by the presence of zinc species. The increased nucleophilic

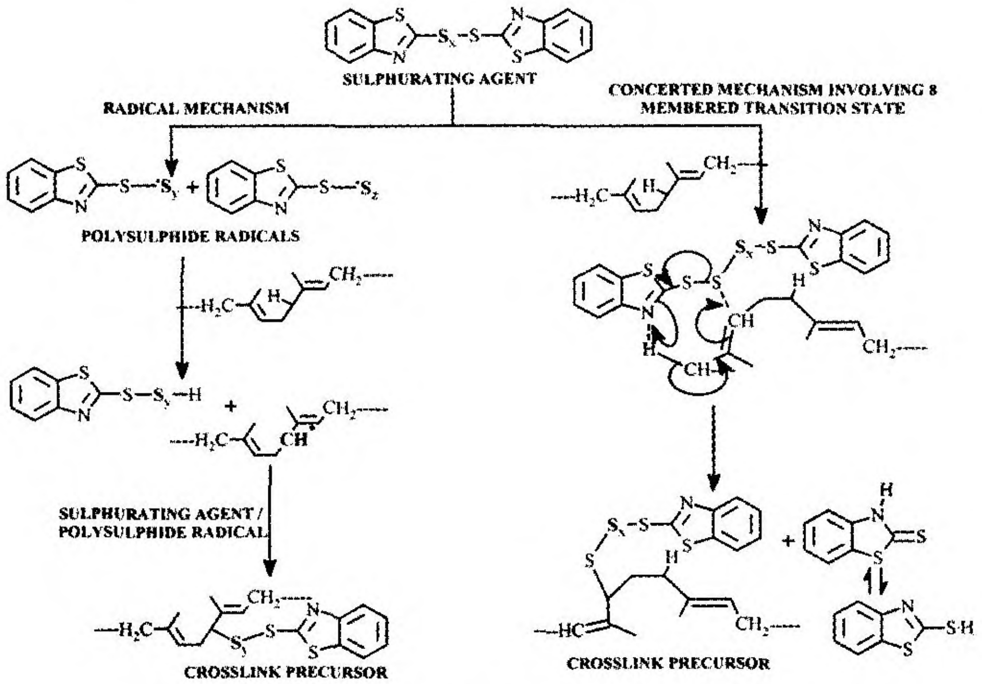

Fig. 12. Formation of crosslink precursors in the absence of activators

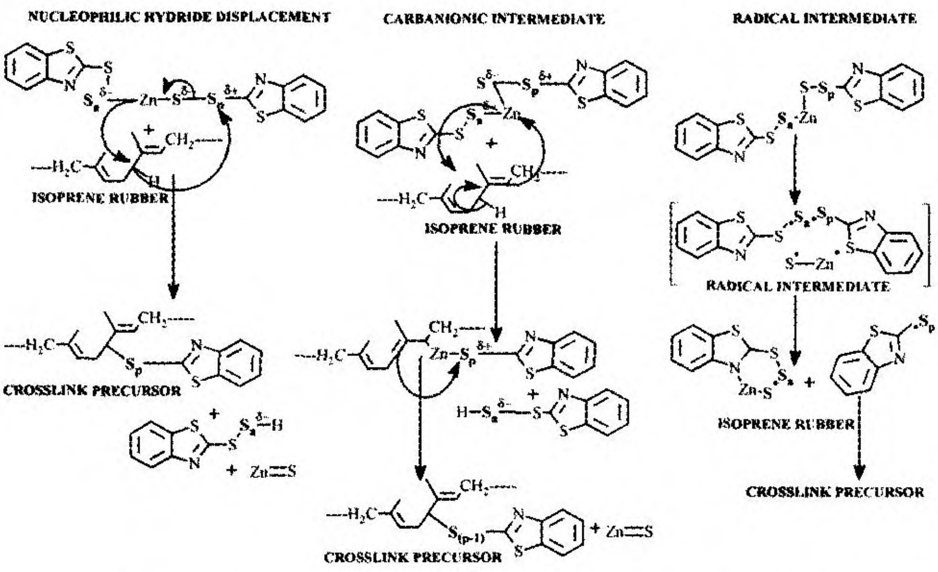

Fig. 13. Formation of crosslink precursors in the presence of activators

character of the sulphur atom adjacent to the zinc ion drives it to attack the allylic site of the rubber hydrocarbon causing a hydride ion elimination which will in turn specifically attack the sulphur atom upon which electro positivity is being created by the presence of zinc ion. These reactions will lead to the formation of a crosslink precursor along with a possible sulphurating agent and zinc sulphide as byproduct.

Crosslink formation

Formation of crosslinks is an inevitable and immediate consequence of crosslink precursor formation. Various mechanisms have been proposed for the conversion of the crosslink precursors into crosslinks. Crosslink formation *via* precursor-precursor interaction (Dogadkin and Beniska, 1958), interaction involving precursor, sulphurating agent and rubber molecule (Bateman *et al*., 1963) and through direct reaction of the crosslink precursor with rubber molecule (Bateman *et al*., 1963; Coran, 1965; 2003) were proposed. Free radical mechanism advocated for activator free systems is given in Figure 14, whereas polar mechanisms which are supposed to give rise to crosslinks in presence of activators like ZnO is being given in Figure 15.

Although both the mechanisms of crosslink formation in the presence of zinc species are catalysed by zinc accelerator complexes the disproportionation reaction pathway seems to be more unlikely to happen because it needs two precursor molecules to diffuse next to each other which cause steric hinderances. Also the formation of monosulphidic crosslinks has

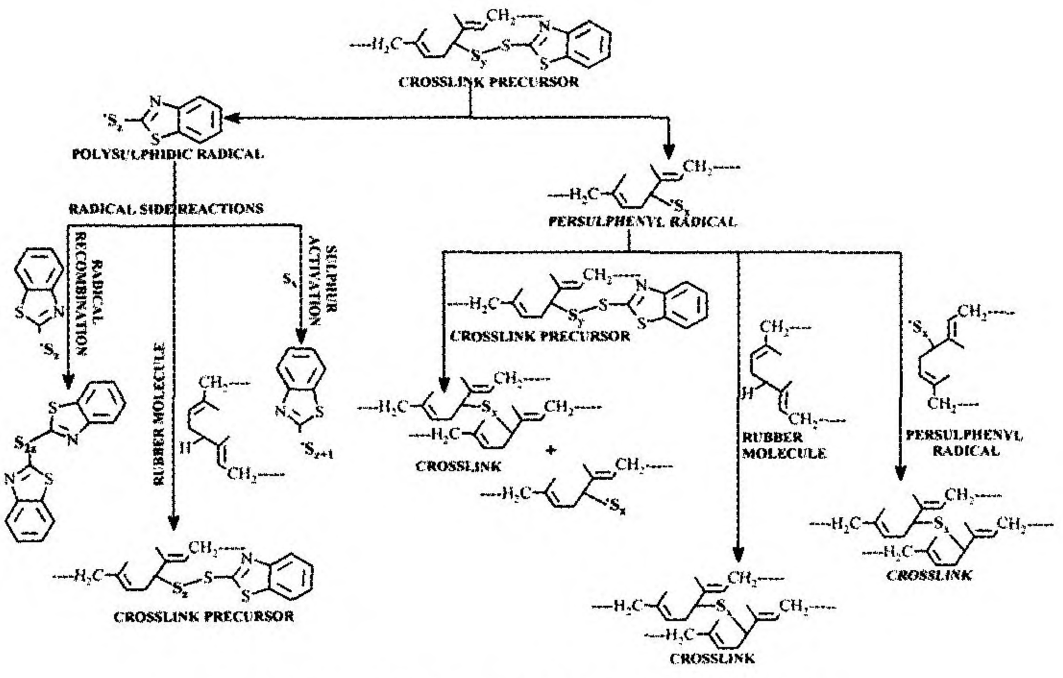

Fig. 14. Formation of crosslinks in the absence of activators

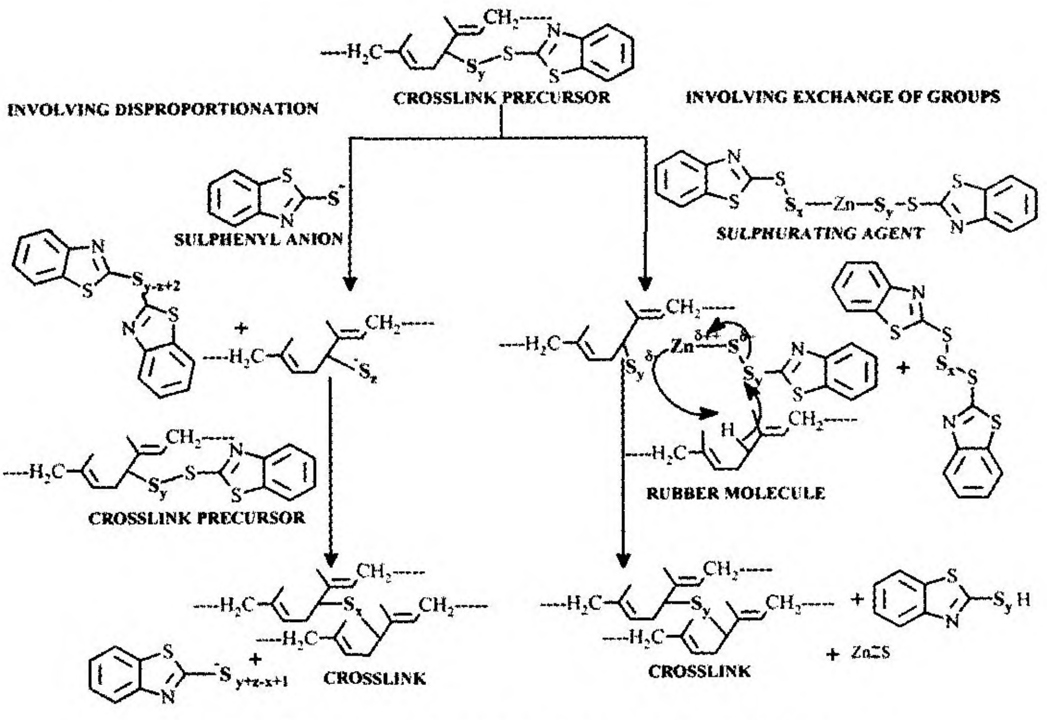

Fig. 15. Formation of crosslinks in the presence of activators

to be considered entirely as the result of desulphuration process in the post crosslinking period, if disproportionation is the mechanism of crosslink formation. These objections indicates that the crosslink formation through the exchange of groups between precursor and rubber might be the prominent pathway (Ghosh *et al.*, 2003).

The radical mechanism of crosslink formation involves the splitting of the crosslink precursor into two active radicals (Coran, 1964; 1965) which can undergo a variety of reactions such as radical recombination (Gradewell *et al.*, 1995; 1999; Kapur *et al.*, 1974), sulphur activation, addition to another rubber molecule to form another crosslink precursor etc. in addition to the crosslink formation (Ghosh *et al.*, 2003).

Crosslink formation by radical mechanism also follows the same steps as that in the case with ionic mechanism. The reaction involving persulphenyl radical and another crosslink precursor and that with two persulphenyl radicals (Ghosh *et al.*, 2003) are similar to that of the already discussed disproportionation reaction observed in the case of ZnO activated system and hence this is probably not the primary mechanism of crosslink formation. The crosslink formation involving the reaction of a persulphenyl radical with a neighbouring rubber chain (Coran, 1964; 1965) might be the major reaction pathway contributing to crosslink formation

Scorch delay reactions

In order to explain the rather long delay periods frequently encountered in accelerated sulfur vulcanization, especially wherein thiazole, sulphenamides or other scorch delay accelerators are used, a model scheme has been proposed by Coran (1964).

According to the model scheme given in Figure 16, crosslink formation will be minimum if the reaction k_4 is much faster than k_3, until A is essentially depleted. Both the reaction through k_3 and that through k_4 are assumed to be much faster than the reaction through k_2 and hence, after the delay required for the depletion of A, crosslink formation will proceed in a first-order fashion. Thus the formation of crosslinks is indeed inhibited by the starting materials and/or their initial reaction products. This treatment of scorch delay has been applied to sulphur vulcanization of natural rubber accelerated by 2,2' -thiobisbenzothiazole (MBTS), 2-(N-cyclohexyl) benzothizaolesulfenamide (CBS), 2-(N-morpholinothio) benzothiazole (MOR or MBS), or 2-(N,N-diisopropyl) benzothiazolesulfenamide (DPBS) and the differences noted between the rates were concluded to be attributed to differences in steric hindrance and stability (Kapur *et al.*, 1974). The mode of action of the above proposed scheme and various other factors that can affect the scorch properties are listed below.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} B^* \xrightarrow{k_3} \alpha Vu$$

$$A + B^* \xrightarrow{k_4} \beta B$$

A- Accelerator and/or its reaction products
B- Crosslink precursor
B*- Activated form of B
Vu- Crosslink α and β adjust stoichiometry

Fig. 16. Coran's model scheme for scorch delay

Effect of zinc-accelerator complex

In MBS system, crosslinking reactions can start only with the formation of the polysulphidic sulphurating species, from MBTS. If the release of MBT from MBS is delayed, MBTS cannot be formed thus delaying the crosslinking reaction as shown in Figure 17. The Delay observed in the onset of crosslinking in presence of ZnO can also be attributed to the inactivity of zinc salt of MBT ($Zn(mbt)_2$), which must break down to

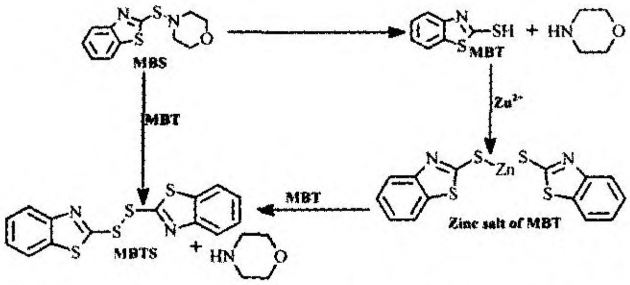

Fig. 17. Effect of zinc- accelerator complex in scorch delay

MBT before participating in the vulcanization process (Gradwell and McGill, 1995; 1996; Heideman *et al.*, 2004). Anyway, this might not be the major contributing factor as a good cure rate follows the scorch period immediately even in the presence of molar excess of ZnO.

Exchange reactions

The delay observed in sulphenamide accelerators may be due to exchange reactions between various accelerator-derived intermediates as depicted in Figure 18. The crosslink precursors are being quenched by accelerator polysulphides or such accelerator derived species until most of the accelerator polysulphides are consumed after which the precursor could form crosslinks (Coran, 1964; Gradwell and van der Merwe, 1999). Campbell and Wise (1964) have experimentally proved that the rate of reaction of the intermediates with the accelerator itself is greater than its reaction with NR during the scorch delay period through absorption chromatographic studies supporting the argument of exchange reactions.

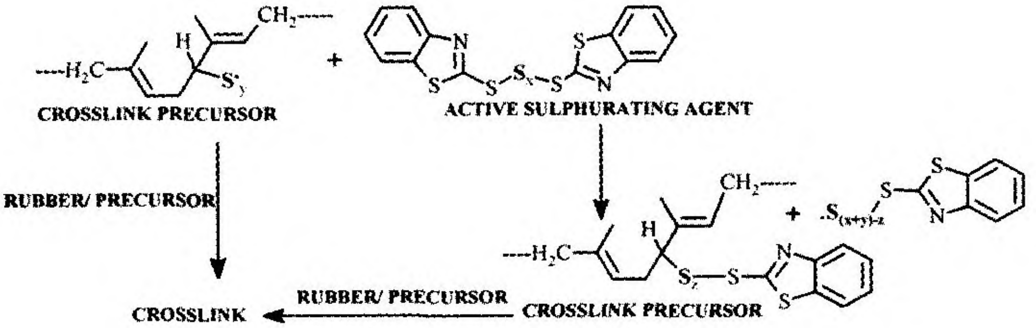

Fig. 18. Scorch delay due to exchange reactions

Formation of amine-terminated precursors

Another reason for the scorch delay observed with sulphenamide accelerators during sulphur vulcanization is attributed to exchange reactions (Ghosh *et al.*, 2003; Gradwell and McGill, 1996; Gradwell and van der Merwe, 1999) between the accelerator and crosslink precursors to form amine-terminated precursors with lower reactivity than benzothiazole terminated precursors. These amine terminated precursors cannot form crosslinks unless and until they are exchanged with MBT or benzothiazole terminated precursor to produce perthiol and sulphenamide or crosslink respectively as shown in Figure 19.

Action of prevulcanization inhibitor (PVI)

It is a well accepted fact that the delay period provided by the various accelerators through aforementioned mechanisms is not sufficient for the necessary pre-cure processing of rubber in many manufacturing processes. Introduction of a prevulcanization inhibitor (PVI) can effectively increase the induction time before actual curing

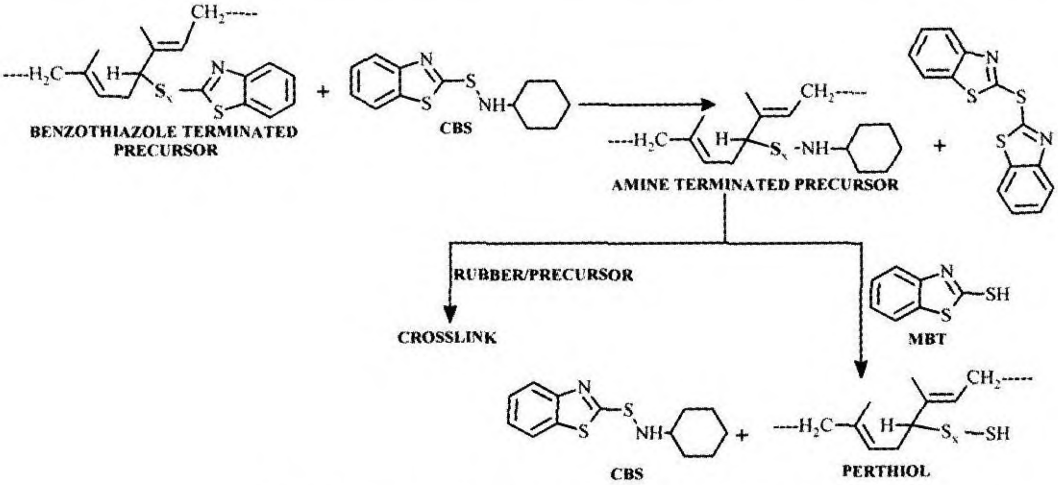

Fig. 19. Scorch delay by amine terminated precursor

commences, while retaining other aspects of cure such as rate of cure, time to maximum cure, maximum crosslink density, etc. (Hopper, 1974; Sullivan *et al.*, 1983; Trivette *et al.*, 1977). A typical PVI has an R-S-N group, with an R group with no proton accepter site and the net activity of the PVI increase by the increase in the number of S-N groups. The characteristic properties expected from a PVI along with scorch safety are (Twiss and Jones, 1935; Sullivan *et al.*, 1983)

1. PVI should react with the actual catalytic accelerator fragment (MBT) much faster than the primary accelerator.
2. The resulting asymmetric disulphide must not take a primary role in crosslinking process, yet it must slowly release the accelerator fragment as crosslinking proceeds.
3. The inhibitor must survive mixing and prevulcanization conditions with minimum loss to unproductive side reactions.
4. They should not affect the colour of the mixing nor impair the ageing properties of the rubber
5. They should be practically free from odour
6. They should be so active that only very small amounts are required to give the desired scorch retarding effect.
7. They should have no adverse effect on the physical properties of the vulcanized rubber.

The most widely used PVI; N-(cyclohexyl thio) phthalimide (CTP) was commercially introduced by Monsanto in 1970 (Morita, 1980) in sulfenamide accelerated sulphur vulcanization. The mechanism of action of PVI is based on the fact that MBTS formation is the key step towards crosslinking and hence if its formation can be arrested, the whole crosslinking mechanism can be checked. MBTS formation is being blocked by CTP by consuming MBT thereby preventing any chance of MBT further reacting with sulfenamides to form MBTS. Kinetic factors also favour this reaction as MBT has greater affinity for CTP than to sulfenamides and hence it will react with CTP alone until all the CTP has been consumed (Gradwell and Stephenson, 2001; Leib *et al.*, 1970; Mukhopadhyay and De, 1979; Scheele and Helberg, 1965; Son *et al.*, 1972; Son, 1973).

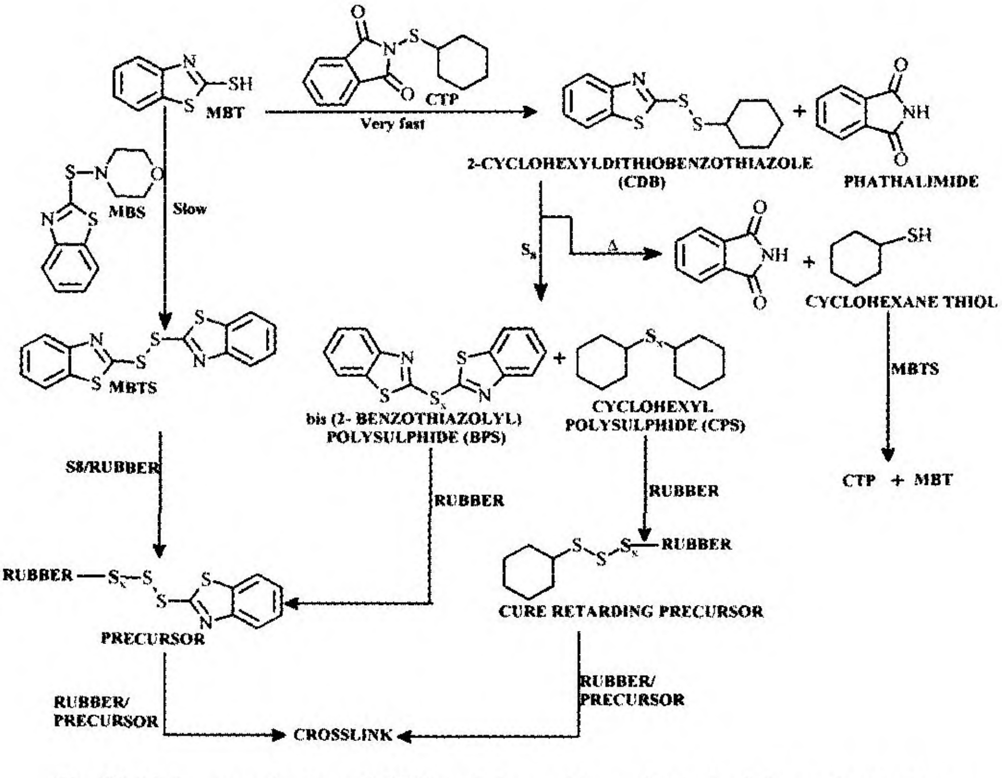

Fig. 20. Mechanism of action of CTP in sulphenamide accelerated sulphur vulcanization

The by-product of CTP action is 2-cyclohexyldithiobenzothiazole (CDB) has been proved to be a lesser scorchy vulcanization accelerator than N-oxydiethylene -2 benzothiazolesulphenamide (OBTS or MBS or MOR), but with slower cure rate (Son, 1973) will accelerate the vulcanization process when actual curing begins. The mechanism of action of PVI is given in Figure 20.

Accelerated sulphur vulcanization via sulphur donors

A number of accelerators (tetramethylthiuram disulphide (TMTD), tetraethylthiuram disulphide (TETD), dipentamethylenethiuram tetrasulphide (DPTT), etc.) can function both as accelerators and sulphur donors. Generally, sulphur donors are used where free sulphur level is to be reduced with the objective of improving thermal and oxidative ageing resistance, to eliminate bloom or to modify processing and curing characteristics (Rodger, 1979). Among the various organic sulphur containing compounds, such as alkyl and cycloalkylene thiuramdisulphides and dithio and perthio- bis amines that can vulcanize unsaturated rubbers in the absence of elemental sulphur, TMTD has been the most studied. Vulcanizates obtained using these compounds in combination with ZnO are characterized by superior thermal and oxidative stability and negligible modulus reversion (Kruger and McGill, 1992) due to the special network structure of the vulcanizate and the formation of a potent antioxidant, zinc dialkyldithiocarbamate (ZDMC) during vulcanization. The network formed in the initial stages of vulcanization will be structurally complex, but will become structurally simpler as crosslinking proceeds to the maximum crosslink density with little cis-trans isomerization of the double bonds, scission of the main chain during cure, conjugated species and cyclic monosulphides (Bateman *et al.*, 1963; Moore and Trego, 1964).

Although extensive research have been undertaken, it is not able to conclude (Shelton and McDonel, 1960) whether the reaction follows a radical (Craig, 1956; Dogadkin and Shershnev, 1960; Geyser and McGill, 1996; Wolfe, 1968) or polar or a combination pathway of both (Coleman *et al.*, 1973; Shelton and McDonel, 1960; Wolfe, 1968). Moore and Watson (1964), Scheele *et al.* (1956), Coleman *et al.* (1973), Bateman *et al.* (1963), Dogadkin and Shershnev, (1960), Versloot *et al.* (1994) and Kruger and McGill, (1992) also put forth their experimental observations for thiuram accelerated vulcanization of isoprene rubber. Among the various mechanisms the combination of thiuram persulfenyl and polyisoprenyl radicals through an irreversible concerted reaction without the formation of a true alkenyl intermediate seems to be more acceptable as C-C crosslinks are negligible in the NR-TMTD-ZnO system (Dogadkin and Shershnev, 1960; Moore, 1958; Savillle and Watson, 1967). True alkenyl intermediate free radicals need true carbon free radical from the rubber hydrocarbon for crosslinks. If that is the case the so formed carbon free radicals can also react among themselves to form C-C crosslinks which is not observed with TMTD vulcanization of NR.

Radical mechanism

According to radical mechanism given in Figure 21, the first step in TMTD-NR vulcanization should be the symmetrical and unsymmetrical decomposition of TMTD into free radicals (Dogadkin and Shershnev, 1960; Kruger and McGill, 1992; Rooyen, 2007) at vulcanization temperatures whose interactive recombination will lead to the formation of accelerator polysulphides (TMTPs) (Coleman *et al.*, 1973; Geyser and McGill, 1996; Kruger and McGill, 1991; 1992). These sulphurating agents will form crosslink precursors on reaction with rubber. Crosslink precursors can form crosslinks either interacting with a precursor molecule or with a rubber molecule just as in the previous cases.

Polar mechanism

In the presence of zinc oxide, TMTD vulcanization of NR may follow a polar route also, as shown in Figure 22, in which the active sulphurating agents are both zinc perthiomercaptides (ZDMC) (Duchacek, 1974; 1978; 1979) and thiuram polysulphides (TMTPs) (Geyser and McGill, 1995; 1996; Kruger and McGill, 1991). The findings of Duchacek (1978; 1979) and kinetic investigations by Scheele and Franck (1959) proved that the formation of zinc

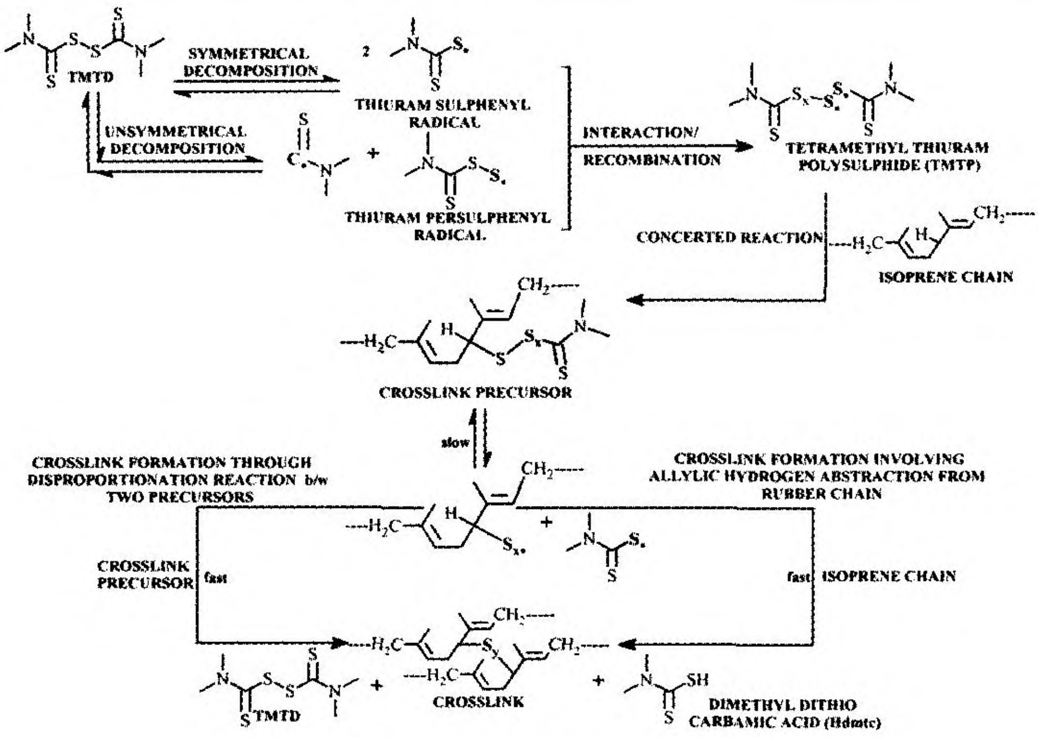

Fig. 21. Vulcanization by TMTD – radical pathway

perthiomercaptides (sulphurating agent) is followed by the formation of network bound accelerator residues (pendent groups/ crosslink precursors) on reaction with rubber hydrocarbon, which will form crosslinks (Geyser and McGill,1996) *via* nucleophilic reactions just as in the case of other vulcanization systems (Bevilacqua, 1959; Bateman *et al.*, 1963; Kruger and McGill, 1992). The precursor may react with a thiuram persulphenyl anion derived from ZDMC to form a rubber polysulphidic anion or with ZDMC itself to form a zinc containing precursor. These two species on reaction with another precursor or isoprene chain respectively will give rise to crosslinks. As per the mechanism, the formation of pendent groups proceeds *via* a concerted reaction between the sulphurating agent and the rubber chain in which the S-S bonds are broken and new C-S bonds are formed through a concerted reaction without the formation of true intermediates.

Formation of mono or disulphidic crosslinks (efficient vulcanization) resulting in a reversion resistant vulcanizate network is being manifested as the highlight of using sulphur donating accelerators such as TMTD as already mentioned. A progressive shortening of initially formed polysulphidic crosslinks is supposed to take place by the extrusion of sulphur from the polysulphidic crosslinks by TMTM which would eventually lead to a heat resistant network with monosulphidic crosslinks (Kruger and McGill, 1992 a, b). But when TMTD is used

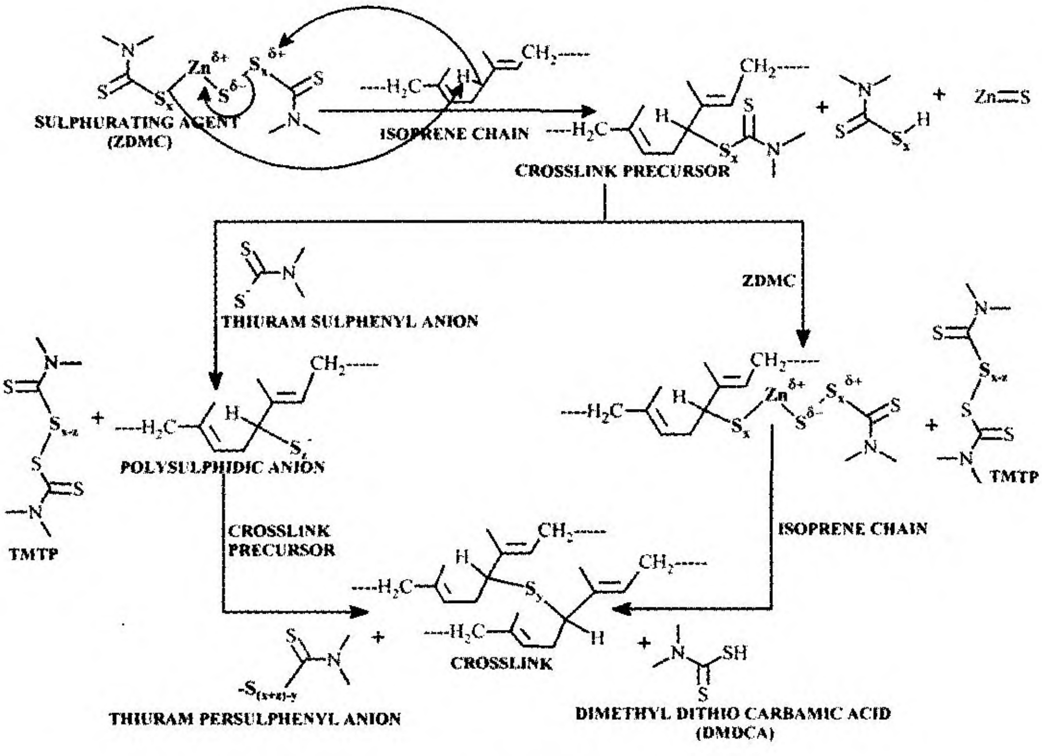

Fig. 22. Vulcanization by TMTD – polar pathway

as an accelerator in the presence of sulphur, *the degree of crosslinking is proportional to* sulphur concentration and at higher sulphur concentration the vulcanizate tend to revert (Scheele and Franck, 1959) as more number of polysulphidic crosslinks are being produced shifting the cure system to an inefficient one.

The role of ZnO in TMTD vulcanization is more prominent than in other cases of sulphur vulcanization, as in the absence of ZnO, dimethyl dithiocarbamic acid (DMDCA) formed as a by-product of pendent group formation and crosslinking (Coleman *et al.*, 1973; Dogadkin and Shershnev, 1960; Kruger and McGill, 1992) will decompose into dimethylamine (Me_2NH) and carbon disulphide (CS_2) which will further trigger various crosslink deteriorating reactions. Me_2NH would be very reactive towards dithiocarbamate species and enhance side reactions (Geyser and McGill, 1996; Kruger and McGill, 1992) consuming various intermediate species required for vulcanization, resulting in degradation of the vulcanizate network. Various reactions that can occur in the absence of ZnO and the mechanism through which they are being arrested in the presence of ZnO are given in Figure 23.

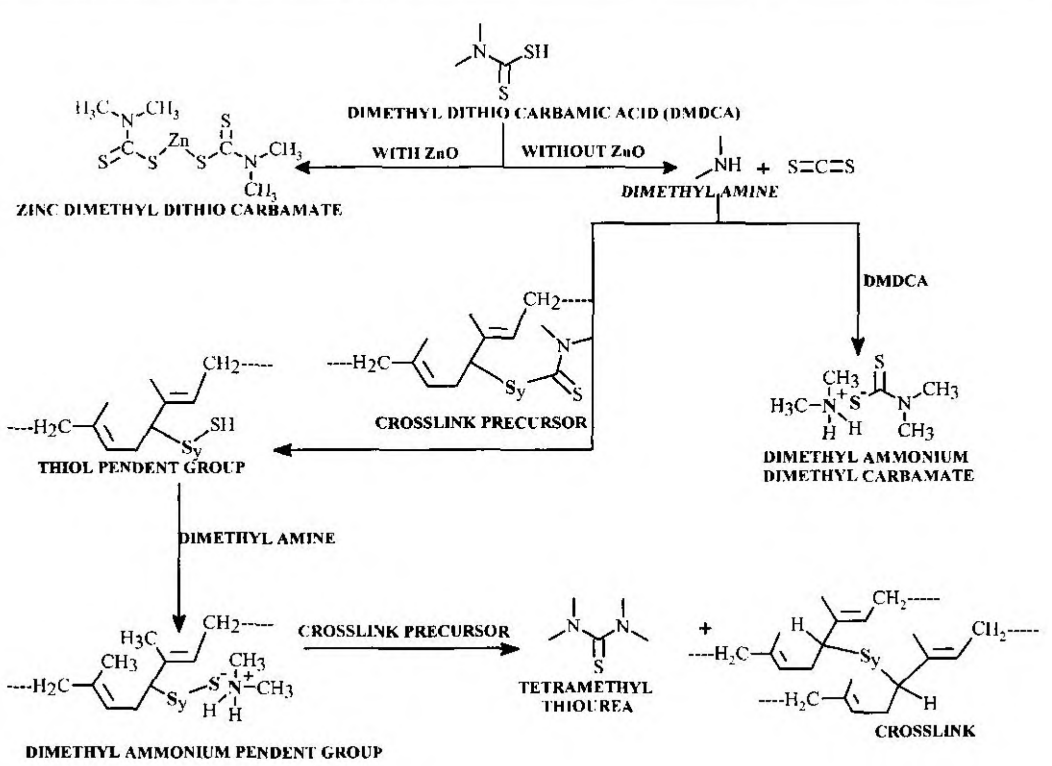

Fig. 23. Role of zinc oxide in TMTD vulcanization

Postcrosslinking chemistry

As we have already mentioned, crosslink desulphuration and crosslink decomposition reactions dominate the post crosslinking chemistry (Morrison and Porter, 1984). After the free sulphur is consumed during vulcanization, the accelerator complex continues to react with polysulphidic crosslinks as though it were elemental sulphur. The reactions include extracting sulphur from the crosslinks (desulphuration), cleaving crosslinks (decomposition), formation of conjugated unsaturation in the main chain etc. (Hoover, 1999). If the desulphuration proceeds rapidly the final network will be highly crosslinked with mainly monosulphidic bonds and there will be relatively few modifications of the cyclic sulphides or conjugated triene type (efficiently crosslinked) (Conover, 1941; Morrel, 1982) or else there will be opportunities for thermal decompositions leading to reversion or loss of crosslinks and to network modifications (inefficiently crosslinked) (Conover, 1941).

Crosslink desulphuration reactions

Desulphuration reactions (Minoura, 1950; Mori and Koenig, 1995; Nieuwenhuizen *et al.*, 1999 a, b) involve the extraction of sulphur atoms from higher ranked sulphur bonds, followed by insertion of the extracted sulphur atoms into the lower ranked sulphur crosslinks. Desulphuration

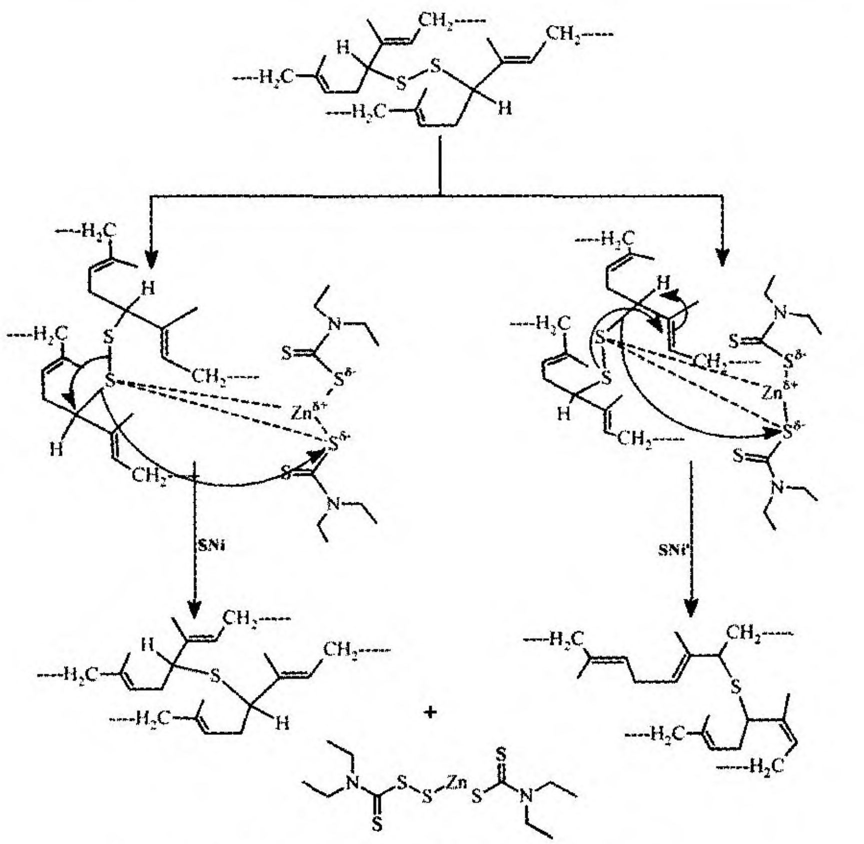

Fig. 24. Mechanism of zinc mediated desulphuration

of rubber bound intermediates would in effect, compete with crosslinking, as it will eventually result in monosulphidic pendent groups which are relatively unreactive and are not precursors to crosslinks. As the temperature of the vulcanizing system is increased, more accelerators are removed as unreactive monosulphidic pendent groups which appears to be a major contributor to the reduction in crosslinking efficiency in EV and semi EV systems with rise in temperature (Bateman *et al.*, 1963; Nieuwenhuizen and Reedjik, 1997). The shortening of crosslinks is often accompanied by changes in position of crosslinks such that the initial allylic crosslinks may get transformed to isoallylic structures.

Bateman *et al.* (1963) proposed a mechanism for zinc mediated desulphuration, involving an intermediate adduct formation between di- or polysulphidic crosslink and the zinc complex, followed by SNi or SNi′ attack along with double bond rearrangement as shown in Figure 24. The reaction assumes the involvement of trithio-zinc, implying

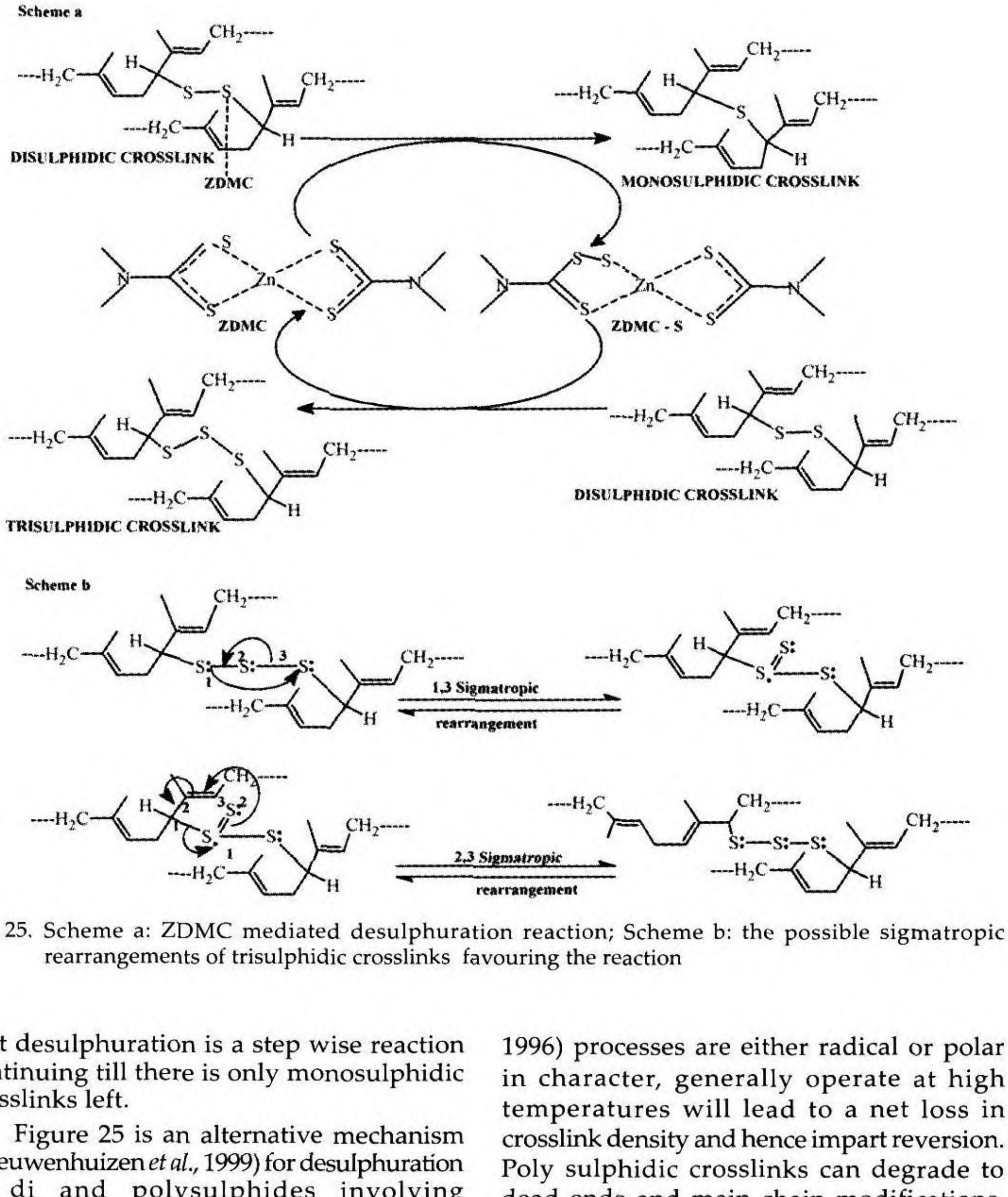

Fig. 25. Scheme a: ZDMC mediated desulphuration reaction; Scheme b: the possible sigmatropic rearrangements of trisulphidic crosslinks favouring the reaction

that desulphuration is a step wise reaction continuing till there is only monosulphidic crosslinks left.

Figure 25 is an alternative mechanism (Nieuwenhuizen *et al.*, 1999) for desulphuration of di and polysulphides involving sigmatropic shift and isomerization of double bond (Nieuwenhuizen *et al.*, 1998).

Crosslink decomposition reactions

Crosslink decomposition (Schotman *et al.*, 1996) processes are either radical or polar in character, generally operate at high temperatures will lead to a net loss in crosslink density and hence impart reversion. Poly sulphidic crosslinks can degrade to dead ends and main chain modifications. Radical decomposition of polysulphidic crosslinks is governed by bond dissociation energies of the bond that is broken. Hence polysulphides of higher lengths are easily dissociated due to their lower bond

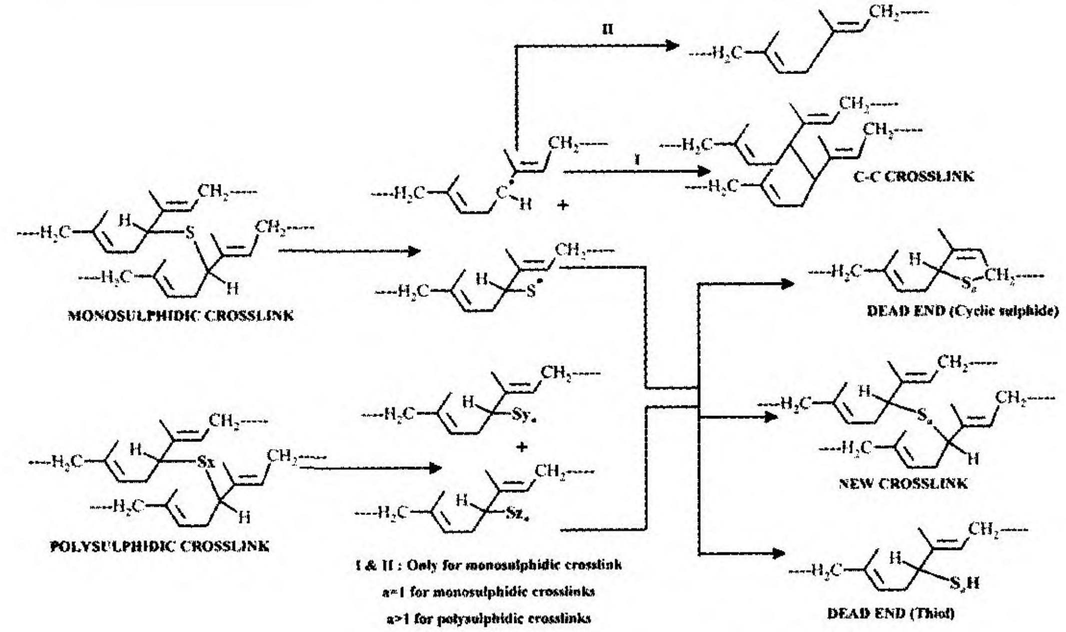

Fig. 26. Radical degradation of cross-links

dissociation energies (approx.150kJ mol^{-1}). Dissociation of di and tri sulphidic crosslinks is more difficult due to their higher bond dissociation energies (289 and 193kJ/mol respectively). Similar degradation of monosulphidic crosslinks (Morrison and Porter, 1984) may lead to the formation of C-C crosslinks where as such a possibility is rare in the case of polysulphidic crosslinks as S-S bond is more easily cleaved than C-S bond. Also the rate of degradation of monosulphidic crosslinks will be far less than that of polysulphidic crosslinks considering the bond dissociation energies of both systems. The radical degradation pathways of crosslinks are given in Figure 26.

But, some alternatives for the degradation of monosulphidic crosslinks other than the radical mechanism are also found in literature. 1, 2-dehydrosulphuration has been established to be an important reversion reaction for monosulphides (McSwkeeney and Morrison, 1983; Morrison and Portor, 1984), that can produce trienes as the final product. 1, 5 hydrogen shifts (Bateman *et al.*, 1963; McSwkeeney and Morrison, 1983; Nieuwenhuizen and Reedjik, 1997) is the predominant degradation mechanism in other cases, if steric and kinetic factors are favourable. Other possible reactions (Nieuwenhuizen *et al.*, 1999) for degradation of crosslinks, such as concerted decomposition of monosulphides to yield $\alpha-\beta$ unsaturated thio aldehydes and polar decomposition of disulphides *via* zinc diethyldithiocarbamate (ZDEC or ZDC) catalyzed 1,4-hydride shift yielding cyclic disulphides were also being investigated using reaction stage modeling (RSM) studies. The concerted mechanism is assumed to operate even at vulcanization temperatures with the only pre-requisite

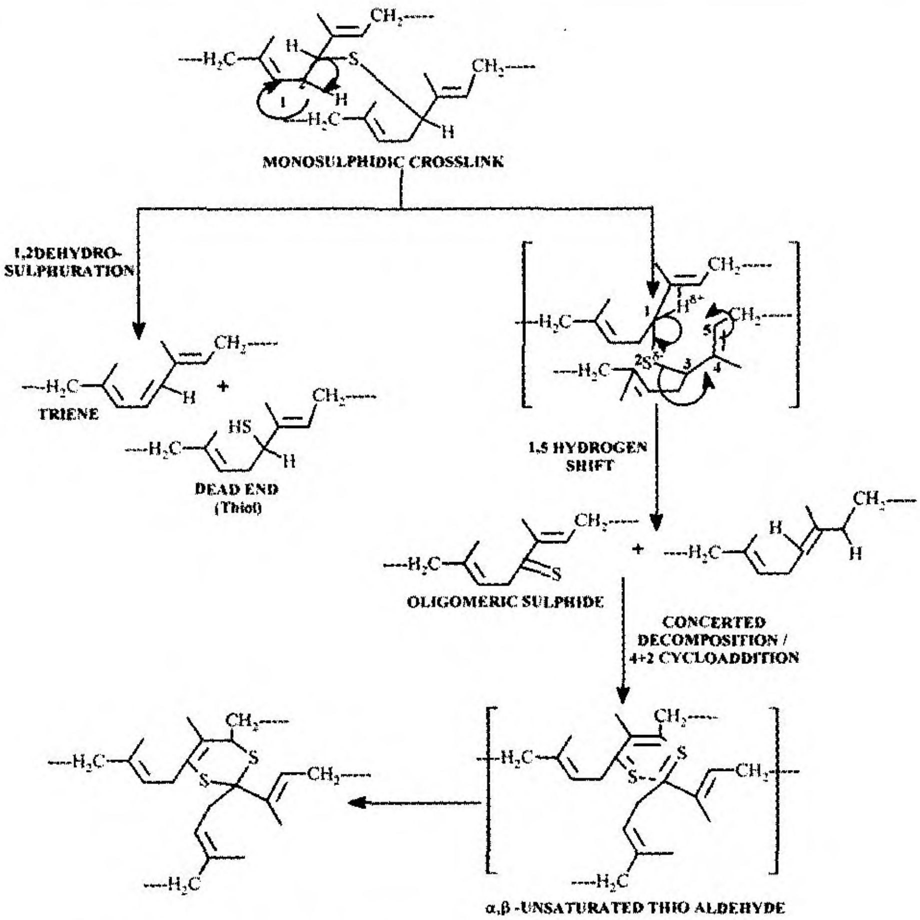

Fig. 27. Degradation of monosulphidic crosslinks by polar pathways

that alpha carbon of the crosslinked sulphur should not be tertiary. Polar degradation possibilities of monosulphidic crosslinks are given in Figure 27.

Tackling reversion

As we have already seen, reversion occurs in sulphur cured NR and synthetic isoprene rubber (IR) when polysulphidic crosslinks are exposed to temperature – time treatment which causes decomposition of polysulphidic crosslinks (Schotman *et al.*, 1996). This phenomenon leads to a reduction in crosslink density and consequently loss of mechanical properties.

The best established compounding method to reduce or minimize reversion is the use of so called efficient cure system thereby diminishing the number of polysulphidic crosslinks and generating reversion resistant mono and disulphidic crosslinks. This approach is successful, if lowering of sulphur does not negatively affect other desired properties of the vulcanizate. But lower sulphur levels will result in lower rubber to metal/fabric adhesion limiting the application of this approach to some extent (Schotman *et al.*, 1996).

The other two major approaches to battle crosslink breaking involves deactivating the detrimental catalytic activity of zinc dithiocarbamates and countering the effect of reversion by substituting a broken crosslink by an alternative one using anti-reversion coagents (Datta *et al.*, 1997; Kok, 1987; Schotman *et al.*, 1996). Anti-reversion coagents are usually *dienophiles like N-benzyl citraconamide,* 1, 3- (bis-citraconimidomethyl) benzene (BCI-MX), tetracyanoethene, maleic anhydride, etc. which can scavenge the dienes and trienes to form Diels-Alder adducts through a concerted (4+2) cyclo addition of a conjugated diene formed during reversion as in Figure 27 with dienophile. The concerted (4+2) cycloaddition is shown in Figure 28.

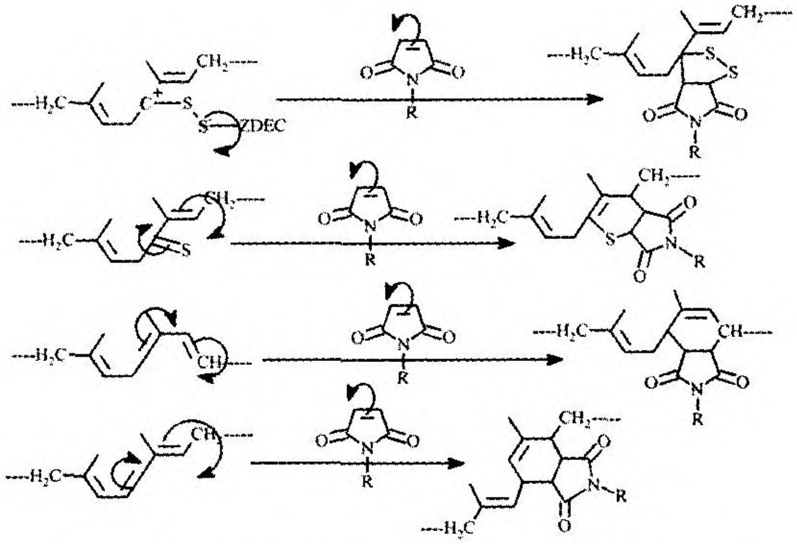

Fig. 28. Scavenging of conjugated dienes and trienes by dienophiles

Among the various retarders employed, *BCI-MX is most commercialized due to its* higher efficiency in battling reversion. This may be attributed to the specialty of its structure which can replace the short conjugated dimers with long BCI-MX bridged dimers, whose lengths are comparable to crosslinks consisting of seven sulphur atoms. Also BCI-MX produces C-C crosslinks which are thermally more stable allowing the rubber to operate at more severe service conditions (Schotman *et al.*, 1996). The structure of the adduct formed by BCI-MX and a diene is shown in Figure 29.

Zinc dithiocarbamates may be deactivated by adding complexing agents

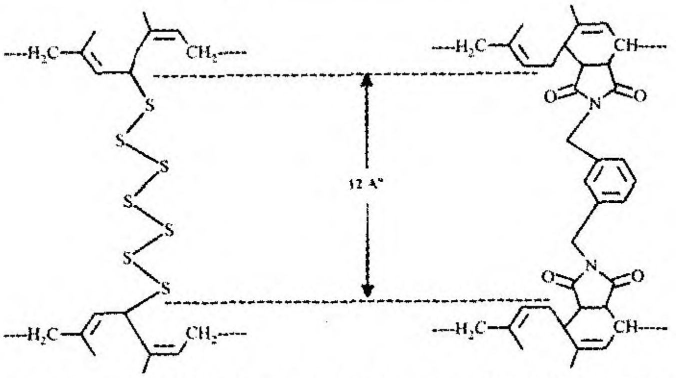

Fig. 29. Comparison of length of Diels Alder adduct formed by BCI-MX with polysulphidic crosslinks

like nitrogen containing ligands such as 1, 10–phenantroline and N-methylimidazole. But these experiments are not yet successful (Nieuwenhuizen *et al.*, 1999).

Accelerated sulphur vulcanization of other polydiene elastomers

Although we have discussed the chemistry of sulphur vulcanization taking the case of natural rubber (NR), accelerated sulphur vulcanization is also suitable for other general purpose rubbers such as synthetic isoprene (IR), polybutadiene rubber (BR), styrene butadiene rubber (SBR) and specialty elastomers such as nitrile rubber (NBR), butyl rubber (IIR), chlorobutyl rubber (CIIR), bromobutyl rubber (BIIR) and ethylene propylene diene rubber (EPDM). Even though natural rubber can be regarded as a general representative of the group, there are some areas upon which the behavior of sulphur vulcanization of natural and synthetic rubbers differs. Let us have a brief discussion over some of such aspects.

The terms efficient and inefficient have already been outlined in terms of usage of sulphur in the vulcanized network. These terms represent two extremes *viz.* efficient vulcanization uses zero or a very low level of sulphur and a high level of accelerator along with a sulphur donor, where as conventional or inefficient system uses higher amount of sulphur compared with accelerator loading.

In NR, efficient vulcanization (EV) result in higher proportion of monosulphidic and disulphidic crosslinks along with minimum main chain modifications giving rise to higher thermal and oxidative ageing resistance. Conventional vulcanized NR has higher proportion of main chain modifications causing poor resistance to thermal and oxidative ageing. The term EV is similarly applicable to other sulphur vulcanizable polymers also. But for SBR, even conventional vulcanization gives a high proportion of monosulphidic crosslinks. Table 3 gives the crosslink distribution pattern for NR and SBR for conventional and efficient vulcanization systems.

Table 3. **Crosslink distribution for NR and SBR**

Vulcanization system	Crosslink type (%)			
	NR		SBR	
	S_1	$S_2 + S_x$	S_1	$S_2 + S_x$
Conventional	0	100	38	62
EV	46	54	86	16

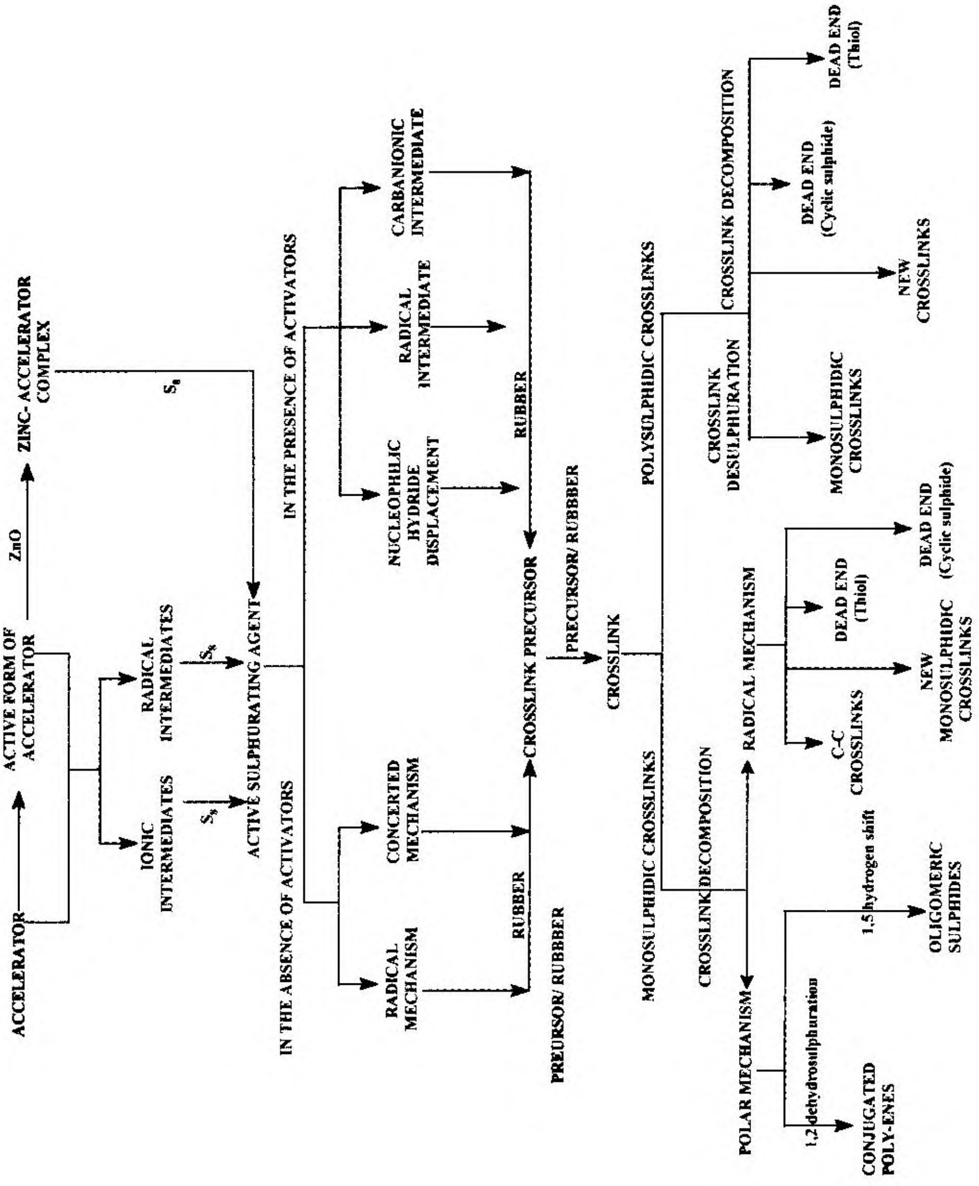

Fig. 30. Summary of steps and processes involved in accelerated sulphur vulcanization

A further difference between NR and other synthetic rubbers is in the mechanism of ageing and lack of reversion. In SBR, oxidative ageing causes minimum main chain breaking and a higher degree of additional crosslinking resulting in increased hardness and modulus and reduced elongation at break. Substantial improvements in oxidative ageing can be obtained in synthetic polymers by EV system. Also the fatigue life of EV cured synthetic polymers is not reduced even with substantial decrease in amount of sulphur.

In the case of EPDM rubber, as a result of the small amount of unsaturation, the vulcanization rate is rather low in comparison with other polydiene elastomers and a relatively large amount of accelerators is needed. Due to the large difference in polarity between polar accelerators and non polar EPDM elastomer, the solubility of the accelerators is limited and usually a mixture of upto five accelerators is applied (Duin, 2002).

SUMMARY

A detailed survey on the sulphur vulcanization of elastomers has been made in this review giving special attention to accelerated sulphur vulcanization of natural rubber. The process of vulcanization has been discussed under three different sections *viz.* accelerator chemistry, crosslinking chemistry and post crosslinking chemistry. A general outlook of the vulcanization process, vulcanization accelerators and the role of activators are also discussed. The mechanism of various reactions involved and the schemes of various reactions are included along with descriptions of the prominent reaction in a group of possible reactions.

The accelerator chemistry deals with the formation of the activator - accelerator complex which can effectively sulphurate the rubber chains giving rise to crosslink precursors. Crosslinking chemistry deals with the formation of crosslink precursor

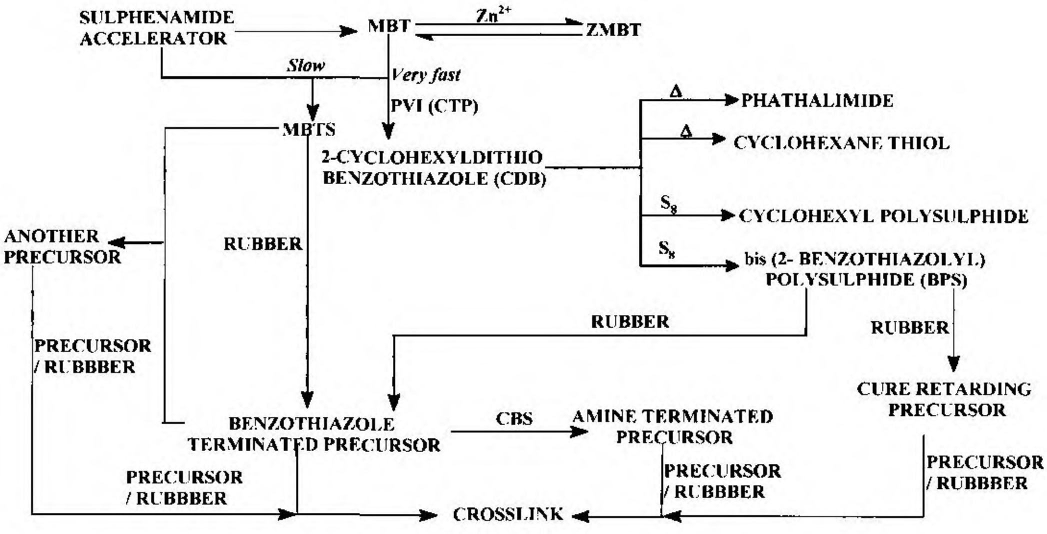

Fig. 31. Scorch delay reactions in a glance.

Table 4. **Comparison of crosslink desulphuration and crosslink decomposition reactions**

	Effects	**Favouring factors**	**Temperature dependence**	**Tackling methods**
Crosslink desulphuration	Results in stable monosulphidic crosslinks and recycling of extruded sulphur	Zinc – accelerator complexes and extra ligands High accelerator sulphur ratio along with zinc salt sufficient enough to solubulize it	Occur even at room temperature	Deactivating zinc – accelerator complexes
Crosslink decomposition	Causes modulus reversion, low crosslink efficiency and main chain modifications	Conventional vulcanization forming polysulphidic crosslinks Increase in temperature	Considerable at 140°C but less at 100°C	Efficient vulcanization. Using anti-reversion co-agents

and the reactions of this precursor leading to crosslinks and the various scorch delay mechanisms. Accelerated sulphur vulcanization *via* sulphur donors is used to minimize the sulphur loading and thereby obtain a reversion free curing due to the higher percentage of mono and disulphidic crosslinks. The various processes involved in the accelerated sulphur vulcanization are summarized (Fig. 30).

Scorch or premature vulcanization is a technical problem often faced by rubber compounders. Although scorch delay to some extend can be achieved through delayed action accelerators, there are many cases were accelerators alone cannot offer the desired scorch time which is being addressed by the use of prevulcanization inhibitors (Fig. 31).

The postcrosslinking chemistry deals with the decomposition and desulphuration of crosslinks. All the properties of the vulcanizate depends on the balance between the three competing reactions *viz.* the formation of crosslinks, the desulphuration of polysulphidic pendent groups and crosslinks eventually into corresponding monosulphides and thermal decomposition of crosslinks resulting in the formation of dead ends, conjugated structures etc. The use of anti-reversion coagents and introduction of EV cure system has been successfully employed to tackle the detrimental effects of reversion. A summarized idea about the crosslink desulphuration and crosslink decomposition processes is given in Table 4.

ACKNOWLEWDGEMENT

The authors gratefully acknowledge the financial support provided by Council of Scientific and Industrial Research (CSIR), New Delhi to Ms. Anu Mary Joseph.

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