CHAPTER - 1

INTRODUCTION

Of all the materials provided by nature for man to use as a material of construction, rubber is unique. Its characteristics of high reversible extensibility fascinates every enquiring mind. Crude rubber mixture can be easily given any desired shape by forming, calendering, profiling, pressure molding, etc. after adding various additives during compounding in the mixing mill. Various articles of different shapes intended for various purposes can be manufactured by employing different production techniques. Vulcanization, which is the last stage in the processing of the rubber mixture, fixes the mixture in the desired shape by converting it from viscous to a highly elastic state. Vulcanization is a crosslinking process whereby individual molecules of a polymer such as rubber are converted into a three dimensional network of interconnected chains. Rubber as used here, refers to any elastomeric substance. Without vulcanization rubber is simply a random collection of long and flexible chains. The chains retain their own identities and can move relative to each other like a liquid.

Unvulcanized rubber resembles to a solid which is capable of undergoing some degree of elasticity when deformed below a certain strain for a short time. The limited elastic behavior

arises from entanglements existing between the very long randomly coiled chains. This pseudocrosslinking effect, however, does not impart the permanance that is required in a rubber for it to have practical utility. By introducing chemical crosslinks in the elastomer by vulcanization such permanance of structure is effectively attained. These cross-links may be chains of sulfur atoms, single sulfur atoms, C-C bonds, polyvalent organic radicals or polyvalent metals ions.

The discovery of the process of vulcanization in 1834 was undoubtedly a major technological breakthrough. It paves the way for the widespread usage of rubbers that affects practically all walks of life. Rubber composites such as tires could not have been possible without this fundamental invention. Amazingly, the basic concept of vulcanization of rubber with sulfur has withstood the test of time for over 150 years; sulfur still remains the key element in vulcani-zing rubber products.

Apart from sulfur there are other crosslinking agents which are commercially used to vulcanize rubber. These are metal oxides, phenolics, quinones, peroxide etc. Heat is normally required to activate the vulcanization process based on these crosslinking agents.

There are available alternate means of effective vulca-nization without the use of a chemical as crosslinking agent.

These include ultraviolet radiation, Cobalt-60 gamma radiation, linear cathode scanned electron beam irradiation and ultrasonic techniques.

1.1 Additives/Compounding Ingredients

Compounding is a process of incorporation of certain additives into the rubber to produce a homogeneous mixture from which after vulcanization products can be made with desirable physical and chemical properties. The essential aspects of compounding are why and how compounding ingredients are selected and put together to yield a useful rubber compound that will be satisfactory for the intended service. The reason for compounding is to incorporate different additives and other substances necessary for vulcanization to adjust the physical properties like modulus, tensile strength etc. of the vulcanized product to the values required. 'Additives' are collectively known as compounding ingredients and belong to widely different classes. The ingredients are classified according to the part they play in the finished product. The classification is somewhat arbitrary as some of the ingredients may have several functions. Accelerator, curing agents, peptizer, plasticizer, fillers, antioxidant, antiozonants, softener fall within these classifications. In addition to these, there are also a number of other miscellaneous and special agents e.g., dyes, pigments, blowing agents, lubricants etc. which

are used in rubber compounding to obtain special effects. On
an average each rubber compound (recipe) will have twelve to
fifteen ingredients each having specific function to perform.
By varying the type and amount of each ingredient, properties
of the final rubber product can be modified. For example ,
by varying the type and amount of accelerators and antioxidants
we can get a product which will have better heat resistance.
aging and physical properties. There are hundreds of new
rubber chemicals which give specific properties to the final
product.

1.1.1 Accelerators

Vulcanization of rubber by sulfur is an extremely slow
and inefficient process. Besides, the storage stability of
the rubber articles and their resistance to aging are unsatis-
factory according to present day standards. So small amounts
of substances, known as vulcanization accelerators, are added
to the rubber stock during compounding to increase the rate
of vulcanization as well as to have a great effect on the
physical and chemical properties of the finished product.

The first synthetic accelerators were inorganic compounds.
Among the basic salts and metal oxides which are or have been
widely used as accelerators, litharge, lime, magnesium oxide
and zinc oxide are the most important ones. Organic vulca-
nization accelerators were first utilized in the rubber indust

more than fifty years ago [1,2] long after the vulcanization
process itself had become known [1,3,4,5].

Oenslager [1,6] noted in 1906 that the introduction of
organic bases like aniline and thiocarbanilide into rubber
compounds improved the quality of low grade rubber and
accelerated the rate of vulcanization [6]. In 1907, aniline
and thiocarbanilide formed part of rubber tires and technical
rubber articles and thus organic bases were the first vulca-
nization accelerators of rubber [7-8]. The introduction of
organic compounds in the vulcanization of rubber, which
began more than 50 years ago, led to revolutionary changes
in the manufacture of rubber products of every description.
It was one of the most important advances which had taken
place in the industry since the discovery of vulcanization.
First, it was found that organic accelerators enabled vulca-
nization times to be greatly reduced [9]. Second, it was found
that they did more than equalize the different vulcanization
behavior of different types of raw rubber [10]. Gradually,
however, it was found that they had considerably more important
advantages, which made them indispensible in the rubber industry
and enabled the quality of rubber products to be steadily
improved. These benefits arose from the shorter curing time
and considerably lower curing temperatures which made the
vulcanization conditions considerably milder for the rubber.
In addition, the proportions of sulfur required for optimum

physical properties could be reduced, thus improving the
resistance of the rubber goods against aging and preventing
the blooming of sulfur. One important consequence of the
use of smaller proportions of sulfur was a flatter vulcaniza-
tion curve (plateau effect) which meant a longer period of
curing time, thereby reducing the risk of overvulcanization
as well as permitting a thorough vulcanization of large and
thick articles.

The more important accelerators can be classified into
the following types according to their chemical compositions.

Aldehyde-Amines

Aldehyde-amine accelerators, known under various trade
names, are the products of condensation of various aldehy-
des[11-13] with amines. Aldehyde-amine accelerator was first
widely used in 1919. When 1-butanal-aniline condensate
is used in rubber compounding, the degree of vulcaniza-
tion is very high. It is a very good secondary accelerator
and less toxic compared to pure amine type accelerators.

Guanidines

Aryl substituted guanidines like diphenyl guanidine were
the first accelerators of this group of compounds. Diphenyl
guanidine was first applied in industry in 1922.

$$\text{(structure: two phenyl-NH groups connected to } C = NH)$$
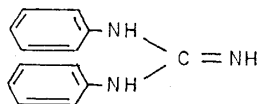
DPG

The guanidines themselves are slow accelerators with rela-
tively slow onset of vulcanization; but they have a powerful
activating effect as secondary accelerators with excellent
mechanical properties of vulcanizates. High modulus, tensile
strength, resilience, outstanding dynamic properties, low
heat build up, and excellent aging properties are some of the
features which make these accelerators so useful even in
modern formulations.

Thiazoles

The year 1921 brought considerable progress in the
development of organic accelerators. C.W. Bedford and L.B.
Sebrell[14,15] in America and G. Bruni and E. Romani[16] in Italy
discovered independently that 2-mercaptobenzothiazole, its
homologues, its disulfides, and its metal salts are very
effective accelerators. 2-Mercaptobenzothiazole and
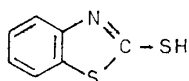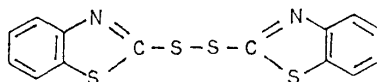
MBT   MBTS

zinc-2-mercaptobenzothiazole have relatively faster onset of

vulcanization and hence the lowest processing safety while

dibenzothiazyl disulfide (MBTS) has a delayed onset of vulca-

nization and so affords higher processing safety. Compounds

with mercapto accelerators generally have a very broad

plateau. They can, therefore, be vulcanized at quite high

temperatures for shorter curing times. 2-Mercaptobenzothiazole

and dibenzothiazyl disulfide are often observed to have a

slight depolymerizing action on rubber, which favorably influ-

ences the processability of the compounds[17].

Sulfenamide accelerators

Compounds containing S-N linkage are, in general,

classified as sulfenamides and are derived by condensing

primary or secondary amines with an -SH containing molecule,

as represented by thiol (-SH) or dithiocarbonates ($-\overset{S}{\overset{\|}{C}}$-SH).

The most widely used sulfenamide accelerators are the

diethyl amine , cyclohexyl amine , dicyclohexyl amine and

morpholyl-derivatives of 2-mercaptobenzothiazole.

The sulfenamides are typical accelerators with a delayed onset of vulcanization. They show a delayed onset of vulcanization compared to dibenzothiazyl disulfide and its combination products. The disubstituted sulfenamide, N,N'-dicyclohexylbenzothiazole-2-sulfenamide (DCBS) was found to give rise to a more sharply defined induction period (decreasing with rising temperature and increasing sulfur concentration), extremely rapid rise in crosslink values and higher crosslinI maxima than the corresponding monosubstituted sulfenamide i.e. N-cyclohexyl benzothiazole-2-sulfenamide (CBS). This sulfenamide is widely used in rubber industry. No other class of
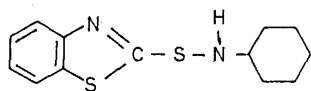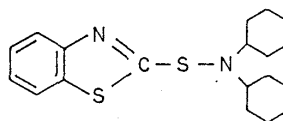
CBS   DCBS

compound so far has been discovered which gives long induction period followed by a rapid crosslinking characteristics of sulfenamide accelerators.

Thiocarbamates

Zinc dithiocarbamates, when used alone ,have a considerably slower rate of vulcanization than ammonium

dithiocarbamates. Zn-dithiocarbamates is used also in solid rubber vulcanization. With Zn-dithiocarbamate, rubber products can be vulcanized in a short time at low temperatures (115-125°C) At higher temperature, as with the sodium dithiocarbamate, the compound has a very narrow plateau and therefore a risk of over-vulcanization. As far as possible, therefore, temperature in excess of 125°C should be avoided.

Thiuram Sulfides

The best known products in this very important class are tetramethyl thiuram monosulfide, tetraethyl thiuram disulfide etc. Thiuram disulfides are fast accelerators with fairly good delayed action. Often thiurams are used not as primary accele-rators but as secondary accelerators, e.g. to raise the rate of

$$CH_3 \diagdown N - C - S - S - C - N \diagup CH_3$$
$$CH_3 \diagup \underset{S}{\overset{\|}{}} \quad \underset{S}{\overset{\|}{}} \diagdown CH_3$$
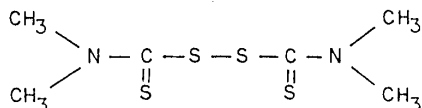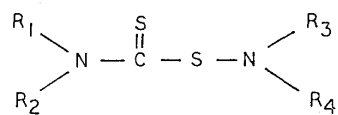
TMTD

vulcanization of mercapto and sulfenamide accelerators. Combi nation with sulfenamides is becoming increasingly important ; it retards the onset of vulcanization to begin with and then gives a particularly fast completion of vulcanization (and hence a steep vulcanization curve) as well as a higher degree of vulcanization.

Thiocarbamoyl Sulfenamides

Certain thiocarbamoyl sulfenamides are powerful, delayed action vulcanization accelerators. These compounds have the general structure as given below. Thiocarbamoyl sulfenamide can give appreciably higher cure rates and cure efficiencies than their benzothiazole sulfenamide analogs.

$$
\begin{array}{c}
R_1 \diagdown \quad\;\; \overset{\displaystyle S}{\underset{\displaystyle \|}{\;}} \qquad \diagup R_3 \\
\qquad N - C - S - N \\
R_2 \diagup \qquad\qquad \diagdown R_4
\end{array}
$$

Thiocarbamoyl Sulfenamide

(R_1, R_2, R_3 & R_4 are alkyl groups)

It is thus seen that common accelerators of vulcanization are basic and acidic compounds comprising nitrogeneous bases and organic sulfur compounds of various types.

1.1.2 Activators

Most accelerators are much more active in the presence of certain substances, called activators, than they are alone. These activators, as such i.e. in absence of an accelerator do not influence vulcanization to any measurable extent. The activating effect of zinc oxide on organic accelerators was studied as early as 1921. The introduction of various metal oxides into rubber mixtures results in a considerable increase in the extent of vulcanization and yiels product with superior mechanical properties[18-19]. It is found that in the

presence of metal oxides the tensile strength and elastic modulus are more than double. But ZnO has no activating effect on certain accelerators like diphenyl guanidine but MgO has. ZnO reacts with polar groups attached to rubber moleculen, which are present initially or introduced by the vulcanization systems.

Barton[20] found that numerous oxidizing agents including mercaptobenzothiazole disulfide (MBTS) could be used in place of zinc oxide. But in general the vulcanizates were of poor quality.

It is considered that the presence of a minimum amount of zinc oxide is necessary even if the accelerator used is a zinc compound[21]. When ZnO is a component in a vulcanizing sulfur-accelerator-fatty acid mix, ZnS might be an expected product because the α-methylenic hydrogens react with sulfur to form H_2S which in turn reacts[22] with ZnO.

Stearic acid

Fatty acids, both saturated and unsaturated, occur in natural rubber and are more common additives in rubber compounds. They are known to contribute various effects. The most commonly recognized ones may be listed as follows, some of them being not essential to vulcanization.

1. Fatty acids are a source of hydrogen and carboxylate ions for buffering the curing system, especially in the presence of ZnO.

2. They have a soulbilizing effect on zinc and other metal ions and organic bases.

3. They are sources of H-atoms for radical reactions, especially the unsaturated acids which also show double bond activity towards curing and aging.

4. They soften natural rubber physically and also may degrade them chemically at curing temperature because of their acid properties.

5. They help in certain mixing operations e.g. in reducing sticking to the surfaces of mixing equipments. They aid in dispersing zinc oxide and may act as a dispersing agent for carbon black.

6. The really important effect of fatty acid is to enhance the effect of ZnO in promoting modulus development (crosslinking) with respect to both rate and final state attained. This behavior is probably limited to the cure period. Thus for a well balanced MBT stock, MBT displaying a very short scorch period, the modulus is enhanced by increased amounts of fatty acid. The rate of curing during the scorch period is decreased by increased amounts of acid and the tendency towards reversion may also be improved.

Consideration of its purity, cost and availability of the various fatty acids, stearic acid is perhaps universally used.

1.1.3 Fillers

Fillers used are of two types, inert and reinforcing. Inert fillers such as various types of whiting, soft clays, barytes, wood flour etc. are used for bulking and cheapening of the vulcanizates. The latter type improves various physical properties of rubber compounds, such as tensile strength, resistance to abrasion and tear, etc. Examples are various carbon blacks, calcium carbonate, calcium silicate etc. Among these reinforcing fillers carbon black plays the most important role as a compounding ingredient for the improvement of various mechanical properties of rubber vulcanizates. Carbon black, which are active rubber fillers, is also known to affect the vulcanization rate in various ways, depending on their identity, pH and other properties. The effect of the amount and nature of carbon black on the rate of exchange of sulfur between mercaptobenzthiazole and elementary sulfur was studied by Blokh and Mamaisur[23]. It is seen[24] that sulfur exchange is accelerated in the presence of carbon black. It is slower in the presence of channel black such as S_{300} EPC (pH 4.3) than in the presence of furnace black such as N 330 HAF (pH 9.0).In the presence

of channel black the vulcanization process is retarded some-
what, while in the presence of furnace black it is accelerated.

1.1.4 Antioxidants

Aging of rubber may be the result of the action of heat,
light, oxygen, ozone, ionizing radiations, repeated deforma-
tions etc. Aging involves free radical chain reactions which
result in both degradation and crosslinking of the rubbers.
In all cases, however, the valuable physical and mechanical
properties are lost, and the aged rubber is no longer suitable
for use. Rubber undergoes complex structural changes during
aging. The viscosities of the rubber solutions also vary
widely during aging depending on the type of accelerator
present.

In order to retard the aging process suitable anti-
oxidants (various amines, phenols and quinones) are added
during compounding of natural and synthetic rubbers.

Miscellaneous Additives

In addition to the above mentioned types of materials
a number of miscellaneous agents e.g. dyes, pigments, blowing
agents etc. are used in rubber compounding to obtain special
effects.

1.2 Binary Accelerator System and their Action in Vulcanization

In modern rubber compounding advantage is frequently taken of combined action of two or more accelerators. If the accelerator combination is properly chosen, not only is prevulcanization prevented, but the vulcanized rubbers also have better physical and mechanical properties. Vulcanization requires less time and may be effected at a lower temperature than when either accelerator is used separately[25-28]. Not all accelerator combinations give a synergistic effect, sometimes the opposite is observed as in case of a mixture of isopropylxanthate with diphenylguanidine.

In early work, the higher activity of binary systems was explained either by the formation of eutectic mixtures or by salt which possessed better solubility in rubber and greater chemical activity[29-30].

It has been known for a long time that amines are powerful activators of the thiazole type accelerators. Jones suspected that the action of bases was similar to that of fatty acids. He found that diphenyl guanidine, like a fatty acid, could act as a transmitter of zinc by forming a soluble zinc diphenyl guanidine compound. Jones' theory can be applied in principle to all accelerators having amine bases soluble in rubber.

Dogadkin and collaborators[31] have tried to generalize the action of different binary accelerator systems. Examining the experimental data concerned with the rate of vulcanization in

the presence of various combinations of the most generally used accelerators, they classified the binary systems with three groups.

1. Systems with mutual activation of the accelerators (combinations of disulfides and mercaptans with nitrogen-containing organic bases and also combinations of disulfides with sulphenamides).

2. Systems with activation of one accelerator only. The vulcanizing activity of such systems does not exceed that of the more active of the two accelerators if used by itself in equimolar amount.

3. Systems with additive effect (combinations of sulfena-mides or disulfides with thiuram monosulfide and also combi-nation of accelerators within the same class of chemical compounds).

A characteristic feature of the performance of the accelerator combination of the first two types (i.e. non additive combina-tions) is that the vulcanization is inhibited in the initial period, after which its rate increases sharply. A slow down of vulcanization during the first 5-10 minutes was observed for chemically different binary systems such as di-2-benz-thiazolyl disulfide, tetramethyl thiuram disulfide, di-2-benzthiazolyl disulfide, N, N-diethyl-2-benzthiazolyl sulfen-amide. This slow down effect may be explained by assuming

that during the initial vulcanization period the accelerators
interact with each other, forming a complex which is less active
as regards to its effect on the kinetics of addition of sulfur
to unvulcanized rubber. In the subsequent stage of the reac-
tion the complex decompose, releasing free radicals which ini-
tiate the reaction between sulfur and unvulcanized rubber and
other processes resulting in crosslinking.

Though the above classifications of binary systems are
very much meaningful, further interpretation of the mechanism
of vulcanization by these systems cannot explain all facts of
binary acceleration. Recent investigations on binary accelera-
tion by some authors provided valuable information. Vulcaniza-
tion can be effectively accelerated in the presence of combina-
tions of an amine salt of dialkyl dithiocarbamic acid and
potassium ethylxanthate or zinc dimethyl dithiocarbamate wit'
DPG[32,33].

It has also been observed that combination of accele-
rators is most effective when (a) the accelerators activate
one another (change in the pH of the system, give better dispersion,
formation of more reactive intermediates etc.), (b) a compound
which is readily dissociated into free radicals is formed by
redox reactions, (c) one or both of the accelerators bring
about a more rapid activation of sulfur (through formation and
decomposition of sulfides) and a more rapid reaction with the
polymer leading to intermolecular crosslinking.

Kemperman[34-37] et al. in their several investigations tried thirty pairs of vulcanization accelerators for synergistic effects by varying the proportion of the accelerators used in two component accelerator systems in NR and SBR stocks. They measured the cure characteristics by vulcameter to determine the effectiveness of the accelerator systems. Of the thirty accelerator pairs tested, twentythree showed positive, three slightly positive and four no observable synergism. The synergism was shown in systems like CBS-ZDC, MBT-TMTD , MBT-ZDC, DPG-ZDC etc.

A 1:1 mixture of mercaptobenzthiazole with hexamethylen. tetramine produces vulcanizates with optimum physical and mechanical properties and with a minimum tendency to scorch[38].

Skinner and Watson[39] studied the binary accelerator systems like CBS-TMTD, MBT-TMTM, MBT-DPG with references to crosslinking efficiency of the system. They found synergistic effect in the above mentioned systems. It is observed that a combination of thiocarbamoyl sulfenamide and benzothiazyl sulfenamide gives higher states of cure, less reversion and a higher percentage of monosulfide crosslinks than when either accelerator is used alone[40]. Maximum synergism was obtained at a molar ratio of about 2 mol of N-oxydiethylene thiocarbamoyl-N'-oxydiethylene sulfenamide (OTOS) to 1 mol of N-oxydiethylene-2-benzothiazyl sulfenamide (MOR). N-Oxydiethylene thiocarbamoyl-N'-oxydiethylene sulfenamide (OTOS) interacts

synergistically with thiazole accelerators[41,42], usually resulting in shortening of actual vulcanization times, good aging and reversion resistance, good compression set and low heat build-up in the conventional vulcanization of NR and SBR stocks. OTOS often gives good storage stability, and processibility at normal and higher temperature. N-Cyclopentamethylene thiocarbamoyl-N'-cyclopentamethylene sulfenamide (CPTCS) and dibenzothiazyl disulfide (MBTS), as binary accelerators in a mixture have been found to provide significant mutual enhanced activity with regard to modulus, tensile strength, hardness and elongation at break in the vulcanization of NR gum stocks[43]. The synergistic activity of the CPTCS-MBTS system is very much dependent upon the accelerator ratios, concentration of sulfur and accelerator, as well as the temperature of vulcanization. Even though the reaction mechanisms of the various accelerators cannot be expressed in terms of one universal equation, they still have a common chemical principle. They all accelerate vulcanization by forming active sulfur fragments and free radicals, including polymeric free radicals, as well as reactive intermediate compounds which readily decompose and are unstable.

As a result of the reaction between these free radicals and sulfur fragments with the chain molecules of the rubber or with polymeric free radicals, tridimen-

sional crosslinking soon occurs at various sites of the chain; this results in far-reaching changes in the mechanical properties of the vulcanizate.

1.3 Dispersion

Inadequate mixing of rubber compounds or the use of unsuitable ingredients can lead to poor dispersion with consequent variation and in some cases failure of the finished product. This is particularly true of accelerators, which are usually added at relatively low temperatures and towards the end of the mixing cycle. As they are very active materials they have a pronounced effect on compound properties. Dispersion-problems due to uneven distribution of accelerator in the compound are relatively easy both to detect and rectify.

Four basic kinds of methods are used to evaluate dispersion of carbon black or other ingredients in rubber viz. optical techniques, electron microscopy, electrical techniques and mechanical techniques. Uneven dispersion of rubber chemicals in the vulcanizate specimen may be detected also by rheometric testing of samples taken from different parts of the compound[44].

Sometimes another type of dispersion problem may be encountered. This can happen when the accelerator forms agglomerates or produce particles in the compound. In this case the particles may or may not be evenly distributed.

The distribution of undispersed particles in the
compound can be improved by additional mixing, and sometimes
putting the compound through a tight nip on the mill which
will help to break up the agglomerates. But this may not be
practical. Sometimes high curing temperatures help to melt
some of the undispersed particles, thus reducing the effect
of poor dispersion.

Dispersion difficulties usually arise when a signi-
ficant proportion of particles in a powder is finer than
one micron.

Roebuck and Moult[44] suggested some points for avoi-
ding the problem of accelerator dispersion :

a) Increase mixing temperatures, e.g. most sulfena-
mide accelerators will melt at mixing temperatures above
$110^{\circ}C$.

b) Use alternative low melting point additives, e.g.
change from thiazole to sulfenamide accelerators.

c) Change order of addition, e.g. any difficultly addi-
tives dispersible *and dispersed early in the mixing cycle.*

d) Increase curing temperatures, e.g. *increased* curing tempera-
ture can be used in non critical compounds to avoid unsightly
spots.

e) In very difficult compounds use predispersions,
e.g. these can be made *by* using high viscosity polymers
which give the best results.

Burnett[45] showed that if a rubber chemical is predis-
persed, it will ensure rapid incorporation into the rubber
compound. This is primarily because accelerators are often
added at the end of a mixing cycle when there is a high
danger of scorch and hence the need for their rapid disper-
sion in order that the batch can be homogenized and cooled
as quickly as possible.

1.4 Vulcanization

The term 'vulcanization' no longer refers to reaction
of rubber with sulfur only, but also with many other subs-
tances whose number is continuously increasing, though sulfur
has remained the principal vulcanizing agent since its early
use by Goodyear and Hancock.

The single most important factor in determining phy-
sical properties is, of course, the degree of crosslinking.
All network properties depend directly or indirectly on
this variable. Vulcanization is a process by which elasto-
meric materials are generally prepared. It consists of the
formation of a three dimensional molecular network by a
chemical which ties together independent chain molecules by
covalent bonds. Vulcanization usually produces network
junctions by the insertion of chemical crosslink s between
polymer chains. The exact nature of these crosslinks is
far from being elucidated and intense experimentation is
still going on in this field. The elucidation of the

mechanism of vulcanization of rubber involving the reaction between sulfur and diene rubbers (natural and synthetic) is also complicated by the fact that/most modern 'curing recipe ' now incorporates, in addition to sulfur and rubber, different compounding ingredients in order to obtain the desired properties. The general contention is that vulcanization is an extremely complex process involving a great variety of different reactions between rubber and sulfur. In the sulfur vulcanization, the basic reaction occurs between the polymer and sulfur. So it would be proper to examine the nature and reactivity of sulfur. By means of infrared spectroscopy Warren and Burwell[46] showed that sulfur exists as S_8 ring and this structure is also retained when it is dissolved in rubber. This has been supported by the studies on diffusion of S^{35} in rubber[47].

The relatively high stability of sulfur is due to the requirement of high energy (about 64 kcal/mol) to split the S_8 ring[48]. This stability of the ring explains the reluctance of sulfur to react. In the vulcanization process accelerators and metallic oxides, acting as promoters, considerably lower the activation energy for a smooth and favorable reaction to occur.

The activated sulfur can exist either in an ionic or in a radical form as shown below[50]:

```
S:S:S      ╱──→Ionic       ────    S:S:S:S:S:S:S:S  (+ ... -)
..  ..    ╱     fission
S   S    ╱
..  ..   ╲
S:S:S     ╲──→Radical      ────    ˙S:S:S:S:S:S:S:S˙
               fission
```
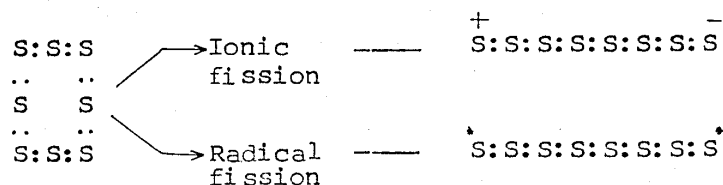
The mode of activation of sulfur has a profound effect upon the reactivity of the polymer.

After being activated by ring splitting, the sulfur is able to react with accelerators, zinc oxide and also with reactive sites on the rubber molecule whether these be α-methylene groups, double bonds, or other sites in such a way that no intermolecular crosslinks are formed initially.

About 4.0-5.5 sulfur atoms are required per chemical crosslink in an unaccelerated vulcanization of rubber, whereas in the presence of accelerators and activators only 1.6 sulfur atoms are consumed on prolonged curing[49]. This means that there occurs a wasteful combination of sulfur during unaccelerated cure and this phenomenon is certainly not desirable as it affects the mechanical properties of the resulting vulcanizates.

In vulcanization, the number of double bonds often remains unchanged, and, instead of addition, the substitution reaction occurs on the α-methylene group to the double bond or to the methyl group of the isoprene unit of natural rubber.

Because of the electron donor activity of the methyl group, which is overcompensated by the electron affinity of the double bond, the α-methylene group in the neighbourhood of the double bond in relation to the methyl group has an extensive electron agglomeration, which makes it particularly reactive.

In those synthetic rubbers, in which the methyl group is absent, the electron affinitive action of the double bond or the action of substituents, such as phenyl group raises the bond strength of the hydrogen atoms in the methylene group, and consequently its reactivity is reduced.

The low crosslink yield in natural rubber when sulfur is used alone is mainly due to the fact that multivalent polysulfide bridges, cyclic sulfides and vicinal bridge links may be formed.

It is now known that several reactions by different mechanisms (radical or ionic) may take place simultaneously or consecutively during vulcanization. There occur primary reactions, in which the vulcanizing agents, accelerators, zinc oxide and possibly fatty acids and rubber hydrocarbons participate to result in unstable intermediate compounds though not in crosslinks. Only subsequently do the cross-linking reactions then take place.
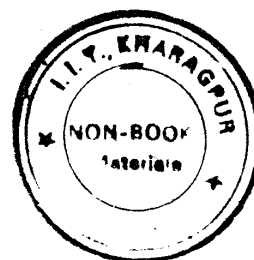
1.4.1   Mechanism of sulfur vulcanization

It has been discussed earlier that elemental sulfur present in the form of an eight-membered ring can be activated either by radical or ionic route so that stable sulfur ring opens up. But whether the former or the latter route prevails during the vulcanization of rubber has not been fully resolved. Farmer and Shipley[51] were among the earlier researchers who made an attempt to elucidate the mechanism of vulcanization of rubber by sulfur only. Through sulfuration experiments conducted on model olefins such as cyclohexene and 1-methylcyclohexene, they proposed a mixed radical and ionic mechanism. This view was later refuted by Bateman et al[52] in favor of an ionic mechanism. Among the model compounds used by Bateman et al was 2,6-dimethyl-2,6-octa-diene, a low mol. wt analog for natural rubber.

Reacting sulfur with 2,6-dimethyl octa-2,6-diene (dihydromyrcene,I), a simple analog of natural rubber, it was possible to isolate a series of different cyclic mono-sulfides as thiacyclohexane (II), thiacyclopentane (III), two unsaturated thiacyclopentanes(IV)and(V),and the conjugated triene (VI)[53-54].

It may be noted that this last compound is at variance with the absence of olefin dehydrogenation observed during the sulfuration of monoolefins, but can be recognized as a direct consequence of the 1,5-diene structure of the olefin.
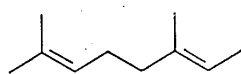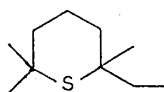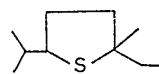
I   II   III
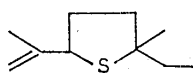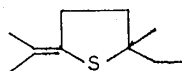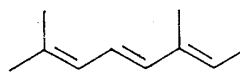
IV   V   VI

In addition to these cyclic monosulfides, intermolecular
sulfur bridges are formed to yield crosslinked larger
molecules (VII) and (VIII).
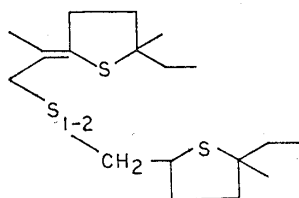
VII
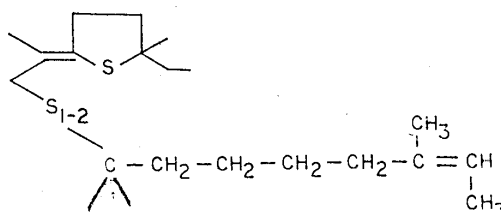
VIII

Electron spin resonance and Raman spectroscopic results

tended to support a predominantly ionic mechanism although

the possibility of a free radical mechanism was not completely

ruled out.

With the progress of the curing time the ratio of cross-

linking sulfur to cyclically incorporated sulfur decreases.

From the findings it can be explained that the reversion

of rubber vulcanizates occurs with the conversion of cross-

linking sulfur into cyclically bound sulfur.

The crosslinking of rubber with sulfur should be regarded

as similar to the reaction which takes place between sulfur

and model substances, especially dihydromyrcene. Here again

the simplest reaction mechanism is that a rubber mercaptan

is formed first, oxidation of which results in the formation

of polysulfides.

$$2 \ RS_xH \xrightarrow[-2 \ H]{\text{oxidation}} RS_x {}^-S_x{}^-R \qquad (1)$$
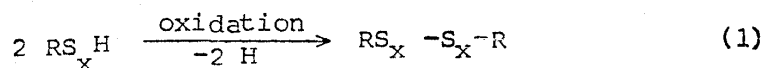
This simple mechanism has been regarded as the most important

crosslinking reaction of rubber[55-57]. Sulfur can also be

used as an oxidizing agent for sulfhydriles.

$$2H - \overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}} - S_xH \ + \ S \ \longrightarrow \ H - \overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}} - S_x - \overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}} - H \ + \ H_2S \qquad (2)$$
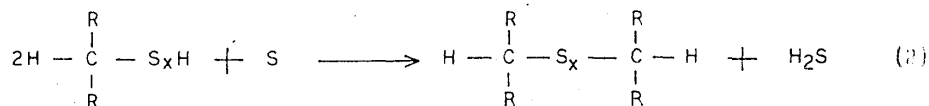
The formation of intermediate rubber mercaptan is, however, not an absolute necessity.

On activation of an S_8 ring bivalent S_8 chain or a lower molecular weight sulfur chain is formed after the ring splitting   which immediately reacts with rubber.

$$
\left[\begin{array}{c} \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} = \overset{}{\underset{CH_3}{C}} - \overset{H}{\underset{H}{C}} \end{array} \right] + \ \dot{S} \cdots \cdots \dot{S} \longrightarrow
$$

$$
\left[\begin{array}{c} \overset{H}{\underset{H}{C}} - \overset{S\cdots\cdots\dot{S}}{\underset{H}{C}} - \overset{}{\underset{CH_3}{C}} = \overset{}{\underset{H}{C}} \end{array} \right] + \dot{H} \qquad (3)
$$
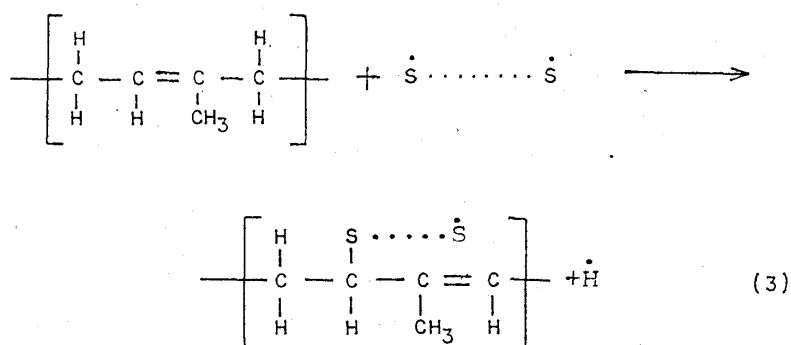
The free sulfur valency reacts with a second active sites on the polymer by radical and/or ionic mechanisms resulting in crosslinking.

$$
\left[\begin{array}{c} \overset{H}{\underset{H}{C}} - \overset{H}{\underset{\underset{\dot{S}}{S}}{C}} - \overset{CH_3}{\underset{}{C}} = \overset{H}{\underset{}{C}} \end{array} \right] + \left[\begin{array}{c} \overset{H}{\underset{H}{C}} - \overset{H}{\underset{}{\dot{C}}} - \overset{CH_3}{\underset{}{C}} = \overset{H}{\underset{}{C}} \end{array} \right] \longrightarrow
$$

$$
\left[\begin{array}{c} \overset{H}{\underset{H}{C}} - \overset{H}{\underset{S}{C}} - \overset{}{\underset{CH_3}{C}} = \overset{}{\underset{H}{C}} \end{array} \right]
$$
$$
\left[\begin{array}{c} \overset{H}{\underset{H}{C}} - \overset{S}{\underset{}{C}} - \overset{}{\underset{CH_3}{C}} = \overset{}{\underset{H}{C}} \end{array} \right] \qquad (4)
$$
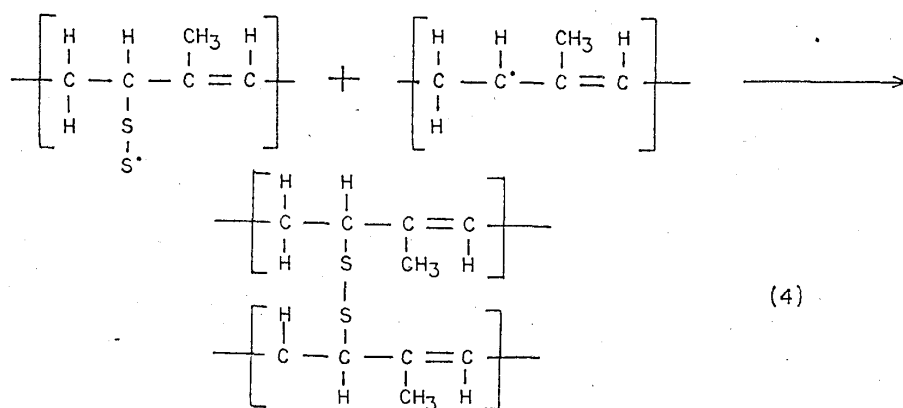
Crosslinking by radical path

$$\left[\begin{array}{c} H \quad H \quad CH_3 \quad H \\ \underset{|}{C} - \underset{|}{C} - \underset{|}{C} = C \\ H \quad S \\ S^- \end{array}\right] + \left[\begin{array}{c} H \quad H \quad CH_3 \quad H \\ \underset{|}{C} - \underset{|}{C} - \underset{|}{C} = C \\ H \quad + \end{array}\right]$$

$$\longrightarrow \qquad \left[\begin{array}{c} H \quad H \quad CH_3 \quad H \\ C - C - C = C \\ H \quad S \\ | \\ \left[\begin{array}{c} H \quad S \\ C - C - C = C \\ H \quad H \quad CH_3 \quad H \end{array}\right] \end{array}\right] \qquad (5)$$
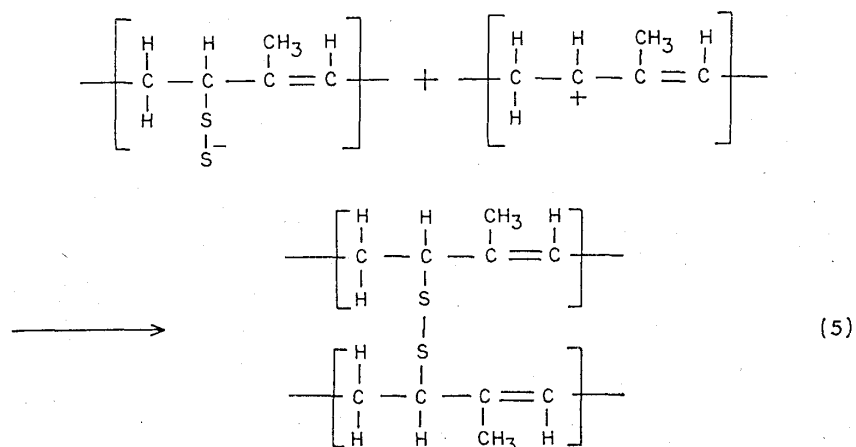
Crosslinking by ionic mechanism

Crosslinks are formed primarily on α-methylene carbon atoms because of the activation by the adjacent double bond and to the electron donor effect of the CH_3 group. This has also been supported by the fact that if methyl iodide is added it is converted to methyl sulfonium iodide in the vulcanizate.[58] According to their model reactions it only appeared possible for thioethers to be added to α-methylene C-atoms.

$$\begin{array}{c} R - C - R \\ | \\ S \\ | \\ R - C - R \end{array} + CH_3I \longrightarrow \left[\begin{array}{c} R - C - R \\ | \\ S - CH_3 \\ | \\ R - C - R \end{array}\right] I \qquad (6)$$
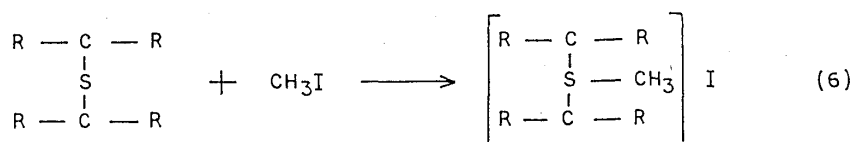
The same reaction is possible also in the case of cyclic sulfur structures[58].

The presence of both intermolecular and intramolecular

sulfur bonds was confirmed by the fact that vulcanization

under identical conditions of two compounds, containing 8. and

2.5 phr sulfur respectively (the latter containing, in addi-

tion to accelerators, zinc oxide and fatty acid), produced

higher modulus in the second compound inspite of the consi-

derably smaller sulfur content[59]. According to Flory and

Rehner[60] the modulus can be regarded as an indication of

the intermolecular bonds which have been formed. The same

reactions with sulfur occur in all 1,5-polyenes as in the

model reactions with dihydromyrcene. Sulfur is absorbed by

polysulfidic bonding in the first, presumably bimolecular,
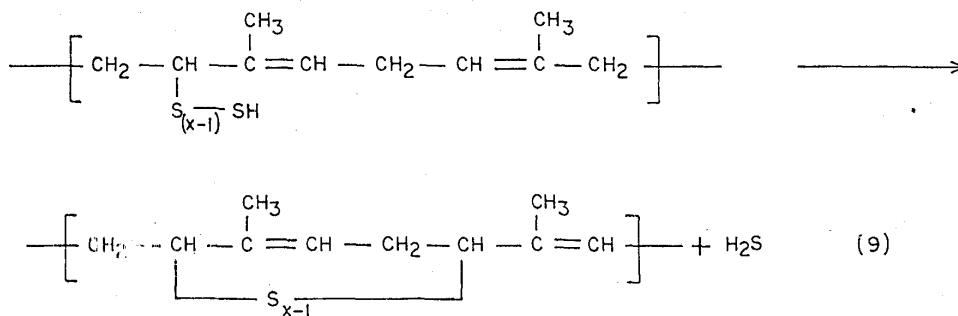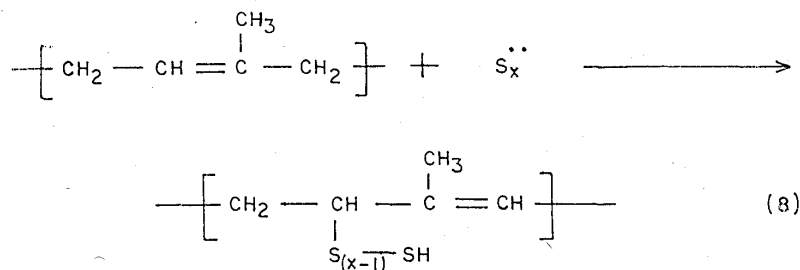
stage of the reaction. The fact that the amount of poly-

$$
\begin{array}{c}
-\!\!\left[CH_2 - CH - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]\!\!- \\
\underset{\displaystyle S_x}{|} \\
-\!\!\left[CH_2 - CH - C = CH - CH_2 - C = CH - CH_2 \right]\!\!- \\
\underset{\displaystyle CH_3}{|} \qquad \underset{\displaystyle CH_3}{|}
\end{array}
\quad\longrightarrow
$$

$$
\begin{array}{c}
-\!\!\left[CH_2 - CH - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]\!\!- \\
\underset{\displaystyle S_{(x-y-1)}}{|} \qquad\qquad \underset{\displaystyle S_y}{|} \\
-\!\!\left[CH_2 - CH - C = CH - CH - C = CH - CH_2 \right]\!\!- \\
\underset{\displaystyle CH_3}{|} \qquad\qquad \underset{\displaystyle CH_3}{|}
\end{array}
\quad + \quad H_2S \qquad (7)
$$
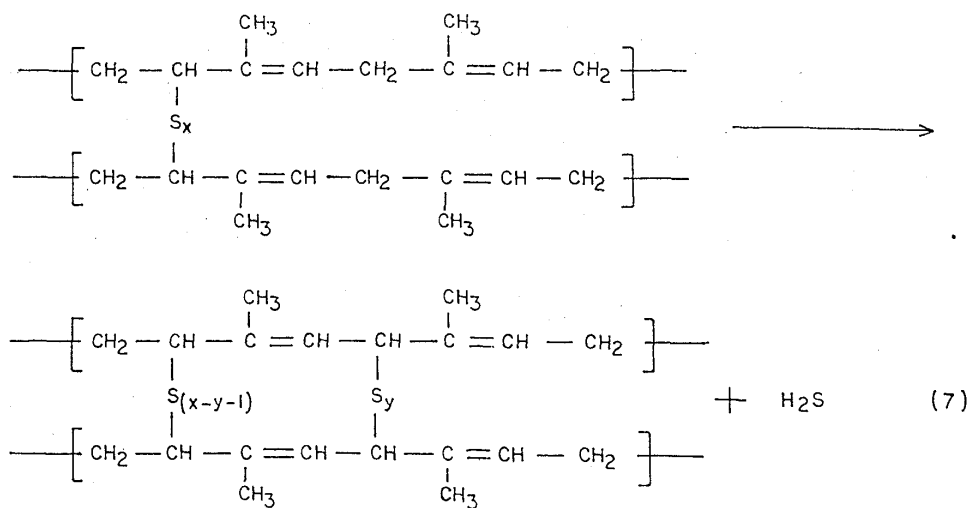
sulfidically bound sulfur reaches a maximum after a certain

reaction time may be due to the occurrence of two conse-

cutive reactions; first, the formation of the polysulfide

and second, its breakdown in the subsequent reaction[61].

Sulfur is first attached as a persulphydride group. Next,

it is added to the double bond, which may take place both

intermolecularly (when a polysulphidic bridge is established)

or intramolecularly when cyclization takes place   (eqs.8-10).

$$-\!\!\left[CH_2 - CH = \underset{\displaystyle \underset{|}{CH_3}}{C} - CH_2\right]\!\!- \;+\; \overset{..}{\underset{..}{S}}_x \longrightarrow$$

$$-\!\!\left[CH_2 - \underset{\displaystyle \underset{|}{S_{(x-1)}SH}}{CH} - \underset{\displaystyle \overset{CH_3}{|}}{C} = CH\right]\!\!- \qquad\qquad (8)$$

$$-\!\!\left[CH_2 - \underset{\displaystyle \underset{|}{S_{(x-1)}SH}}{CH} - \underset{\displaystyle \overset{CH_3}{|}}{C} = CH - CH_2 - CH = \underset{\displaystyle \overset{CH_3}{|}}{C} - CH_2\right]\!\!- \longrightarrow$$

$$-\!\!\left[CH_2 - CH - \underset{\displaystyle \overset{CH_3}{|}}{\underset{\displaystyle S_{x-1}}{\underline{\qquad C \qquad}}} = CH - CH_2 - CH - \underset{\displaystyle \overset{CH_3}{|}}{C} = CH\right]\!\!- + H_2S \qquad (9)$$

$$\left[CH_2 - CH - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH \right] + \left[CH_2 - CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 \right]$$
$$\underset{\underset{\displaystyle SH}{|}}{\overset{\displaystyle S_{x-1}}{|}}$$

$$\longrightarrow \quad \left[CH_2 - CH - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH \right] \quad + H_2S \qquad (10)$$
$$\overset{\displaystyle S_{x-1}}{|}$$
$$\left[CH_2 - CH - C = CH \right]$$
$$\underset{\displaystyle CH_3}{|}$$
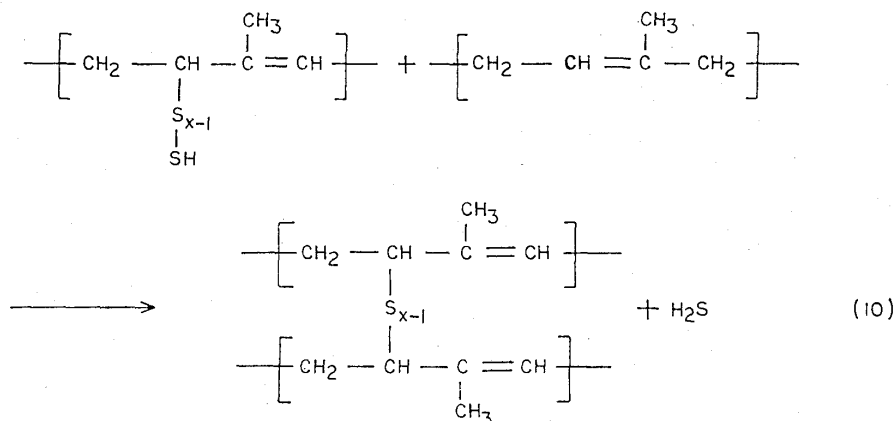
The addition reaction referred to above is very fast, for the crosslinking and the reduction of the sulfur concentration appear to take place at the same speed[62]. The progress of the reaction between the rubber hydrocarbon and sulfur, which leads to simple crosslinking, is shown in eqs. 11-14.

$$\left[CH_2 - CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 \right] + \overset{..}{\underset{}{S_x}} \longrightarrow \left[CH_2 - CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{.}{C}H \right] + \overset{.}{S_x}H \qquad . (11)$$

$$\left[CH_2 - CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{.}{C}H \right] + S_8 \longrightarrow \left[CH_2 - CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH \right] + \overset{..}{S}_{8-x} \qquad (12)$$
$$\underset{\underset{\displaystyle S_x}{.}}{|}$$

$$\left[CH_2-CH=\underset{\underset{\overset{|}{S_x}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \right] \quad + \quad \left[CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2 \right]$$

$$\longrightarrow \quad \left[CH_2-CH=\underset{\underset{\overset{|}{S_x}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH \right]$$

$$\left[CH_2-\overset{|}{CH}-\overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}-CH_2 \right] \qquad\qquad (13)$$

$$\left[CH_2-CH=\underset{\underset{\overset{|}{S_x}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH \right] \quad + \quad \left[CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2 \right] \longrightarrow$$

$$\left[CH_2-\overset{|}{CH}-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}-CH_2 \right]$$

$$\left[CH_2-CH=\underset{\underset{\overset{|}{S_x}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH \right] \quad + \quad \left[CH_2-CH=\overset{\overset{CH_3}{|}}{C}-\overset{\cdot}{CH} \right]$$

$$\left[CH_2-\overset{|}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2 \right] \qquad\qquad (14) \ .$$
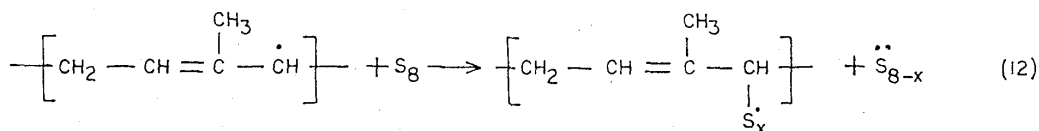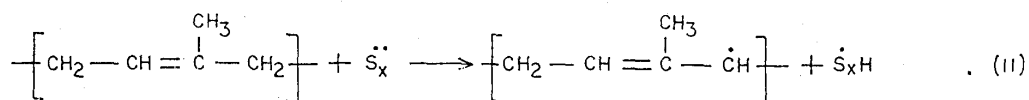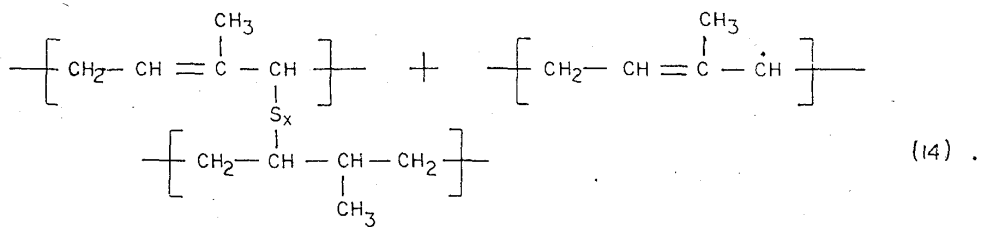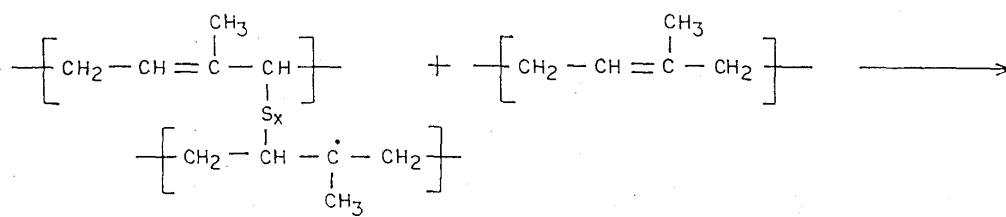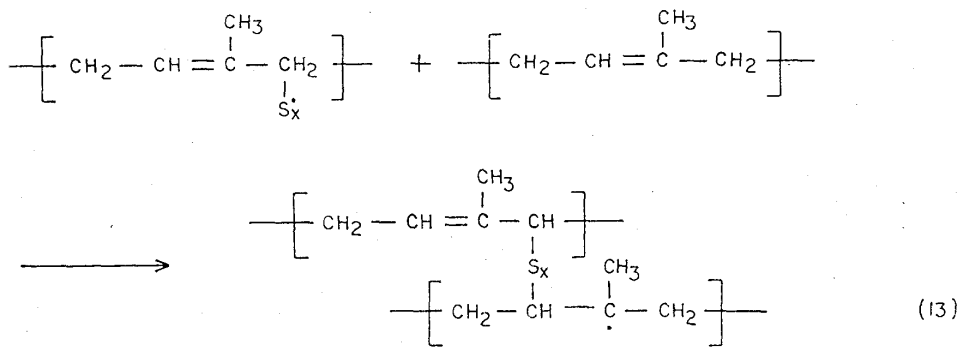
A typical structure of accelerator-free sulfur vulcanizates is the following[63]
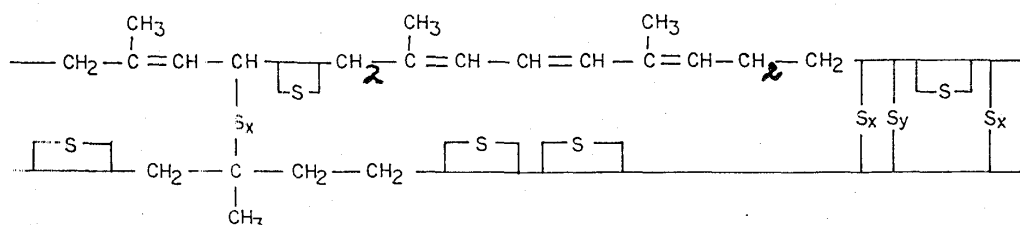
1.4.2 Mechanism of accelerated sulfur vulcanization

In the process of rubber vulcanization, the organic accelerators undergo complex transformations through decomposition and reconstitutions of new active compounds, and also by reacting with sulfur, hydrogen sulfide, functional group of carbon blacks, rubber molecules and other components of rubber mixture. The use of modern instrumental methods (isotopic exchange of sulfur atoms, electron paramagnetic resonance spectroscopy etc.) made it possible to gain considerable knowledge of the mechanism of acceleration of rubber vulcanization by organic reagents.
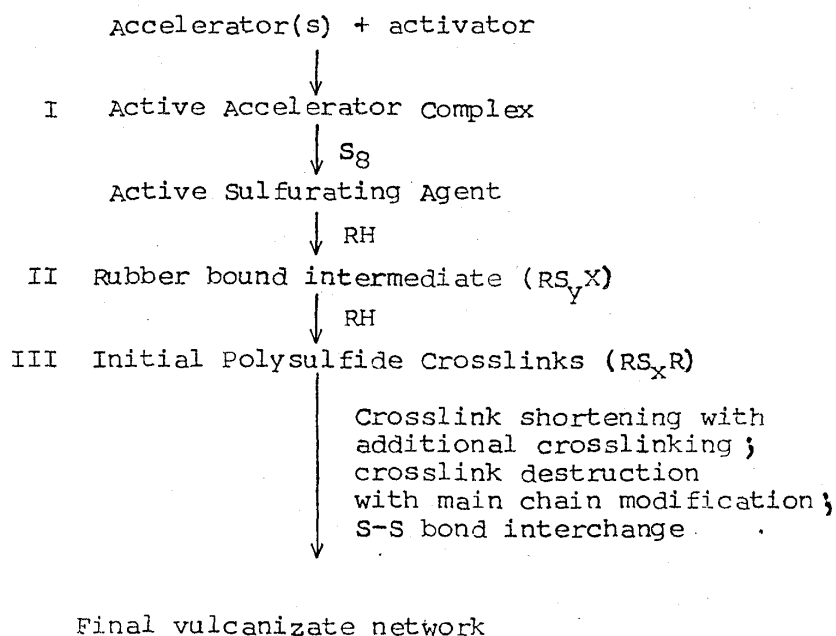
The reaction mechanism of organic accelerators is complex and varied and cannot be described by any one general type of equation. The detailed mechanism of action of the different accelerators will naturally be different. Many theories of the effect of accelerators on vulcanization have been suggested.

None of these is of a general nature; practically, there is an
individual theory for each type of accelerator.

Vulcanization of rubber by sulfur in the presence of an
accelerator or a combination of accelerators in general is now
widely accepted as occurring according to a mixed ionic and
radical mechanism[64].

An outline reaction scheme for the course of sulfur
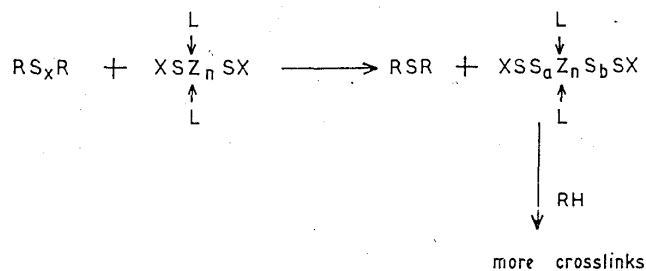vulcanization of NR is now generally accepted[63].

$$Accelerator(s) + activator$$

I   Active Accelerator Complex
    $\downarrow$ S_8
    Active Sulfurating Agent
    $\downarrow$ RH

II   Rubber bound intermediate (RS_yX)
     $\downarrow$ RH

III   Initial Polysulfide Crosslinks (RS_xR)

Crosslink shortening with
additional crosslinking ;
crosslink destruction
with main chain modification ;
S-S bond interchange

Final vulcanizate network

$\underline{/}$ R - Rubber chain, H - Usually an allylic hydrogen atom

X - Accelerator residue $\underline{/}$

The critical features of this scheme were the identification
of an accelerator terminated polysulfidic pendent group as the

rubber bound precursors to crosslinks and the postulation that
the initially formed crosslinks were polysulfides which subse-
quently u derwent a number of competing reactions. Since the
scheme was first proposed, further evidence for the existence
and identity of the rubber bound intermediates has been
obtained[65-67] ; but there is as yet no general agreement on
the chemical nature of the active sulfurating agent in parti-
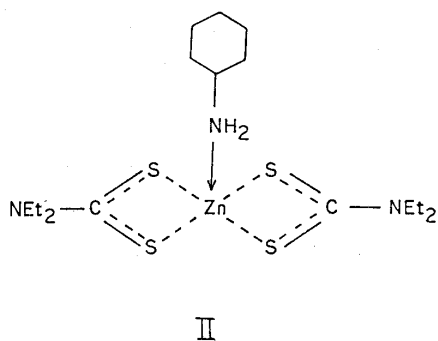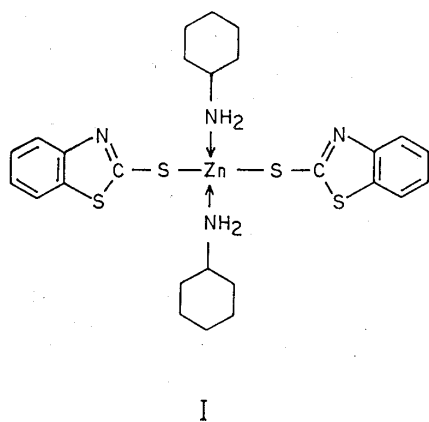cular, as to whether it contains zinc or not[68-69] .

In the transformation of the initial polysulfide network
into the more complex 'final' network present in the vulcani-
zate, two principal reactions were identified.

The first reaction is desulfuration (Reaction 1) giving
rise to crosslink shortening and leading eventually to mono-
sulfide crosslinks. This reaction was shown to be affected
by zinc complexes derived from the accelerator (or sulfur donor)
and the zinc compounds present in the rubber mix.

$$RS_xR \;+\; XS\overset{\underset{\displaystyle L}{\downarrow}}{\underset{\underset{\displaystyle L}{\uparrow}}{Z}_n}SX \longrightarrow RSR \;+\; XSS_a\overset{\underset{\displaystyle L}{\downarrow}}{Z}_nS_bSX$$

$$\downarrow RH$$

more crosslinks

L = Ligand

X = Accelerator residue

I

II

I and II are formalized structures and represent the stochio-
metry but not necessarily the actual structures of the complex.
The sulfur removed from the polysulfides is able to sulfurate
more olefin to form additional crosslinks.

The second reaction is the thermal decomposition leading
to cyclic,monc and disulfide, conjugated diene and trienes in
the rubber backbone, and zinc sulfide. Monosulfide[70] crosslinks
were found to be resistant to such decomposition upto about 170°C.
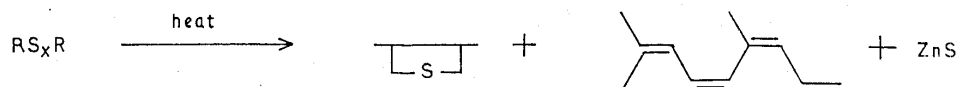

The balance between these two reactions was found to determine,
in a large measure, the type of vulcanizate network formed. If
the concentration of Zn-accelerator-thiolate complexes such
as I and II in the rubber is high, the polysulfide crosslinks

are desulfurated rapidly to stable monosulfidic ones and a heat
resistant network with a high degree of crosslinking is
formed. This is the so called efficient vulcanization
system. If the zinc complexes are present in low concen-
tration or are insufficiently soluble, desulfuration is
slow and, unless the vulcanization temperature is low, the
polysulfide crosslinks suffer thermal decomposition with
consequent modulus reversion and extensive modification of the
main chain (conventional or inefficient vulcanization).

The concentration of zinc-accelerator-thiolate
complexes in the rubber is not the only factor determining
the balance of the two reactions in NR. Both the rate of
desulfuration of polysulfide crosslinks and the rate of
their thermal decomposition depend upon the positions of
attachment of the sulfur chains to the backbone rubber
chains and the detailed structure of the hydrocarbon at
the ends of the crosslinks. In the course of normal accele-
rated vulcanization, there are three different positions of
attack on the polyisoprene backbone; two of these are
methylene groups in the main chain (labelled d and a in III) and
the third is the side-chain methyl group (labelled b in III).
Direct analysis of the distribution of the sites of attack
cannot yet be made on actual rubber vulcanizates, and infor-
mation had to be obtained solely by sulfuration of the model
olefin 2-methyl-2-pentene and more recently 2,6-dimethyl-2,

6-octadiene. The former (IV) models the α-methylic site but
only one of the α-methylenic sites of polyisoprene; the latter
(V) models all three sites. But at the present time these are
not all supported by the synthesis of relevant studies.
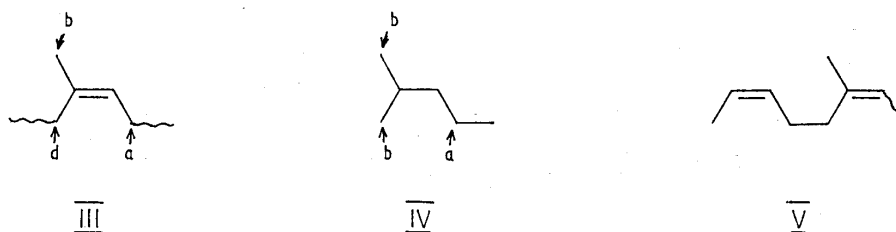
Because allylic rearrangements are common in subsequent reac-
tions of the sulfurated rubber, sulfur substituents appear not
only on allylic carbon atoms but on isoallylic carbon atoms also.

1.4.3 Type of crosslinks in rubber vulcanization and the
     influence of the nature of crosslinks and the crosslink
     density on the mechanical and thermal (aging) properties
     of vulcanizates)

In designing a vulcanizate for a particular application the
following factors are to be carefully manipulated. These are
(i) selection of a polymer to suit the end uses of the product,
(ii) selection of antidegradants to confer protection in service,
(iii) ultimate cost of the product, and (iv) selection of cura-
tives to suit the processing/curing conditions.

The single most important factor in determining physical
properties is, of course, the degree of crosslinking. All

and the presence of other rubber bound side products of vulca-
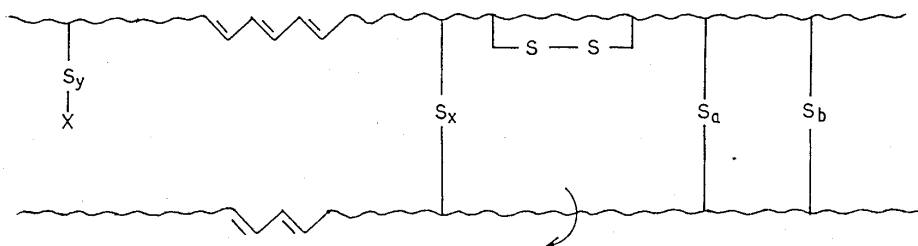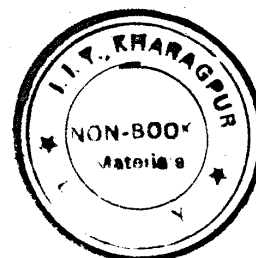nization influence physical properties.

Figure -1.1

Generalized structure of a sulfur vulcanizate of a diene rubber,

a, b, x,) = 1-6, x = accelerator residue, e.g. 2-benzthiazolyl,

dialkylth ocarbamoyl etc. curved arrow signifies cis-trans

isomerization.

In general, diene rubbers form not only mono, di and
also
polysulfidic crosslinks, but pendent sulfidic groups terminated

by an accelerator residue, cyclic sulfides, conjugated diene

and triene units, cis-trans isomerized olefin units and viscinal

crosslinks (Fig.1.1)

Sulfur vulcanizing systems normally form di- and poly-

sulfidic species which are not only thermally fugitive but are

highly susceptible to nucleophilic, electrophilic and free

radical attack.

network properties depend to some extent on this variable

although not always in a straightforward way (Table 1.1).

Table 1.1

Influence of Degree of Crosslinking on Physical Properties

of Vulcanizates

Property	Change with increase in degree of crosslinking
Properties dependent only on the degree of crosslinking	
Stiffness (modulus)	increases
hardness	increases
Properties partly dependent on degree of crosslinking	
breaking elongation	decreases
resilience	increases
heat build up	decreases
solvent swelling	decreases
creep, stress relaxation	decreases
set	decreases
abrasion resistance	increases
infatigue cracking	increase
tensile strength, tear strength	increases, then decreases
lower temperature crystallization	decrease in rate

In the case of sulfur vulcanization also, the position
is further complicated because the nature of the crosslink

Type of linkages in rubber network	Bond energies KJ/mol
$-C-S_x-C$, $(x>2)$	268
$-C-S_2-C-$	268
$-C-S-C-$	285
$-C-C-$	352

Di- and especially polysulfidic crosslinks not only display poor thermal aging resistance but, as a consequence of their high chemical reactivity, affect other physical properties (Table 1.2) also.

Table 1.2

Influence of Di- and Polysulfidic Crosslinks on Vulcanizate Properties

Property	Change with increase in proportion of di- and polysulfides
creep, stress relaxation	increases
set	increases
incremental swelling	increases
tensile strength, tear strength	increases
resilience	increases
fatigue failure	decreases
heat resistance	decreases
thermal aging resistance	decreases

Table 1.3

Influence of Main-Chain Modifications on the Properties of

Vulcanizates

Property	Change with increase in degree of modification		
	Olefinic[a]	Cyclic sulfide	Pendent group
resilience	decreases	decreases	
strength[b]	decreases	decreases	little effect
fatigue failure	decreases	decreases	little effect
swelling in hydro-carbon oil	decreases	decreases	little effect
oxidative aging resistance	decreases	decreases	decreases
low temperature crystallization	rate decreases	rate decreases	decreases

[a] Includes conjugated diene and triene groups and cis-trans isome. ed units

[b] Especially high-temperature strength