

Polymer Science

Polymer Additives and Compounding

Additives for Rubbers

Dr. Utpal Kumar Niyogi
Deputy Director
Division of material Science
Shri Ram Institute for Industrial Research
19, University Road
Delhi – 110007

(23.07.2007)

CONTENTS

[Introduction](#)

[Vulcanizing agents](#)

[Accelerators](#)

[Activators](#)

[Retarders](#)

[Fillers](#)

[Antidegradants](#)

[Softeners](#)

[Peptizers](#)

[Colours and Pigments](#)

[Tackyfyng agents](#)

[Blowing agents](#)T

Key Words

Vulcanization, Recipe, Crosslink, Pendant, Hinder, Scorch, Synergistic, Reinforcement, Cluster, Structure, Aggregate, Agglomerate, Nerve, Hysterisis, Tack

Introduction

In its original state an elastomer is generally not very strong, does not maintain its shape after a large deformation, can be very sticky having even its consistency as chewing gum, has limited resistance to solvents and is prone to attack by oxygen, ozone etc. In a nutshell, useful articles cannot be made from it without modification. It is therefore necessary to blend an elastomer with certain additives to optimize properties to meet a given service application or set of performance parameters. This process of blending of various ingredients with elastomers, each having a specific function either in processing, vulcanization or end use of the product is known as 'compounding' and the formulation thus developed is a 'recipe'.

All the ingredients used are normally given in amounts based on a total of 100 parts of the rubber and used with a notation 'phr'. Thus when comparing various recipes, the effects of varying any ingredient used is easily recognized when the physical properties or processing parameters are compared. Product performance requirements will dictate the initial selections of the compounding ingredients. These additives must be environmentally safe, meet occupational health and safety requirements, be processable in the product manufacturing facilities and be cost effective.

Compounded rubber has many unique characteristics not found in other materials, such as dampening properties, high elasticity and abrasion resistance. Hence rubber has found use in applications such as tires, conveyor belts, large dock fenders, building foundations, automotive engine components, hose, shoe soles and a wide range of domestic appliances. The major classes of additives are:

- | | |
|-----------------------|-------------------------|
| a) Vulcanizing agents | g) Softeners |
| b) Accelerators | h) Peptizers |
| c) Activators | i) Colours and Pigments |
| d) Retarders | j) Tackyfying agents |
| e) Fillers | k) Blowing agents |
| f) Antidegradants | |

Each class of the additives will be discussed in this chapter.

a) Vulcanizing Agents

In order for a rubbery polymer to attain an effectively high elastic state, it is necessary to lightly crosslink the highly flexible polymer molecules to prevent them from slipping past each other on application of a stress. In the rubber industry this process is known as 'vulcanization'. Vulcanization increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force by the insertion of crosslinks between polymer chains forming a crosslinked molecular network.

The crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber (mixed with vulcanizing agents) in a mold under pressure.

Ever since the discovery of the process by Charles Goodyear in the USA in 1839 and its exploitation by Thomas Hancock in London from 1843 onwards, it has been the usual practice to vulcanize diene polymers with sulfur although alternative agents such as metal oxides, difunctional compounds and peroxides are also used for specific

elastomers. The most common agent used is sulfur, as it enters into reactions with majority of unsaturated rubbers to produce vulcanizates.

Initially when vulcanization was accomplished by using elemental sulfur at a concentration of 8 parts per 100 parts of rubber (phr), it required 5 hours at 140°C. The addition of zinc oxide reduced the time to 3 hours. The use of accelerators in concentrations as low as 0.5phr. has further reduced the time to as short as 1 to 3 minutes. As a result, elastomer vulcanization by sulfur without accelerator is no longer of much commercial significance. Even though unaccelerated sulfur vulcanization is not of practical importance, its chemistry has been the object of much research and study.

Sulfur is combined in the vulcanization network in a number of ways (Fig 1). As crosslinks, it may be present as monosulfide, disulfide or polysulfide [Fig 1 (a)], but it may also be present as pendant sulfides terminated by moiety X, derived from accelerator [Fig 1(b)], or cyclic monosulfides or disulfides [Fig. 1(c)]. An estimate of the number of sulfur atoms for each crosslink formed has been made; unaccelerated rubber-sulfur vulcanizates may give a figure of 40-45, whilst in the conventional accelerated sulfur vulcanizates this 'inefficiency' figure may drop to 10-15. Special 'efficient' vulcanizing systems can reduce it still further to 4 or 5.

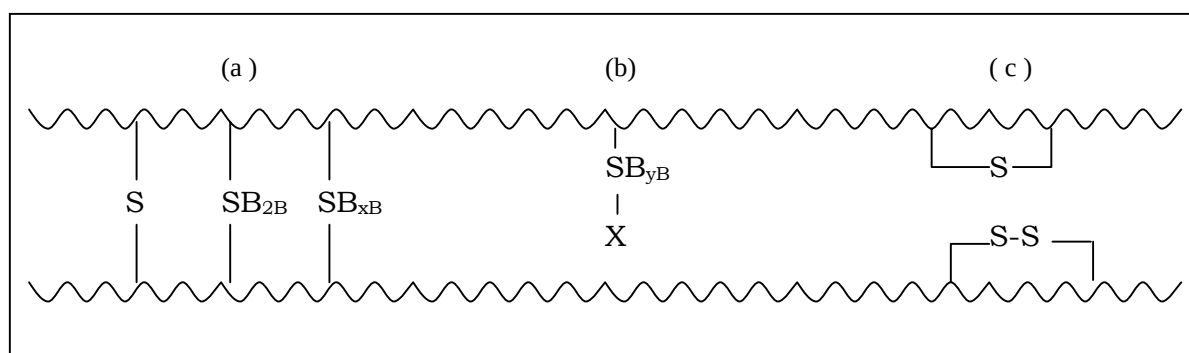


Fig 1. Structural features of a sulfur- vulcanized natural rubber network.

The chemistry of unaccelerated vulcanization is controversial. Many slow reactions occur over the long period of vulcanization. A proposed mechanism involving free radicals is given in fig.2

Accelerators and similar sulfur bearing chemicals can be used for the vulcanization of natural and styrene- butadiene rubbers in recipes using very small amounts of elemental sulfur. Generally in these 'low-sulfur' cures, less than 1 phr of sulfur is used in combination with 3 to 4 phr of the sulfur donor and in some cases no elemental sulfur is added to the recipe.

The compounds used decompose at the vulcanization temperature and release radicals, which combine with the chains to form crosslinks. With these systems, efficient cross linking occurs as most of the sulfur is combined in crosslinks containing one or two sulfur atoms with little or no cyclic sulfur present. Consequently, this form of vulcanization produces products, which resist ageing processes at elevated temperatures much more effectively than those produced with normal curing systems. However, due to the large amounts of the sulfur donors used, these systems are more expensive than normal sulfur cures and are only used when necessary.

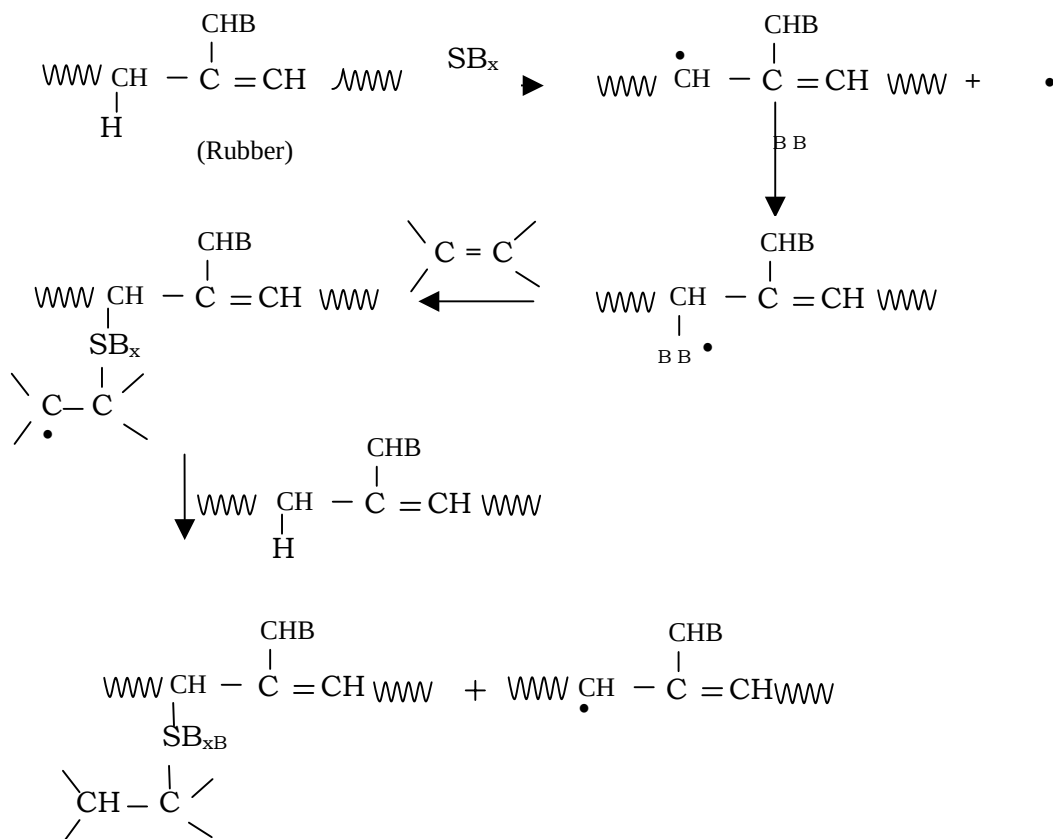


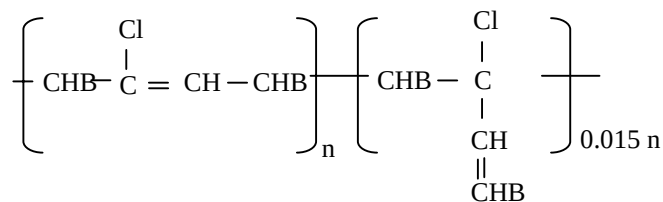
Fig 2. Unaccelerated vulcanization by sulfur, free radical mechanism

Most non-sulfur vulcanizing agents belong to one of the three groups i) metal oxides ii) difunctional compounds, or iii) organic peroxides.

Metal Oxides

Carboxylated nitrile, butadiene, and styrene - butadiene rubbers may be crosslinked by the reaction of zinc oxide with the carboxylated groups on the polymer chains. This involves the formation of zinc salts. Other metal oxides are also capable of reacting in the same manner

In case of neoprenes, the double bond is 'hindered' by the neighbouring chlorine atoms, and so vulcanization with sulfur is not possible. Neoprenes can be represented by the structure:



Neoprenes are generally vulcanized by reaction with metal oxides; zinc oxide is generally used along with magnesium oxide. Neoprenes can be vulcanized in the presence of zinc

oxide alone; however, magnesium oxide is necessary to give scorch resistance. The reaction is supposed to involve the allylic chlorine atom (active chlorine) which is the result of the allylic shift of chlorine atom occurring during small amount of 1,2 polymerization. Fig 3 is given for the vulcanization of neoprene rubber by the action of zinc oxide and magnesium oxide.

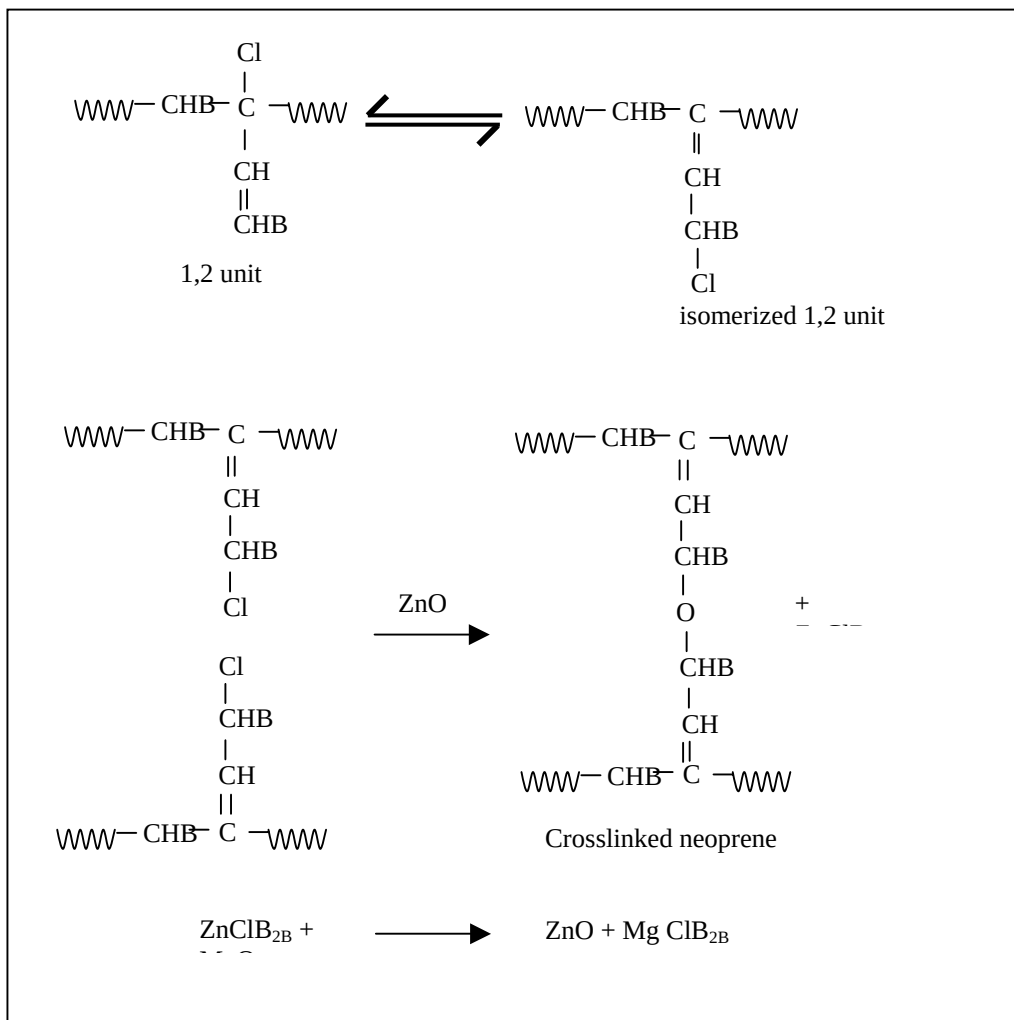
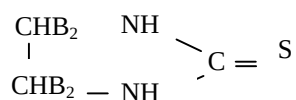


Fig 3. Mechanism of crosslinking of neoprenes by the action of zinc oxide and magnesium oxide

Magnesia is included in the formulation to act as a scavenger for the chlorine atom also. More rapid vulcanization is achieved by the use of organic accelerator eg. ethylene thiourea (ETU),



Difunctional Compounds

Certain difunctional compounds form crosslinks with rubbers by reacting to bridge polymer chains into three dimensional networks. Phenolic resins are used with NR, BR and SBR, quinone dioximes with butyl, and diamines with fluororubbers.

Diene rubbers such as NR, butyl and BR can be vulcanized by action of phenolic compounds, usually disubstituted by $-\text{CH}_2-\text{X}$ groups, where X is OH or a halogen as per the scheme in Fig 4.

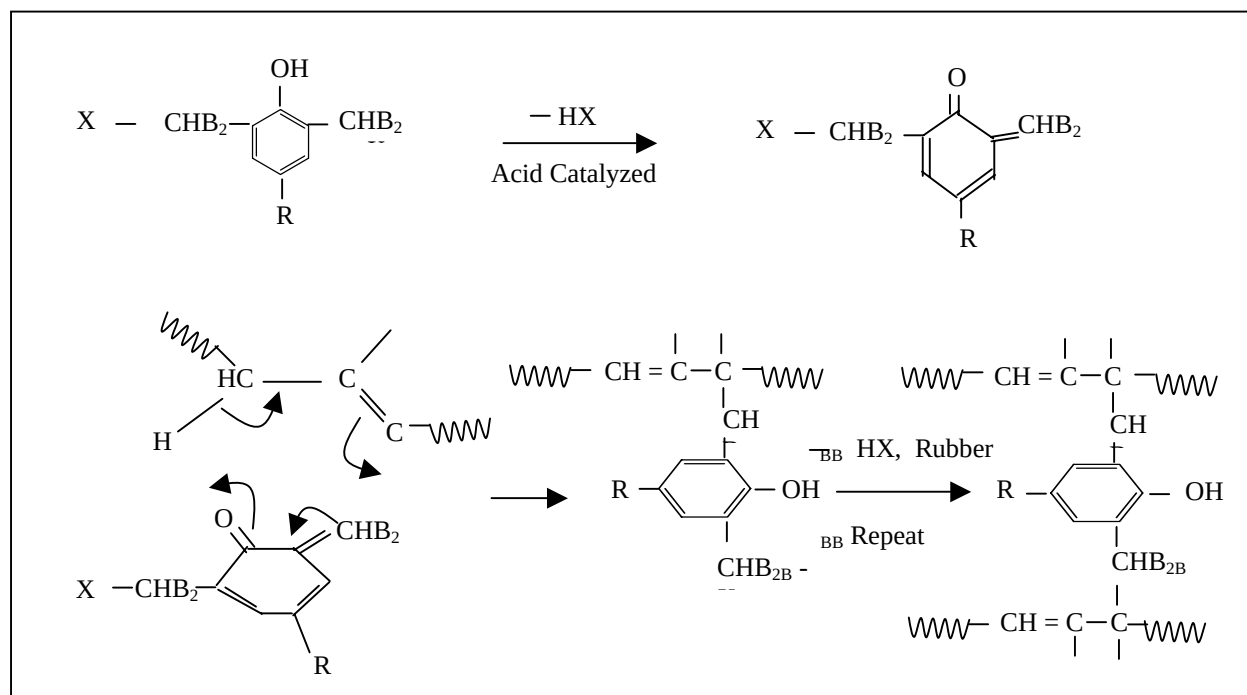
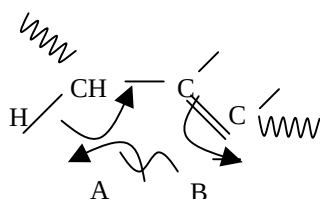


Fig 4. Vulcanization by phenolic curatives

The crosslinking of butyl with p-quinone dioxime proceeds through an oxidation step by an oxidizing agent such as red lead and the reaction has been proposed to take place via the formation of dinitrosobenzene as an intermediate, followed by addition of this intermediate to two molecules of rubber with removal of two hydrogen radicals, which react with the polymer or with more nitrosobenzene when quinone dioxime will be regenerated. The mechanism is given in Fig 5.

The chemical structural requirements for these types of vulcanization is that the elastomer molecules must contain allylic hydrogen atoms. The attacking species from the vulcanization systems must contain sites for proton and electron acceptances in proper steric relationship. This will then permit the following rearrangement, where A is the proton acceptor site and B is the electron acceptor site:



Vulcanizing agent

This is an explanation for the fact that this type of vulcanization is not possible by double bond per se without allylic hydrogens in the elastomer molecules.

The basic ingredients for vulcanization of fluorocarbon rubbers comprise a metal oxide (ZnO, MgO or PbO) with a diamine such as hexamethylenediamine carbamate. The vulcanization probably occurs in three stages: hydrogen fluoride is eliminated in the presence of basic materials to form regions of unsaturation; difunctional agents then react through additions to

double bonds or through substitution of an allylic fluoride atom to form chemical crosslinkages. Finally, during the high temperature post cure, conjugated double bonds are formed which undergo Diels – Alder condensation, and subsequent aromatization leads to very stable aromatic crosslinks.

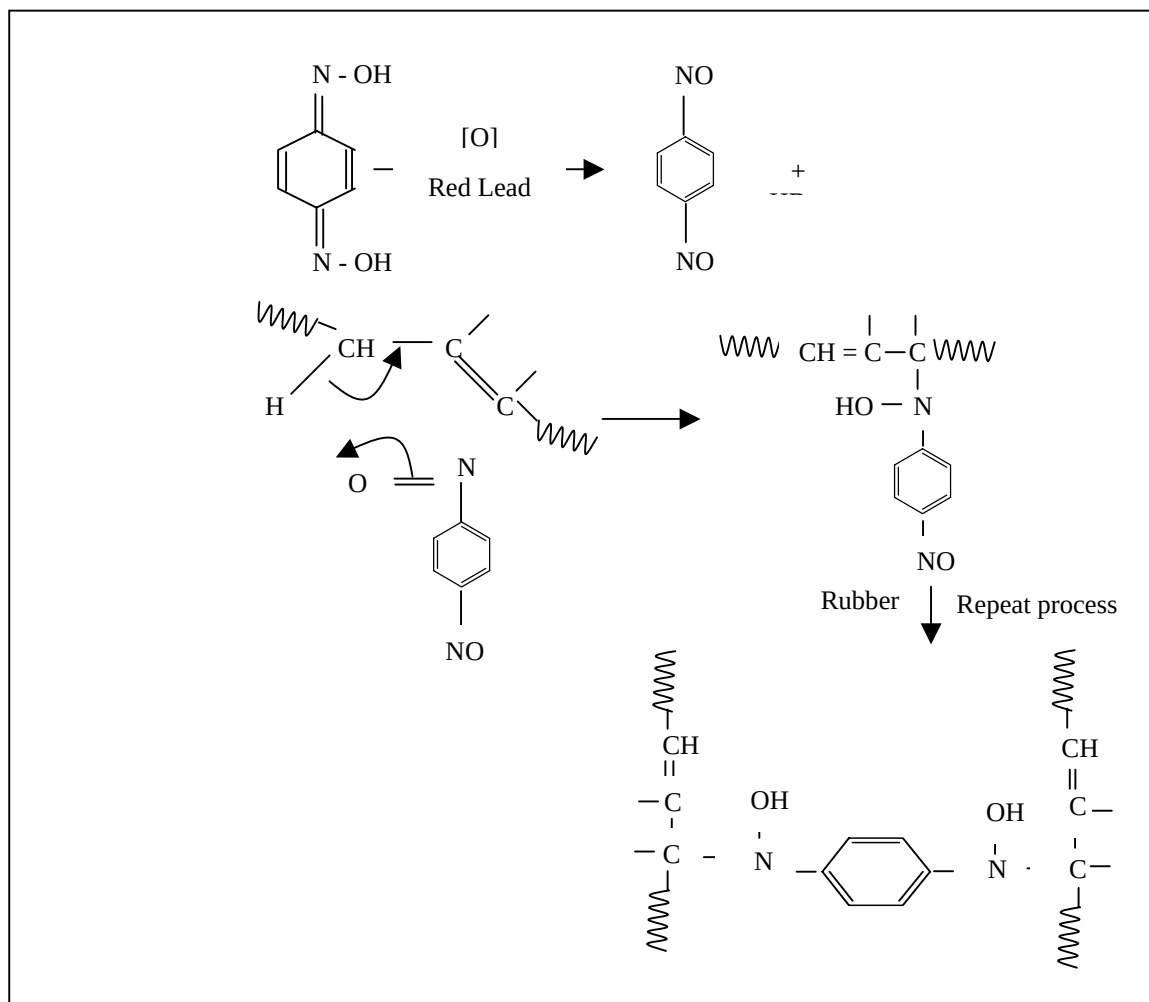


Fig. 5. Vulcanization by quinone dioxime

Organic peroxides

Organic peroxides are useful for crosslinking saturated as well as unsaturated polymers or those which contains no sites for attack by other vulcanizing agents. This type of vulcanizing agent does not enter into polymer chains but produces radicals which form carbon – carbon linkages between adjacent polymer chains. They are useful for ethylene-propylene rubber (EPR) and silicone rubber. They are not generally useful for vulcanizing butyl rubber, poly (isobutylene –co-isoprene), because of a tendency towards chain scission rather than crosslinking when the polymer is subjected to the action of a peroxide.

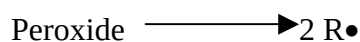
Elastomer derived from isoprene and butadiene are readily crosslinked by peroxides. However, many of the vulcanizate properties are inferior to those of accelerated sulfur vulcanizates. Peroxide vulcanizates of these diene rubbers may be essential when improved thermal ageing and compression set properties are required.

Some widely used peroxides for crosslinking of elastomers are given in Table 1.

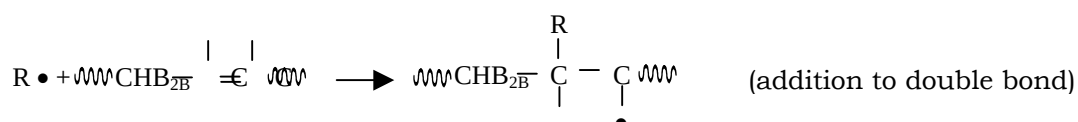
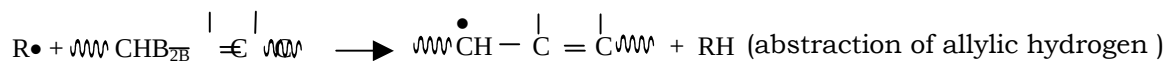
Table 1. Organic peroxides for vulcanization

Chemical Name & Formula	Remarks
$\begin{array}{c} \text{O}=\text{C}-\text{O}-\text{O}-\text{C}=\text{O} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{Benzoyl peroxide} \end{array}$	➤ Used for silicone rubber ➤ Not suitable for olefin rubbers
$\begin{array}{c} \text{O}=\text{C}-\text{O}-\text{O}-\text{C}=\text{O} \\ \quad \quad \\ \text{Cl}-\text{C}_6\text{H}_3-\text{Cl} \quad \text{Cl}-\text{C}_6\text{H}_3-\text{Cl} \\ \text{2,4 Dichlorobenzoyl peroxide} \end{array}$	➤ Used for silicone rubber ➤ Not suitable for olefin rubbers
$\begin{array}{c} \text{CHB}_3 \quad \quad \text{CHB}_3 \\ \quad \quad \\ \text{CHB}-\text{C}-\text{O}-\text{O}-\text{C}-\text{CHB}_3 \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{Dicumyl peroxide} \end{array}$	➤ Used for natural and synthetic olefin rubbers ➤ Also used for silicone rubber
$\begin{array}{c} \text{CHB}_3 \quad \quad \text{CHB}_3 \\ \quad \quad \\ \text{CHB}-\text{C}-\text{CHB}_{2\text{B}}-\text{CHB}-\text{C}-\text{CHB}_{3\text{B}} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{CHB}-\text{C}-\text{CHB}_{3\text{B}}-\text{CHB}-\text{C}-\text{CHB}_{3\text{B}} \\ \quad \quad \\ \text{CHB}_3 \quad \quad \text{CHB}_3 \\ \text{2,5-Di-(t-butyl peroxy)-2,5-dimethyl hexane} \end{array}$	➤ Used for natural and synthetic olefin rubbers ➤ Also used for silicone rubber
$\begin{array}{c} \text{CHB}_3 \quad \quad \text{CHB}_3 \\ \quad \quad \\ \text{CHB}-\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{CHB}_{3\text{B}} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{CHB}-\text{C}-\text{CHB}_{3\text{B}}-\text{CHB}-\text{C}-\text{CHB}_{3\text{B}} \\ \quad \quad \\ \text{CHB}_3 \quad \quad \text{CHB}_3 \\ \text{Di-(t-butyl peroxy)-p-diisopropyl benzene} \end{array}$	➤ Used for natural and synthetic olefin rubbers ➤ Also used for silicone rubbers

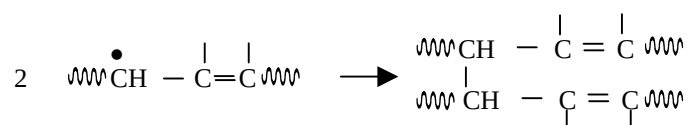
The initiation step in peroxide induced vulcanization is the decomposition of the peroxide to give free radicals:



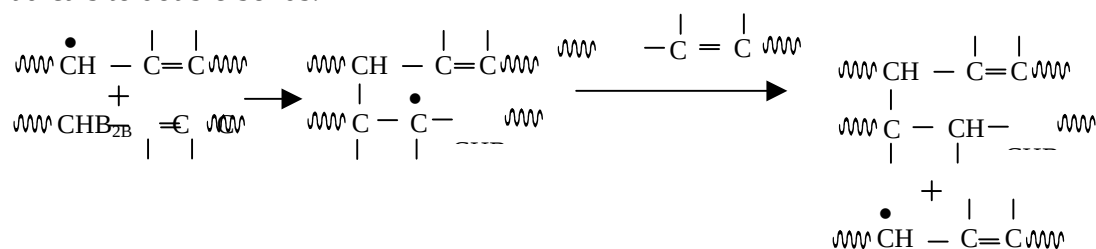
where R is an alkoxy, alkyl or acyloxy radical, depending on the type of peroxide used e.g. benzoyl peroxide gives benzoyloxy radicals, and dicumyl peroxide gives cumyloxy radicals. In case of unsaturated hydrocarbon elastomers such as butadiene or isoprene, the next step is the abstraction of a hydrogen atom from an allylic position on the polymer molecule or the addition of the peroxide – derived radical to a double bond of the polymer molecule.



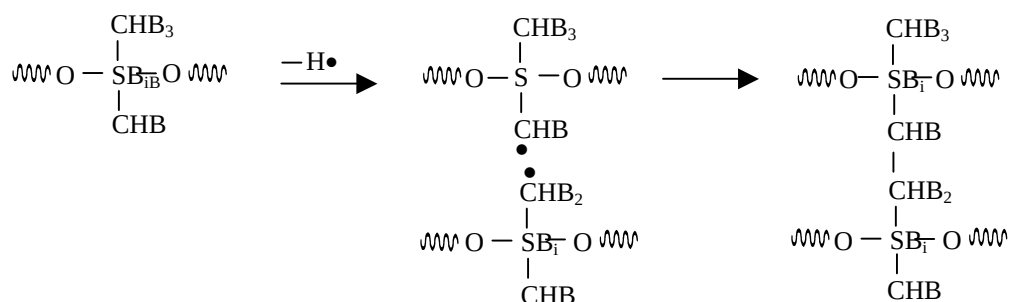
For isoprene rubber, the abstraction route predominates over radical addition, two polymeric free radicals then unite to give a crosslink.



Crosslinks can also form by a chain reaction that involves the addition of polymeric free radicals to double bonds.



In case of crosslinking of saturated dimethyl polysiloxane rubbers, the mechanism is hydrogen atom abstraction due to attack by peroxides on the methyl group of the polymer followed by polymeric radical coupling leading to crosslinking.



When vinyl groups are also present in the polymer, the vulcanization reaction is quicker and

the main attack is undoubtedly at these reactive sites.

b) **Accelerators**

It is now a common practice to use sulfur in conjunction with several other additives. First amongst them are accelerators, which are of many types. In the absence of an accelerator, about 8-10 parts of sulfur is required and the vulcanization can prolong for hours; much of the sulfur is consumed in intramolecular rather than crosslinking reactions. Use of about 1 phr accelerator with 2-3 phr sulfur, enables effective vulcanization to occur not only in shorter time (which in extreme cases may be seconds rather than minutes), but also gives vulcanizates with much better properties.

Though accelerating effect of aniline on sulfur vulcanization was discovered by Oenslager in 1906, its reaction product with carbon disulfide, thiocarbanilide, was first introduced as an accelerator in 1907. Further development led to guanidine accelerators. Thiurams and dithiocarbamates were first used as accelerators in 1919. Though these are the most active accelerators in respect of both crosslinking rate and extent, they give little or no scorch resistance and therefore cannot be used in many commercial processes. Thiurams, dithiocarbamates and xanthates find practical applications in latex technology where problems of scorching are less likely to occur.

It is important that the vulcanizing system should give not only a rapid and effective crosslinking at the desired vulcanizing temperatures but also that it should resist premature vulcanizing (scorching) at the somewhat lower temperature that may be required to mix, extrude, calender or subject the rubber to other shaping operation before crosslinking.

The first delayed action accelerators were introduced in 1925 as 2-mercaptobenzothiazole (MBT) and 2-benzothiazyl disulfide (or 2,2'-dithiobisbenzothiazole) (MBTS). Even more delayed action and yet faster curing vulcanization became possible in 1937 with the introduction of sulfenamides such as N-cyclohexylbenzothiazole-2-sulfenamide (CBS), N-t-butylbenzothiazyl-2-sulfenamide (TBBS) and N-morpholinothiobenzothiazole (MTBT). Further progress was made in 1968 with the availability of a highly effective premature vulcanization inhibitor (PVI), N-cyclohexyl thiophthalimide (CTP) which can be used in small concentration together with sulfenamide accelerators. This additive is frequently used to independently control scorch resistance with little or no effect on crosslinking rate.

The reduction in the amount of time required for vulcanization is generally accomplished by changing the amounts and / or types of accelerators used. There are some common practice used by rubber compounders to arrive at suitable recipes for specific applications:

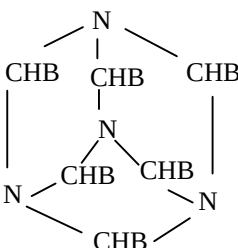
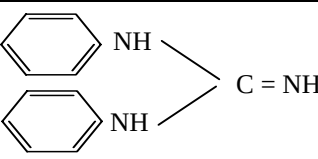
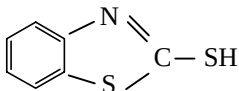
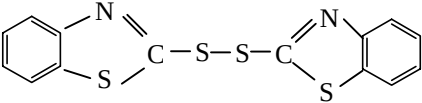
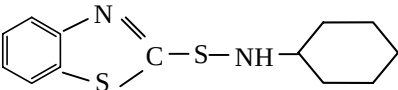
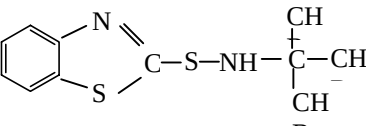
- a) Single accelerator systems (primary accelerators) which are of sufficient activity to produce satisfactory cures within specified time.
- b) Combinations of two or more accelerators, consisting of the primary accelerator which is used in the largest amount, and the secondary accelerator which is used in smaller amounts (10-20% of the total) in order to activate and improve the properties of the vulcanizate. Combinations of this type usually produce a synergistic effect as the final properties are somewhat better than those produced by either accelerator separately. For example, when a mixture of a

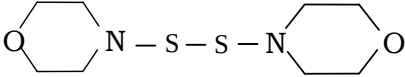
benzothiazole with smaller amounts of a dithiocarbamate or thiuram or amine is used, each accelerator activates the other and high crosslinking rates can be obtained.

- c) Delayed action accelerators, not affected by processing temperatures (thus providing some protection against scorching) but produce satisfactory cures at ordinary vulcanization temperatures.

Table 2 lists some of the principal accelerators in each of the main types with examples and remarks on their properties.

Table 2. Accelerators for sulfur vulcanization

Types	Examples	Remarks
Aldehyde – amines	 Hexamethylene Tetramine (HMT)	➤ Moderately test ➤ Primary accelerator for NR and synthetic rubbers ➤ Occasionally used as secondary plasticizer ➤ Used in self curing adhesive
Guanidines	 1,3 Diphenyl Guanidine (DPG)	➤ Moderately fast ➤ Secondary accelerator for thiazoles, sulfenamides and thiurams
Benzothiazoles	 Mercaptobenzothiazole (MBT)  Dibenzothiazyl disulfide (MBTS)	➤ Fast accelerator ➤ Apt to be scorchy ➤ General purpose ➤ Primary accelerators for NR & synthetic rubber ➤ Delayed action ➤ Safe processing ➤ Moderate cure rate ➤ Primary accelerator for NR & SBR
Sulfenamides	 N-cyclohexylbenzothiazyl sulfenamide (CBS)  N-t-butyl -2- benzothiazyl sulfenamide(TBBS)	➤ Delayed action, semiultra ➤ Safe processing ➤ Moderate cure ➤ For NR and synthetic rubbers ➤ Delayed action ➤ primary accelerator for NR and synthetic rubbers

Types	Examples	Remarks
Dithiocarbamates	$\left\{ \begin{array}{c} \text{CB}_{2\text{B}} \diagdown \\ \text{---} \\ \text{CB}_{2\text{B}} \diagup \\ \text{---} \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S}^- \right\}_2 \text{ZnP}^{++\text{P}}$ Zinc diethyldithiocarbamate (ZDC) $\begin{array}{c} \text{CB}_{2\text{B}} \diagdown \\ \text{---} \\ \text{CB}_{2\text{B}} \diagup \\ \text{---} \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S}^- \text{NaP}^+$ Sodium diethyldithiocarbamate (SDC)	➤ Delayed action ➤ Safe processing ➤ Primary accelerator for NR & synthetic rubbers ➤ Ultra accelerator ➤ Low temperature use ➤ Water soluble ultra accelerator used for latex
Thiurams	$\begin{array}{c} \text{CHB} \diagdown \\ \text{CHB} \diagup \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S} - \text{S} - \overset{\text{S}}{\parallel} \text{C} - \begin{array}{c} \text{CHB}_{3\text{B}} \diagdown \\ \text{CHB}_{3\text{B}} \diagup \end{array} \text{N}$ Tetramethylthiuram disulfide (TMTD) $\begin{array}{c} \text{CHB} \diagdown \\ \text{CHB} \diagup \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S} - \overset{\text{S}}{\parallel} \text{C} - \begin{array}{c} \text{CHB}_{3\text{B}} \diagdown \\ \text{CHB}_{3\text{B}} \diagup \end{array} \text{N}$ Tetramethyl thiurum monosulfide (TMTM)	➤ Ultra accelerator ➤ Safe, especially good for IIR & CR ➤ Excellent for fast press cure ➤ Ultra accelerator ➤ Booster for thiazoles especially for nitrile rubber
Xanthates	$\left\{ \text{CB}_{4\text{B}} - \text{O} - \overset{\text{S}}{\parallel} \text{C} - \text{SP}^- \right\}_2 \text{ZnP}^{++\text{P}}$ Zinc butyl xanthate (ZBX) $\begin{array}{c} \text{CHB}_{3\text{B}} \diagdown \\ \text{CHB}_{3\text{B}} \diagup \end{array} \text{CH} - \text{O} - \overset{\text{S}}{\parallel} \text{C} - \text{SP}^- \text{NaP}^+$ Sodium isopropyl xanthate (SIX)	➤ Low temperature ultra accelerator ➤ Water soluble ultra accelerator for latex work
Morpholines	 4,4' - dithiobismorpholine	➤ Used principally as vulcanizing agent for NR & synthetic rubbers ➤ Provides excellent heat ageing properties

Typically a recipe for the vulcanization system for an elastomer represented by $\text{>CH} - \overset{\text{I}}{\text{C}} = \text{CH} -$ (NR, IR, SBR, NBR, IIR, CIIR and EPDM rubbers), contains:

Zinc oxide	-	2-10 phr
Stearic acid	-	1-4 phr
Sulfur	-	0.5 – 4 phr
Accelerator	-	0.5-2 phr

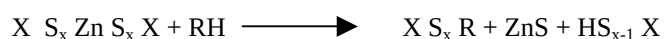
Where zinc oxide and stearic acid are vulcanization activators. Representative recipes for accelerated sulfur vulcanization are given in table 3.

Table 3. Accelerated sulfur vulcanization systems, phr

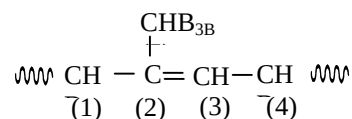
Ingredients	NR		SBR		NBR		I I R		EPDM	
	1	2	1	2	1	2	1	2	1	2
Zinc oxide	5.00	6.00	4.00	3.00	2.00	5.00	5.00	3.00	5.00	2.50
Stearic acid	0.50	0.50	2.00	3.00	3.00	1.00	2.00	2.00	1.00	0.50
Sulfur	2.50	3.50	1.75	2.00	2.00	1.50	2.00	2.00	1.50	0.75
MBTS	0.25	-	-	-	-	1.50	-	0.50	-	-
MBT	-	0.50	-	-	-	-	0.50	-	0.50	0.25
TMTD	0.04	-	-	-	-	-	1.50	1.00	1.50	-
TMTM	-	-	-	-	-	-	-	-	-	0.75
CBS	-	-	1.00	2.00	2.00	1.50	-	-	-	-
DPG	-	-	0.80	-	-	-	-	-	-	-
Cure Temp. °C	141	141	153	153	153	153	153	153	160	165
Cure Time, Min	20	40	25	30	30	25	40	20	20	55

Chemistry of vulcanization with accelerated sulfur

The initial step in vulcanization seems to be the reaction of sulfur with the zinc salt of the accelerator to give a perthio-salt, $\text{XS}_x \text{Zn S}_x \text{X}$, where X is a group derived from the accelerator (eg. thiocarbamate or benzothiazyl groups). This salt reacts with the rubber hydrocarbon RH, to give a rubber bound intermediate and a perthio-accelerator group which, with further zinc oxide will form a zinc perthio-salt of lower sulfur content; this may again be an active sulfurating agent, forming intermediates $\text{XS}_{x-1} \text{R}$. In this way each molecule of accelerator gives rise to a series of intermediates of varying degrees of polysulfidity.



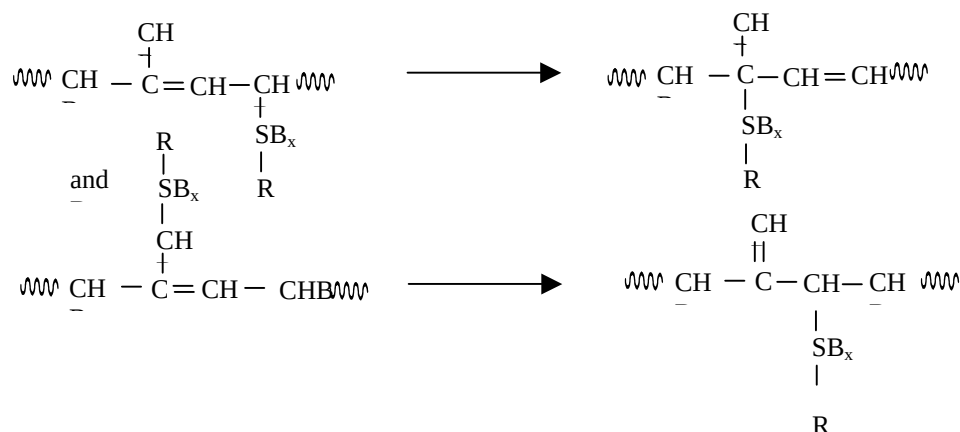
The hydrogen atom which is removed, is likely to be attached to a methylene group in the α -position to the double bond i.e. in natural rubber, the hydrogen atoms at position 4 and 5 are the most labile in this type of reaction,



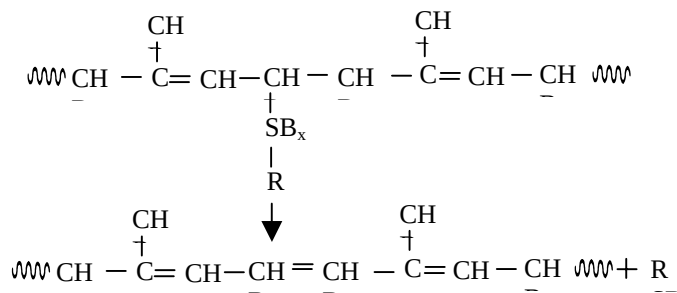
The intermediate XS_xR then reacts with a molecule of rubber hydrocarbon RH to give a crosslink, and more accelerator is regenerated:



Further, on prolonged heating, the degree of polysulfidity of the crosslinks decreases. This process is catalyzed by $\text{XS}_x\text{ZnS}_x\text{X}$ and can result in additional crosslinks. Moreover, the crosslinks which were initially at positions 4 and 5 undergo an allylic shift resulting in new configurations:



Simultaneously, disappearance of crosslinks of the disulfide and polysulfide type occurs,



with formation of conjugated trienes.

This destruction of crosslinks may lead to the formation of the cyclic sulfide though it needs to be investigated in details. In the light of above reactions, it may be concluded that, if the desulfuration proceeds fast as in the case of the recipe NR 100/S 0.4/CBS 6.0/ZnO 5.0/lauric acid 1.0, the final network will be highly crosslinked with mainly monosulfidic bonds and relatively less occurrence of cyclic sulfide or conjugated triene which may be termed as 'efficiently crosslinked'.

On the other hand, if desulfuration proceeds slowly as in the case of the compound, NR 100/S 2.5/CBS 0.6/ZnO 5.0/ Lauric acid 0.7, there are ample possibilities for thermal decomposition leading to loss of crosslinks (reversion) and to modified network. The crosslinks thus survive will be di-or poly-sulfidic and hence will be liable to further decomposition; such a network is ‘inefficiently crosslinked’.

d) Activators

These additives are used to increase the vulcanization rate by activating the accelerator so that it performs more effectively.

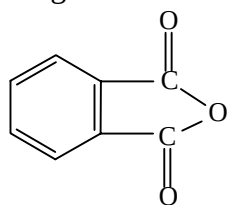
Accelerator activators are grouped as follows:

- (i) **Inorganic Compounds (mainly metal oxides):** Include zinc oxide, hydrated lime, litharge, red lead, white lead, magnesium oxide. Zinc oxide is the most common and is generally used in combination with a fatty acid to form a rubber soluble soap in the rubber matrix. The majority of metal oxide are used in coated or treated forms in order to disperse more readily in the rubber mixtures. Normal use level is 2 to 5 phr.
- (ii) **Organic acids:** Normally used in combination with metal oxides such as zinc oxide; they are generally monobasic fatty acids or mixtures of the types, stearic, oleic, lauric, palmitic and myristic acids, and hydrogenated oils from palm, castor, fish, and linseed oils. The usage of each particular type depends on the accelerator used and the amounts of compounding ingredients present. Normal use level is 1 to 3 phr.

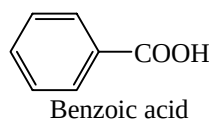
It is believed that fatty acids with zinc oxide (or other metal oxides) give a salt that form intermediate complexes with the accelerators. The complex thus formed is more effective in activating the sulfur present in the mixture, thus increasing the reaction rate.

e) Retarders

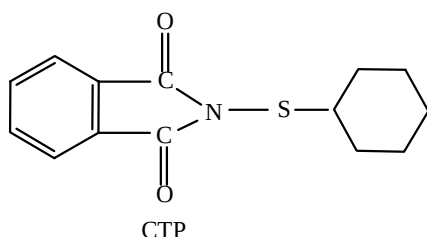
These ingredients are used to reduce the accelerator activity during processing and storage i.e. to prevent scorch during processing and prevulcanization during storage. They should either decompose or not interfere with the accelerator during normal curing at elevated temperature. In general, these materials are organic acids such as salicylic acid, phthalic anhydride (PA) which function by lowering the pH of the mixture thus retarding vulcanization. Presently, though N - (cyclohexylthio) phthalimide (CTP) is the largest tonnage retarder used in rubber industry, N-nitrosodiphenylamine (NDPA) and thiosulfonamides also constitute special class of retarders. The use of retarders should be avoided, if possible, by the proper selection of accelerator – sulfur combination and careful control of processing conditions.



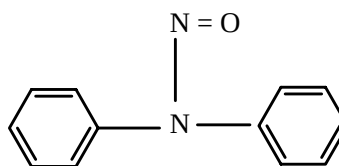
Phthalic anhydride



Benzoic acid



CTP



NDPA

e) Fillers

The use of fillers in rubber is almost as old as the use of rubber itself. It has been observed since long that incorporation of particulate fillers such as carbon black increases the strength of vulcanized rubbers significantly, even more than tenfold by reinforcing it. Thus it is hardly surprising that relatively few applications of elastomers use the polymer in the unfilled state.

Reinforcement has been defined as the incorporation of small particles of materials, known as fillers, into rubber which improves the modulus and failure properties (tensile strength, tear resistance and abrasion resistance) of the final vulcanizate. In general, when a reinforcing agent is added to a base pure gum recipe, that agent imparts greater stiffness and higher ultimate tensile strength than would be obtained by using an equal volume of a common filler, e.g. coarse particle size whiting. The usual quantities of these materials are, 10-50 parts per 100 parts by volume of rubber.

The degree of reinforcement provided by a filler depends on a number of variables, the most important of which is the development of a large polymer-filler interface which can be furnished only by the particles of colloidal dimensions. Spherical particles 1 μm in diameter have a specific surface area of 6 m^2/cm^3 . This constitutes roughly the lower limit of significant reinforcement. The upper limit of useful specific surface area is of the order of 300-400 m^2/cm^3 , and is set by the considerations of dispersibility, processability of the unvulcanized mix, and serious loss of rubbery characteristics of the composites. In general, the finer reinforcing agents require more energy for their dispersion into rubber and the plasticity of the resultant mix is lower. Therefore, it is more difficult to process in operations following mixing. This effect of reinforcing agents on the properties of the rubber - filler mixture is of great practical significance and, for the manufacture of some products, it may be a more important factor in the selection of reinforcing agents than their effect on the vulcanizate properties.

The most common reinforcing fillers are, carbon blacks and silicates. Silicates, clays, whiting (calcium carbonate) and other mineral fillers are used extensively where a high degree of reinforcement is not required. Carbon blacks represent the most important class of reinforcing fillers, both in tonnage and in variety of properties.

Carbon Black

As has already been mentioned, carbon blacks constitute the most important class of reinforcing fillers for rubbers. They are prepared by incomplete combustion of hydrocarbons or by thermal cracking. Most of the carbon blacks used today is made by oil furnace process. A fuel, either gas or oil, is burnt in an excess of air, producing a turbulent mass of hot gases into which the feed stock (generally a residual oil of high aromatic and low asphaltene content) is injected. Reaction to form finely divided carbon is completed within milliseconds and the black is separated from the combustion gases by means of cyclones and filter bags. It is mixed with water in pin-type mixers and then dried in horizontal rotating drums. The yield from the furnace process varies from 25% to 75% of the available carbon, depending upon the particle size; particle diameter ranges from 20 nm to 80 nm. The main types of carbon blacks are: FEF (Fast Extrusion Furnace), HAF (High Abrasion Furnace), SAF (Super Abrasion Furnace) and ISAF (Intermediate Super Abrasion Furnace) blacks. ISAF Black is the one used mostly for treads of passenger car and truck tyres.

In the thermal process, oil, or more frequently, natural gas is cracked at 1300°C in absence of oxygen in a hot refractory surface. The recovery is about 40% - 50% of the available carbon and blacks thus obtained range in particle diameter from 120 nm to 500 nm. Main types of these blacks are: FT (Fine Thermal) and MT (Medium Thermal).

In the now obsolete and virtually extinct channel process, natural gas is burnt in small burners with a sooty diffusion flame and the carbon is deposited by the impingement of the flame on a cool surface such as a large rolling drum or on to slowly reciprocating channel irons. The deposited black is scraped and collected. The yield from this very inefficient process is 5% or less, but very fine blacks can be made, the particle diameters ranging from 9 nm to 30 nm.

The five most important properties of carbon black are: (i) Particle size, (ii) structure, (iii) physical nature of the surface, (iv) chemical nature of surface and (v) particle porosity.

(i) **Particle Size:** The particles of carbon black are not discrete but are fused “clusters” of individual particles. The fusion is especially pronounced with very fine carbon blacks. However, the reinforcement imparted by the black is not influenced by the size of the clusters but greatly by the size of the particles within it. The particle size of various grades of carbon blacks is given in table 4.

Table 4. Particles size of various types of carbon black fillers

Type Name	Type Code	Average particle diameter (nm)
Super abrasion furnace	SAF	20 (Oil furnace)
Intermediate super abrasion furnace	ISAF	23 (Oil furnace)
High abrasion furnace	HAF	23 (Oil furnace)
Fast extrusion furnace	FEF	40 (Oil furnace)
General purpose furnace	GPF	50 (Oil furnace)
Semi-reinforcing furnace	SRF	60 (Oil furnace) 80 (Gas furnace)
High modulus furnace	HMF	60 (Gas furnace)
Fine thermal	FT	180
Medium thermal	MT	470

(ii) **Structure:** The term “structure” refers to the joining together of carbon particles into long chains and tangled three-dimensional aggregates. This aggregation of the particles takes place in the flame during carbon black manufacture. By virtue of their irregular morphology, the aggregates are bulky, and occupy an effective volume considerably larger than that of the carbon itself. ‘High structure’ refers to a high degree of bulkiness, manifested in low bulk density and a high capacity to absorb oil. In rubber technology it is customary to associate high structure of filler with high modulus of vulcanizate. The

thermal process produces blacks with little or no structure. On the other hand, the oil furnace process, using highly aromatic raw materials gives blacks of high structure. Structure is normally measured by determining the total volume of the air spaces between aggregates per unit weight of black. The test is done by measuring the volume of a liquid (Dibutyl phthalate, DBP), required to fill the voids.

The gross morphology of reinforcing silicas is similar to that of carbon blacks, except that fusion tends to be more extensive with precipitated silicas. Clays and other mineral fillers exhibit essentially no structure in the sense considered here.

(iii) Physical nature of particle surface: The carbon atoms in a carbon black particle are present in layer planes. Diffracted-beam electron micrographs have shown that in the blacks with low reinforcing potential (thermal blacks), the layers are highly oriented. They are mainly parallel to the surface, have regular spacing and are quite large with very few defects in their network structure. On the contrary, blacks with high reinforcing potential, show less crystallite orientation. Their particles are more irregular in shape, the layers are much smaller, less frequently parallel and have more defect; this may indicate the presence of significant amounts of 'non-graphitic' carbon.

It is possible that the nature of the carbon atoms at the surface of a particle may affect rubber reinforcement. The carbon atoms can be relatively un-reactive if they are an integral part of the layer plane, more reactive if attached to a hydrogen atom, and very reactive if present as a resonance stabilized free radical.

(iv) Chemical nature of particle surface: Carbon blacks consist of 90%-99% elemental carbon. The other major constituents are (combined) hydrogen and oxygen. The hydrogen comes from original hydrocarbon and is distributed throughout the carbon black particles, oxygen is confined to the surface. The principal groups present are, phenolic, ketonic and carboxylic together with lactones which are chemically combined.

(v) Particle porosity : The surface of carbon black particles are not smooth owing to the attack on them by high-temperature oxidizing gases immediately after their formation. Oxidation takes place at the 'non-graphitic' atoms and can progress into the particle to give pores.

Effects on rubber properties: In general terms, the smaller the 'particle size', the poorer the processability and the higher the reinforcement. The effect of 'structure' is more noticeable on processing properties than on the properties of the vulcanizate. In general, the higher the structure, the stiffer and less 'nervy' the unvulcanized compound and the harder the vulcanized material. The term 'nerve' relates to the elastic recovery from deformation of a raw rubber when a stress is removed from it.

The role of the physico-chemical nature of the surface in the rubber reinforcement is still not fully understood. It has been postulated that a black with high structure gives a high modulus rubber, not because the carbon black agglomerate restrict the crosslinked network but because the high shear forces during mixing break these agglomerates down to give active free radicals capable of reacting with rubber. High structure, however, does not increase either tensile strength or tear resistance – the two properties usually associated with reinforcement. On the other hand, it has been shown that, as a carbon black is progressively graphitized by heat treatment, tensile strength and tear resistance progressively decrease, indicating that the physico-chemical nature of the surface is important.

As far as the chemical nature of the surface is concerned, experimental evidences overwhelmingly point to the existence of chemical bonds or chemisorptive linkages i.e. interactions of higher energy physical adsorption. First, carbon black surfaces contain functional groups capable of reacting with polymer molecules to form grafts during processing and vulcanization and second, numerous reactions of hydrocarbon polymers with carbon black have been demonstrated. In fact, several possible mechanisms exist by which grafts may be formed. For example, carbon blacks chemisorb olefins at vulcanization temperatures. The degree of chemisorption is increased in the presence of sulfur. Shear generated polymeric free radicals have been shown to graft to the carbon black surface during mixing. The crosslinking rate of a rubber is affected by phenolic and carboxylic groups; the black slows the rate of cure in proportion to its total acidity. Channel black for example, is slower curing than furnace black. However, on the whole, the physical adsorption activity of the filler surface is of much more importance than its chemical nature for the mechanical properties of general purpose rubber.

Carbon black particles with 'pores and cracks' have higher surface areas than blacks of similar particle size without such features. This can result in cure retardation owing to the increased adsorption and inactivation of rubber curatives.

Main effects of filler characteristics on vulcanizate properties Although rubber properties are interconnected and relate to the combination of all filler properties, a brief summary of the main influence of each of the four filler characteristics is given below:

1. Smaller particle size (larger external surface area) results in higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity and higher mooney viscosity, with minor effects on extrusion shrinkage and modulus.
2. An increase in surface activity (physical adsorption) results in modulus at the higher strain ($\geq 300\%$), higher abrasion resistance, higher adsorption properties, higher 'bound rubber' (discussed later) and lower hysteresis.
3. An increase in persistent structure (bulkiness) results in lower extrusion shrinkage, higher modulus at low and medium strains (upto 300%), higher mooney viscosity, higher hysteresis and longer incorporation time. Higher electrical conductivity and heat conductivity are found for higher structure blacks. This property is interrelated with surface activity, structure changes on fillers without surface activity (graphitized black) showing the effects indicated above only rather faintly. At constant high activity, the structure effects are most pronounced.
4. Porosity results in higher viscosity and higher electrical conductivity in the case of carbon blacks.

Fillers are known to influence the crosslinking reaction during vulcanization, e.g. the retardation of cure by channel blacks compared to furnace blacks, hard clay as compared to whiting, or some silicas as compared to silicates, all having corresponding particle size. In most cases, the cause of this retardation may be attributed to acidity of the filler indicated by the pH of its aqueous slurry, influencing the kinetics of the crosslinking reaction. The slurry pH of a channel black is 4-4.5, of a furnace black 7-9; for clay and whiting the values are approximately 4.5-5.5 and 8-10; for silica it varies from 3.5-7, whereas silicates approach 10.

The mixing stage in the course of the production of a vulcanizate introduces more variance in the mechanical properties than any other step. The primary process in mixing of carbon black and rubber is the penetration of the voids between the aggregates by the rubber; the primary products are concentrated agglomerates held together by the rubber vehicle. When all voids are filled with rubber, the black is considered 'incorporated' but not yet dispersed. Immediately after and even during mixing of their formation, these concentrated agglomerates are subjected to high shear forces that tend to break them down again into smaller and smaller units until the final dispersion is reached. However, this effect will not be so evident with coarse fillers. High structure fillers incorporate more slowly than low structure fillers, but once incorporated, the former disperses more easily and rapidly than their low structure counter part.

During the milling process, rubber chain molecules become attached to reinforcing fillers, so they are no longer soluble in the usual rubber solvents; this process is the basis for the formation of 'bound rubber'. It continues after mixing and eventually a system of interconnecting chain and particle results, which appears as an insoluble fragile black gel containing all the black and part of the rubber (the bound rubber). The process may continue for weeks at room temperature and is accelerated by increasing the temperature. Bound rubber is usually expressed quantitatively as the percentage of the rubber originally present, i.e. a compound of 50 parts of black and 100 parts of rubber with a bound rubber of 35% has 35 parts of rubber bound to 50 parts of black.

Bound rubber can be considered as a measure of surface activity and, because of this, the percentage of bound rubber may run parallel to rubber properties related to surface activity such as modulus, abrasion resistance and hysteresis. The formation of bound rubber is usually explained by assuming that mechanical breakdown of polymer chain molecules results in the appearance of free radicals at the newly formed chain ends. Reactive sites on the filler surface then combine with these free radicals to form the bound rubber. Since there are many sites on a filler particle, it can act as a giant crosslink. The amount of bound rubber first increases with milling and then goes down, as the polymer (natural rubber) breakdown becomes the dominating factor.

Application in rubber compounding: Between 90% and 95% of the total carbon black produced is used in rubber industry, and approximately 80% of this is used in the manufacture of tyres and related products such as inner tubes and retreading compounds.

By far the largest amount of carbon black used today is of the furnace type. Furnace blacks are practically used in every type of black-filled rubber article. The high structure, high reinforcing furnace grades are used in synthetic rubber treads to give increased tread life. The low reinforcing furnace grades are used in carcasses, the high reinforcing ones in treads. The fine particle blacks are used where high strength and resistance to abrasion are required, i.e. in conveyor belt-covers and certain types of footwear. The coarse particle blacks are used in such articles as hose, cables, footwear uppers, mechanical goods, and extrusions.

The thermal blacks are used in inner linings and inner tubes. They provide a low degree of reinforcement and can be used at high loading. They are used in V-belts because of their low heat build-up, and other applications are in mats, sealing compounds, and mechanical goods.

Non black fillers

Addition of silica to a rubber compound offers a number of advantages such as improvement in tear strength, reduction in heat build up and increase in compound adhesion in multi component products, such as tires. Two fundamental properties of silica and silicates influence their use in rubber compounds, ultimate particle size and extent of hydration. Other physical properties such as pH, chemical composition and oil absorption are of secondary importance.

Silicas, when compared to carbon blacks of the same particle size, do not provide the same level of reinforcement, though the deficiency of silica largely disappears when coupling agents are used with it. In general, silicas produce relatively greater reinforcement in more polar elastomers such as NBR and CR than in non polar polymers such as SBR and NR. The lack of reinforcement properties of silica in NR and SBR can be corrected through the use of silane coupling agents.

Some other filler systems are worthy of mention, not because of their reinforcement qualities but because of their high consumption. These include kaolin clay (hydrous aluminium silicate), mica (potassium aluminium silicate), talc (magnesium silicate), limestone (calcium carbonate), and titanium dioxide. As with silica, the properties of clay can also be enhanced through treatment of surface with silane coupling agents. Such clays show improved tear strength, an increase in modulus, improved adhesion of components in multi component products, and improved ageing properties.

Calcium carbonate is used as a low-cost filler in rubber products for static applications such as carpet underlay. Titanium dioxide finds extensive use in white products such as white sidewalls of tires where appearance is important.

f) Antidegradants

The presence of carbon-carbon double bonds renders elastomers susceptible to attack by oxygen, ozone and also thermal degradation. The oxidation of elastomers is accelerated by a number of factors including heat, heavy metal contamination, light, weather, fatigue, oxygen, ozone and atomic radiation.

The loss in physical properties associated with natural and accelerated ageing processes, is normally caused by either chain scission resulting in reduction of chain length and average molecular weight, cross linking resulting in a three dimensional structure and higher molecular weight, and chemical alteration of the molecule by introduction of new chemical groups.

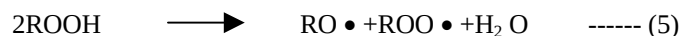
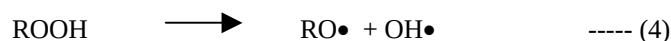
Natural rubber, polyisoprene, and butyl rubbers degrade predominantly by chain scission resulting in a weak, softened stock often showing surface tackiness. Chemical analysis shows the presence of aldehyde, ketone, alcohol and ether groups resulting from oxidative attack and mostly at α - hydrogens and double bonds. SBR, neoprene, EPDM, polybutadiene and acrylonitrile degrade by crosslinking, giving boardy and brittle compounds with poor flexibility and elongation.

Since all rubber like materials, whether natural or synthetic, cured or uncured, contain a certain amount of chemical unsaturation, they are subject to chemical attack by oxygen. Generally, when 1-2 weight % oxygen is combined with most polymers, the product is no longer useful. By speeding up the effect of oxygen, metallic salts are some of the most powerful catalysts of oxidation, manganese, copper, iron, nickel and cobalt being the worst; however, vulcanization helps to diminish their harmful effects. Consequently antidegradants are added to retard or prevent the polymer breakdown, to improve the ageing qualities, and to extend the service life of the product involved.

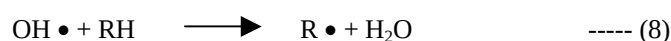
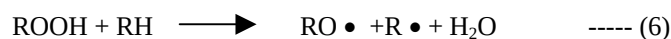
Mechanism of degradation : The degradation of unsaturated elastomers is an autocatalytic, free radical chain reaction. It has been established that attack commences on the α - methylenic carbon atom in the chain. A hydrogen atom is extracted and, in the presence of oxygen, an oxidative chain reaction is initiated which if unchecked, propagates autocatalytically.



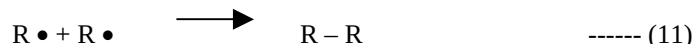
Whilst the $\text{R}\bullet$ radical again reacts as in equation (2), the hydroperoxide may decompose as follows:



or may react as follows:



Reaction (2) to (8) form a series of chain reactions, where reaction (3) is the rate determining stage. Cleavage of hydroperoxide as in reaction (4) also occurs by absorption of UV light. The chain reaction terminates as:

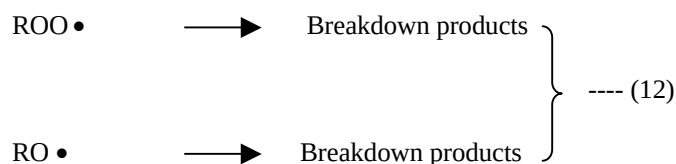


If reactions (10) and (11) occur more than once per hydrocarbon molecule (radical), chain extension will take place and, if occur on an average more than twice, crosslinking will result.

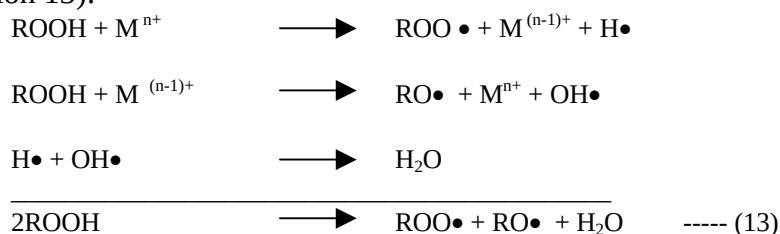
Like any other chemical process, the rate of reaction will increase with temperature and increase in service temperature will thus accelerate the degradation of rubber. Ultraviolet light initiates free radical oxidation at the exposed surface of an elastomeric product to

generate a layer of oxidized rubber. Heat, moisture or high humidity can then initiate crazing of the surface, which subsequently can be abraded off. Such degradation of surface is more severe with non-black stocks than with black compounds.

It is also possible that reactions may occur which cause decomposition of the peroxide radicals by the following reaction scheme:

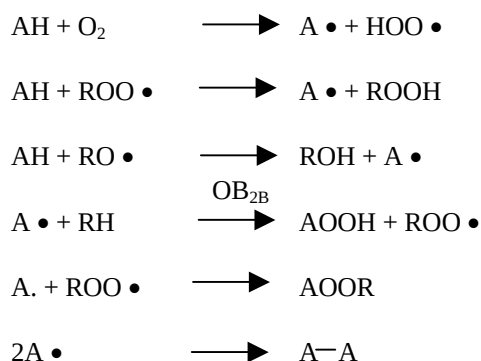


Trace quantities of transition metal ions greatly accelerate the rate of oxidation by catalyzing the decomposition of hydroperoxides to radical species. The metal catalyst is an active hydroperoxide decomposer in both its higher and lower oxidation states. In the overall reaction, two molecules of hydroperoxide are decomposed to peroxy and alkoxy radicals (equation 13):



Whether decomposition or crosslinking occurs, is therefore, a function of both the polymer type and environmental conditions.

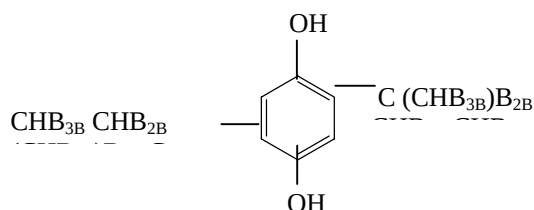
Antioxidants : A proper stabilizer or antioxidant has to function by interrupting the degradation reaction sequence (1) to (12) either by (a) capturing the free radicals formed, and / or (b) by ensuring that the peroxides and hydroperoxides produced decompose into harmless fragments without degrading the polymer and without initiating new free radicals capable of propagating the reaction chain. Possible inhibition reactions are:



The majority of commercially available inhibitors belong to two main chemical classes: amines and phenolics, which represent respectively staining and non-staining types. In general the amines are used only where color is not important. Phosphites are mainly used as stabilizers for SBR.

The non- staining antioxidants are subdivided in four groups: phosphites, hindered phenols, hindered bisphenols, and hydroquinones.

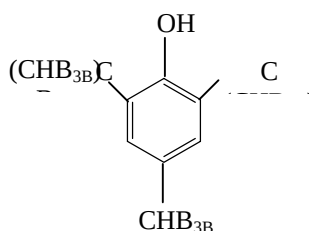
Whereas **phosphites** such as tri (mixed mono-and di-nonyl phenyl) phosphite are used as synthetic rubber (eg. SBR) stabilizers, hydroquinones such as 2,5 - di - tert - amyl hydroquinone are used in adhesives.



2, 5 - di - tert - amyl - hydroquinone

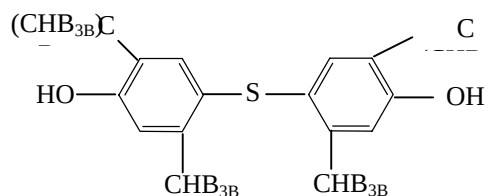
Hindering the phenolic hydroxyl group with at least one bulky alkyl group in the ortho position appears necessary for high antioxidant activity. Nearly all-commercial phenolic anti-oxidants are hindered in this manner (examples 2,6, di - tert - butyl - p - cresol). Steric hindrance decreases the ability of a phenoxy radical to abstract a hydrogen atom from the substrate and produce an alkyl radical capable of initiating oxidation. However, because of their low molecular weight hindered phenols tend to be volatile and hence hindered bisphenols such as 4,4' - thiobis (6-t-butyl -m- cresol) are the most persistent of four classes of materials because of their low volatility.

Hindered Phenol



2, 6 di - tert - butyl - p - cresol

Hindered bis phenol

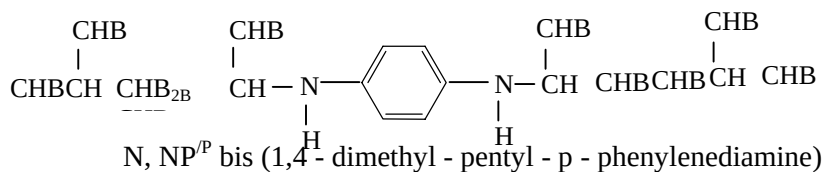


4, 4^P thiobis (6 - t- butyl - m - cresol)

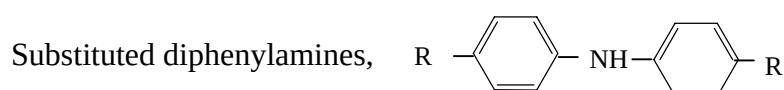
Hindered phenols are employed as stabilizers for uncured, unsaturated elastomers during processing and storage in relatively low concentrations, i.e. ca 0.1% - 0.5%. According to use requirements, up to 3% of a phenolic or amine antioxidant is added before vulcanization.

Staining antioxidants: Antioxidants derived from p-phenylenediamine and di-phenylamine are highly effective scavenger of peroxy radicals. They are more effective than the phenolic antioxidants for the stabilization of easily oxidisable unsaturated elastomers. p-phenylene diamine derivatives are used primarily for elastomers containing carbon black because of their intense staining effects.

N, N' - disubstituted-p-phenylenediamines, such as N,N' - bis (1,4 - dimethyl - pentyl - p - phenylenediamine) are used in greater quantities than other classes of antioxidants.



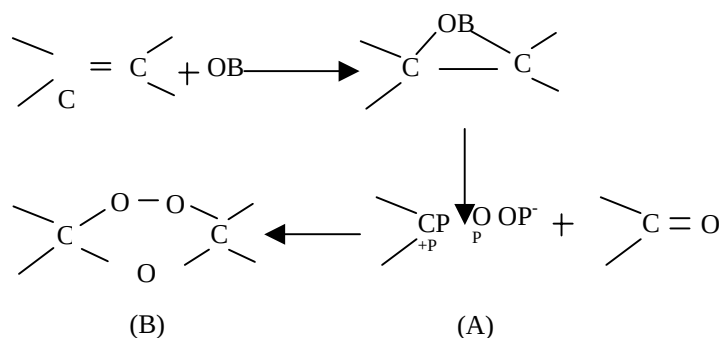
These products protect unsaturated elastomers against oxidation and degradation by ozone.



(where $R =$ alkyl, usually $C_7 - C_9$ or an alkoxy, e.g. CH_3O) are especially useful in synthetic rubbers e.g. for neoprene type. They are rarely used alone, usually found as a constituent of proprietary antiflex cracking - antioxidant blends. They tend to show a directional improvement in compound fatigue resistance.

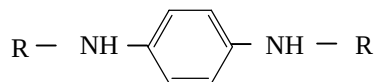
Polymerized dihydroquinolines in different degree of polymerization influence migratory and long term durability properties. They are good general purpose antioxidants and also are effective against heavy metal pro-oxidants such as nickel and copper ions.

Antiozonants: When diene rubbers are exposed to ozone under stressed conditions, cracks develop which are perpendicular to the direction of stress. The mechanisms of ozone attack and its inhibitions are not well understood. It is probable that ozone attacks rubber by the following mechanism:



It is believed that an antiozonant reacts with either the zwitterion (A) or the ozonide (B) to form an inert protective film. Every time this film is broken, is repaired by the formation of fresh film produced from the three reactants (rubber, ozone and antiozonant) in situ.

Para phenylenediamines (PPDs) are the only class of antiozonants used in significant quantities in combating the ozone - initiated degradation. The general structure of PPDs is:



They not only serve to protect rubbers from ozone but also improve resistance to fatigue, oxygen, heat and metal ions.

There are three general categories of paraphenylenediamines, which are listed as follows:

1. **Dialkyl PPDs:** The substituent R groups are both alkyls, as is di isopropyl p - phenylenediamine. The R group can range from C3 upto C9. They induce higher levels of scorch in a compound than other classes of PPDs and also migrate faster than other classes due to their low molecular weight. However, they lack consistency.
2. **Alkyl – aryl PPDs:** One substituent R group is aromatic ring, other is an alkyl group. The most widely used one is N-1, 3 dimethylbutyl-N' - phenyl - p - phenylene diamine. This antiozonant shows good dynamic protection, good static protection when combined with wax, better compound processing safety and scorch safety and slower migratory properties, thus rendering long product life.
3. **Diaryl PPDs:** these are less active than alkyl - aryl PPDs and have a tendency to bloom. They contain two aromatic pendant groups, as in diphenyl-p-phenylenediamine or di- β -naphthyl-p-phenylenediamine.

Waxes are an additional class of materials used to improve ozone protection of rubber primarily under static conditions. Wax protects rubber against static ozonolysis by forming a barrier on the surface. Wax migrates from the bulk of the rubber continuously, maintaining an equilibrium concentration at the surface. Microcrystalline wax migrate to the rubber surface at a slower rate than paraffin wax and performs best at high service temperature whereas paraffin waxes protect best at low temperatures. It can be noted that under dynamic conditions, the protective wax film breaks down, after which the antiozonant system in the rubber formulation will take over as the primary stabilizer system for ozone protection. Waxes are used to ensure protection against ozone for products in storage such as tires in a warehouse.

The selection criteria governing the use of antidegradants are as follows:

- 1) **Discoloration and Staining:** For elastomers containing carbon black, more active amine antioxidants are preferred; phenolics are mainly used in light colored goods, where color retention is imported.
- 2) **Volatility:** As a rule, the higher the molecular weight of the antioxidant the less volatile it will be, though hindered phenols tend to be highly volatile compared with amines of equivalent molecular weight. Thus correct addition of antioxidants in the compound is critical for avoiding any loss of material.
- 3) **Solubility:** Low solubility of an antioxidant cause blooming to the surface with consequent loss of protection of the product. Therefore solubility of antidegradants, particularly antiozonants, controls their effectiveness. They should not be extracted by water or other solvents, such as hydraulic fluid, during their service life.
- 4) **Chemical Stability:** Stability of antidegradants against heat, light, oxygen and solvents is required for durability.
- 5) **Concentration:** Most antidegradants have an optimum concentration for maximum effectiveness after which the material solubility becomes a limiting factor, para-phenylenediamine offer good oxidation resistance at 0.5 – 1.0 phr and antiozonant

protection in the range 2.0 – 5.0 phr. Above 5.0 phr para – phenylenediamine tends to bloom.

g) Softeners

Softeners include a wide variety of oils and synthetic organic materials, which do not react chemically with rubbers but serve primarily as processing aid. They are used for a number of reasons. Some of these reasons are:

- to decrease the viscosity and thereby improve the workability of the compound
- to reduce mixing temperature and power consumption
- to reduce hardness
- to reduce low temperature brittle point
- to aid in the dispersion of fillers
- to reduce mill and calender shrinkage
- to provide lubrication to aid in extrusion and molding

The most important class of the softeners are hydrocarbon oils which fall into one of the three primary categories; paraffinic, naphthenic and aromatic. All the three classes of oils used at 2-10 phr, contain high levels of cyclic carbon structures; difference are in the number of saturated and unsaturated rings. For general all round properties, the naphthenics are preferred. The proper selection of the oils for inclusion in a formulation is important. The oil must be compatible with the rubber and the other compounding ingredients used in the recipe. Incompatibility will result in poor processing characteristics and / or bleeding in the final products.

Certain esters of organic acids or phosphoric acid are used as plasticizers in the circumstances where petroleum oils may be unsuitable, e.g. because of incompatibility with the polymer. They are used particularly in NBR and CR polymers as processing aids. Examples are, dibutyl phthalate (DBP), dioctyl phthalate (DOP), poly (propylene adipate) (PPA), trixylyl phosphate (TXP) etc.

h) Peptizers

Peptizers are generally used to lower the viscosity of uncured compounds. They function in the thermomechanical and thermooxidative breakdown of rubbers, as oxidation catalysts at high temperatures but as radical acceptors at low temperatures. They have little effect on vulcanization properties. Examples of peptizers are, pentachlorothiophenol, phenyl hydrazine, certain diphenyl sulfides, and xylyl mercaptan. Peptizers are most effective in natural rubber, SBR and polyisoprene, but they are relatively ineffective in other synthetic rubbers.

Each peptizer has an optimum loading in a compound for maximum efficiency. Peptizers such as pentachlorothiophenol are generally used at 0.1 – 0.25 phr level. This enables significant improvement in compound processability, reduction in energy consumption during mixing and improvement in compound uniformity. High levels can, however, adversely affect the compound properties, as excess peptizer continues to catalyze polymer breakdown during the service life of the product.

i) **Colors And Pigments**

Colorants are the materials used for coloring non-black rubber goods. They must be stable to curing conditions, color fast, should be free from staining or bleeding, and reasonably priced.

Colorants are commonly chemically classified as inorganic white and colored pigments, polymer – soluble organic colorants (dyes), carbon black pigments and organic pigments (e.g. metal flakes). Pigments are virtually insoluble in rubbers whereas dyes are soluble. The term pigment is linked with a specific range of particle size (~ 0.01 to $\sim 1.0 \mu\text{m}$). Coloration with pigments requires dispersion; coloration with dyes involves a dissolving process. Dyes can only absorb light and do not scatter it and are therefore transparent, whereas the optical effect of pigments is based on reflectance resulting in opaque and colored materials. With all colored pigments that selectively absorb and reflect, the shade is influenced by particle size. To be efficient, they should have a strong covering power. No reflectance occurs when the particle sizes are very small.

Intensive research on organic pigments has produced a variety of such materials which are stable to curing conditions and to light, and are non-bleeding either to adjacent rubber compounds or to other finishes. Many of these pigments are available as pastes or as masterbatches in rubber, which greatly assist in dispersion and lead to appreciable economics in the amount needed to produce the color required in the final compounds. Certain rubber soluble dyestuffs are also used to produce delicate shades in translucent materials.

Inorganic pigments are generally insoluble in the rubber in which crystal or particulate structure is retained to some degree; color results from the dispersion of fine particles throughout the rubber. Some of the inorganic pigments, which are used for coloring rubbers, are:

- i) Titanium dioxide: A white pigment, mainly used for its whitening power in tire sidewalls, hospital accessories, floor tiles etc.
- ii) Zinc carbonates: A white powder, cheaper than titanium dioxide, used when maximum whiteness is not required.
- iii) Antimony sulfides: Antimony trisulfide gives strong crimson color (crimson antimony) or red-orange color (golden antimony) depending on presence of sulfur and other chemicals like antimony tetrasulfide or calcium sulfate.
- iv) Cadmium sulfide: Gives colors ranging from yellow through orange to deep red.
- v) Chromium oxide: A dull green pigment
- vi) Iron Oxide: Mainly ferric oxides, with a range of colours from deep red, through orange to yellow depending on the method of preparation, are available.
- vii) Mercuric sulfide: Gives strong bright red color (vermilion)
- viii) Nickel titanate: Highly stable yellow pigment.
- ix) Ultramarine blue: It is sulfur – containing complex of silicates. The colors vary from deep blue to greenish shades.

The inorganic materials usually give rather dark colors in rubber compounds; for brightly colored materials more expensive organic pigments are used which are available in a wide range of colors and shades.

j) **Tackyfyng Agents**

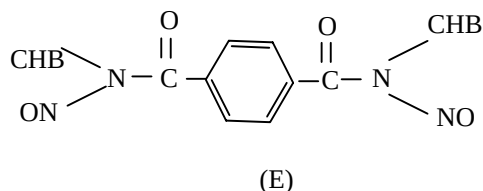
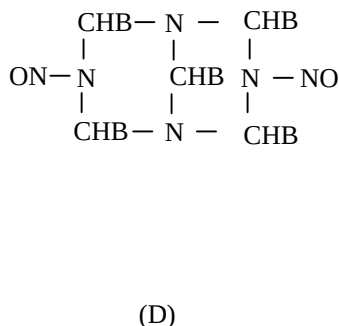
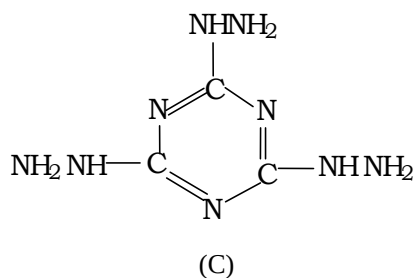
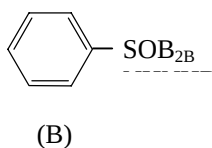
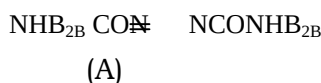
Natural rubber displays a phenomenon known as 'natural tack'. When two clean surfaces of masticated rubber (rubber whose molecular weight has been reduced by mechanical shearing) are brought into contact, the two surfaces become strongly attached to each other. This is a consequence of interpenetration of molecular chain ends followed by crystallization. Amorphous rubbers such as SBR do not exhibit such tack and it is necessary to add tackyfyng agents such as rosin derivatives and polyterpenes to impart tack for efficient compounding. Other tackifiers include pine tar, coumarone resins, petroleum resins and non-reactive phenolic resins.

k) **Blowing Agents**

Many polymers are used in cellular form in which the polymer matrix contains gas filled cells which may or may not be intercommunicating. Over the years many methods have been devised for preparing cellular polymers such as sponge and microporous rubber; the most important ones are the following:

- i) Incorporation of a chemical compound which decomposes at some stage of the processing operation to yield volatile reaction products such as N_2 , CO_2 , H_2O , NH_3 etc. These are known as chemical blowing agents.

Most widely used blowing agent is azodicarbonamide (A). However hydrazide derivatives such as benzene sulfonhydrazide (B), hydrazine derivatives e.g. trihydrazinotriazine (C), nitrosoamine derivatives such as dinitrosopentamethylene tetramine (D), terephthalamide derivatives such as N,N' -dimethyl- N,N' -dinitrosoterephthalamide (E) and in a few cases inorganic bicarbonates such as sodium bicarbonate, are also used as chemical blowing agents.



- ii) Physical blowing agents liberate gases as a result of physical processes such as evaporation or desorption at elevated temperatures or reduced pressures. This class includes mostly volatile liquids, e.g. freons, aliphatic hydrocarbons, powdered solid carbon dioxide.

- iii) Diffusion of gases into the polymer under pressure with subsequent expansion of the composition at elevated temperatures after decompression.

Suggested Readings

1. Rubber Technology and Manufacture, C.M. Blow, Ed., Hewnes Butterworths, London, 1971
2. Rubber Technology, Maurice Morton, Ed., Van Nostrand Reinhold Company, New York, 1973
3. Plastics Materials, J.A. Brydson, 7th Edn., Elsevier, India, 1999.
4. Rubber, Natural and Synthetic, H.J. Stern., Maclaren, London, 1967.
5. Vanderbilt Rubber Handbook, G.G. Windspear ed., R.T. Vanderbilt Co. Inc., New York, 1968.
6. Reinforcement of Elastomer, G.Kraus, Wiley – Inter science, New York, 1965
7. Vulcanization and vulcanizing agents, W. Maclaren, London, 1967
8. Vulcanization of Elastomers, G. Alliger. and I.J. Sjothun, Eds., Reinhold, New York, 1964
9. Science and Technology of Rubber, J.E. Mark, B. Erman, F.R. Eirich, Eds., 2nd Edn., Academic, San Diego, 1994.
10. The Chemistry and Physics of Rubber – Like substances, L. Bateman, Ed., John Wiley & Sons, New York, 1963
11. Rubber Chemistry, J. A. Brydson, Applied Science, London, 1978
12. Encyclopedia of Polymer Science & Engineering, M. Grayson and J.I. Kroschwitz, Eds., 2nd Edn., Wiley, New York, 1987.
13. Kirk – Othmer Encyclopedia of Chemical Technology, 3rd Edn., Wiley Interscience, New York, 1978