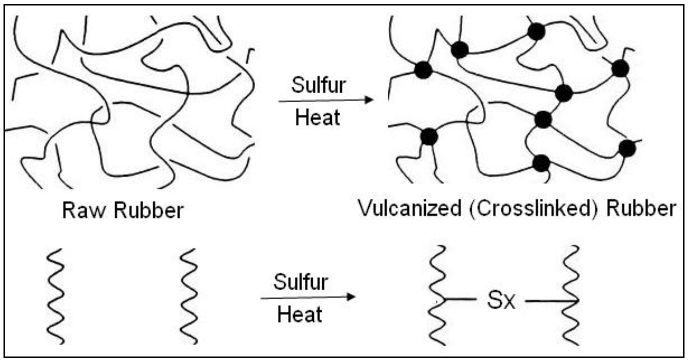
Vulcanization & Accelerators

Vulcanization is a cross linking process in which individual molecules of rubber (polymer) are converted into a three dimensional network of interconnected (polymer) chains through chemical cross links(of sulfur).



The vulcanization process was discovered in 1839 and the individuals responsible for this discovery were Charles Goodyear in USA and Thomas Hancock in England. Both discovered the use of Sulfur and White Lead as a vulcanization system for Natural Rubber. This discovery was a major technological breakthrough for the advancement of the world economy.

Vulcanization of rubbers by sulfur alone is an extremely slow and inefficient process. The chemical reaction between sulfur and the Rubber Hydrocarbon occurs mainly at the C = C (double bonds) and each crosslink requires 40 to 55 sulphur atoms (in the absence of accelerator). The process takes around 6 hours at 140°C for completion, which is uneconomical by any production standards. The vulcanizates thus produced are extremely prone to oxidative degradation and do not possess adequate mechanical properties for practical rubber applications. These limitations were overcome through inventions of accelerators which subsequently became a part of rubber compounding formulations as well as subjects of further R&D.
Following is the summary of events which led to the progress of ‘Accelerated Sulfur Vulcanization'.

Event	**Year**	**Progress**
- Discovery of Sulfur Vulcanization: Charles Goodyear.	1839	Vulcanizing Agent
- Use of ammonia & aliphatic ammonium derivatives: Rowley.	1881	Acceleration need
- Use of aniline as accelerator in USA & Germany: Oenslager.	1906	Accelerated Cure
- Use of Piperidine accelerator- Germany.	1911	New Molecules
- Use of aldehyde-amine & HMT as accelerators in USA & UK	1914-15	Amine Accelerators
- Use of Zn-Alkyl Xanthates accelerators in Russia.	1919-20	New Molecules
- Use of Thiurams & Dithiocarbamates -Germany.	“	Speed Control
- Effect of ZnO on cure rate, discovery of DPG, MBT, MBTS.	1919-22	Delayed Action
- R & D efforts for more effective delayed action accelerators.	1930	Delayed Action
- Sulfenamide accelerator developed- USA.	1937	Delayed Action
- Several other Sulfenamide accelerators developed	1945 …	Delayed Action
- Pre Vulcanization Inhibitor CTP- USA	1970	PVI
- Post Vulcanization Stabilizers	1990s…	PVS

Sulfur remains the most successful and economical cross linking agent even today!

Sulfur as vulcanizing agent has a limitation that, the elastomers must contain chemical unsaturation (C=C double bonds) for sulfur cross linking. The structure of speciality elastomers EPDM and Butyl had to be chemically modified to make sulfur vulcanization possible for their commercial success.

Other chemicals used for cross linking of polymers are Sulfur Monochloride, Tellurium, Selenium, Thiuram accelerators, Polysulphide polymers, p-Quinonedioximes, Metallic Oxides, Organic Peroxides, Di-isocyanates, etc. (mostly for specialized applications).

In the case of fully saturated elastomers organic peroxides are often used for cross linking.

Accelerators:

An accelerator is defined as the chemical added into a rubber compound to increase the speed of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiency.

Accelerator also Decreases the Quantity of Sulphur necessary for vulcanization and thus improving 'aged' properties of the rubber vulcanizates.

Classification of Accelerators:

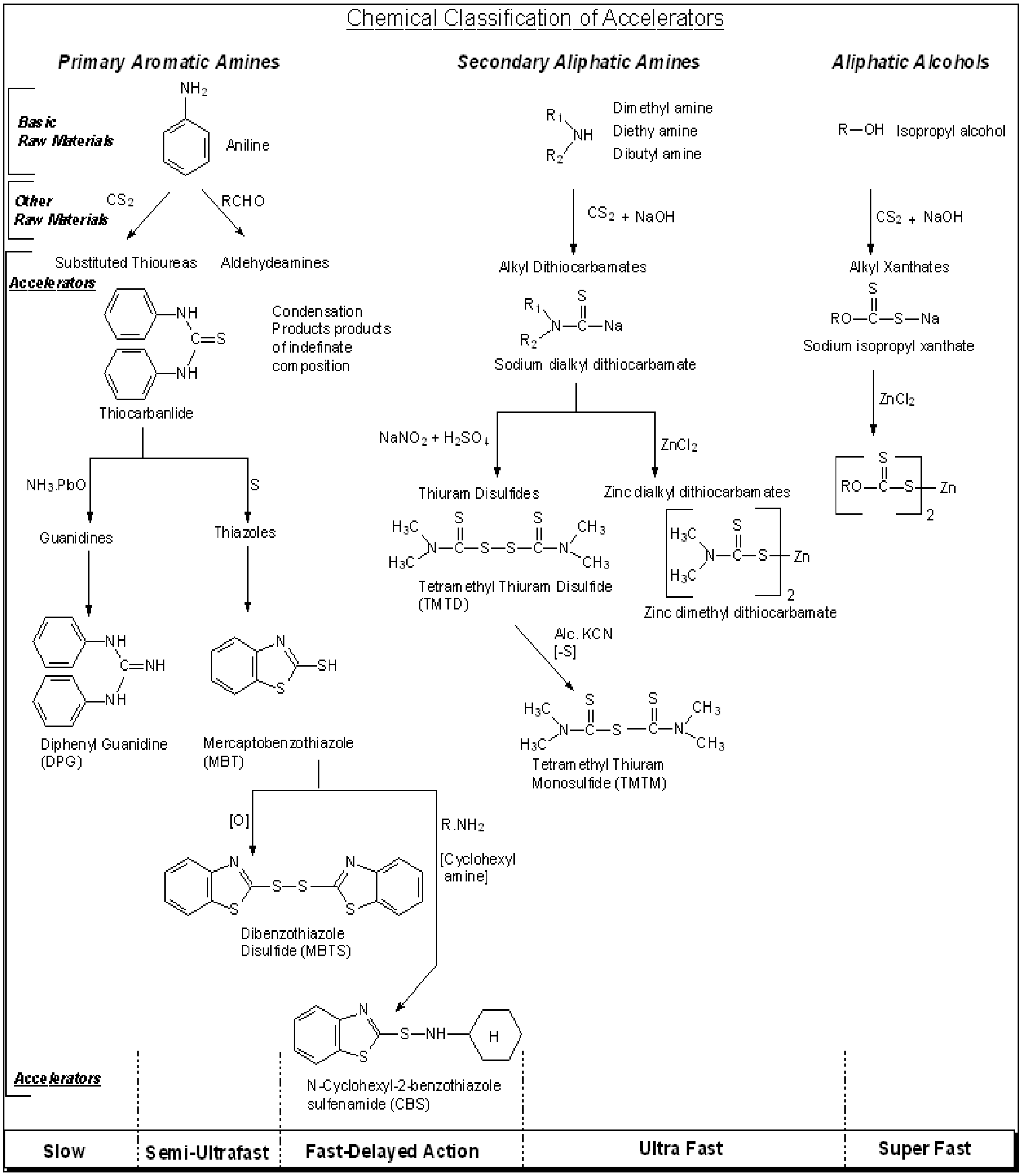
Accelerators	*Chemical Group*	*Vulcanization Speed*
BA, HMT	Aldehyde Amine	Slow
DPG, DOTG	Guanidine	Slow
MBT, MBTS, ZMBT	Thiazole	Semi Ultra fast
ZBDP	Thiophosphate	Ultra fast
CBS, TBBS, MBS, DCBS	Sulfenamides	Fast-Delayed action
ETU, DPTU, DBTU	Thiourea	Ultra fast
TMTM, TMTD, DPTT, TBzTD	Thiuram	Ultra fast
ZDMC, ZDEC, ZDBC, ZBEC	Dithiocarbamate	Ultra fast
ZIX	Xanthates	Ultra fast

Accelerators are also classified as Primary and / or Secondary accelerators based on the role they play in a given compound.

Generally, Thiazoles and Sulfenamide accelerators play a role of being Primary Accelerators due to their characteristics such as good processing safety, a broad vulcanization plateau and optimum cross link density as well as desired reversion delay that they offer. The Primary Accelerators are used at 0.5 to 1.5 phr dosages in most rubber compounds.

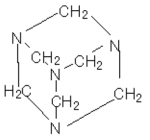
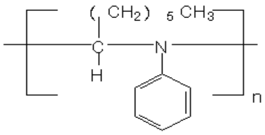
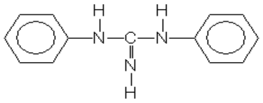
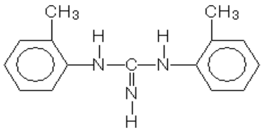
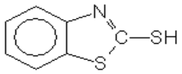
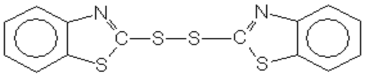
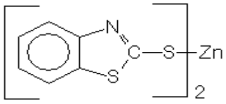
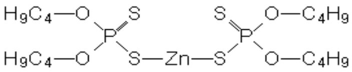
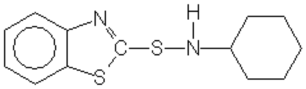
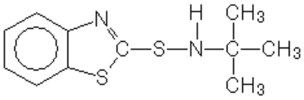
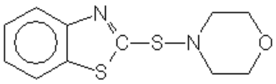
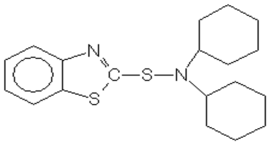
The basic accelerators such as Guanidines, Thiurams, and Dithiocarbamates etc are used as Secondary accelerators to activate the primary accelerators. The use of secondary accelerators increases the speed of vulcanization substantially but at the expense of scorch safety. The dosages of the secondary accelerators are generally between 10-40% of the primary accelerator.

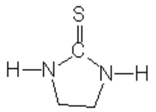
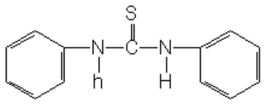
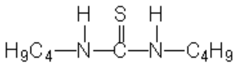
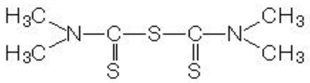
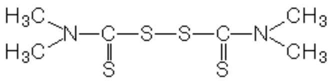
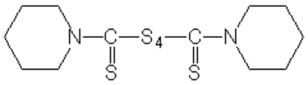
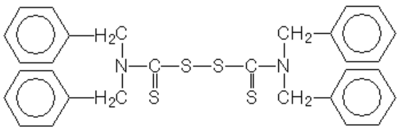
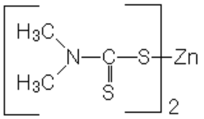
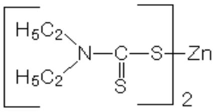
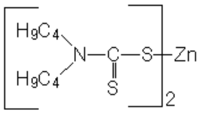
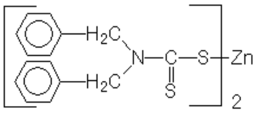
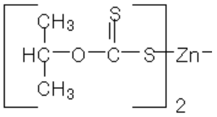
Accelerators some times are also be classified according to the chemical groups to which they belong.



Over 150 different chemicals belonging to different classes of composition are known to function as accelerators for rubber vulcanization of which around 50 accelerators are most commonly used by the Rubber Industry.

Commonly used Accelerators:

Accelerator	Chemical Structure	Remarks
Hexamethylene Tetramine (HMT)		Group: Amines. Speed: Scorchy & Slow cure rate. Use: As a secondary accelerator
Heptaldehyde-Aniline condensation Product (BA)		Group: Aldehyde-Amines. Speed: Scorchy & Slow cure rate. Use: As a Primary accelerator.
Diphenyl Guanidine (DPG)		Group: Guanidines. Speed: Scorchy & Slow cure rate. Use: As a Primary & Secondary accelerator
N, N'-Diorthotolyl Guanidine (DOTG)		Group: Guanidines. Speed: Scorchy & Slow cure rate. Use: As a Primary & Secondary accelerator
2- Mercaptobenzothiazole (MBT)		Group: Thiazoles. Speed: Scorchy Ultra fast. Use: As a Primary accelerator
2-2'-Dithiobis(benzothiazole) (MBTS)		Group: Thiazoles. Speed: Less scorchy than MBT. Ultra fast. Use: As a Primary accelerator
Zinc-2-mercaptobenzothiazole (ZMBT)		Group: Thiazoles. Speed: Scorchy. Ultra fast. Use: As a Primary accelerator
Zinc-O,O-di-N-phosphorodithioate (ZBDP)		Group: Thiophosphate. Speed: Scorchy. Ultra fast. Use: As a Primary accelerator
N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
2-(4-Morpholinothio)-benzothiazole (MBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
N,N'-dicyclohexyl-2-benzothiazole sulfenamide (DCBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator

Accelerator	Chemical Structure	Remarks
Ethylene Thiourea (ETU)		Group: Thioureas Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Di-pentamethylene Thiourea (DPTU)		Group: Thioureas Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Dibutyl Thiourea (DBTU)		Group: Thioureas Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Tetramethylthiuram Monosulfide (TMTM)		Group: Thiurams Speed: Ultra fast. Use: As a Primary / Secondary accelerator. Not a sulfur donor
Tetramethylthiuram Disulfide (TMTD)		Group: Thiurams Speed: Ultra fast. Use: As a Primary / Secondary accelerator, Sulfur donor
Dipentamethylenethiuram tetrasulfide (DPTT)		Group: Thiurams Speed: Ultra fast. Non-nitrosamine Use: As a Primary / Secondary accelerator, Sulfur donor.
Tetrabenzylthiuram Disulfide (TBzTD)		Group: Thiurams Speed: Ultra fast. Use: As a Primary/ Secondary accelerator, Non-nitrosamine, Sulfur donor.
Zinc dimethyldithiocarbamate (ZDMC)		Group: Dithiocarbamates Speed: Ultra fast. Use: As a Primary / Secondary accelerator.
Zinc diethyldithiocarbamate (ZDEC)		Group: Dithiocarbamates Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Zinc dibutyldithiocarbamate (ZDBC)		Group: Dithiocarbamates Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Zinc dibenzyldithiocarbamate (ZDBC)		Group: Dithiocarbamates Speed: Ultra fast. Use: As a Primary/ Secondary accelerator, Non-nitrosamine.
Zinc-Isopropyl Xanthate (ZIX)		Group: Xanthates Speed: Super fast. Use: As a Primary accelerator.

Selection of Accelerators for Rubber Compounds:

Before selecting an Accelerator system for the manufacture of a particular rubber product, following points have to be taken into account.

- ✓ *Solubility in rubber (high solubility required to avoid bloom & improve dispersibility),*
- ✓ *Processing operations & their temperatures the rubber compound is be required to undergo,*
- ✓ *Adequate Scorch Time desired for 'scorch free' processing & storage stability,*
- ✓ *The Cure rate requirements,*
- ✓ *Reversion characteristics desired (delayed reversion on over cure),*
- ✓ *Vulcanization method to be used (mode of heat transfer),*
- ✓ *Maximum vulcanization temperature available,*
- ✓ *Cure cycle desired at the available vulcanisation method and temperature,*
- ✓ *Requirements of vulcanizates properties (to decide the type & state of cure),*
- ✓ *Effectiveness over a wide range of cure temperatures & Suitability for use with different polymer blends,*
- ✓ *No adverse effects on other properties / materials (e.g. bonding, ageing, adhesion, non-rubber components in the rubber product),*
- ✓ *No known health hazards upon usage as chemical / its decomposition products and easy to handle nd dust suppressed physical form.*
- ✓ *No adverse effects during end-use of the rubber product (e.g. accelerators used in the manufacture of rubber articles intended for food contact / surgical use),*
- ✓ *Stability of the accelerator as a chemical (e.g. problems with the use of decomposed sulphenamide accelerators),*

A. Thiazole Class Accelerators:

This class of accelerators include commercially available and widely used accelerators such as MBT, MBTS and ZMBT (NaMBT the sodium salt of MBT also finds applications in few latex goods manufacture).

Thiazoles are medium-fast primary accelerators with only moderate processing safety. Thiazoles are most widely used accelerators in the rubber industry for the production of wide variety of goods such as cycle tyres and tubes, footwear, beltings, hoses and other moulded and extruded goods.

Thiazoles are activated by Zinc oxide / Stearic acid combination and produce flat cure with vulcanizates having very good reversion resistance.

Activity of Thiazole accelerators with respect to cure characteristics can be summarised as follows:

1. Scorch Safety → Longer…. (MBT < MBTS < ZMBT)
2. Cure Rate → Faster….. (ZMBT < MBTS < MBT)
3. Crosslink Density → Higher at equal dosage….. (ZMBT < MBT < MBTS)

Thiazoles act as retarders of cure in rubber compounds accelerated using Thiurams (TMTD/TMTM)/Dithiocarbamates (ZDC, ZDBC) or ETU class accelerators as main accelerator and also reduce bloom of Thiurams and dithiocarbamates in EV cure systems.

All thiazole accelerators can be further boosted to increase speed of vulcanisation by using small quantities of basic accelerators such as DPG, DOTG, TMTM, TMTD, ZDC, etc

Thiazole accelerators can be retarded using small proportion of Pilgard PVI or other retarders like NDPA, pthalic anhydride, salicylic acid, etc.

Addition of extra Stearic acid or partial replacement by sulphenamide accelerator also control scorch to some extent.

Thiazoles are particularly preferred for rubber to metal bonding applications as amine-accelerators affect the rubber-metal bond strength.

B. Sulfenamide Class Accelerators:

The sulfenamide class accelerators include CBS, TBBS, MBS, DCBS etc. and are most popular in the tire industry due to their **delayed action as well as faster cure rate offered by them during vulcanization of rubber compounds containing furnace blacks**.

The sulfenamide accelerators are the reaction products of 2- Mercaptobenzothiazole with basic amines such as Cyclohexylamine / Tert-Butylamine / Morpholine / Dicyclohexyl amine etc.

These accelerators provide wide range of crosslink densities depending on type and dosage of accelerator used and exhibit flat & reversion resistant cure. Progressive increase in dosage of sulfenamide accelerator shows improvement in scorch delay, cure rate and state of cure.

Sulfenamide accelerators can be boosted by using DPG, DOTG, TMTM, TMTD type basic accelerators for further increasing the cure rate (but at the expense of scorch safety).

Sulfenamide accelerators can be effectively retarded using small proportion of Pilgard PVI (CTP) without affecting their rate of cure.

Vulcanizates of sulfenamide accelerators have a typical 'aminic' odour and exhibit higher stress-strain properties along with better resilience and flex-fatigue resistance as compared to Thiazoles.

Sulfenamide accelerators decompose rapidly in the presence of steam and hence are preferred for manufacture of open steam cured rubber products requiring faster onset of cure for better shape retention. However, this advantage is lost in the case of hot air cured products.

Sulfenamide accelerators are usually incorporated in the rubber compound at the end of mixing cycle when temperature is above melting point of the accelerator to ensure proper dispersion. Generation of excess heat is avoided to prevent decomposition of sulfenamide accelerator. In case sulfenamide accelerator is to be added at a later stage; addition in the form of sulfenamide rubber master batch is recommended.

Activity of sulfenamide accelerators can be summarised as follows:

1. Scorch safety → Longer (CBS < TBBS < MOR < DCBS}
2. Cure Rate → Faster (DCBS < MOR < CBS < TBBS)
3. Crosslink density → Higher at equal dosage (DCBS < MOR < CBS < TBBS)

Sulfenamide accelerators have limited storage stability and the rate of degradation is greatly influenced by storage conditions such as humidity & heat and hence, is used on a strictly first in-first out basis. Sulfenamide accelerators should be stored in a cool & dry atmosphere (Below 30°C & 60% RH) and away from acids / acidic substances / fumes to prevent rapid degradation.

C. Thiuram Class Accelerators:

Thiuram class includes accelerators such as TMTM, TMTD, TETD, TBzTD and DPTT.

Thiurams are ultra-fast accelerators for NR, SBR, BR, NBR and other highly unsaturated rubbers and the most preferred primary accelerator for sulfur cured low-unsaturation content rubbers like butyl (IIR) and EPDM.

Thiurams are widely used as secondary accelerator generally at 0.05 - 0.4 phr with thiazole / sulfenamide class accelerators to achieve faster curing rate, higher crosslink density with a compromise on scorch safety and vulcanizate exhibit lower heat build up compared to DPG/DOTG activated sulphenamide cures.

Thiurams exhibit longer processing safety compared to dithiocarbamate accelerators. Thiurams, when used as vulcanising agents (2.5 - 3.0 phr) in the absence of sulfur; the vulcanizates attain high degree of state of cure exhibiting high tensile strength, high modulus, lower elongation at break, higher rebound resilience at elevated temperatures and lower tear resistance.

Thiurams are also used along with Guanidine in Polychloroprene compounds to achieve good processing safety.

In combination with Dithiocarbamates and Xanthates, Thiurams have retarding effect without changing the rate of vulcanisation.

Thiuram accelerators do not discolour the vulcanizates & the products are tasteless.

Activity of various thiuram accelerators with respect to cure characteristics can be summarised as follows :

1. Scorch Safety → Longer (TMTD < TETD << TMTM)
2. Cure Rate → Faster (TMTM = TETD = TMTD)
3. Crosslink density at equal dosage → Higher (TMTM = TETD = TMTD)

D. Dithiocarbamate Class Accelerators

Dithiocarbamate class includes accelerators such as ZDMC, ZDEC, ZDBC, ZBzDC etc.

Dithiocarbamate accelerators are widely used as ultra fast accelerator for NR latex based compounds and also find applications as primary or secondary accelerators in most dry rubber based sulfur cured compounds.

The dithiocarbamate class accelerators require Zinc oxide and Stearic acid for activation and produce rapid vulcanization.

Dithiocarbamates exhibit very low scorch safety, faster cure rate and higher crosslink density and the rubber products can be vulcanized in a short time at low temperature (115 - 120°C). Compounds accelerated with dithiocarbamates have a very narrow plateau hence reversion due to over cure can take place very rapidly.

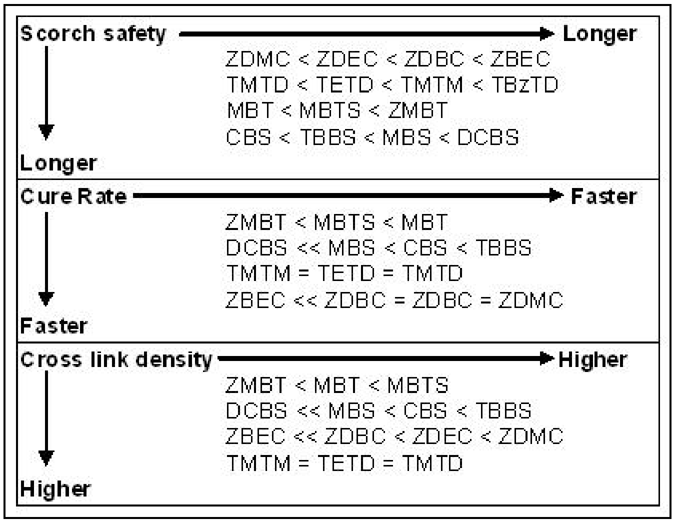
Low unsaturation content rubbers such as EPDM and IIR can be cured using dithiocarbamate as a secondary accelerator (at relatively higher dosage) along with thiuram class accelerators as primary accelerators.

Dithiocarbamate accelerators have limited solubility in rubber compounds and hence excess quantity tends to bloom on the surface of the vulcanizates. Dithiocarbamates are non-staining and non-discolouring even on exposure to light and are suitable for the manufacture of transparent goods.

Activities of various dithiocarbamate accelerators with respect to cure characteristics in dry rubber compounds can be summarised as follows:

1. Scorch Safety → Longer (ZDMC < ZDEC < ZDBC)
2. Cure Rate → Faster (ZDBC = ZDEC = ZMDC)
3. Crosslink density at equal dosage → Higher (ZDBC = ZDEC = ZDMC)

Summary: Cure Activities of the Accelerators:

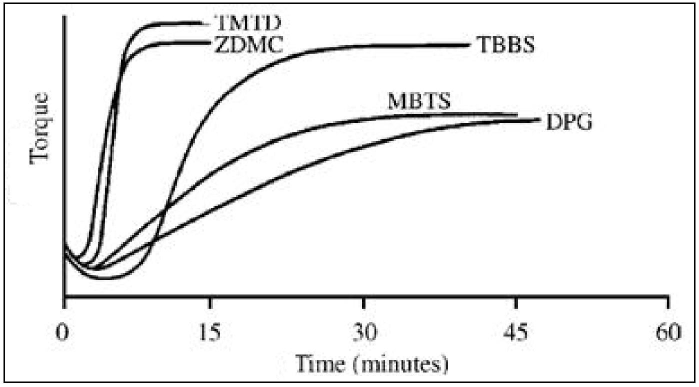


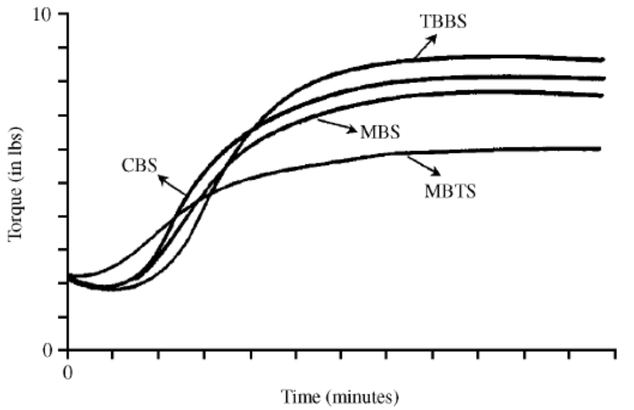
Scorch safety → **Longer**
ZDMC < ZDEC < ZDBC < ZBEC
TMTD < TETD < TMTM < TBzTD
MBT < MBTS < ZMBT
CBS < TBBS < MBS < DCBS
Longer

Cure Rate → **Faster**
ZMBT < MBTS < MBT
DCBS << MBS < CBS < TBBS
TMTM = TETD = TMTD
ZBEC << ZDBC = ZDBC = ZDMC
Faster

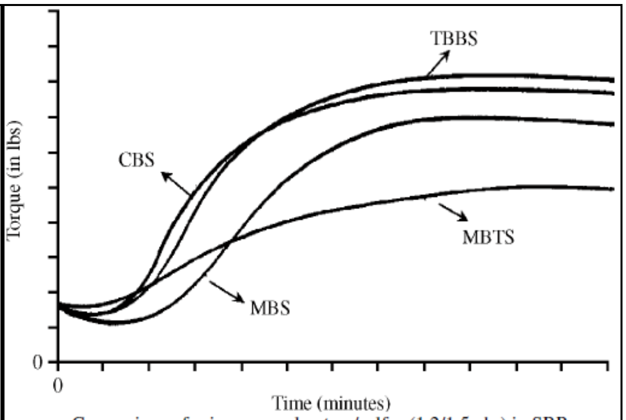
Cross link density → **Higher**
ZMBT < MBT < MBTS
DCBS << MBS < CBS < TBBS
ZBEC << ZDBC < ZDEC < ZDMC
TMTM = TETD = TMTD
Higher

Rheographs: Accelerators 0.5 phr + Sulfur 2.5 phr in NR compound @ 145°C:





Comparison of primary accelerators/sulfur (0.5/2.5 phr) in NR at 144 °C



Comparison of primary accelerators/sulfur (1.2/1.5 phr) in SBR

Above Rheographs clearly indicate the Scorch characteristics, the Rate of cure and the State of cure offered by commonly used individual accelerators.

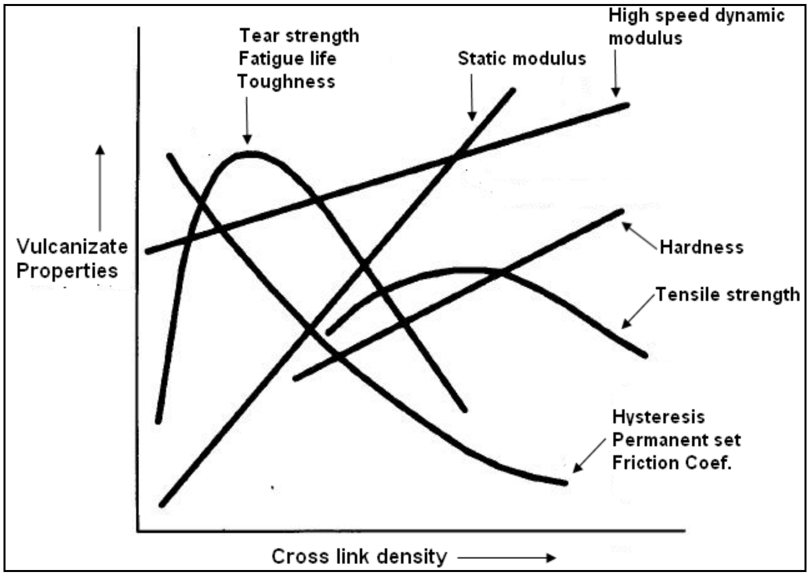
Vulcanization System (Cure system):

A typical sulfur vulcanization system consists of following ingredients:

Zinc oxide	3.0	to	10 phr
Stearic acid	1.0	to	4 phr
Accelerator	0.5	to	4 phr
Sulfur	0.5	to	3 phr

In this vulcanization system; for a particular rubber compound, selection of appropriate accelerators is a very important task since both the accelerator type as well as dosage greatly influence processing and vulcanizate properties of the rubber compound.

- ***Cross link density & Vulcanizate properties:***



Cross link density is = Number of molecules of cross linked units *per unit weight* of the cross linked polymer.

Degree of cross linking = Number of *molecules of cross linked basic units* per total number of polymer basic units.

Vulcanizate Properties of a rubber vulcanizate depend strongly on the cross link density. Properties like static modulus, dynamic modulus & hardness increase as the cross link density increases. The fracture properties like Tensile Strength and Tear Strength pass through a maximum value as the cross link density increases and then decrease.

Avg Molecular Wt of the polymer between two adjacent cross links (Mc) is related to the tensile strength of the vulcanizate. [The practical value of Mc is 8000-10000 i.e.114 to 144 repeating monomer units between the two cross links if the monomer has a Mol. Wt =70]. When un-crosslinked rubber is stressed; the rubber molecule chains readily slide over one another and detangle. At slow rate the fracture occurs at low stress by viscous flow without breaking any chemical bonds. The introduction of few cross links increases the molecular weight of the chain creating a branched molecule and a broader molecular weight distribution. This creates more difficulties for the branched chains to detangle & thus increasing the tensile strength of rubber.

Rubbers have an optimum range of cross link density for their practical usage. The cross link level has to be high enough to prevent fracture due to viscous flow but low enough to avoid brittleness.

The degree and type of cross links are most important factors for achieving the desired vulcanizate properties. The type of cross links depends on:

- *Sulfur dosage,*
- *Accelerator type,*
- *Accelerator / Sulfur ratio,*
- *Cure time.*

Generally, high Accelerator / Sulfur ratio and longer cure time increase the number of monosulfide cross link formation at the expense of polysulfide cross links. Such vulcanizates exhibit better heat stability, lower compression set and longer reversion time as compared to polysulfide predominant net work due to better stability of C-S bonds as compared to S-S bonds. On the other hand; vulcanizates containing higher proportions of polysulfide cross links offer higher tensile strength, tear strength & flex-fatigue resistance due to the ability of S-S bonds to break reversibly and there by locally releasing high stresses which could initiate failure.

Sulfur cure systems for highly unsaturated general purpose rubbers are classified as:

- *Conventional Cure (CV),*
- *Efficient Vulcanization Cure (EV)*
- *Semi Efficient Vulcanization Cure (SEV).*

This classification is based on the ability of the system to combine sulfur / sulfur donor and polymer chains with sulfur cross links (of desired types, proportions & with desired total cross link density). Sulfur & Accelerator dosages and Accelerator: Sulfur ratios are the differentiating factors of this classification.

Vulcanization System	**Conventional (CV)**	**Efficient (EV)**	**Semi Efficient (Semi EV)**
Sulfur Dosage, phr	2.0-3.5	0.4-0.8	1.0-1.7
Accelerator Dosage, phr	0.4-1.2	2.0-5.0	1.2-2.4
Accelerator/Sulfur Ratio	0.1-0.6	2.5-12.0	0.7-2.5

Conventional Vulcanization System (CV):

This term is used for natural rubber, polyisoprene and butadiene based synthetic rubber compounds, when relatively higher dosages of sulfur (above 1.5 phr) and lower dosages of accelerators (0.5 to 1.0 phr) are used.
The combined sulfur with rubber exists predominantly in the 'Polysulfidic cross links' form and the amount of free sulfur and the ratio of free sulfur to accelerator varies from rubber to rubber. A fair degree of wasted sulphides and main chain modifications are present in the vulcanizate. In SBR & BR vulcanizates poly and di-sulfidic cross links are predominant. The conventional vulcanization system gives poor reversion; oxidative heat and long term flex resistance. However; the vulcanizates exhibit good tensile and tear strength, good fatigue and low temperature resistance. Typical conventional curing systems for various elastomers are given below:

Ingredients	*Conventional Cure Systems*		
Polymer	*NR*	*SBR*	*NBR*
Zinc Oxide, phr	5.0	5.0	5.0
Stearic Acid, phr	2.0	2.0	1.0
Sulfur, phr	2.5	2.0	1.5
CBS, phr	0.6	1.2	1.0

Efficient Vulcanization System (EV):

This term is used for natural rubber, polyisoprene and butadiene based synthetic rubber compounds, when very low dosages of sulfur (below 0.4-0.5 phr) and higher dosages of accelerators (2.5 to 5.0 phr) are used.
EV Systems may comprise of a sulfur donor instead of elemental sulfur or a combination of low concentration of elemental sulfur (less than 0.5 phr) and high concentration of accelerators. Sulfur donors capable of donating one / two sulphur atoms are used. The EV system makes efficient use of sulfur for cross linking and produces a network containing thermally stable Monosulfidic & Disulfidic cross links with much less chain modifications. The short sulfur cross links provide poor tensile & tear strength, poor flex-fatigue life and abrasion resistance. However EV cure systems offer good heat aging and compression set resistance. These cure systems are generally used for rubber products with thick cross section and for products with static applications.Typical EV curing systems for various elastomers are given below:

Ingredients	*EV Cure Systems*					
Polymer	*NR*		*SBR*		*NBR*	
CBS, phr	3.0	1.0	1.5	1.2	2.0	1.5
TMTD, phr	-	1.0	3.0	1.2	3.0	1.5
DTDM, phr	-	1.0	-	1.2	-	1.5
Sulfur, phr	0.5	-	0.3	-	0.3	-

Semi Efficient Vulcanization System:

This term is used for natural rubber, polyisoprene and butadiene based synthetic rubber compounds, when sulfur and accelerator concentrations are between those of conventional vulcanizing system and the EV system. The Semi-EV cure systems are an attempt to find out a compromise between CV & EV cure. The Semi EV system has found particular application in NR where compromise between heat ageing and fatigue life is often necessary. Typical Semi EV cure systems for various polymers are given below.

Ingredients	*Semi-EV Cure Systems*					
Polymer	*NR*		*SBR*		*NBR*	
CBS, phr	1.5	0.6	2.5	1.0	1.0	1.2
TMTD, phr	0.5	-	-	-	1.0	-
DTDM, phr	-	0.6	-	1.0	-	1.2
Sulfur, phr	1.5	1.5	1.2	1.2	1.0	1.0

The number of Sulfur atoms in a cross link:

The number of Sulfur atoms in a cross link depend on the type of cure system used for vulcanization.

Vulcanization System	*Sulfur atoms per cross link*
Un-accelerated sulfur vulcanization	40 - 45
Conventional (accelerator-sulfur) cure	10 - 15
Semi-Efficient Vulcanization (Semi - EV cure)	5 - 10
Efficient Vulcanization (EV - cure)	4 - 5
Elemental sulfur less Vulcanization (Sulfur donor cure)	less than 4

Type of cross links:

The type and distribution of cross links in a given cure system also depends on the type of cure system used.

Cure	NR Conventional		NR-EV	
Sulfur , phr	2.5	2.5	0.4	0.4
CBS , phr	0.6	0.6	6.0	6.0
Cure Temperature , °C	140	140	140	140
Cure Time, minutes.	40	70	40	70
Cross link Types				
% Polysulfidic	48	33	0	0
% Disulfidic	38	33	26	9
% Monosulfidic	14	33	74	91

The Semi EV Cure has about 35% Monosulfidic, 35% Disulfidic & 30% Polysulfidic cross links.

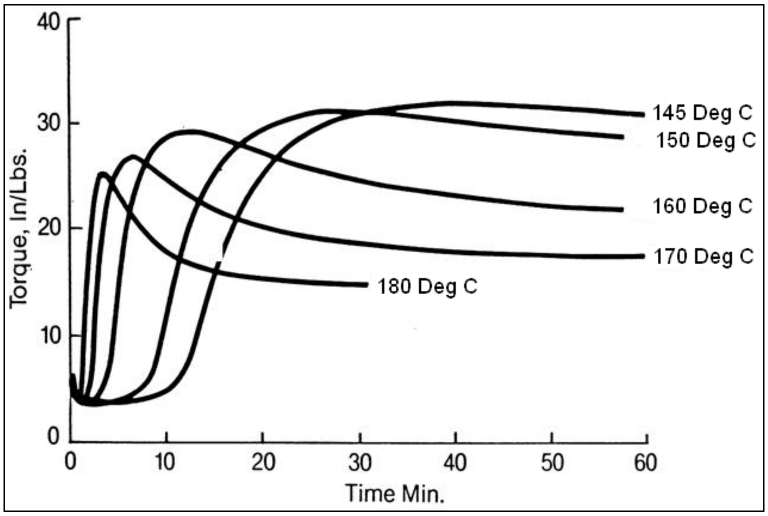
Effect of Cure Systems on Cross link types and vulcanizate properties:

The cure system selected influences the properties of the vulcanizates as summarized in the following table.

Cure System	Conventional	Semi-EV	EV
Poly + Disulfidic cross links, %	95	50	20
Monosulfidic cross links, %	5	50	80
Cyclic sulfides concentration	High	Medium	Low
Reversion Resistance	Low	Medium	High
Heat aging Resistance	Low	Medium	High
Flex-Fatigue Resistance	High	Medium	Low
Heat Build-up	High	Medium	Low
Tear Resistance	High	Medium	Low
Compression Set	High	Medium	Low

Effect of vulcanization temperature:

Vulcanization temperature has a significant effect on crosslink structure. Optimum properties are obtained when curing is done at the lowest possible temperature. However, to increase productivity, higher temperatures are frequently used. The modulus decreases with increase in cure temperature irrespective of type of accelerator used, which could be recovered to a great extent by increasing dosages of accelerators.

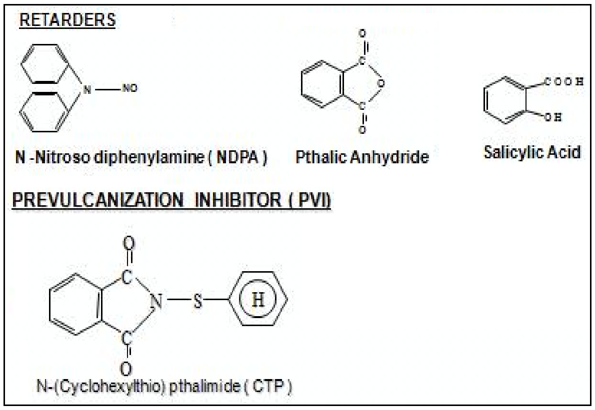


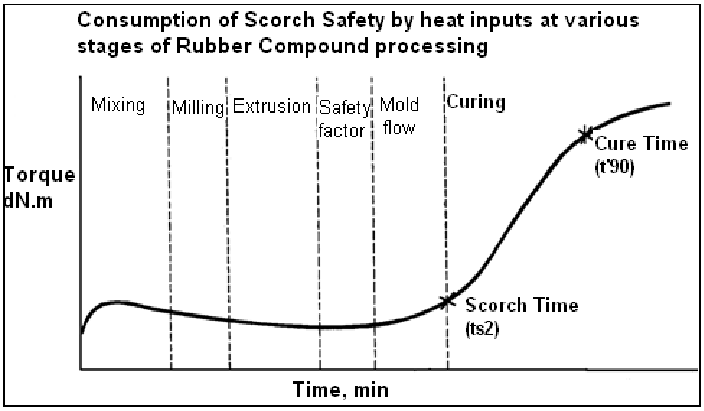
Retarders:

A proper balance of rubber processing safety and faster curing rates is essential for the increased productivity and economic use of high value rubber processing equipments. Often higher processing temperatures are used along with faster accelerator combinations and higher vulcanization temperatures are used to reduce the vulcanization time.

Sometimes the rubber processing temperatures reach a temperature just 10°C below the actual vulcanization temperature and this induces 'onset' which is known as *Scorch or Premature Vulcanization.* The 'scorch' at a little advanced stage renders rubber compound useless for further processing or vulcanisation. Only few 'scorched' particles reduce the physical properties of the vulcanizate drastically.

To avoid scorch with faster curing systems and / or with higher processing temperatures and prolonged storage; ‘Retarders' or ‘Pre Vulcanization Inhibitors (PVI) ' are added during compounding.





Traditionally, salicylic acid, pthalic anhydride, acetyl salicylic acid and NDPA (N-nitroso diphenylamine) were used as retarders at 0.3 - 1.0 phr levels. However, the acidic retarders retard cure rate and are ineffective with Sulphenamides. The NDPA retarder causes severe staining; is less effective with PPD class antidegradants and cannot be used with MBS or DTDM type Morpholine derived products because of possible formation of a suspect carcinogen N-nitrosomorpholine.

Pre Vulcanization Inhibitor:

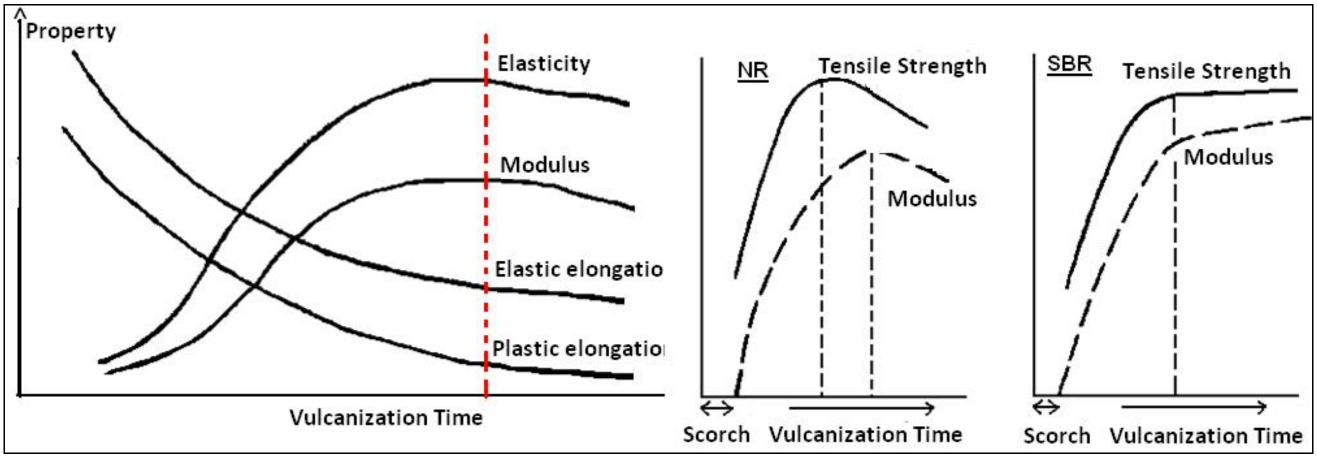
Pre Vulcanization Inhibitor (PVI) N-cyclohexyl thiopthalimide (CTP) has solved most of the problems associated with conventional retarders. CTP is most effective at sulphur dosages between 1.5-1.3 phr. CTP is very sensitive with sulfenamide accelerators and hence it is important to determine the optimum dosage of CTP needed for obtaining the desired processing safety for a given compound under prevailing processing conditions.

Generally 0.1 – 0.2 phr dosage is of CTP is sufficient. Excess CTP dosage should be avoided as it can delay the cure time or render the product under cured. CTP exhibits a linear relationship between its dosage and the scorch time offered. CTP is most effective with the fastest curing polymers and the approx. order of response is NR > NBR > SBR > EPDM > IIR > CR.

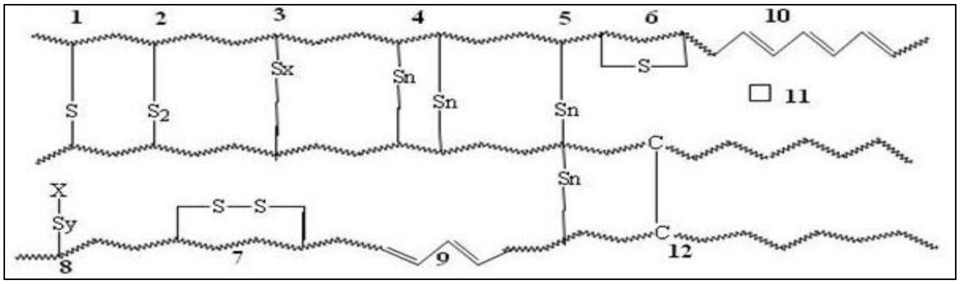
Sulfur Vulcanization Chemistry:

Many studies have been carried out to understand the mechanism of rubber vulcanization with sulfur in the presence of accelerators and activators. Vulcanization is the phenomenon of formation of cross links with rubber macromolecules. These cross links can be made up of sulfur atoms or they can have some other chemical composition if other cross linking agents are used. Transformation of rubber from plastic to elastic state, lack of solubility in organic solvents, limited swelling ability, as well as modification of certain important physico-mechanical properties, like tensile strength, elasticity, elasticity modulus, relative and plastic elongation, plastic compression, heat evolution, swelling stability, permeability to gases, resistance to low temperatures, can be explained by the presence of these cross links.

In the case of natural rubber NR both tensile strength and modulus display a peak followed by a decrease of their values. The latter phenomenon is called Reversion. In the case of styrene-butadiene rubber (SBR) the tensile strength remains approximately constant, while the modulus increases (marching cure) and when the vulcanization time is too long leading to over cure, sudden reduction of elongation at break occurs, which is not observed in the case of natural rubber. The variation of mechanical properties (tensile strength, elasticity modulus) depends on nature of the polymer.

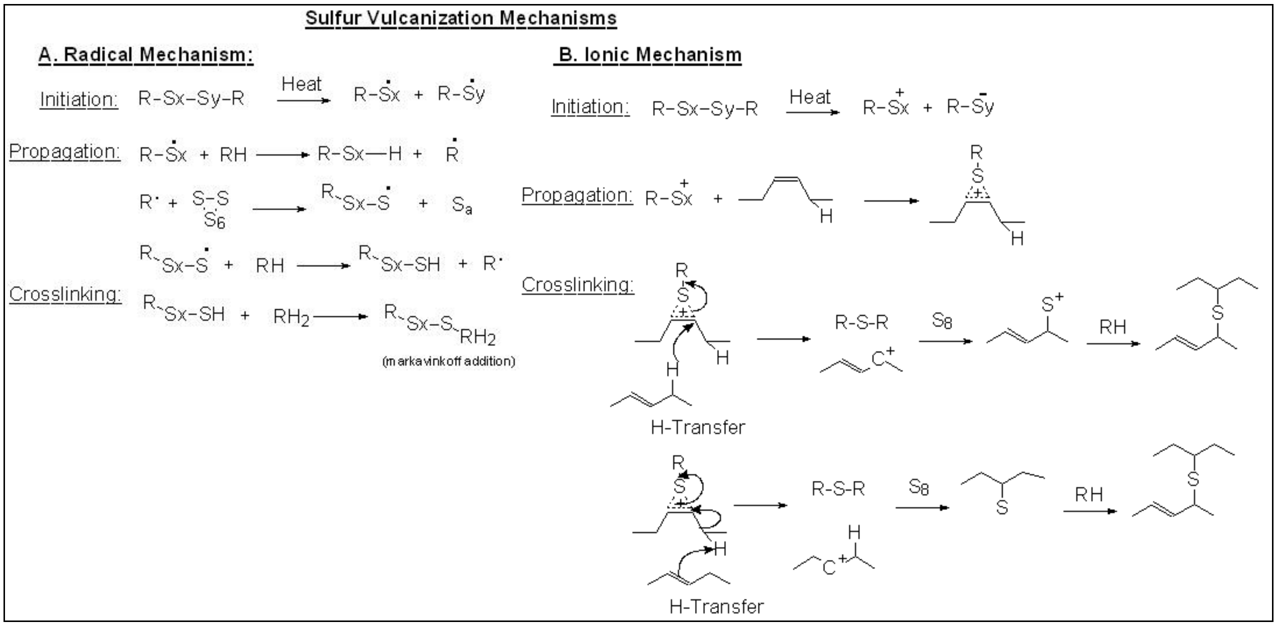


Typical Chemical Groups present in Sulfur Vulcanized Natural Rubber:



1. Monosulfidic cross links.
2. Disulfidic cross links.
3. Polysulfidic cross links.
4. Parallel vicinal cross links (n=1 to 6) attached to adjacent main chain atoms & act as a one cross link.
5. Cross links that are attached to common or adjacent carbon atom.
6. Intra-chain cyclic monosulfides
7. Intra-chain cyclic disulfides.
8. Pendent sulfidic group terminated by moiety X derived from accelerator.
9. Conjugated diene.
10. Conjugated triene.
11. Extra net-work material.
12. Carbon-Carbon cross links (probably absent).

Cross links which form bridges between the chains are stress bearing members contributing to elasticity and strength. Cyclic sulfides, accelerator fragments, vicinal cross links do not contribute to elasticity. ‘Sx’ refers to cross links consisting of more than two sulfur atoms (Polysulfidic cross links). ‘Sx’ gets desulfurated to form di or mono sulfidic cross links with the action of heat (as low as at 90 - 100°C).



Accelerated Sulfur Vulcanization:

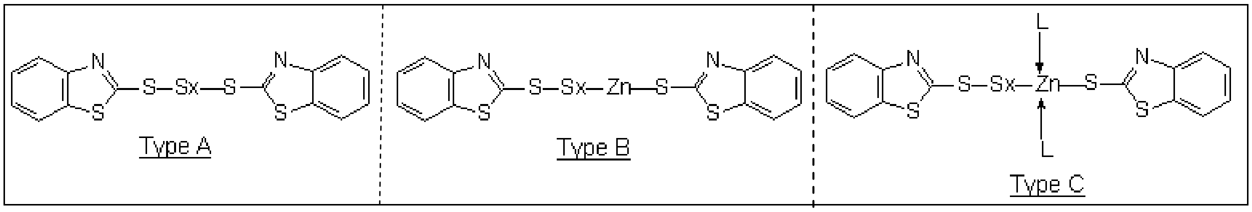
The accelerated sulfur vulcanization chemistry is very complex since several chemical reactions start at the same time following their own speeds at the selected vulcanization temperature. Both radical and ionic reactions are involved and the resultant effect depends largely on the compounding formulation. The crosslink structure depends on the nature of rubber, ratio of sulphur to accelerator and temperature of vulcanization. Following table summarizes the dependence of compounding formulation on the type of reactions.

Type of mechanism	*Cure System*
Radical	NR + CBS + Sulfur
	NR + TMTD + Sulfur
	NR + TMTD
	NR + Sulfur
Ionic	NR + TMTD + Sulfur + ZnO + St.acid
	NR + TMTD + ZnO
Mixed (Radical + Ionic)	NR + CBS + Sulfur + ZnO + St.acid

Three competing reactions occur simultaneously during vulcanization.

- *Cross linking,*
- *Desulfuration*
- *Degradation.*

The first step in accelerated sulfur vulcanization is the formation of 'Accelerator-polysulfide' by reaction of Accelerator + Zinc Oxide + Stearic acid + Sulfur. In the absence of Zinc Oxide molecule of the Type A is formed. The organic pendent group in this Type A molecule is Benzothiazole. (When other than thiazole accelerator is used; the organic pendent group will be different but the polysulfidic nature is the same.)

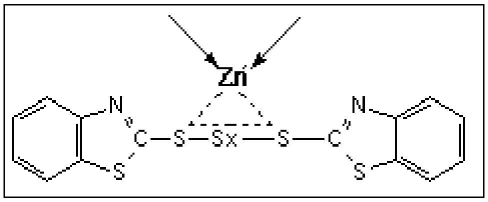


Type A

Type B

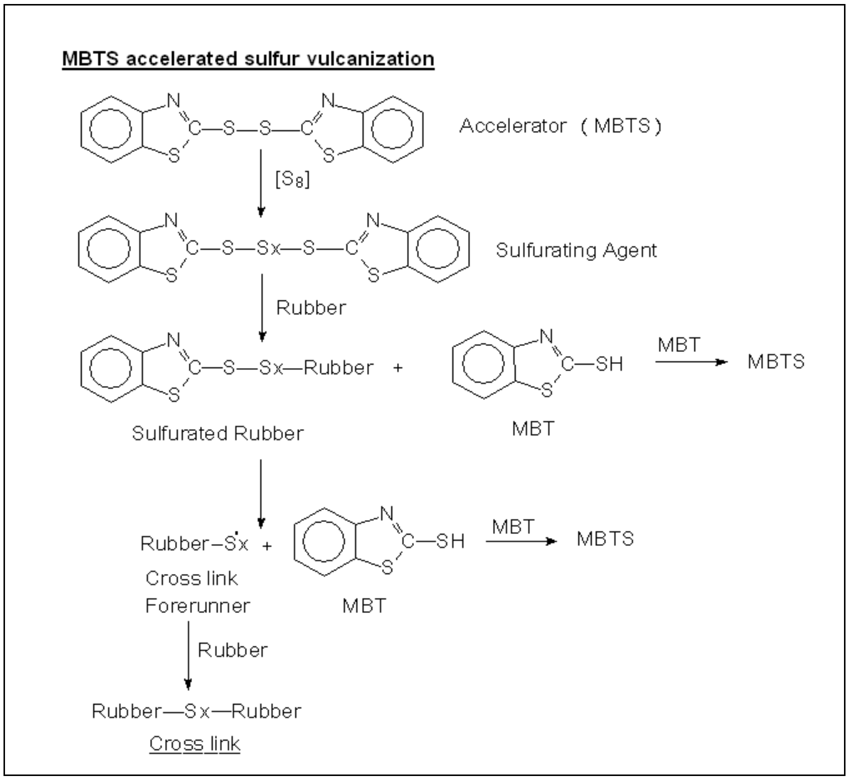
Type C

In the presence of Zinc Oxide molecule of the Type B is formed. The organic pendent group in this Type B molecule is Benzothiazole. In the presence of an amine legend L (released by decomposition of sulfenamide) a molecule of the Type C is formed. These structures suggest that Zn is covalently bonded as a part of polysulfidic chain in the accelerator species. It is also possible that Zn forms a complex with sulfur in the Accelerator-polysulfide as shown below:

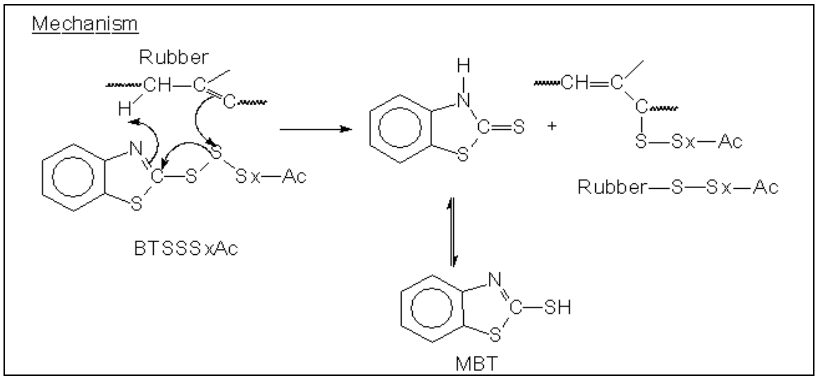


All these molecules are capable of sulfurating rubber chains and are considered as 'Active Sulfurating Agents'.

Thiazole accelerated sulfur vulcanization:



- In the presence of heat MBTS molecules react with sulfur to form a ‘Sulfurating Agents’ of the type - Monomeric Polysulfides **Ac-Sx-Ac**.
- The Polysulfide Sulfurating Agent molecules react with rubber molecules to form ‘Sulfurated Rubber Molecules of the type- polymeric polysulfides **Rubber-S-Sx-Ac** and release MBT molecules. Two MBT molecules react to form MBTS again.
- The Sulfurated Rubbers decompose into **Rubber-**$\mathbf{S}_x^{\cdot}$ type radicals which are the ‘Cross link Forerunners’ and in the process release MBT molecules. Two MBT molecules react to form MBTS again.
- A Cross link Forerunner combines with another rubber molecule to form Rubber-Sx-Rubber Cross link.



Sulfenamide Accelerated Sulfur Vulcanization:

Three major aspects which decide the activity of a sulfenamide are:

- The basicity of the amine and the steric hindrance offered by it. (The amine may be primary or secondary. More the basicity of the amine; shorter is the scorch time and faster is the cure rate. Sterically hindered amines offer longer scorch delay and slower cure rates.)
- The strength of S-N bond. (Well stabilized S-N bond offers longer scorch delay.)
- The presence of MBT molecule. (Accelerator of sulfur vulcanization.)

The innovations for development of sulfenamide accelerators were focused on improving the scorch safety of NR based tire compounds and improving their storage stability. New sulfenamide accelerators were introduced to accommodate the extra scorch safety required for the processing of new fine particle size hard carbon blacks which offer higher abrasion resistance for the tire tread compounds.

It is now generally accepted that the sulfenamide accelerator in the presence of sulfur decomposes due to heat into MBT & respective amine.

MBT thus formed auto catalytically reacts with remaining sulfenamide molecules to form MBTS and release amine molecules.

These two reactions offer the scorch delay exhibited by the sulfenamide accelerators.

Elemental sulfur then reacts with the MBTS giving a polysulfide (MBPT) which is an active Sulfurating agent.

MBPT attacks the allylic position of the rubber molecule to form a polythio-mercapbenzothiazyl group attached to the polymer chain (and is known as pendent group or rubber bound intermediate or cross link precursor).

The sulfenamide decomposition is an autocatalytic reaction due to the presence of MBT and its rate is proportional to the amount of MBT present.

Sulfur gets exclusively attached to the polymer chain at the allylic position in the presence of accelerator (where as sulfur is attached to other positions of the rubber chain due to the radical mechanism in the absence of an accelerator).

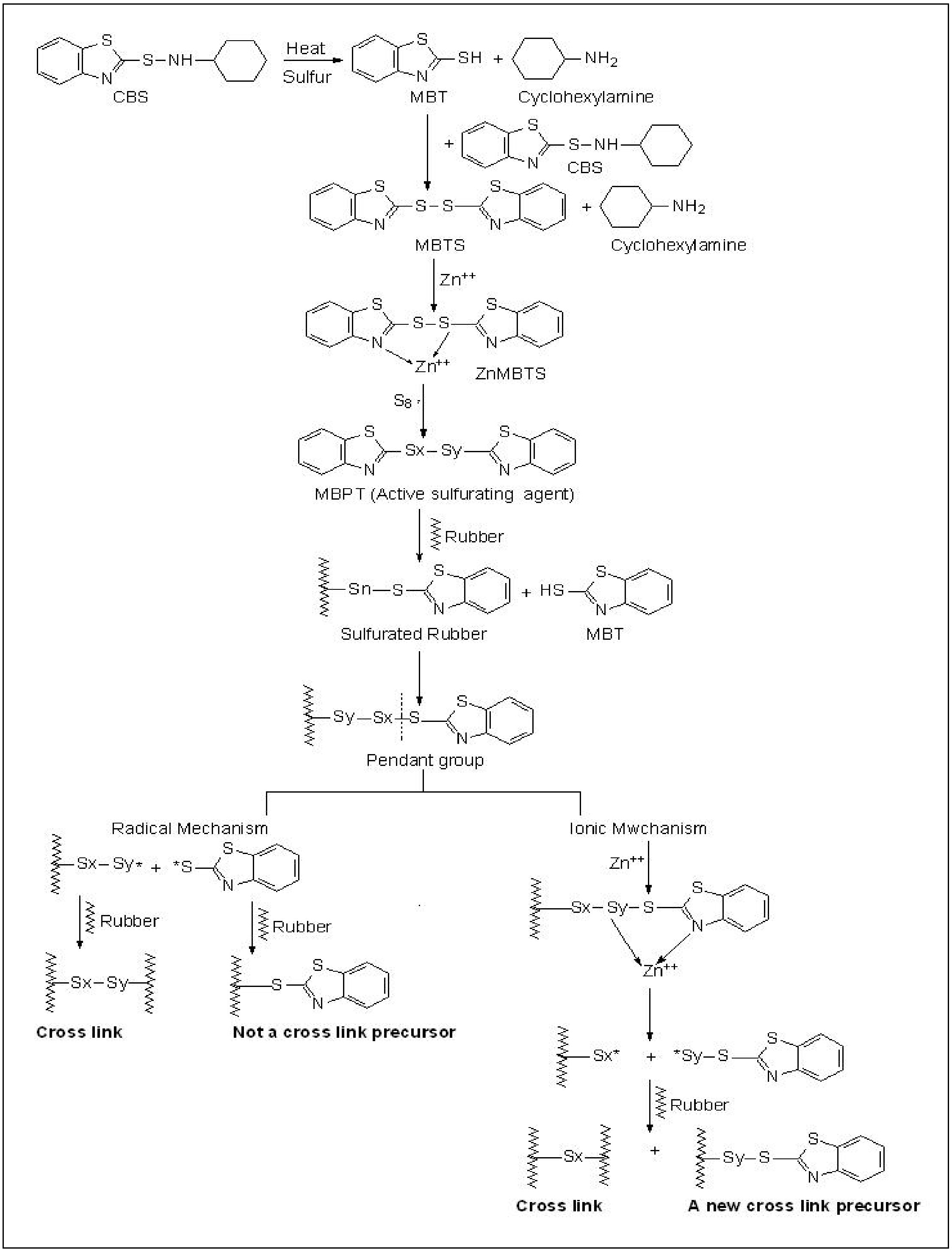
In the final step second rubber molecule is attacked to the cross link precursor by the MBT addition to form a cross link containing 1, 2, 3 or more sulfur atoms.

Only the last step of cross link formation is detected in the Rheometer curve.

This mechanism confirms that the cross linking of rubber with sulfur takes place at C=C double bonds and thus saturated rubbers cannot be cross linked by sulfur.

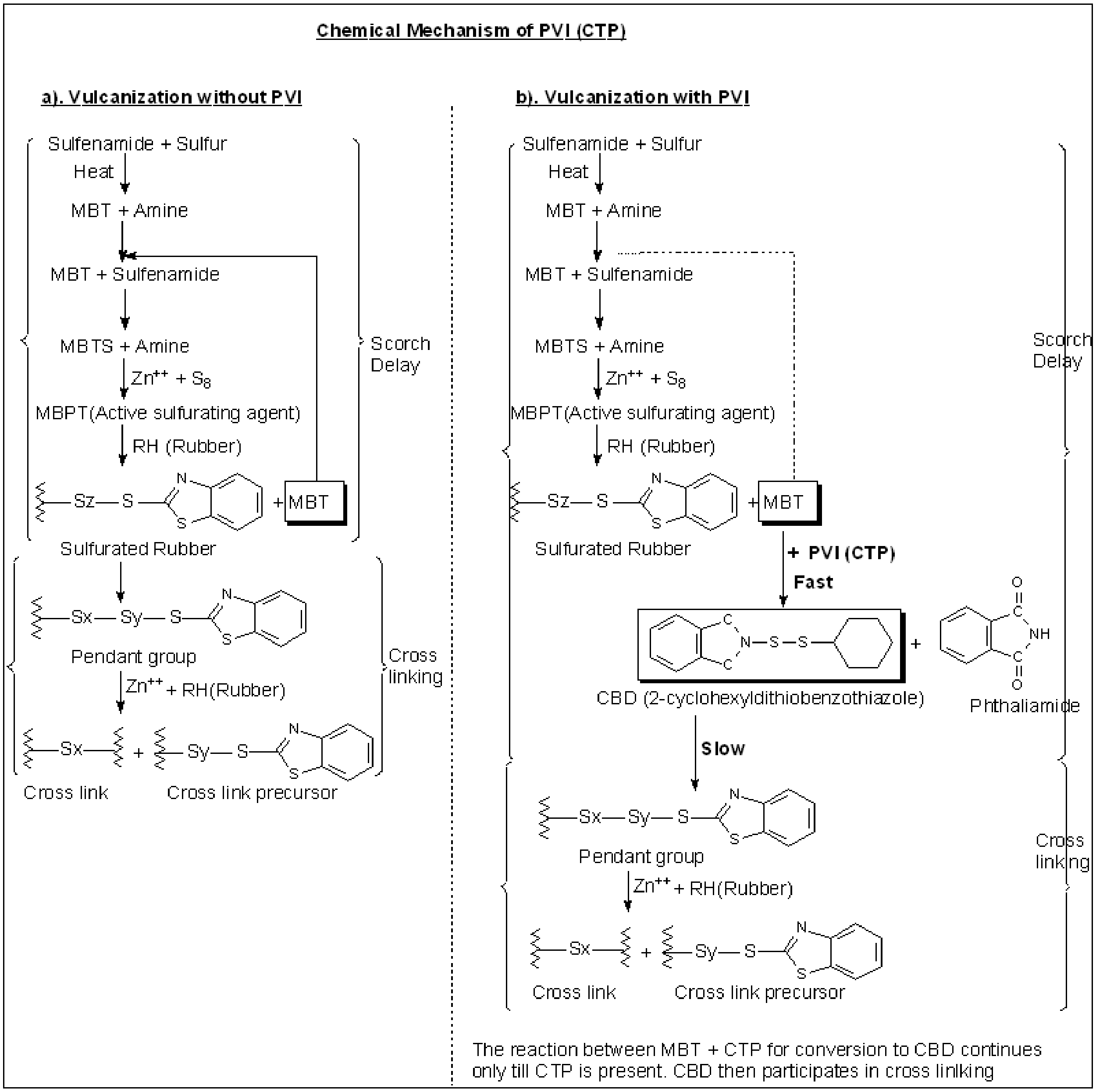
The generally accepted scheme of sulfenamide accelerated sulfur vulcanization is as follows:

CBS Accelerated Sulfur Vulcanization:



Pre Vulcanization (Scorch) Inhibition chemistry of CTP:

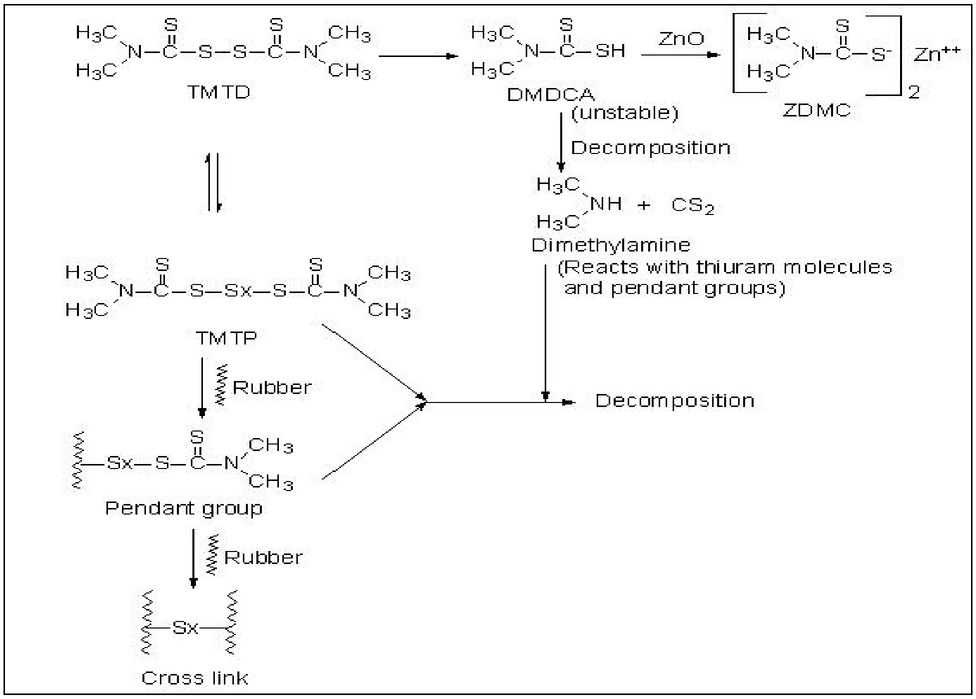
In the absence of PVI; sulfenamide decomposes into MBT and amine. MBT thus released initiates autocatalytic decomposition of sulfenamide accelerator. Sulfur Cross linking does not start as long as the sulfenamide is not depleted. MBT then gets converted to MBTS for cross linking to start via formation of active Sulfurating agent followed by sulfurated rubber & pendant groups.



In the presence of PVI (CTP); the MBT released is instantly converted to CBD and this reaction continues till CTP is present. CTP thus scavenges the auto catalyst MBT required for the formation of cross link precursor and delays the scorch. CBD itself is a delayed action accelerator and its quantity depends on the dosage of CTP added. CBD then participates in the cross linking process like any other sulfenamide accelerator.

Thiuram accelerated vulcanization:

Although Thiuram accelerators can be used as primary accelerators these are extremely scorchy and exhibit very fast curing rate. When these are used as primary accelerators for low temperature cure or rapid high temperature cure they produce cross links of shorter lengths which are heat and reversion resistant.
Thiuram accelerator TMTD has 13.3 % available sulfur for cross linking and it also acts as an accelerator of vulcanization and hence its chemistry of vulcanization is complex. In the thiuram accelerated sulfur vulcanization both ionic and radical chemical reactions take place at the same time.



During TMTD accelerated vulcanization in the presence of Zinc Oxide dimethyl dithiocarbamic acid DMDCA is formed as a by-product. DMDCA is highly unstable and decomposes into Dimethyl amine (DMA) and carbon di sulfide (CS_2). DMA then rapidly reacts with TMTD and destroying the TMTD molecules and the pendant group. These reactions do not involve ZnO but ZDMC is also formed by reaction with DMDCA releasing water which prevents destruction of TMTD & Pendant groups. Thus the presence of ZnO is necessary.

Post Vulcanization Net work reactions:

The initially formed cross links are predominantly polysulfidic. During post cross linking or product service these polysulfidic cross links get degraded (into cyclic polysulfides, dienes, ZnS etc.) and desulfurated (into more stable mono or disulfidic cross links). Such rearrangements change the original vulcanizate properties considerably.

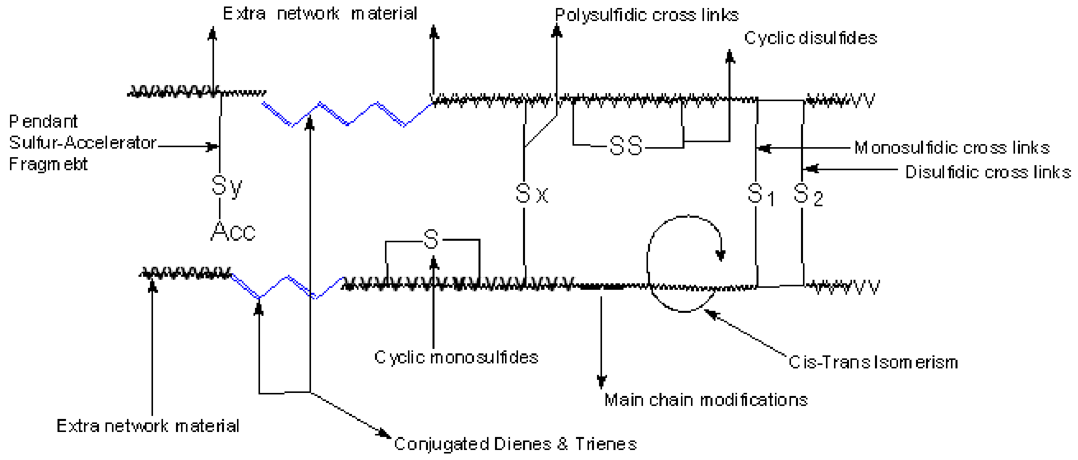
$R\text{-}S_x\text{-}Ac \rightarrow$ Cyclic Sulphides + Dienes + ZnS *(Degradation)*

$R\text{-}S_x\text{-}Ac \rightarrow R\text{-}S_{x\text{-}y}\text{-}Ac + S_{x\text{-}1}$ (*Desulfuration)*

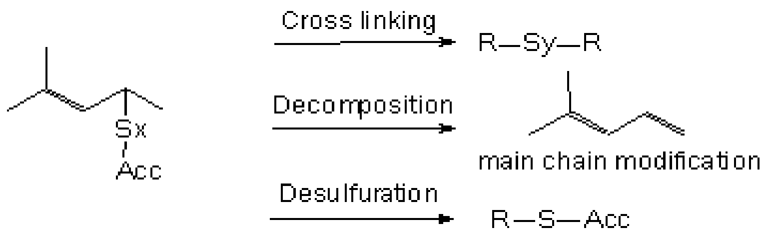
$R\text{-}S_y\text{-}R \rightarrow R\text{-}S\text{-}R + S_{y\text{-}1}$ *(Monosulfidic Cross links)*

$R\text{-}S_{x+y}\text{-}R + Ac\text{-}S_x\text{-}Ac \rightarrow R\text{-}S_x\text{-}R + Ac\ \text{-}S_{y+z}\ \text{-}Ac$ (*Sulfur Exchange)*

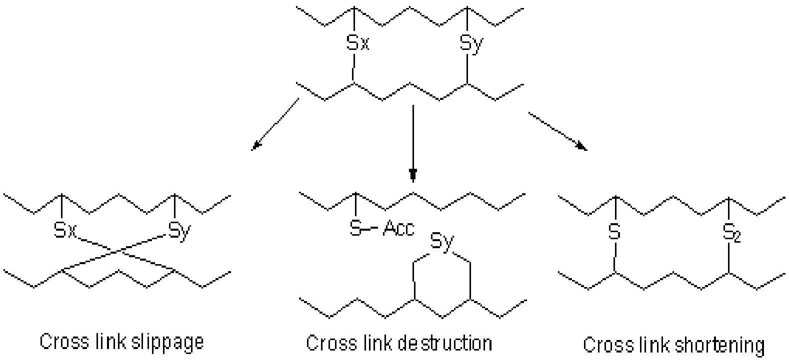
Post Vulcanization Network and onset of Reversion



Fate of cross link precursor

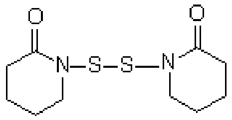
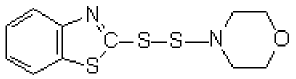
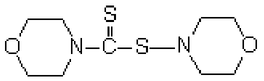
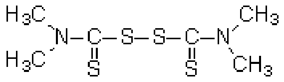
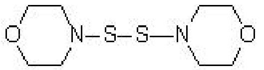
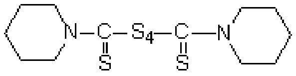


Fate of polysulfidic cross links in network



Sulfur Donor Vulcanization System:

Sulfur Donors

Material	Chemical Structure	Mol Wt.	Melting Point, °C	Active Sulfur, %
N, N-Craptolactam disulfide (CLD / DTDC)		224	120	11.1
2-morhilino-dithio benzothiazole (MBSS)		284	130	11.3
N-oxydiethylene thiocarbamyl-N'- oxydiethylene sulfenamide (OTOS)		248	130	12.9
Tetramethylthiuram Disulfide (TMTD)		240	155	13.3
4, 4'-Dithiodimorpholin (DTDM)		236	135	13.6
Dipentamethylene thiuram tetrasulfide (DPTT)		384	130	16.6

A vulcanization system in which there is no elemental sulphur present and all the sulphur available for the cross-linking is provided by the partial decomposition of sulphur containing materials (chemicals). (Note: Such cure systems offer EV type cures).

Sulphur donors are of two types. First, those which exhibit accelerator activity and also can directly substitute sulphur (e.g. DTDM, Craptolactam disulphide) without any major change in vulcanization characteristics and the second type (e.g. DPTT, TMTD) which mainly function as accelerators also so that adjustments in cure system are necessary. The amount of active sulphur present in sulphur donors is different for each chemical.

Sulphur donor cure system provides a stable vulcanization network with 80 % mono & disulphide type cross links. When the cure time is extended beyond the optimum cure the disulfidic cross links get converted to mono sulfidic cross links.

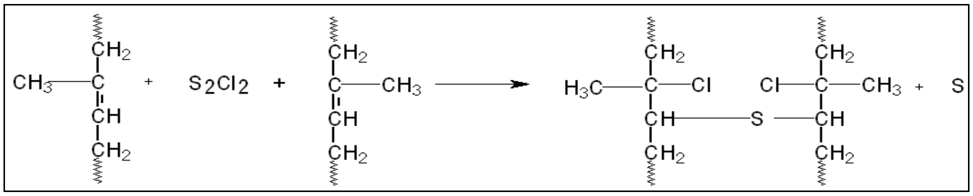
The network structure gives high heat and reversion resistance as well as compression set resistance but comparatively poor flex-fatigue and tear resistance properties.

This type of cure systems are used for manufacture of rubber products which cannot contain high amounts of elemental sulphur or are intended for applications requiring high heat and compression set resistance without emphasis on flex-fatigue resistance. The sulphur donors are also used for high temperature and Semi-EV cures to protect vulcanizates from reversion effects.

Sulfur Monochloride (S_2Cl_2) Cure:

Rubber can be vulcanized by exposure to S_2Cl_2 vapors on when immersed in a 5 % solution of S_2Cl_2 in petroleum naphtha / CS_2 .

The vulcanization reactions take only a few seconds at room temperature and hence known as cold cure' method. This method is used only for thin-walled products, proofing or for instantly cross-linking an adhesive film. Not very popular due to high toxicity of S_2Cl_2 solution and poor aging properties of the vulcanizate.

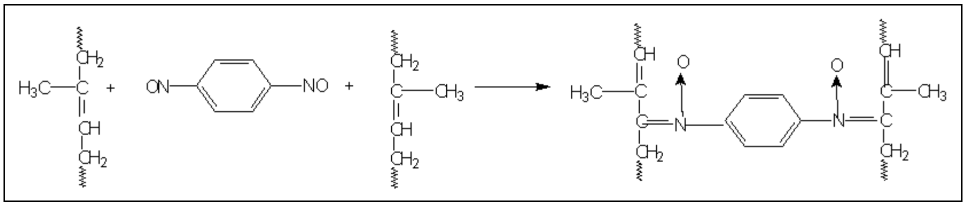


Non-sulfur Vulcanization Systems:

A vulcanization system not requiring free or donated sulfur. *(These are based on metal oxides, organic peroxides etc.)*

Quinone Dioxime Cure:

Para Benzoquinonedioxime and dibenzoyl quinine dioxime can cure many rubbers through their free radical reactions.



This type of cure is mainly used for butyl rubber (IIR) where sulfur cures are undesirable (too slow or sulfur presence is objectionable).

Combination of CDO/Dibenzo-CDO with ZnO, MBTS, Lead oxide can produce faster cure rates in IIR which can be suitable for continuous vulcanization process (e.g. cables).

The vulcanizates exhibit good tensile and compression set resistance properties and heat aging resistance.

Phenol Formaldehyde Resin Cure:

Phenol formaldehyde resins with para-alkyl substitutes can be used as vulcanizing agents for olefin rubbers (both high and low unsaturation rubbers). Resin cure gives carbon-carbon cross links with rubber via Methylol group and are stable under heat.

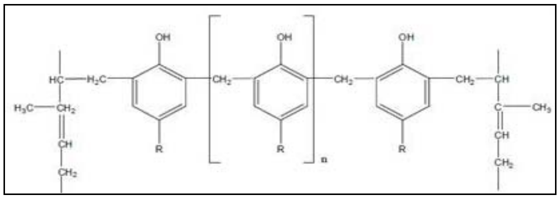
Vulcanization with resin alone is a very slow process even at high temperatures but addition of catalysts such as FeCl3, SnCl2 or polymers which liberate halogen acids (e.g. polychloroprene, chlorosulphonated polyethylene, etc). Increase the rate and state of vulcanization. The halogenated PF resin (e.g. brominated

PF resin) are self activating type hence inclusion of halogen donors is not necessary when halogenated PF resins are used as vulcanizing agents.

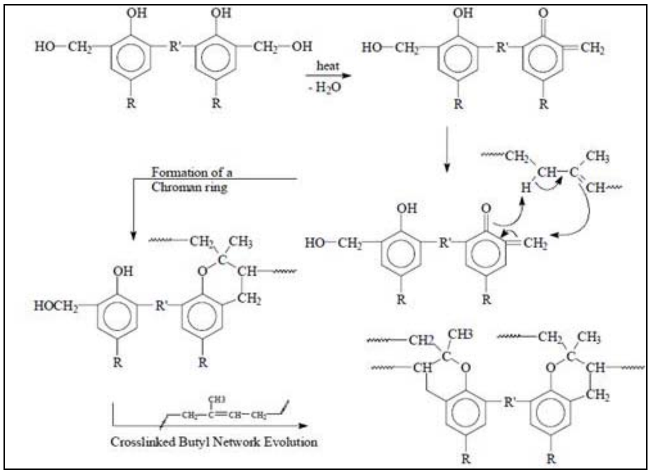
PF Resin cures are adversely affected by Amine type antioxidants and conventional rubber accelerators.
The physical properties of PF Resin cured NR are similar to those of peroxide cured NR. PF Resin cured butyl rubber is highly reversion resistant and exhibits very good heat and ozone resistance. The use of PF resin cure is limited to butyl rubber based tire curing bladders and air bags.

Cross linking mechanism

a). Through α-hydrogen



b) Through Chroman structure formation



Organic Peroxide Cure:

Organic peroxides are derived from hydrogen peroxide

$$\mathbf{H-O-O-H} \rightarrow \mathbf{R-O-O-H} \rightarrow \mathbf{R-O-O-R'}$$

(Hydrogen Peroxide) (Hydroperoxide) (Organic Peroxide)

Peroxide is defined as a chemical compound that contains oxygen – oxygen bonds. This bond breaks on heating to yield free-radical fragments (known as homolytic cleavage – two electrons of the bond are separated).

$$\mathbf{R-O-O-R'} \rightarrow \mathbf{HEAT} \rightarrow \mathbf{R-O^{\cdot} + {}^{\cdot}O-R'}$$

Free radical fragments **$R-O^{\cdot}$ & $^{\cdot}O-R'$** are highly reactive & initiate formation of cross links in the polymer.
The stability of peroxide bond depends on the composition of R & R'. The R & R' groups can be inorganic (e.g. sodium peroxide) or organic (e.g. benzoyl peroxide). The cross linking mechanism of peroxide vulcanization can be described as follows:

Three major steps are involved,
Peroxide undergoes hemolytic cleavage to form two alkoxy radicals as a result of (heat) energy input.

$$\mathbf{R-O-O-R} \rightarrow \mathbf{HEAT} \rightarrow \mathbf{2\,R-O^{\cdot}}$$

An alkoxy radical abstracts a hydrogen atom from a polymer chain

$$\mathbf{R-O^{\cdot} + P-H} \rightarrow \mathbf{P^{\cdot} + ROH}$$

Two radicals on adjacent polymer chains couple to form a carbon-carbon bond.

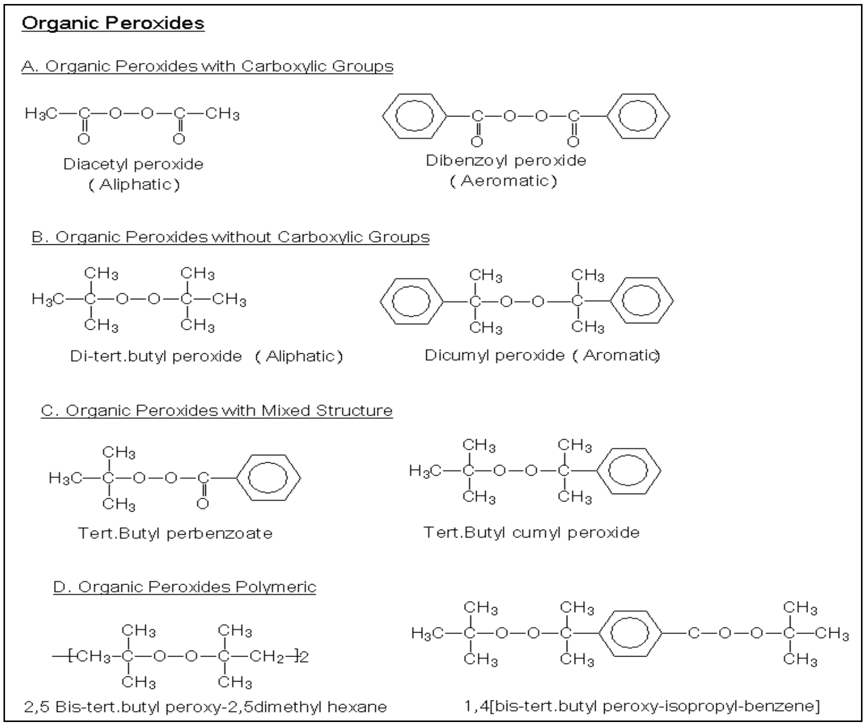
$$2P^{\cdot} \rightarrow P - P$$

The formation of C **- C** bond as a crosslink is an important feature of peroxide vulcanization. Thus, neither the peroxide nor the by-products are part of the crosslink hence the inherent polymer stability is retained after cross linking. The rate determining step is hemolytic cleavage of the peroxide molecule (which is completed in few seconds-or minutes). This is a first order reaction and the rate of this reaction is proportional to the concentration of the peroxide present at any time and is also controlled by the energy available for homolytic cleavage. The rate of radical formation depends on the temperature of the system.

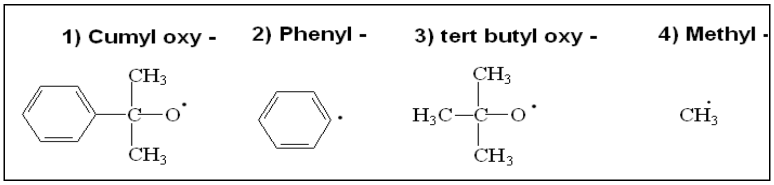
The cure time and temperature are related to the half life of the peroxide. (Half life is the time required for half the peroxide to decompose at the reaction temperature).The peroxides which have short half life can initiate cross linking at lower temperatures. The amount of peroxide remaining at any time = Initial concentration x 0.5 n (where n = number of half lives. (i.e. ½ half life remains after one half life, ¼ the half life remains after two half lives, 1/8th half life remains after three half lives and after five half lives about 97 % of the peroxide gets decomposed). For typical peroxides used in the rubber industry; the half life drops to about 1/3 rd for each 10°C increase in the temperature.

Peroxide cross linking is possible for NR, IR, BR, CR, SBR, NBR, HNBR, Silicone rubbers, polyurethane rubbers, EPM, EPDM, Polysulphide rubber, polyethylene, EVA, ABS *and not possible for IIR, CIIR, Epichlorohydrin, Polypropylene, Polybutene, Polyisobutene, & PVC.*

Classification 0f Organic Peroxides:



Peroxides with carboxylic acid groups exhibit low sensitivity to acid groups, have lower decomposition temperatures and are not useful in the presence of carbon black. Peroxides without carboxylic groups are very sensitive to acids, exhibit higher decomposition temperature and are less sensitive to oxygen. Aliphatic substituted peroxides are favorable over aromatic substituted peroxides. The preferred peroxides are those which form following radicals.



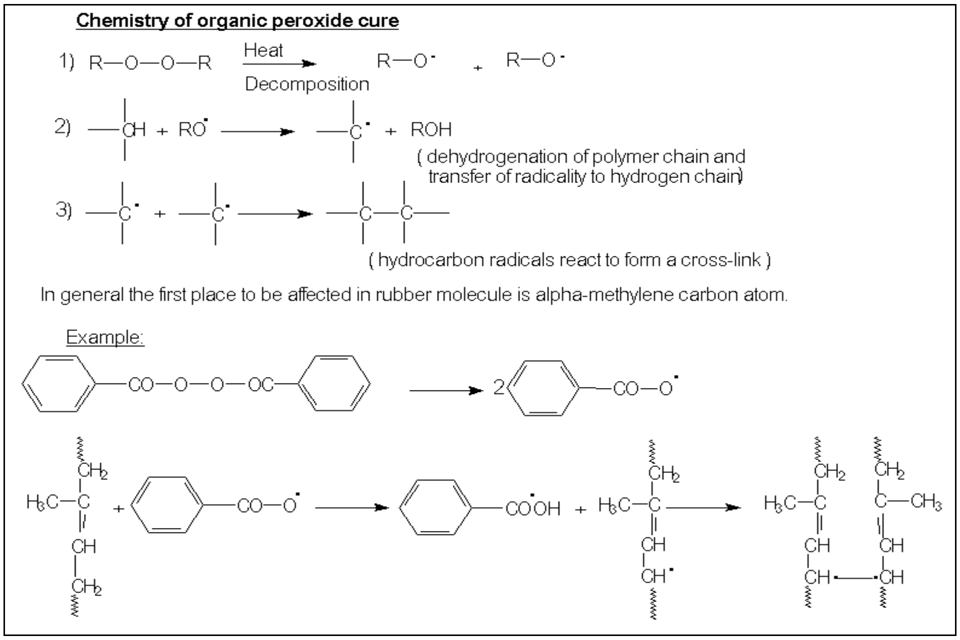
When symmetrical peroxides are used; two radicals of similar activity are formed which initiate cross linking reactions. In case of mixed peroxides; the more reactive radical acts as a cross linker and the other remains inactive. For most organic peroxides, the presence of oxygen during cure is not desired as the same causes degradation of the rubber very rapidly (hence sticky surface). For this reason; peroxide cure cannot be used for hot air or UHF heating cured products.

Advantages of Peroxide Cure over sulphur cure are:

- Simple formulation, long term compound storage stability and possibility of using higher processing temperatures.
- Rapid cure at high temperature and yet no reversion.
- Low compression and permanent set, high temperature resistance and no extractable constituents.
- Non-staining, non-blooming and non-discoloring.
- Co-vulcanization of saturated and unsaturated rubbers.

Disadvantages of Peroxide Cure are:

- High sensitivity to oxygen during cure.
- Process oils, antioxidants, resins, acidic clays and other acidic materials used in compounding can affect peroxide cure significantly and hence their selection is critical.
- Vulcanizate properties such as tensile strength, tear strength, flex- fatigue resistance, abrasion, etc. are significantly affected.
- Acceleration / retardation is mainly temperature dependant
- Foul odor to cured products in some cases.
- Long cures and higher curing temperatures required and post cure is necessary in most cases.
- Higher cost of peroxides and vulcanization process.



The peroxide cures are co-activated by polyvalent compounds such as Triallyl cyanurate (TAC), malic acid or reactive acrylic derivatives which produce several consecutive reactions with one peroxydic initiation. These get involved in the cross linking scheme and increase the cross link density apart from exhibiting some plasticizing effect.

Following table summarizes the organic peroxides popularly used in the Rubber Industry along with their key properties.

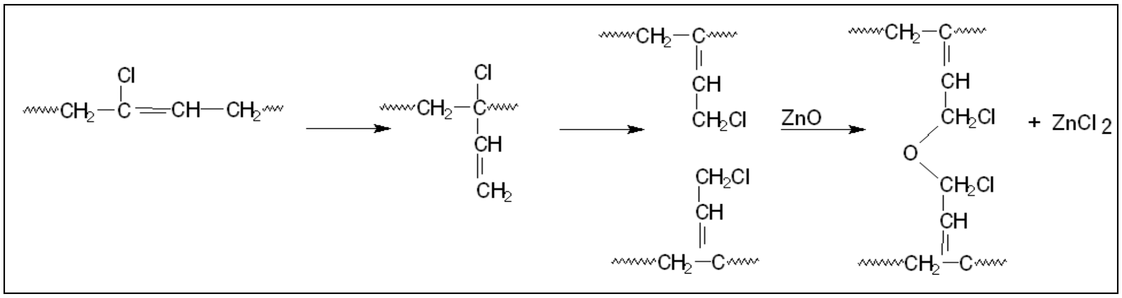
Chemical Name	10 hr. HLT, °C	Active Oxygen, % w/w	Rheometer Parameters		
			Temp, °C	T_2, min	T_{90}, min
Dibenzyl Peroxide	73	6.47	120	2.5	7.5
Tert-butyl peroxy benzoate	105	8.07	150	3.5	7.0
Dicumyl Peroxide	115	5.87	180	2.0	7.0
Bis (tetrabutylperoxy Isopropyl) benzene	117	9.26	180	3.0	12.0

Most peroxides that are commonly used in rubber compounding formulations are very stable and require high temperatures (above the rubber processing temperatures) for decomposition to occur. The extent of peroxide decomposition depends on its thermal history which includes both time and temperature. The relative measure of peroxide stability is 10 hr half life temperature (10 hr HLT). This is the temperature that is required to decompose 50 % of peroxide in ten hours. The 10 hr HLT varies greatly amongst peroxides. The peroxides which have a low 10 hr HLT decompose at a faster rate than those having higher values. Relatively stable peroxides (higher 10 hr-HLT) provide higher scorch resistance but generally exhibit slower curing rates.

Rubber	Dicumyl peroxide (98%), phr.	Bis (tert.butylperoxyisopropyl) benzene (98%), phr.
NR, IR	0.80 – 1.65	0.50 – 1.00
BR	0.40 – 0.75	0.20 – 0.50
CR	0.40 – 1.10	0.25 – 0.70
SBR	0.70 – 1.50	0.45 – 1.00
NBR	1.00 – 1.65	0.60 – 1.00
AU (Ester type)	1.90 – 3.20	1.20 – 2.00
EU (Ether type)	1.30 – 2.60	0.80 – 1.60
EPM, EPDM	2.50 – 4.00	1.50 – 2.50
PE	0.60 – 2.70	0.35 – 2.40
EVA	0.80 – 1.80	0.60 – 1.20
Safe processing Temperature, °C (= Scorch Time > 20 minutes)	120	130
Typical cross linking Temperature, °C	170	180
Typical Cure Times, minutes	12.0 – 15.0	12.0 – 15.0

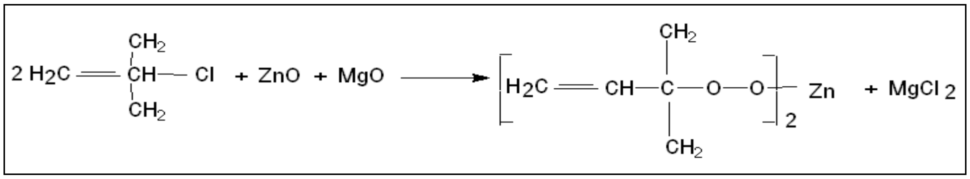
Metal Oxide Cure:

Metal oxide cure is used for non-olefin rubbers like Polychloroprene, Chlorosulphonated polyethylene, etc. which contain some active group through which they can be cross linked. In case of Polychloroprene, the double bond is ‘hindered’ by the neighboring chlorine atom and hence vulcanization by sulphur is not possible. The allylic shift of chlorine atom in the presence of zinc oxide makes cross linking possible as shown below.



MgO is included in the vulcanization system to act as a scavenger of chlorine atoms (and acceptor). Use of ZnO alone gives a fast on-set of cure (scorchy) and vulcanizates have poor mechanical properties. MgO when used alone is very safe but takes long time to vulcanize. Vulcanizates have moderate mechanical properties.

When a combination of ZnO – 5 phr + MgO – 4 phr is used, the cross linking effect is stronger and the scorch safety is within acceptable limits. Only Calcined and extra light MgO is used for high activity and is generally added first in the mixing cycle. Fine particle size ZnO is preferable and due to its scorchy behavior it is added at the end of the mixing cycle. Lead oxide and Red lead are used as vulcanizing agents for polychloroprene when lower absorption and higher acid resistance is desired. (The chlorides of lead are insoluble in water / acid). Lead oxide exhibits faster cure rates than Red Lead in case of Sulphur modified CR, however, the mercaptan modified CR responds in the similar manner to Lead Oxide as well as Red Lead. The cross linking mechanism in the presence of ZnO + MgO combination may be represented as follows :



Here, ZnO is main cross linking agent and MgO is a chlorine acceptor. However, ZnO also serves as a chlorine acceptor (like MgO) and small amounts of MgO do take part in cross linking reaction.

Practical Test Methods for Monitoring Vulcanization

Stress-Strain Properties

Test sheets vulcanized for various cure times at a particular vulcanization temperature are prepared. The test samples are tested for stress-strain properties using a tensile testing machine. The values of the modulus at 100, 200, 300 % elongation, the ultimate tensile strength, elongation at break, tear strength, etc. are plotted against the vulcanization time at the selected temperature. The values of each cure time represent the state or degree of vulcanization.

A plot of tensile strength Vs cure time reveals that the tensile strength values initially increase with the cure time and then pass through an optimum value before showing a decreasing trend as the cure time increases.

The cure time at optimum value of tensile strength is the state of optimum vulcanization at the vulcanization temperature as far as tensile strength is concerned. The optimum state of vulcanization could be different for different properties and according to end-property requirements the optimum state of vulcanization is determined. The optimum state of vulcanization could be different for different properties and according to end-property requirements the optimum state of vulcanization is determined.

Measurement of tensile modulus at 100 % elongation (E) is directly proportional to the crosslink density (1/2 Mc) which is expressed by following relationship.

$$E = \frac{3\,Pr\,RT}{2\,Mc}$$

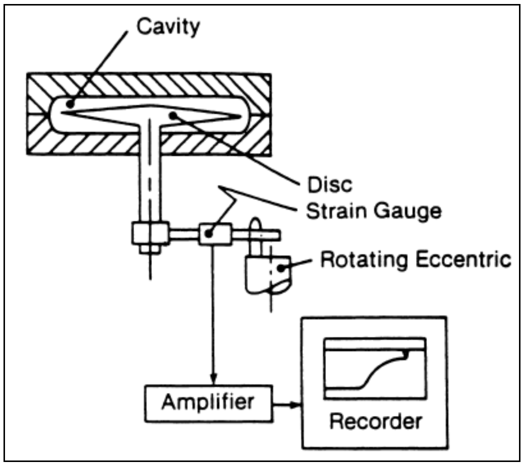
where, Pr = Density of Rubber ,
R = Universal gas constant,
T = Absolute Test Temperature,
Mc = Number average relative mol. mass between the cross links.

The accuracy of 100 % modulus measurements may raise some concern and hence often 300 % modulus is measured for day to day quality control in a factory.

Curometers

Curometers are designed for the testing of uncured elastomeric materials and produce a continuous cure curve of unvulcanized rubber compound sample which can be used to determine the curing characteristics.

Oscillating Disc Rheometer (ODR):

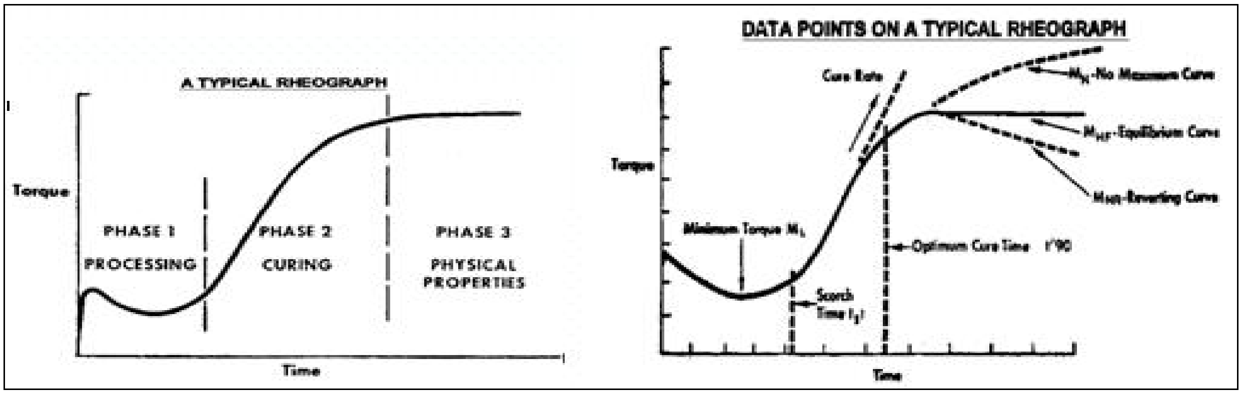


Uncured rubber sample is confined in a die cavity located in electrically heated platens. The die temperature can be selected within the range of 100 – 200 °C. The cavity is formed by a fixed lower die and a moveable upper die. The dies are kept closed during the test by a pneumatic pressure ram.

The rotor consists of a biconical disc with integral shaft. The rubber sample completely surrounds the biconical disc. The disc is oscillated at 100 cpm through an arc of 1°, 3° or 5° by a motor driven eccentric. The reciprocal motion is transmitted from the eccentric to the shaft through a connecting link and a torque arm.

The force required to oscillate the disc (and thus apply a shearing strain to the specimen) is measured electronically by the torque arm transducer. (The torque arm transducer consists of semi conductor strain gauges bonded to each side of the torque arm).

This force (torque) is plotted on the recorder against time continuously which represents the cure curve (curing characteristics) during the testing period. The recorder also plots the test temperature continuously.



The curve represents the developments of properties in a rubber compound at a given curing temperature.

The increase in torque level during vulcanization is proportional to the number of cross links formed per unit volume of rubber.

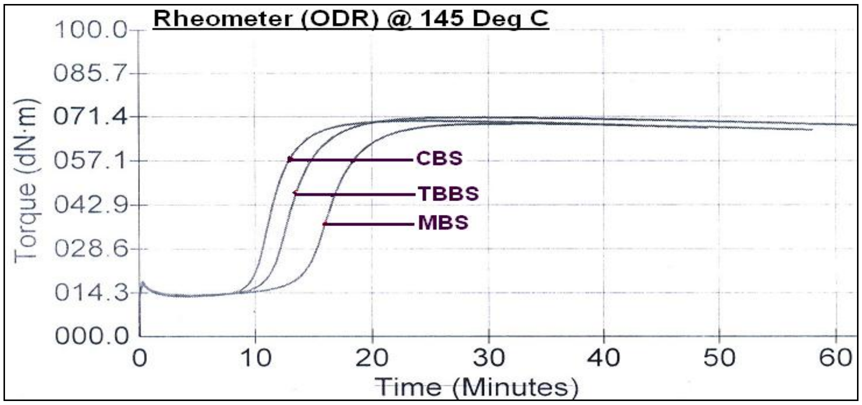
A very good correlation can be obtained for a compound or a family of compounds where the ‘curing system ‘is the only variable.

No direct comparison can be made when either the polymer of level of filler loadings is changed.

Rheometer curves can be used as compound development tools to study the rate and state of cure on variations of the cure system as well as for routine QC tools for batch to batch release in a factory.

Typical Example: Sulfenamide accelerators in NR-BR Truck Tread Compound:

NR	80.00		
BR	20.00		
ZnO	5.00		
St. Acid	2.00		
6PPD	2.50		
TMQ	1.00		
N220	55.00		
Aromatic Oil	10.00		
PVI	0.15		
Sulfur	1.60		
Total	177.25		
CBS	**1.2**	**-**	**-**
TBBS	**-**	**1.08**	**-**
MBS	**-**	**-**	**1.15**



Rheometer (ODR) Test at 145°C, Arc-3°	**CBS**	**TBBS**	**MBS**
Minimum Viscosity, (ML), dN.m	13.08	13.12	13.51
Maximum Viscosity, (MH 100), dN.m	70.03	71.21	69.15
(MH 100 - ML), dN.m	*56.95*	*58.09*	*55.64*
Scorch Time : t S2 , min	*8.70*	*9.48*	*11.45*
Time to 50% Cure t'c50, min	*11.01*	*12.64*	*15.79*
Time to 80% Cure t'c80, min	12.72	14.75	18.04
Time to 90% Cure t'c90, min	*14.11*	*16.63*	*19.79*
Time to 100% Cure t'c100, min	24.48	21.55	33.86
Reversion Time, trev98, min	42.00	51.00	51.15
Cure Rate, (tc90 - tS2), min	5.41	7.15	8.34

Moving Die Rheometer (MDR):

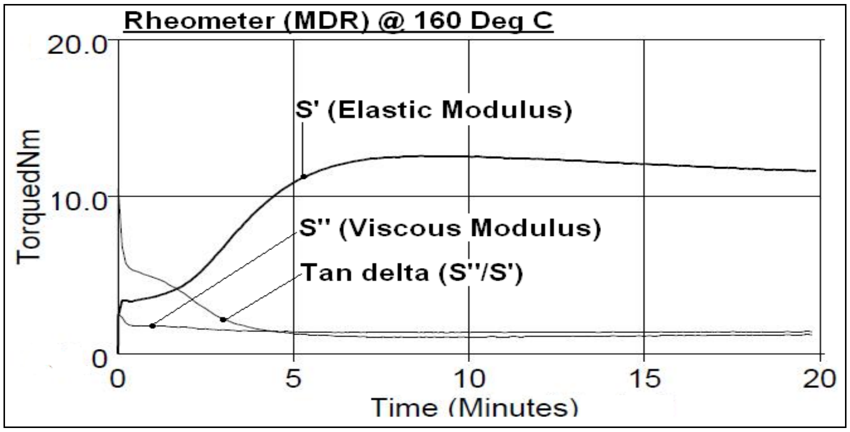
The Moving Die Rheometer (MDR) is an improvement over ODR where several limitations of ODR have been overcome.

The improvements in MDR (over ODR) include reduction of time lag between the test sample temperature and the die cavity temperature. The friction between the rotor and the test cavity by elimination of rotor itself. Uniform shear to a smaller sample ensuring very little work input into the sample and orientation effects are eliminated, heat transfer rate from dies is very rapid and temperature gradient within the sample is very small, the temperature measurement is done at the die-surface and the torque is measured in a reactive manner and hence elastic and viscous responses can be separated and measured simultaneously with the cure data throughout the test.

The viscous response S" (out of phase with the strain applied is typically 0.1 to 0.5 times of the elastic response S' (in phase with the strain applied). The viscous response S" provides information on stock processing characteristics as well as, (late in the test run on cured sample), to see if predictions can be made regarding finished product performance.

The elastic response S' is a measure of state of cure at any point of time on the cure curve at the given temperature of cure. The tan delta (= S" / S') also can be continuously plotted on the MDR since both S' & S" values are also measured continuously.

Thus one can monitor the rate and state of cure as the cure is in progress. A typical MDR Rheograph of NR-BR Tread compound is given below:



Test ID	ML	MH	Ts1	Ts2	Tc10	Tc50	Tc90	CRI (90/2)	Td @ ML	Td @ MH
0001	3.36	12.59	1.88	2.43	1.82	3.48	5.77	30.00	0.55	0.110

Chemical Method: (Swelling in solvent)

Vulcanized rubber does not dissolve but swells in solvents and the extent of swelling depends on cross link density. A tightly cured sample will swell less than a lightly cured sample. Equilibrium swelling in benzene can be used to determine the cross link density

$$\text{Cross link density } V_e = \frac{\text{Number of Net work chains}}{\text{Volume of the unswollen net work}}$$

The Crosslink Density is determined as follows:
The test sample is extracted in acetone for 16 hr to remove any soluble material and then dried at 70°C to remove acetone. Its weight is recorded. The sample is allowed to swell in benzene for 7 days at 25°C. Assuming that there are 2 cross for each elastically effective network chain; the cross link density can be calculated using following equation:

The volume fraction of the polymer in the swollen net work is calculated by assuming addivity of volumes and is used to arrive at the cross link density by the Flory-Rehner Equation:

$$Ve = \frac{-[\text{logn } (1 - Vr) + Vr + (X_1 V_r^2)]}{V_1 [(V_r^{1/3} - Vr) / 2]}$$

Where,

Ve=Effective number of chains in a real net work per unit volume [Cross link density (mol/cm^3)]

V_r=Volume fraction of rubber in the swollen network.

$$\text{i.e.} = \frac{\text{Weight of dry rubber / Density of dry rubbe}}{\frac{\text{Weight of dry rubber}}{\text{Density of dry rubber}} + \frac{\text{Weight of solvent absorbed by rubber}}{\text{Density of solvent}}}$$

V_1=Molar volume of solvent (cm^3/mol), X_1=Polymer solvent interaction parameter *(NR & Benzene = 0.437, SBR & Benzene = 0.442, NBR-Med ACN & Benzene = 0.390).*

Determination of Cross link type:

The sulfur cross links may be a mixture of Polysulfide (S atoms >3), Disulfide and Monosulfide cross links. Their distribution varies depending on the cure system used. Chemical probes can be used to determine the type of cross links.

The proportion of polysulfidic cross links is determined by using a chemical probe piperidine-propane-2-thiol which is capable of cleaving only the polysulfidic cross links. The benzene extracted test sample is placed under nitrogen and treated with 0.2 M solution of propane-2-thiol dissolved in 0.4 M piperidine in heptane solvent at 25°C for 6 days to break only the polysulfidic cross links. A comparison of original cross link density and the value obtained after the probe treatment provides the concentration of the polysulfidic cross links.

The same sample is further treated with 1 M hexane-1-thiol in piperidine for 48 hr to cleave disulfidic (and polysulfidic cross links) and the cross link density is determined. This gives the cross link proportions of Monosulfidic cross links+ C-C bonds.

Thus, determination of cross link density before and after the treatment of the sample with specified probes allows the assessment of mono, di and polysulfidic concentrations of cross links in a vulcanized test sample.

Example:

Base formulation: NR-100, ZnO-5.0, St.acid-1.5, CBS-1.5, DTDM-1.5, Sulfur-0.5.

Cure	Cross link density $(2Mc)^{-1}$	Poly-sulfides	Di-sulfides	Mono-sulfides
	(x 10^5 g.mol / gm rubber)			
Cure t'c90 @ 150°C	3.36	0.93 (27.68 %)	0.80 (23.81 %)	1.62 (48.21 %)
Cure t'c90 @ 160°C	3.18	0.86 (27.04 %)	0.75 (23.58 %)	1.56 (49.06 %)

……