Rubber Production Methods:

In 1906, it was found that aniline and other amines accelerated sulfur vulcanization. Since that time, emphasis has been placed on nitrogen- and sulfur-containing organic compounds.

Important milestones along the way have been the discovery of dithiocarbamates in 1918, of 2 mercaptobenzothiazole (MBT) in 1921, and of benzothiazole sulfenamides in 1937.

Accelerators and accelerator systems are chosen on the basis of their ability to control the following processing/performance properties of rubber compounds:

1. Time delay before vulcanization begins (scorch safety)

2. Speed of the vulcanization reaction after it is initiated (cure rate)

3. Extent of the vulcanization after the vulcanization reaction is complete

(state of cure)

4. Other factors such as green stock storage stability, fiber or steel

adhesion, and bloom tendency

Table 1 Recognized Industry Abbreviations for Accelerators

Abbreviation	Chemical name	Flexsys trade name
CBS	*N*-Cyclohexyl-2-benzothiazolesulfenamide	Santocure CBS
CTP	*N*-(Cyclohexylthio)phthalimide	Santogard PVI
DBTU	*N*,*N*′-Dibutylthiourea	
DCBS	*N*,*N*-Dicyclohexyl-2-benzothiazolesulfenamide	Santocure DCBS
DETU	*N*,*N*′-Diethythiourea	
DOTG	Di-*o*-tolylguanidine	
DPG	Diphenylguanidine	Perkacit DPG
DPTH	Dipentamethylenethiuram hexasulfide	
DTDM	Dithiodimorpholine	Sulfasan DTDM
ETU	Ethylenethiourea	
MBS	2-(Morpholinothio)benzothiazolesulfenamide	Santocure MBS
MBT	2-Mercaptobenzothiazole	Perkacit MBT
MBTS	Benzothiazyl disulfide	Perkacit MBTS
NDPA	*N*-Nitrosodiphenylamine	
PEG	Polyethylene glycol	
TBBS	*N*-*t*-Butyl-2-benzothiazolesulfenamide	Santocure TBBS
TDEDC	Tellurium diethyldithiocarbamate	Perkacit TDEC
TETD	Tetraethylthiuram disulfide	Perkacit TETD
TMQ	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	Flectol TMQ
TMTD	Tetramethylthiuram disulfide	Perkacit TMTD
TMTM	Tetramethylthiuram monosulfide	Perkacit TMTM
TMTU	Trimethylthiourea	
ZBDC	Zinc dibutyldithiocarbamate	Perkacit ZDBC
ZBPD	Zinc *o*-di-*n*-butylphosphorodithioate	Vocol ZBPD
ZDEC	Zinc diethyldithiocarbamate	Perkacit ZDEC
ZDMC	Zinc dimethyldithiocarbamate	Perkacit ZDMC
ZMBT	Zinc salt of 2-mercaptobenzothiazole	Perkacit ZMBT
6PPD	*N*-1,3-Dimethylbutyl-*N*-phenyl-*p*-phenylenediamine	Santoflex 6PPD
ETPT	Bis(diethyl thiophosphoryl) trisulfide	
BDITD	Bis(diisopropylthiophosphoryl) disulfide	

There are many classes of compounds that can serve as accelerators in vulcanization processes as shown in Table 1.

Table 2 Accelerator Classes

Class	Response speed	Acronyms
Aldehyde-amine	Slow	—
Guanidines	Medium	DPG, DOTG
Thiazoles	Semi-fast	MBT, MBTS
Sulfenamides	Fast, delayed action	CBS, TBBS, MBS, DCBS
Dithiophosphates	Fast	ZBPD
Thiurams	Very fast	TMTD, TMTM, TETD
Dithiocarbamates	Very fast	ZDMC, ZDBC

Accelerators can be classified chemically and functionally. The principal chemical classes of accelerators in commercial use today are listed in Table 2.

ACTIVATORS

The most organic accelerators and cure systems requires the use of inorganic and organic activators. Zinc oxide is the most important inorganic activator, but other metallic oxides have also profound effect on the extent of cure achievable in accelerated sulfur vulcanization. The most important organic activators are fatty acids, although weak amines, guanidines, ureas, thioureas, amides, polyalcohols, and amino alcohols are also used.

As shown below,

The Mechanism of Zinc-Mediated Accelerated Sulfur

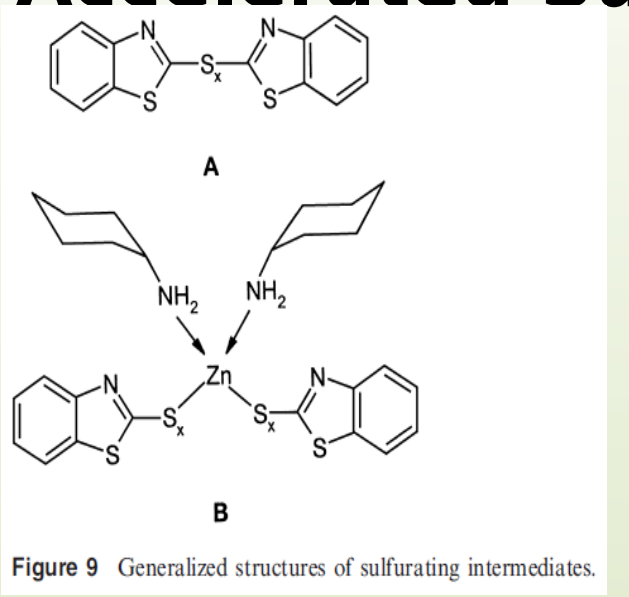


Figure 9 Generalized structures of sulfurating intermediates.

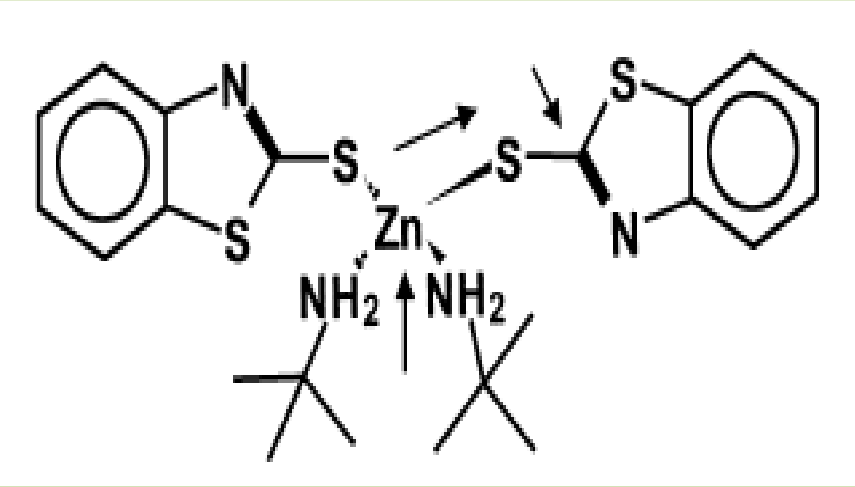
In fact, the most active contain the -N=C=S-H functionality. This is the common structural unit found in all of the 2-mercapto-substituted nitrogen heterocyclic accelerators.

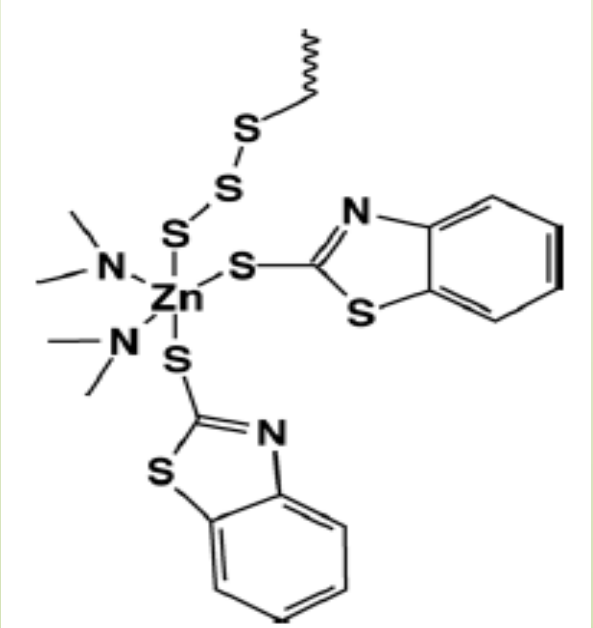
Sulfur may be activated by reaction of the amine with the sulfur molecules, which generates ammonium polysulfide anions or polysulfidic radical anions. These combine or react to form amine polysulfides or alkylammonium polysulfides, which have been proposed as intermediates in vulcanization.

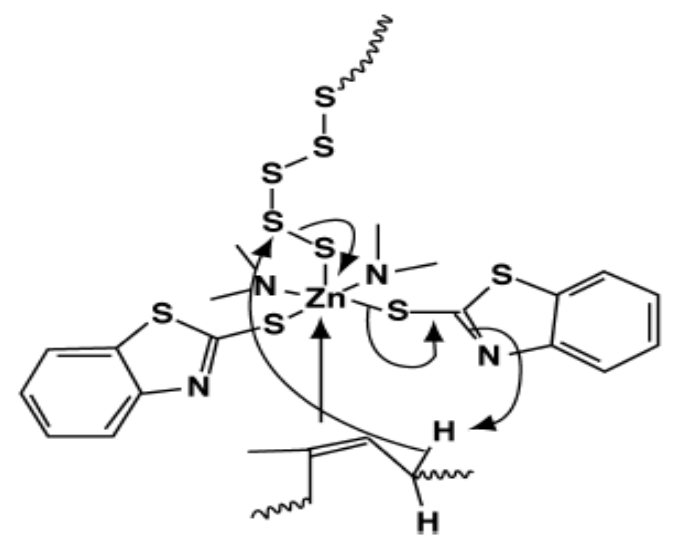
sulfur–amine reaction product subsequently reacts with the

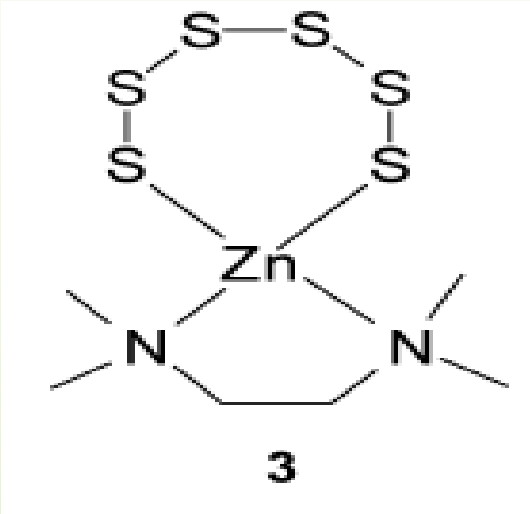
The four parameters act on the rate of vulcanization.

1. Electron density in the Zn–S bond (electron–electron repulsion)
2. Electron density in the C=N bond (electron–electron repulsion)
3. Interaction parameter for an N-H bond (measure of the quality of interaction of the amine ligand wit
4. Molecular surface area





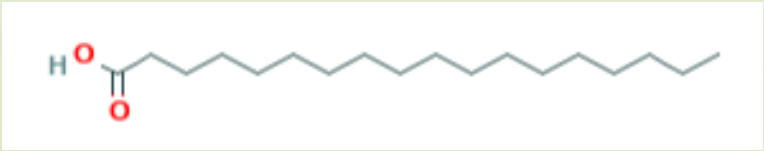




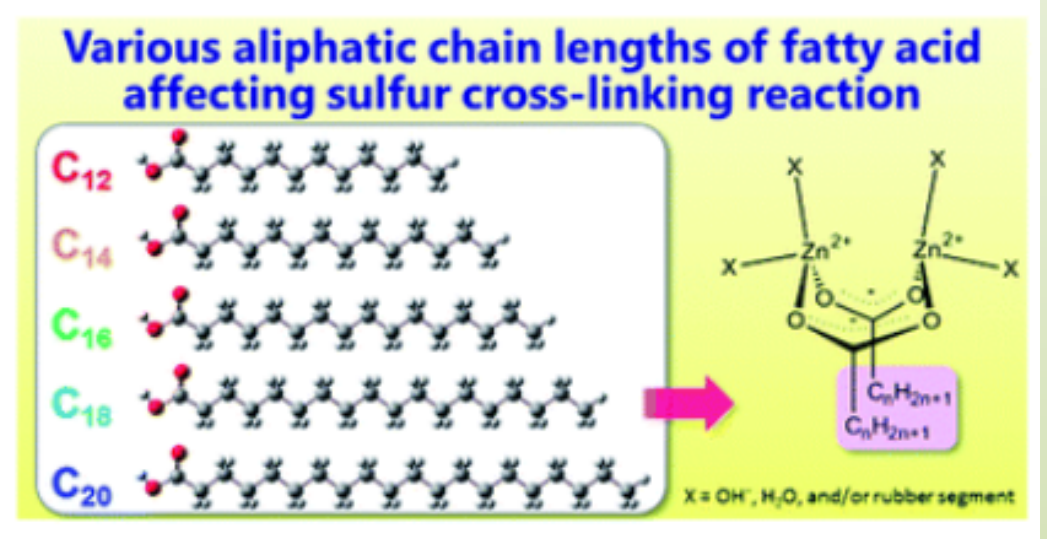
Today use a combination of zinc oxide and stearic acid as the activating system. In general the use of the activators zinc oxide and stearic acid improves the rate and efficiency of accelerated sulfur vulcanization.

In the absence of an accelerator, the activators zinc oxide and stearic acid are ineffective in increasing the number of cross-links produced.

The addition of zinc oxide to the accelerated stock as the only activator produces a dramatic effect and a well-cured stock. This demonstrates the critical role of zinc in accelerated sulfur vulcanization. Most natural rubbers and some synthetics contain enough fatty acids to form soluble zinc salts (from added zinc oxide) that interact with the accelerators.



Stearic acid



Sulfenamide-accelerated cures will release free amine, which produces a soluble zinc amine complex from the zinc oxide.

RETARDERS

Santogard PVI (N-cyclohexylthiophthalimide) was the first rubber chemical able to delay the onset of sulfur vulcanization in a predictable manner. Santogard PVI is almost the ‘‘ideal’’ retarder, because small additions (0.1–0.5 phr) produce large increases in processing safety

Unlike other retarders (e.g.,N-nitrosodiphenylamine), Santogard PVI will not decompose over the normal range of processing and curing temperatures.

Although the highest response occurs with sulfenamides, Santogard PVI is active with nearly all accelerators for sulfur-curable elastomers but normally ineffective with peroxide, resin, or metal oxide curing systems. It is not normally used in latex formulations. Santogard PVI is most effective with the fastest curing polymers, and an approximate orde

NR > NBR > SBR > EPDM > IIR