

accelerators and accelerator systems

Part I: Primary Accelerators

Sulfur, by itself, is a slow vulcanizing agent. With high temperatures and long heating periods, one obtains unsatisfactory crosslinking efficiency with unsatisfactory strength and aging properties. Only with vulcanization accelerators can the quality corresponding to today's level of technology be achieved. The multiplicity of vulcanization effects demanded can not be achieved with one universal substance, a large number of diverse materials are necessary.

introduction

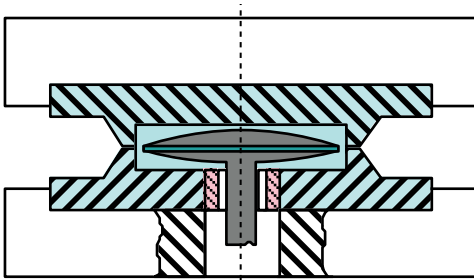
The use of sulfur alone for curing is both time consuming and inefficient. A typical cure with sulfur alone will use 5-20 phr (parts per hundred rubber) sulfur and require 5-15 hours to complete at 266-320°F. This is a result of the slow reaction between the rubber and large number of sulfur atoms to form the crosslinks. Surely, sulfur curing could benefit from the use of any additive which would accelerate the formation of crosslinks.

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

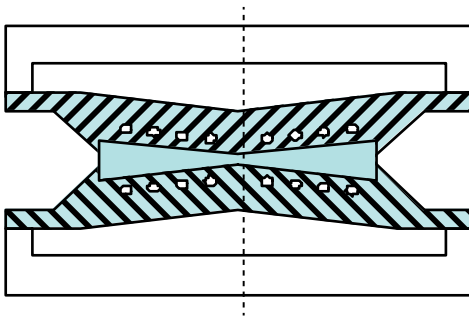
There is a wide variety of accelerators available to the compounder. For ease in understanding, it is useful to classify accelerators by chemical structure. One such classification, made by the ASTM is as follows: 1. Thiazoles (Mercapto), 2. Sulfenamides, 3. Guanidines, 4. Dithiocarbamates, 5. Thiurams, 6. Specialty Accelerators. The focus here will be on two types of primary accelerators, thiazoles and sulfenamides.

vulcanization

To understand the action of accelerators, vulcanization of rubber and its chemical changes must be understood. The science of determining the vulcanization (curing) properties of a rubber compound is known as Rheology. Rheology is a cure curve produced by a rheometer, either ODR or MDR, which measures torque changes produced by pressure and heat over time.



ODR – Oscillating Disc Rheometer



MDR – Moving Die Rheometer

A typical cure curve obtained from a rheometer is shown in *Figure 1*. The initial portion of the curve is called the scorch period where much of the accelerator chemistry is involved. As time goes on torque increases and attains a maximum value. The time required to attain 90% of the maximum torque is termed as the optimum cure time where the time required to attain 10% of the maximum torque is termed the scorch time. The choice of accelerator in the process of sulfur vulcanization determines the kind of network structure and consequently leads to the specific material properties. The chosen accelerator affects the cure rate and scorch safety, as well as the number and the average length of the formed crosslinks. Both the number and the length of the crosslinks have an influence on physical properties of rubber.

Vulcanization Terms

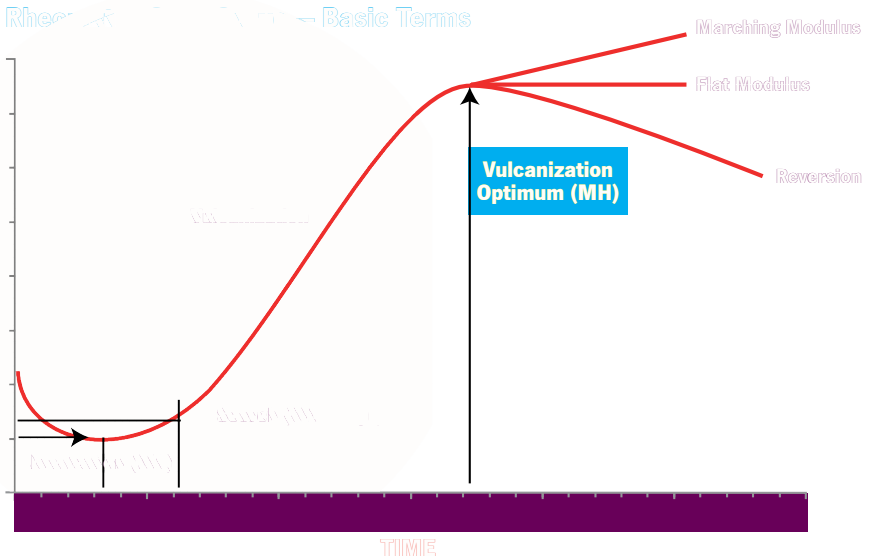


Figure 1: Typical rheograph showing different stages of curing.

selection of accelerator system

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

- Expected shelf life of the compound
- Accelerator's solubility in rubber (high solubility to avoid bloom and improve dispersibility)
- Various processing stages the rubber must be required to undergo
- Adequate processing safety for "scorch free" processing operations
- Faster cure rate for economical production of the rubber product
- No reversion on oven cure
- Vulcanization method to be used (mode of heat transfer)
- Maximum vulcanization temperature available
- Cure cycle desired for the available vulcanization method, the temperature, and the vulcanizate properties required
- Effectiveness of the accelerator system over a wide range of cure temperatures and suitability for use with different polymers

- No adverse effects on other properties (e.g. bonding, aging, adhesion, etc.) and no adverse effects on non-rubber components in the rubber product
- No known health hazards upon usage as a chemical and of its decomposition products on cure
- No adverse effects during end-use of the rubber product (e.g. accelerators used in the manufacturing of the rubber articles intended for food contact, surgical use, etc.)
- Stability of the accelerator as a chemical (e.g. problems with the use of decomposed sulfenamide accelerators)
- Easy to handle and dust suppressed physical form

Selection of a good acceleration system is one of the more difficult problems in compounding. The system chosen must have good raw stock storage stability, and its time delay before vulcanization starts must be sufficient to allow efficient mixing and processing. It must be compatible with the cure method used. For example, a thick, rubber-covered roll may have a curing period of several hours at temperatures of 200–300°F; on the other hand, an insulated electric wire may have its rubber covering cured in a matter of seconds at 388°F. The latter temperature is that of saturated steam at 200 psi pressure used in the continuous vulcanization of rubber-insulated wiring. Once vulcanization has started, it must proceed at a satisfactory rate to an appropriate state of cure. Finally, the accelerator must produce a vulcanizate that gives good adhesion to fibers or metal if it is a composite article, has crosslinks that are suitable for aging or flexing, and doesn't bloom.

Accelerator choice is critical.

primary accelerators

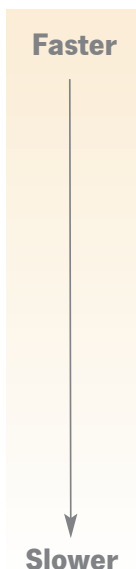
A choice of suitable accelerators for compounding must be selected from a large number of organic compounds. These contain nitrogen or sulfur, or both. They have been developed over a period of many years and the type and amount depends on the elastomer used, the predetermined processing requirements, and the anticipated curing rates.

Accelerators are typically classified as primary or secondary. Primary accelerators usually provide considerable scorch delay, medium to fast cure, and good modulus (crosslink density) development. Secondary accelerators usually produce scorchy, very fast curing stocks. Primary accelerators are sulfenamides and thiazoles. Secondary accelerators are dithiocarbamate, thiurams, guanidines, and specialty accelerators.

Scorch Rates of Some Commonly Used Accelerators

Secondary “Kickers”

CuDD
DPTT
Bismet
TMTD
ZDMC
TM/ETD
ZDEC
DPG
TETD
DOTG
TDEC
TMTM
TB₂TD
ZDBC



Primary

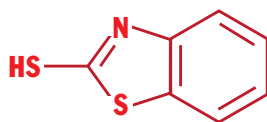
MBT
MBTS
ZMBT
CBTS
BBTS
Cure-Rite 18
OMTS
OBTS
DCBS

By far the most popular accelerators are the thiazoles and derivatives of the thiazoles, the sulfenamides. Probably over 70% of the accelerators used are of these types. Their good qualities are the effective acceleration they provide at medium and high temperatures and their wide range of curing rates and scorching characteristics. Quite frequently they are paired with a secondary accelerator to derive maximum levels of processing safety and vulcanization rate.

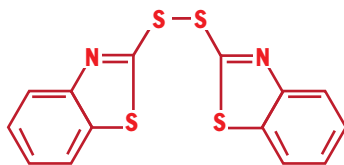
Thiazole Types

Raw materials for thiazoles are aniline, carbon disulfide, and sulfur. The chief thiazole accelerators are 2-mercaptobenzothiazole (MBT), benzothiazole disulfide (MBTS), and the zinc salt of 2-mercaptobenzothiazole. The zinc salt is rarely used in dry compounding but is used more in latex foams and dipped goods. Both MBT and MBTS can cause scorching problems when used alone in furnace black natural rubber stocks. MBTS is somewhat safer to process than MBT. It is common practice to use a kicker with MBT and MBTS. MBTS is often used with DPG to give a safe, flexible system in many mechanical goods stock. A starting cure system for an SBR stock might be 1.5 MBTS, 0.15 TMTD, and 2.80 sulfur.

MBT or 2-mercaptobenzothiazole was the first thiazole to be used commercially in the rubber industry. It is highly reactive and used effectively in applications requiring a good degree of activity at lower temperatures: 142°C (287°F) or below, and in slower curing synthetics. MBT imparts flat curing properties and also imparts good aging characteristics. Combinations of MBT with ultra accelerators are used where faster curing is needed and an increase in scorch can be tolerated. An example would be curing systems for compounds designed for continuous curing in hot air or liquids at 232°C (450°F) and higher.



MBTS or benzothiazole disulfide was originally developed for safe processing rubber compounds cured at or above 142°C (287°F). MBTS continues to be used widely in compounds of all types for many major commercial applications. Its activity and scorch properties can be controlled over a wide range by using various combinations of MBT and ultra accelerators with MBTS. MBTS acceleration is the ideal starting point in new compound development, especially in mineral-filled types for such applications as soles and heels or molded goods.



ZMBT or zinc-2-mercaptobenzothiazole is a modified thiazole. It is mainly used in latex. ZMBT has much higher scorch safety. It also imparts the flat curing properties and good aging characteristics given by MBT.

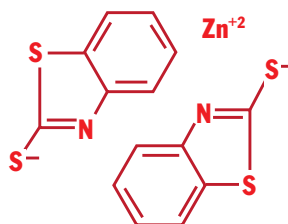


Figure 2 compares the cure rate of thiazoles. The formula is SBR based.

SBR	100.0 phr
ZnO	5.0 phr
SA	2.0 phr
Sulfur	1.8 phr
Thiazole	1.2 phr

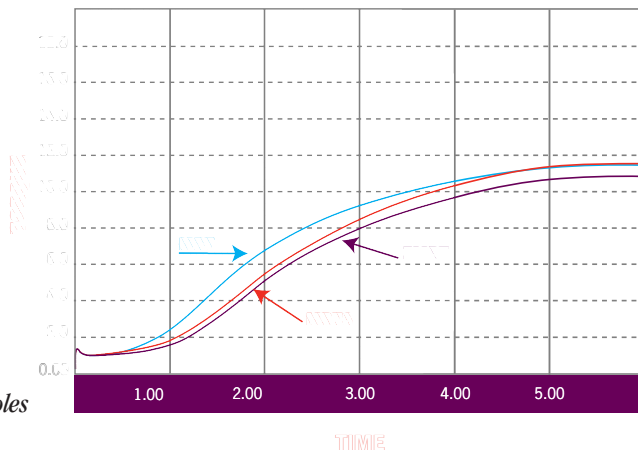


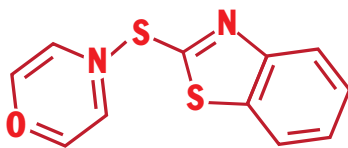
Figure 2:
Cure Rate of Thiazoles

Sulfenamide Types

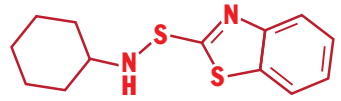
Sulfenamides are made in two ways: by the reaction of 2-mercaptobenzothiazole with an N-chloramine and by oxidation of the appropriate amine salt of 2-mercaptobenzothiazole.

The various amine functional groups of sulfenamides reflect their scorch time and cure rate differences. If the amine is highly basic, the scorch time is lower, the cure rate faster. In terms of processing safety, Benzothiazyl 1,2-dicyclohexyl sulfenamide is the highest, with N-cyclohexyl-2-benzothiazole sulfenamide the lowest. The trend is to use the modifications of the original sulfenamide accelerators that give greater processing safety. A popular accelerator is N-tert-butyl-2-benzothiazolesulfenamide (BBTS). Besides giving a longer scorch delay, BBTS gives higher modulus than CBTS, so dosage can possibly be reduced 10%. Very frequently the sulfenamides are used with secondary accelerators like TMTD.

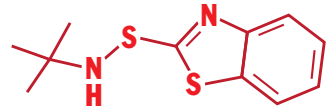
OBTS or N-oxydiethylene benzothiazole-2-sulfenamide is considered a preferred delayed action accelerator by many compounds for natural and synthetic rubber compounds requiring maximum processing safety and flat curing characteristics. Overall properties of natural and synthetic compounds with OBTS acceleration are generally above those obtained with thiazoles.



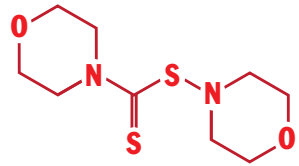
CBTS or N-cyclohexyl-2-benzothiazolesulfenamide is used in natural and synthetic rubber. It is faster curing than OBTS, develops higher modulus and is somewhat scorchier.



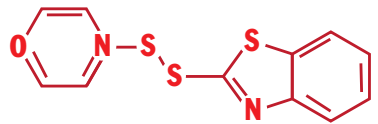
BBTS or N-tert-butyl-2-benzothiazolesulfenamide accelerator is less scorchy and faster curing than CBTS in natural and synthetic rubbers. In many compounds the dosage can be reduced 10% compared with other sulfenamides.



Cure-Rite 18 or N-oxydiethylene thiocarbamyl-N-oxydiethylene sulfenamide is a very efficient delayed action accelerator. Combinations of Cure-Rite 18 with other sulfenamides give high modulus and good aging due to the efficient use of sulfur.



OMTS or 4-Morpholinyl-2-benzothiazole disulfide is faster curing in natural or synthetic rubber than other sulfenamides. It develops high modulus and good aging in low sulfur stocks. Good aging can be attributed to its sulfur donating capability, which is particularly evident when used in combination with a dithiocarbamate and Cure-Rite 18.



DCBS or benzothiazyl 1,2-dicyclohexylsulfenamide is a delayed action accelerator. DCBS provides the longest delay for on-set of cure. It is most suitable for thick cross sections. DCBS is very sensitive to activation by basic secondary accelerators like DPG, DOTG, TMTM, and TMTD. Small dosages of these kicker accelerators produce response.

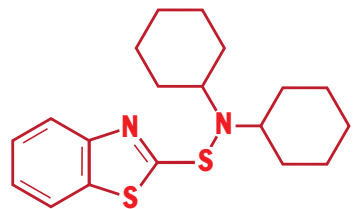


Figure 3 compares the cure rate of sulfenamides. The formula is SBR based.

SBR	100.0 phr
ZnO	5.0 phr
SA	2.0 phr
Sulfur	1.8 phr
Sulfenamide	1.2 phr

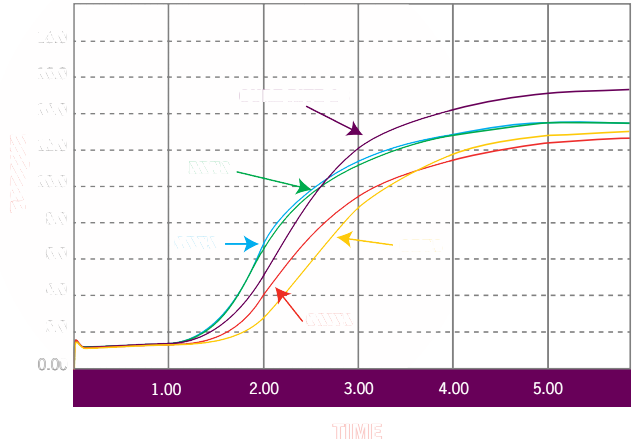


Figure 3:
Cure Rate of Sulfenamides

polymer – accelerator interaction

Accelerators respond differently to different elastomers. The greater the unsaturation (double bonds) in the polymer structure, the faster the cure characteristics. *Figure 4* shows the response between sulfenamide OBTS and different elastomers on cure rate and state. Where a 50-part carbon black stock of natural rubber might use 2.25 parts of sulfur and 0.5 part of a sulfenamide accelerator, a similar SBR 1500 stock might use 1.75 parts of sulfur and 0.80 part of the same accelerator. Again, rubbers like IIR (butyl) and EPDM, which are saturated (low to no double bonds), should not have more sulfur than can be accommodated with the available double bonds. To get faster curing, accelerator levels may be raised to a point that bloom occurs. This defect can be prevented by using small amounts of several accelerators so that the accelerator residues are soluble in the rubber.

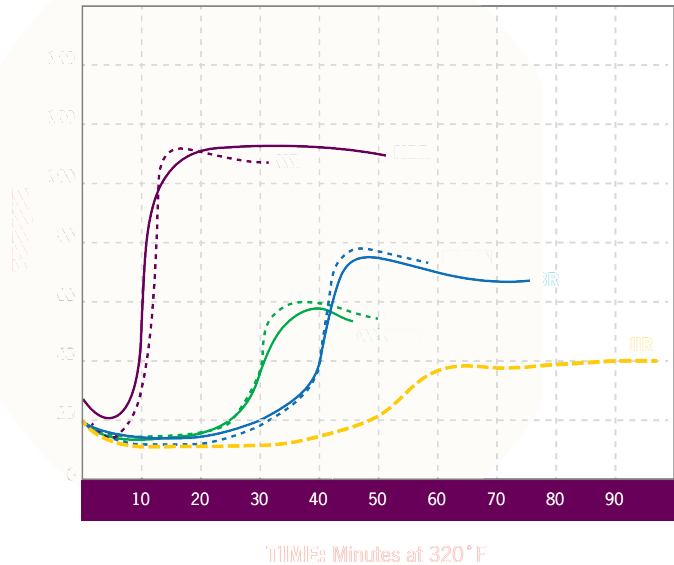
Polymer Cure Curves - Same Cure System

Compound Formulation

Elastomer	100.0
ZnO	5.0
Stearic Acid	2.0
Sulfur	1.8
MBS	1.2

The greater the unsaturation in the polymer's backbone, the faster the cure characteristics.

Figure 4:
Various Polymer Interactions
with OBTS



summary

Accelerator choice is critical. Selecting a good accelerator system is difficult. Many parameters, such as raw rubber storage stability, processability, scorch, crosslinking, and cured rubber requirements to name a few, come into consideration. Primary accelerators, thiazoles and sulfenamides, are the most popular accelerators and offer a good start. Their good qualities are the effective acceleration they provide at medium and high temperatures and their wide range of curing rates and scorching characteristics. They usually provide considerable scorch delay, medium to fast cure, and good modulus development. Refining necessary parameters can be accomplished with the addition of secondary accelerators. This topic will be covered in Part II: Secondary Accelerators.



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