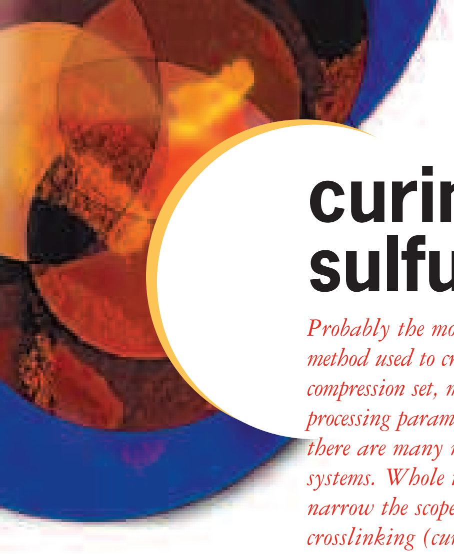


curing with sulfur and sulfur donor systems

Probably the most complex issues in rubber compounding are the cure systems. The method used to crosslink the elastomers is crucial to finished properties(i.e. heat resistance, compression set, modulus, flexibility, and resilience to name a few) as well as critical to processing parameters(scorch time, cure time, reversion or marching modulus). Also, there are many materials that can be combined into an almost infinite array of cure systems. Whole textbooks have been written discussing curing and curing agents. To narrow the scope a little, this Solutions paper will concentrate on the most popular crosslinking (curing) method, sulfur and those materials that donate sulfur.

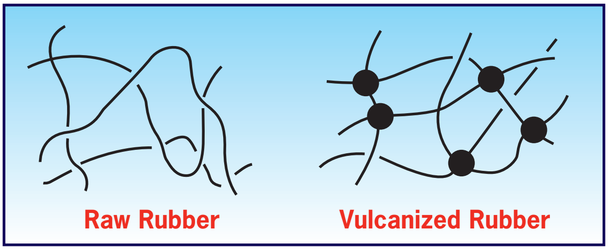
The process of crosslinking is called curing or vulcanization and the chemicals used for curing are referred to as curing agents or cure systems.

Charles Goodyear has been credited for the earliest method of crosslinking. His process, heating rubber with sulfur, was first successfully used in Springfield Massachusetts, in 1841. It was found heating natural rubber with sulfur resulted in improved physical properties. However, the curing time took about 5 or more hours and the vulcanizates suffered from poor physical properties, such as poor heat aging.

Since those days, the process and the resulting vulcanized articles have been greatly improved. Some of the improved areas were speeding up the crosslinking reaction by the introduction of accelerators and accelerators that donate sulfur. The combination of sulfur with various accelerators is used to dramatically improve various properties of the crosslinked article such as compression set, heat aging, and dynamic properties. (See Table 1 to determine which of Akrochem's broad line of Sulfurs may be best suited for your application)

fundamentals of crosslinking:

Crosslinking is the process of adding certain chemicals to elastomers to give it useful properties such as strength, stability, and elasticity. The elastomer long chain molecules are converted into a three dimensional elastic network by joining (crosslinking) the molecules at certain points along the polymer chain. Example of this crosslinking is shown below.



Crosslinks

The cure rate is the speed at which a rubber compound increases in modulus (crosslink density) at a specified crosslinking temperature or heat history. Cure time refers to the amount of time required to reach specified states of cure at specified cure temperature or heat history. An example of cure time is the time required for a given compound to reach 50% or 90% of the ultimate state of cure at a given temperature often referred to as t50 and t90 respectively. (See Fig.1) Determining what is the optimum cure time for a small curemeter specimen is not the same as determining the optimum cure time for a thicker rubber article cured in a factory setting.

Table 1: SULFURS

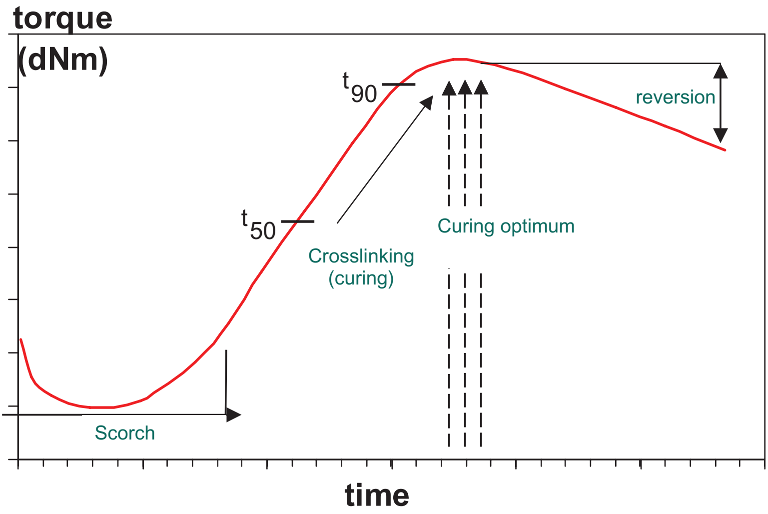
DESCRIPTION/APPLICATIONS:

Sulfur is the most frequently used vulcanizing agent in rubber. Akrochem offers a broad line of sulfurs, to meet specific applications:

- Rubbermaker's Sulfur is the most widely used, general purpose grade.
- OT and 1% OT Sulfur offer two levels of oil to minimize dust.
- Fine, treated sulfur is similar to RM grade but with more consistent particle grind size and slightly less dusting.
- Superfine Sulfur is an especially fine-ground form of Rubbermaker's Sulfur.
- MC-98 Sulfur is an extremely fine particle size Sulfur treated with magnesium carbonate (thus the ash content) to improve dispersibility and reduce caking. Because sulfur has low solubility in nitrile rubber, MC-98 is used to gain maximum dispersion in NBR. However, MC-98 can be used in any sulfur-curable polymer when optimum dispersion is desired.
- MC-HOT Sulfur is a high oil-treated (HOT) version of MC-98. Oil treatment reduces dust and improves dispersibility even more. MC-HOT is the ultimate powdered sulfur for dispersion.
- Flaked Sulfur is for industrial uses and not typically used in rubber.

Akrochem Name	**Sulfur Purity %**	**Heat Loss**	**Ash**	**Oil Content**	**Passing through 80 mesh**	**Passing through 100 mesh**	**Passing through 200 mesh**	**Passing through 325 mesh**
Rubbermaker's (RM) Sulfur	99.5	0.15	0.10	0.0			90% min	
OT Sulfur	99.0	0.15	0.10	0.5			90% min	
1% OT Sulfur	98.0	0.15	0.15	1.0	99.9%min			
Fine Treated Sulfur	99.5	0.10	0.15	—-		99.5 % min	91% min	
Superfine Sulfur	99.5	0.15	0.10	—-				95% min
MC-98 Sulfur	97.5	0.15	2.10	—-				98% min
MC-HOT Sulfur	96.4	0.15	2.60	1.0			99% min	90% min
Flaked Sulfur-Crude * ½" sieve	99.5	0.15	0.10	—-	95% min*			

Fig. 1: Schematic of a Cure Curve

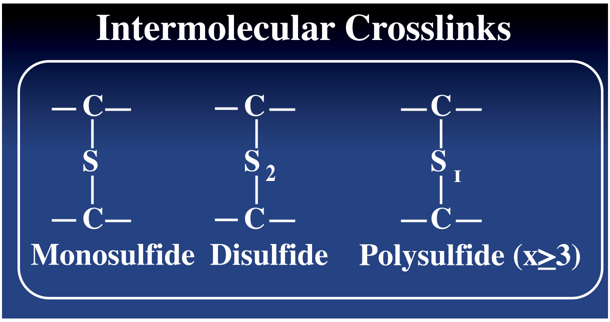


efficiency of sulfur crosslinking

Sulfur linkages have proven to be the easiest to produce rubber products with excellent elastic properties especially flexing, tearing, and dynamics. A typical rubber formula uses a higher sulfur amount (1.5-3.0phr) in combination with lesser amounts of accelerators to increase rate and **efficiency** of cure. This "general purpose" or **conventional** cure system is satisfactory for many applications. However, the higher ratio sulfur cure produces mostly crosslinks containing 3-8 sulfur atoms. This leaves the S-S bond as the weak link in the vulcanized product. The S-S bond is susceptible to breakage from exposure to heat or stress. This limits the use of high sulfur cures to applications that see less than 180 – 200F (82-93C). The primary method to improve heat resistance of sulfur bonds is to **decrease** the number of single and double S "x-links". This is accomplished by reducing sulfur levels incrementally (depending on how much heat resistance is needed) and replacing free sulfur (elemental sulfur) with accelerators that donate sulfur (called sulfur donors) that can become part of the X- link. (See **Fig. 2 and Fig. 3**)

Fig. 2: Type of Sulfur Bridge bonding energy (kJ/mol)

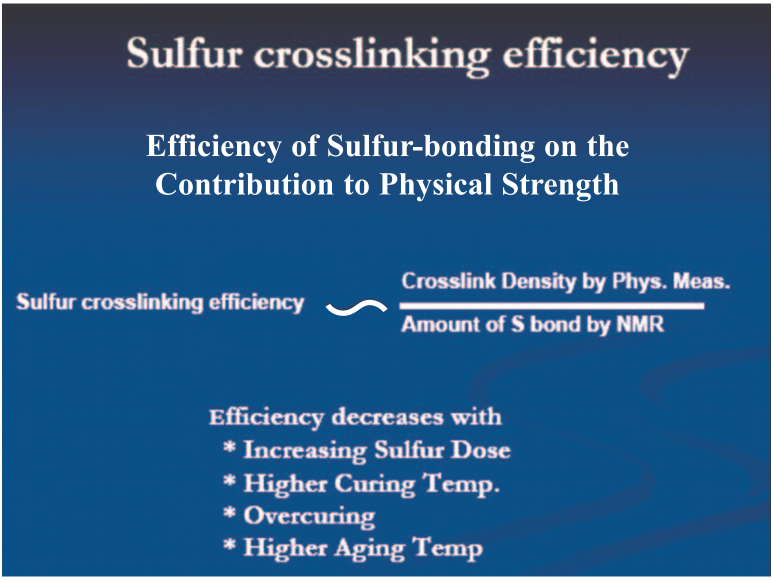
Polysulfidic	$-C-S_x-C-$	$(x \geq 3)$	< 270
Disulfidic	$-C-S_2-C-$		270
Monosulfidic	$-C-S-C-$		285
Carbon-Carbon	$-C-C-$		350



As one can see the carbon-carbon bond has a higher bond energy (350kJ) than the sulfur-carbon bond (285kJ) formed by the EV (Efficient Vulcanization) sulfur cure system and a much stronger bond strength than the sulfur-sulfur bond (< 270 kJ) formed by a CV (Conventional Vulcanization) sulfur cure system.

When we refer to bond energy or bond strength we are referring to the amount of energy required to break a bond. The higher bond strength means greater heat is needed to break the bond. This leads to better heat resistance and lower compression set properties for vulcanizates (cured rubber articles).

Fig. 3: Efficiency of Crosslinking

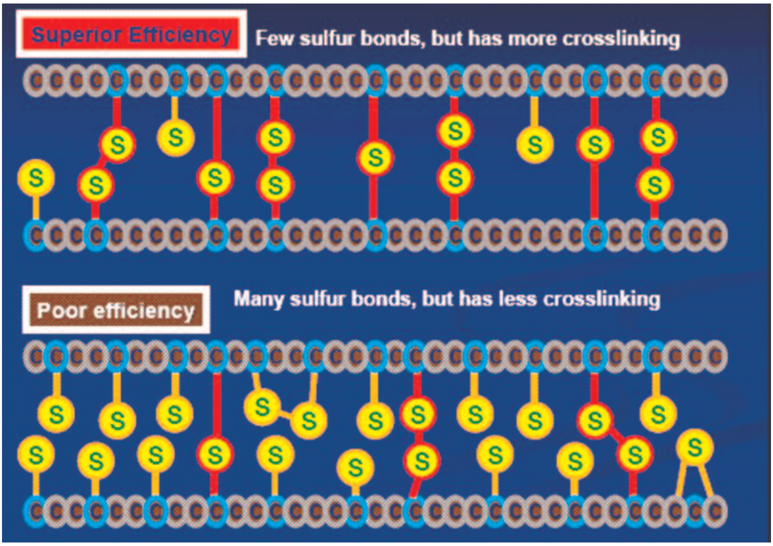


Sulfur crosslinking efficiency

Efficiency of Sulfur-bonding on the Contribution to Physical Strength

$$\text{Sulfur crosslinking efficiency} \sim \frac{\text{Crosslink Density by Phys. Meas.}}{\text{Amount of S bond by NMR}}$$

Efficiency decreases with
- * Increasing Sulfur Dose
- * Higher Curing Temp.
- * Overcuring
- * Higher Aging Temp



Superior Efficiency

Few sulfur bonds, but has more crosslinking

Poor efficiency

Many sulfur bonds, but has less crosslinking

type of crosslink systems and the effect on physical properties

Based on the sulfur/accelerator combinations, three popular crosslinking (cure) systems were introduced. They are called conventional (CV), semi-efficient (SEV), and efficient (EV) crosslinking (cure) systems. The proper selection of crosslinking (cure) systems is dictated by many factors such as, desired end properties, processing parameters, and environmental conditions to name a few.

It is well established that the degree of crosslinking strongly influences different properties such as:

- Tensile stress and elongation at break
- Dynamic damping and rebound resilience
- Tear Resistance
- Compression Set
- Resistance to fluids or swelling

Excellent heat aging and compression set properties are obtained with the shorter crosslinks, while tensile strength, rebound resilience and flex fatigue properties are obtained with the polysulfidic crosslinks.

EV systems are those where a low level of sulfur and correspondingly high level of accelerator or sulfurless curing are employed in vulcanizates for which an extremely high heat and reversion resistance is required. In the conventional curing (CV) systems, the sulfur dosage is high and correspondingly the accelerator is low. The CV systems provide better flex dynamic properties but worse thermal and reversion resistance. For optimum levels of mechanical and dynamic properties of vulcanizates with intermediate heat, reversion, flex and dynamic properties, the so-called semi-EV systems with intermediate level of accelerator and sulfur are employed. Typical levels of accelerator and sulfur in EV systems, semi-EV, and CV, are shown in **Table 2**.

Table 2: Crosslink Structure and Properties of CV, Semi-EV, and EV

	SYSTEMS		
FEATURES	**CV**	**Semi-EV**	**EV**
Poly- and disulfidic crosslinks(%)	95	50	20
Monosulfidic crosslinks	5	50	80
Cyclic sulfide(conc.)	High	Medium	Low
Non-cyclic sulfide(conc.)	High	Medium	Low
Reversion Resistance	Low	Medium	High
Heat aging resistance	Low	Medium	High
Fatigue resistance	High	Medium	Low
Heat buildup	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set(%)	High	Medium	Low
Sulfur Level (phr)	2.0	1.0	.5

Many studies have documented both the advantages (increased age resistance), and the disadvantages (impaired fatigue resistance) of EV and semi-EV systems. The worse fatigue resistance correlates to lower amounts of polysulfidic crosslinks in the network. The CV systems provide higher amounts of poly- and disulfidic crosslinks and higher proportions of sulfidic and non-sulfidic modifications. This combination provides high flex fatigue resistance but at the expense of heat and reversion resistance.

A second approach involves modifying cure systems to generate vulcanizates with more disulfidic and monosulfidic crosslinks which have greater chemical and thermal stability than the polysulfidic crosslinks and main chain modification to conventional vulcanizates. Such cure system modifications are accomplished via sulfur donors or high ratios of accelerators to sulfur. These cure systems are sometimes called Sulfurless or low sulfur cure systems.

sulfur donors

Aside from the sulfur itself, sulfur bearing compounds that liberate sulfur at the vulcanization temperature can be used as vulcanizing agents. These are called sulfur donors.

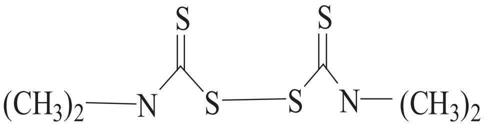
Generally sulfur donors convert initially formed polysulfides to monosulfides which is characteristic for EV and semi-EV systems.

A few sulfur donors are given in **Fig. 4** which includes Akrochem Accelerator R (DTDM), which can directly substitute sulfur. Akrochem TMTD can act simultaneously as a vulcanization agent or an accelerator. The amount of active sulfur, as shown in **Fig. 4** is different for each compound. Sulfur donors may be used when a high amount of sulfur is not tolerated in the compounding recipe, for example, high temperature vulcanization of rubber. They are used in EV and SEV systems. Sulfur donors are used to generate a network capable of resistance to degradation on exposure to heat.

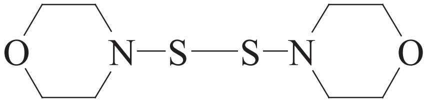
The main advantage of sulfur donors is that they reduce the normal blooming of sulfur in unvulcanized compounds. The onset of cure occurs later than with free sulfur. The splitting of thiuram tetrasulfides and morpholine derivatives results simultaneously in the formation of accelerators or activators, which make the vulcanization proceed particularly fast.

To acquire the benefits described above and also to prevent sulfur blooming, it is generally sufficient for a part of the vulcanization sulfur to be substituted by sulfur donors. In most instances phrs of a sulfur donor are used instead of one part of sulfur in order to reach a comparable degree of crosslinking.

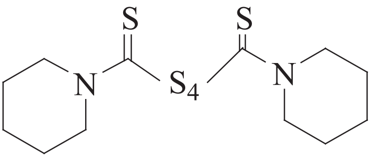
Fig 4: SULFUR DONORS



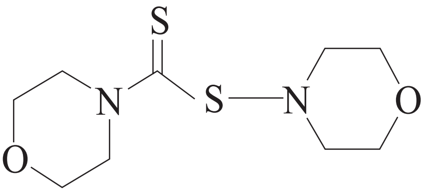
Akrochem TMTD
(Tetramethyl Thiuram Disulfide)
(1 .0 Active Sulfur)



Akrochem Accelerator R (DTDM)
(4,4'-Dithiodimorpholine)
(1 .0 Active Sulfur)



Akrochem DPTT
(Dipentamethylene Thiuram Tetrasulfide)
(.0 Active Sulfur)



Akrochem Cure-Rite 18
(OTOS) (Thiocarbamyl Sulfenamide)
(1 .0 Active Sulfur)

compounding with cv, sev, and ev systems

In natural rubber, EV and semi-EV systems can provide remarkable resistance to marching modulus. Control can generally be realized without fatigue compromises. The choice of cure systems depends in part on the processing conditions required. Sulfur donors normally give longer processing safety and better green stock storage than the use of high accelerator/low sulfur systems. However the latter may be better in the long overcure situations.

Sulfur donors are used to replace part of or all of the elemental sulfur to improve thermal and oxidative aging resistance. They may also be used to reduce the possibility of surface bloom and to modify curing and processing characteristics. Two chemicals have been developed over the years to function as sulfur donors- alone or in combination with sulfur. They are Akrochem TMTD and Akrochem Accelerator R (DTDM). Akrochem TMTD is used to provide significantly improved heat and aging resistance. (See **Table 3** and **Fig. 5 through Fig. 9**)

TABLE 3 : Test Data

Curing System	**Conventional**	**Semi-EV**	**EV**
INGREDIENTS	**1**	**3**	**4**
Natural Rubber	100.00	100.00	100.00
HAF Carbon Black (ASTM N-330)	50.00	50.00	50.00
Zinc Oxide	3.50	3.50	3.50
Stearic Acid	2.50	2.50	2.50
Aromatic Oil	4.00	4.00	4.00
Antioxidant	2.00	2.00	2.00
SULFUR	**2.50**	**1.20**	**0.25**
CBS	0.50	0.80	2.20
TMTD	0.00	0.40	1.00
PHYSICAL PROPERTIES			
Cure System	**Conventional**	**Semi-EV**	**EV**
Cured minutes @140°C	30	30	40
Durometer - Shore A @RT	68	67	61
Tensile Strength			
Unaged	4146	4132	3862
Aged 120hrs@100°C	966	2215	3251
%Retention	13	54	84
Elongation - %			
Unaged	490	490	555
Aged 120hrs@100°C	130	305	470
%Retention	17	62	85
300% Modulus - psi			
Unaged	1264	1278	951
Aged 120hrs@100°C	--------	1207	1079
Compression Set (%)			
Unaged	44	19	21
Aged	36	17	19
Crescent Tear @ RT			
Unaged	86	77	--------
Aged 1344hrs@70°C	40	51	--------
Fatigue Life (kilocycles to failure)			
Unaged	120	58	--------
Aged 1344hrs@70°C	9	27	--------

Fig. 5 Cure System Comparison

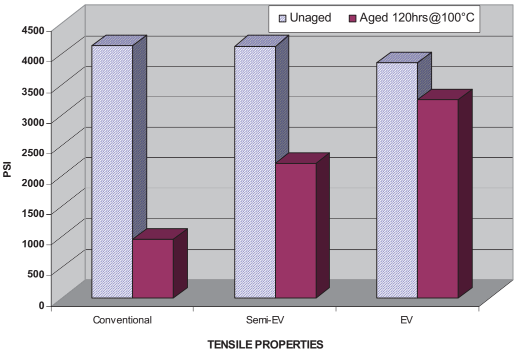


Fig. 6 Cure System Comparison

Cured 30mins@140°C

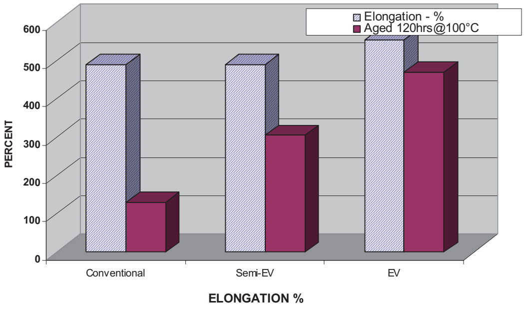


Fig. 7 Cure System Comparison

Cured 30mins@140°C

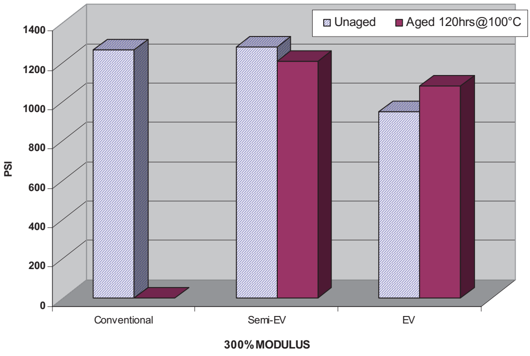


Fig. 8 Cure System Comparison

Cured 30mins@140°C

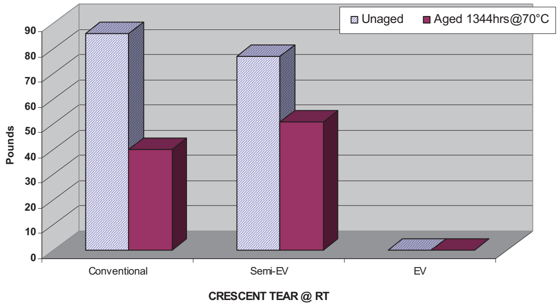
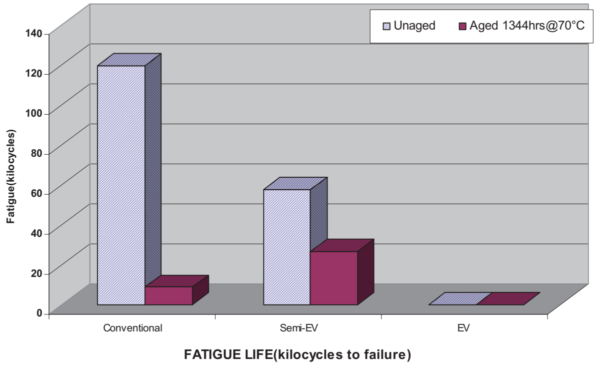


Fig. 9 Cure System Comparison

Cured 30mins@140°C



application: examples of sulfur curing

Below are examples of actions to take when considering different compounding goals with sulfur cure systems.

Goal #1: To improve aging resistance of an initial CV system

Action Change to a higher accelerator/sulfur ratio, e.g. EV

	CV System	→	**EV System**
Akrochem CBS	0. phr to		1. phr
Akrochem MC-9 Sulfur	. phr to		0. phr
Akrochem Accel. R (DTDM) Sulfur Donor			1. phr
Akrochem TMTD			1. phr

Goal #2: To Reduce cure time

Action 1. Increase accelerator
. Increase accelerator level and reduce sulfur level (EV system, i.e.)
. Use a faster accelerator

summary

As you can see various approaches can be used to modify cure systems to meet ones needs. In sulfur cure systems, zinc oxide or magnesium oxide, stearic acid or other fatty acids or its metal salts are required to activate the curing reaction using accelerators, depending on the objectives of the cure system.

To improve aging resistance, high accelerator to sulfur ratio referred to as efficient vulcanization (EV) is used. This system gives higher monosulfidic crosslinks, which are less flexible than polysulfidic thus lower dynamic properties. The conventional cure system, high sulfur to accelerator ratio, gives higher polysulfidic crosslinks hence better dynamic fatique properties.

It is the job of the compounder to determine which sulfur cure system will give him the best properties for the end use product.

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