accelerators and accelerator systems

Part I: Primary Accelerators

Sulfur, by itself, is a slow vulcanizing agent. With high temperatures and long heating periods, even slow vulcanization results in low yield and low strength and the vulcanizates show poor aging properties. Only with vulcanization accelerators can the quality correspond 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.

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 in the 266-320°F range. 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 permit vulcanization to proceed at lower temperatures and with lower energy density. 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,

The focus here will be on two types of primary accelerators, thiazoles and sulfenamides.
vulcanization

In order to understand the nature of vulcanization, vulcanization of rubber and the chemical changes that occur need to be understood. The process of vulcanizing the vulcanization (curing) properties of a rubber compound is known as vulcanization. A cure is comprised of a characteristic, often 100% or 150%, which means that the change produced by pressure and heat occurs.

A typical cure curve obtained from a schematic is shown in Figure 1. The initial portion of the curve is called the scorch period after which the accelerator chemistry is activated. In time, the cure goes as the maximum stress and attains a maximum value. The time required to attain 90% of the maximum stress is termed as the optimum cure time where the time required to attain 90% of the maximum stress is termed as the scorch time. The choice of accelerator in the process of sulfur vulcanizes determines the kind of rubber structure and composition leads to the specific desired properties. The chosen accelerator affects the cure rate and scorch time, as well as the stability and the overall length of the crosslinks formed. Both the number and the length of the crosslinks have an influence on the physical properties of rubber.
Vulcanization Terms

Figure 2: Typical diagram showing different stages of curing.

selection of accelerator system

When selecting an accelerator system for the vulcanization of a particular rubber product, the following points must be taken into account:

- Expected shelf life of the compound
- Accelerator’s stability in rubber (high stability to avoid fluxes and excess disposal)
- Various processing states the rubber must be exposed to (e.g., mixing, extrusion)
- Adequate processing safety for ‘fresh free’ processing operations
- Safety issues on the eventual production of the rubber product
- No reaction on area cure
- Vulcanization method to be used (speed of heat transfer)
- Maximum vulcanization temperature available
- Cure cycle determined for the available vulcanization method, the temperature, and the vulcanization properties required
- Effectiveness of the accelerator system over a wider range of cure temperatures and availability for use with different polymers
- No adverse effects on other properties (e.g., hardness, aging, adhesion, etc.)
- No adverse effects on the rubber compound in the rubber product
- No negative health hazards upon usage as a chemical and of its decomposition products on cure
- No adverse effects during use of the rubber product (e.g., accelerators used in the manufacturing of the rubber articles intended for food contact qualification, etc.)
- Stability of the accelerator as a chemical (i.e., problems with the use of decomposed sulfur-based accelerators)
- Easy to handle and dose properly (physically)

Inclusion of a sulfur accelerator system is one of the most difficult problems in compounds. The sulfur chosen must have good cure on blend stage and in the following blow. It accelerates the cure of the accelerator to allow efficient mixing and processing. It must be compatible with the cure method used. For example, a thiol, sulfur curable rubber has a curing speed of around 100% in 20 minutes; curable rubber containing a mixture of sulfur is faster at 60% in 5 minutes. The temperature is that of cured stocks at 200°C for various used in the compound or accelerators of rubber until mixing. For evaluation of their properties, rubber can be used to a temperature of 150°C to an approximate range of cure. Finally, the accelerator must produce a vulcanization that gives good adhesion to fibers or metal. If it is a composite article, less crumbly that are suitable for aging of living, and don't bloom

Accelerator selection is critical.

### Primary accelerators

A choice of suitable accelerator for compounding must be selected from a large number of organic compounds. These various categories into viable, or both. They have been developed over a period of many years, and the type and amount depend on the elastomer used, the production processing requirements, and the end-use product. Accelerators are typically classified as primary or secondary. Primary accelerators usually promote considerable sulfur diffusion, moderate to fast cure, and good results (catalyst density development). Secondary accelerators provide secondary, fast cure rate, and high curing efficiency. Primary accelerators are sulfides and thiabenzothiazoles. Secondary accelerators are thio-oxadiacarbenes, thio-oxadiazoles, and specially, primary accelerators.
### Search Rates of Some Commonly Used Accelerators

<table>
<thead>
<tr>
<th>Secondary &quot;Victims&quot;</th>
<th>Primary</th>
</tr>
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<tbody>
<tr>
<td>GBM</td>
<td>MRTS</td>
</tr>
<tr>
<td>GETS</td>
<td>MRTS</td>
</tr>
<tr>
<td>TMTD</td>
<td>MRTS</td>
</tr>
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<td>TNSC</td>
<td>MRTS</td>
</tr>
<tr>
<td>TCDSC</td>
<td>MRTS</td>
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<td>TCD</td>
<td>MRTS</td>
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<tr>
<td>TCDSC</td>
<td>SICDSC</td>
</tr>
<tr>
<td>TNSC</td>
<td>SICDSC</td>
</tr>
<tr>
<td>TNSC</td>
<td>SICDSC</td>
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</tbody>
</table>

#### Thimane Types

The vast majority of thimanes are carbon, carbon-diamond, and silicone. The chief thimane accelerators are: 3-naphthaleneethanethiol (3NETH), benzene-carboxyaldehyde (BCA), and the new salt of naphthaleneethanethiol (NEET). The salt is not only used to the compelling fact that it is used more in lame forms and rigid forms. Both BCA and MRTS can cause remarkable problems when used in various black and carbon fiber rods. MRTS is somewhat easier to process than BCA. It is common practice to use a higher with BCA and MRTS. BCA is known with BCA to give a softer thimane in shape than BCA. A softer thimane is useful for an MRTS stack to 1.5 MRTS, 1.5 TMTD, and 2.00 mrad (10).
MBF or 2-methoxythiophenol is the first
thiol to be used commercially in the rubber
industry. It is highly reactive and used
effectively in applications requiring a good
degree of aging at lower temperatures (14°C (57°F) or below), and in slower
curing systems. MBF imparts fast curing properties and also imparts good
aging characteristics. Combination of MBF with other accelerators are used
when faster curing is needed and an increase in cured can be tolerated. An
example would be aging systems for compounds designed for continuous
curing at hot or heated vulcanizing temperatures (152°C (306°F) and higher).

MBT or benzothiazole disulphide was
classically developed for use in processing
rubber compounds cured at or above
14°C (57°F). MBT continues to be used
widely in compounds of all types for many
more commercial applications. Its activity
and sulfur properties can be controlled over a wide range by using various
combinations of MBT and other accelerators with MBT. MBT accelerates in the
cold starting point in cure compound development, especially in natural
filled types for such applications as tires and belts or molded goods.

ZMBT or zinc-2-methylbenzoate is a
modified thioate. It is mainly used in tires.
ZMBT has much higher cured rubber. It also
imparts the fast curing properties and good
aging characteristics given by MBT.
Figure 3 compares the cure rate of bisazoles. The formula is MRR based.

<table>
<thead>
<tr>
<th>MRR</th>
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<tr>
<td>220</td>
<td>0.00</td>
</tr>
<tr>
<td>375</td>
<td>0.00</td>
</tr>
<tr>
<td>525</td>
<td>0.00</td>
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</table>

**Sulfinamidone Types**

Sulfinamidones are made in two steps by the reaction of 2-methylbenzimidazole with an 8-quinolinic acid and catalysts of the appropriate aromatic salt of 5-methylenbenzoic acid.

The various amino-functional groups of sulfinamidones select their scratch time and cure rate difference. If the aromatic is high in the scratch time, the cure rate (as in terms of pressure-sulfurized)-1.25-styryl-bis-1-sulfinamidone is the highest, with 0.5-catalyzed 1-hydroxy-substituted-sulfinamidone the lowest. The trend is to use the modifications of the original sulfinamidone-acid that give greater pressure-sulfurizing-acid accelerators from 1.5-hydroxy-sulfinamidones (MRR). Besides giving a longer scratch delay, MRR gives higher results than MRR, so change can possibly be induced in 10% very frequently the sulfinamidones are used with succinimide accelerators that TOT.

**MRR** and 5-methylbenzimidazole-2-sulfamic acid is used to prepare delayed action antifungal by using compositions for natural and synthetic milieus for their applications, changing reactive-mixing and using catalysts. Overall, foils of natural and synthetic compounds with MRR accelerators are generally those dissimilar with others.
In the diagram, several primary accelerators are depicted, each with its own structural formula. The text describes the properties and uses of each accelerator:

- **CGEB** (Cylohexyl-1,2-bis(aminohexyl)acetate): A highly effective accelerator for sealants and adhesives. It is faster curing than HEB, develops higher modulus, and shows promise in automotive applications.

- **HEB** (Hexyl-1,2-bis(aminohexyl)acetate): A highly effective accelerator for sealants and adhesives. It is faster curing than CGEB, develops higher modulus, and shows promise in automotive applications.

- **Cure-All 18** (Cylohexyl-1,2-bis(aminohexyl)acetate): A highly effective accelerator for sealants and adhesives. It is faster curing than CGEB, develops higher modulus, and shows promise in automotive applications.

- **MMA** (Methyl Methacrylate): A highly effective accelerator for sealants and adhesives. It is faster curing than CGEB, develops higher modulus, and shows promise in automotive applications.

- **CGEB** (Cylohexyl-1,2-bis(aminohexyl)acetate): A highly effective accelerator for sealants and adhesives. It is faster curing than HEB, develops higher modulus, and shows promise in automotive applications.

- **SUE** (Styrenated Butadiene): A highly effective accelerator for sealants and adhesives. It is faster curing than CGEB, develops higher modulus, and shows promise in automotive applications.

- **DBS** (Di-2-hydroxyethylphosphine): A highly effective accelerator for sealants and adhesives. It is faster curing than CGEB, develops higher modulus, and shows promise in automotive applications.
Polymer Cure Curves - Same Cure System

<table>
<thead>
<tr>
<th>Compound Formulation</th>
<th>E/0.5</th>
<th>E/0</th>
<th>Shore A/0</th>
<th>Shore A/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hevea</td>
<td>100</td>
<td>5.0</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Synthetic HLR</td>
<td>1.2</td>
<td></td>
<td></td>
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This graph is a representation of the polymer’s behavior. It shows the cure characteristics.

Figure 4: Steady Polymer Automations with MIN.

**Summary**

Accelerator choice is critical. Selecting a good accelerator option is difficult. Many parameters, such as cure rate, storage stability, processability, workability, crosslinking, and cured rubber properties need to be considered. Primary accelerators, thiazoles and thienylbenzothiazoles, are the most popular accelerators and offer a good shelf. Their good properties are the effective accelerators they provide at medium and high temperatures and their wide range of curing rates and crosslinking characteristics. They usually provide considerable scorch delay, an adequate cure rate, and good modulus development. Defining secondary parameters can be accomplished with the addition of secondary accelerant. This topic will be covered in Part II. Secondary Accelerants.