2. Sulfenamides
in rubber curing systems.

The ultra accelerators allow faster curing of a compound than can be obtained with other classes of accelerators such as
basic, (c) chemical type, (d) by acceleration speed such as slow, medium,
ultra accelerated compounds to produce optimum physical properties in a shorter
time than what is obtained with primary accelerators.

In addition to the greatest degree. Generally, smaller quantities of sulfur can be used in
rubber product, the following considerations must be taken into account.

- The curing rates of the rubber compound should be constant within the overall range of
torque after the start of vulcanization. One must select ultra/secondary accelerators that work
to cause pre-cure at room temperature.
- Selection of the proper ultra/secondary accelerator is very important to a compounder. It can
determine the number of cycle times one can run. The ultra/secondary levels in a compound can
also be used.

- Ultra/Secondary Accelerator System

I. Ultral Speed Accelerator

II. Secondary Accelerator

III. Ultra/secondary Accelerator System

In selecting the ultra/secondary accelerator route for the manufacture of a particular
rubber product, the following considerations must be taken into account:

- Exposure to time of the compound
- Ultral Accelerator’s solubility in rubber
- The interaction of the ultral accelerator with the primary accelerator
- The number of processing stages the compound undergoes
- The limit of sulfur added to the compound
- Ease of use can be economical production of the rubber product
- Determination of sulfur levels and its effect on the levels of ultra accelerators
- The curing method and (e.g. injection, compression, or transfer molding)
- Maximum vulcanization temperature available
- Cure rates and the availability vulcanization method, the temperature, and the
  vulcanization required
- The interaction of the ultra/secondary accelerator with the primary accelerator
- The ultra/secondary accelerator effect on other ingredients required
- To have thorough knowledge open space (a) and chemistry of the vulcanizing
  principles involved
- To achieve effective during out of the rubber product (e.g. accelerators and in
  manufacturing, all the rubber articles involved for food contact, surgical use, etc.)
- To achieve effective vulcanization rates and within the overall range of
torque after the start of vulcanization. One must select ultra/secondary accelerators that work
to cause pre-cure at room temperature.
- Selection of the proper ultra/secondary accelerator is very important to a compounder. It can
determine the number of cycle times one can run. The ultra/secondary levels in a compound can
also be used.

II. Secondary Accelerator

Secondary accelerators are compounds that are not effective on their own. They are
usually used to modify the action of primary accelerators. They have the capability of
having a synergistic effect with other ingredients in a compound. Their major functions are that they
produce increased cure rate (zinc oxide based) and cure rate with sulfur and/or sulfur based
compounds. They have the capability to increase cure rate and obtain required physical properties
in a shorter time.

III. Ultra/secondary Accelerator System

Ultra/secondary Accelerator System is a combination of primary accelerator(s) and
ultra/secondary accelerators. It was designed to provide a combination of ultra/secondary
accelerators and primary accelerators in order to achieve efficient use of these
accelerators to achieve optimum curing. Ultra/secondary Accelerator System is a combination of
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combination of ultra/secondary accelerators and primary accelerators in order to
achieve efficient use of these accelerators to achieve optimum curing.

Cure Acceleration and Accelerator Systems Part I covered the meaning of vulcaniza-
tion, interaction of accelerators at which time they are sometimes called “secondary” accelerators. In
addition to the greatest degree. Generally, smaller quantities of sulfur can be used in
rubber product, the following considerations must be taken into account.

For the most popular ultra/secondary accelerators are the dithiocarbamates and
thiuram-based. They are all organic compounds that work in synergy with sulfur or other sulfur
compounds. Their major functions are that they produce increased cure rate (zinc oxide based) and cure rate
with sulfur and/or sulfur based compounds. They have the capability to increase cure rate and obtain
required physical properties in a shorter time.

Dithiocarbamate Type

Dithiocarbamates are powerful accelerators that are rarely used alone with a secondary
accelerator to derive maximum levels of processing safety and vulcanization
(ultra/secondary). They require a synergistic effect with other ingredients in a compound. Their major
functions are that they produce increased cure rate (zinc oxide based) and cure rate
with sulfur and/or sulfur based compounds. They have the capability to increase cure rate and obtain
required physical properties in a shorter time.
accelerators and accelerator systems

Part I: Ultra/Secondary Accelerators

Introduction

The Ultra/Secondary Accelerator System Part I covers the discussion, explanation, and application of ultra/secondary accelerators. In this section, we introduce the general concept of vulcanization and the primary accelerators. The focus will be on the types of ultra/secondary accelerators, the thiazoles and sulfenamides and their role in rubber curing systems.

In addition to Part I, accelerators are classifiable by ASTM as:

- Semi-ultra, which gives lower modulus than can be obtained with other classes of accelerators such as thiurams.
- Ultra, which gives lower modulus and shorter scorch times which are in continuous production. Low sulfur content rubber such as a four and three with thiram can be vulcanized at high temperature (140°C) for wire insulation, as well as for rubber tubing and pipes. DZDC with 50 parts of curing activity in DMQ formulations.

Semi-ultra accelerators are considered to be faster than the thiazoles and sulfenamides.

Primary accelerators are utilized.

Other types of rubber compounds are:

- Natural rubber
- SBR stocks the system might be 0.6 ZMDC, 0.75 parts of thiazole, 1.8 parts of sulfur.

- Melt viscosity
- Curing method used (e.g., injection, compression, or transfer molding)
- Secondary accelerator’s solubility in rubber
- Interaction of the ultra/secondary accelerators with the polymer system
- The ultra/secondary accelerators effect on other ingredients in a compound
- The ultra/secondary accelerators effect on over-cures. CuDD shows a lower modulus, tensile strength, lower compression set, and a marked plateau modulus, tensile strength, lower compression set, and a marked plateau

Ultra/Secondary 

<table>
<thead>
<tr>
<th>Ultra/Secondary</th>
<th>Number</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
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<tr>
<td>Secondary</td>
<td>0.61</td>
<td>0.40</td>
</tr>
<tr>
<td>Total</td>
<td>1.00</td>
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</tr>
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</table>

Dithiocarbamates

Dithiocarbamate in rubber is a powerful accelerator which speeds vulcanization. In latex, it is especially recommended for SBR, or in cord and tube production and other applications requiring rapid curing.

TMTD is also the most effective accelerator in chlorinated rubber, and Butyl. It is a powerful antioxidant to obtain maximum aging, especially in mineral filled compounds.

ZDEC is an active form of Zinc Dibutyl Dithiocarbamate. In latex it is less likely to cause pre-cure at room temperature. TDEC or ZDHC in smectic stabilized epoxides. TDEC or ZDHC in smectic stabilized epoxides.

ZDEC in a base of ZDHC gives a better holding strength than the thiazole. The incorporation of thiram and other ingredients is a compound. The correct amount of accelerator in a compound will give satisfactory cure activity in EPDM formulations.

ZDEC or ZDHC (Zinc Dibutyl Dithiocarbamate) is a powerful accelerator which speeds vulcanization. It is especially recommended for SBR, or in cord and tube production and other applications requiring rapid curing.
Part II: Ultra/Secondary Accelerators

Before selecting an ultra/secondary accelerator system for the manufacture of a particular compound, determine the amount of storage time (shelf-life) a compound can withstand. The correct selection of ultra/secondary accelerator system will allow sufficient scorch delay before the onset of vulcanization and high properties required (butyl), and EPDM. Dithiocarbamates have good tensile and resiliency. They have slightly lower scorch rates than thiurams. The ultra/secondary accelerators often produce scorchy, very fast curing rates.

Dithiocarbamate Types

- **ZDBC**
  - Or Zinc dibutyl dithiocarbamate is used as a stabilizer in hot melts. It is also useful as a secondary accelerator for the continuous vulcanization of butyl rubber.
  - It is an active form of Zinc diethyl dithiocarbamate.

- **ZBED**
  - Or Zinc dibenzyl dithiocarbamate is a typical ultra-accelerator at normal curing temperatures. It is also recommended as a booster for thiazoles. It may be used in combination with other accelerators to adjust the cure rate.

- **ZDMC**
  - Or Zinc di(2-mercaptobenzyl) dithiocarbamate is an ultra-accelerator which is active at normal curing temperatures. It is also useful as a secondary accelerator for the continuous vulcanization of butyl rubber.

ZDMC or ZDEC is an ultra-accelerating accelerator for sulfur and sulfur based compounds that can be used in an ultra/secondary or thioamide system. It is a powerful accelerator which is strongly activated by a thioamine. SAA-30 gives powerful acceleration at low sulfur levels. It is also useful as an ultra-accelerator for the continuous vulcanization of butyl rubber.

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accelerators and accelerator systems Part II: Ultra/Secondary Accelerators

As mentioned in Part I, accelerators are classify by ASTM as:...

Introduction

In addition to the greatest degree. Generally, smaller quantities of sulfur can be used in

selection of ultra/secondary accelerator systems

For example, although the Ultra/Secondary Accelerator system for the manufacture of a particular rubber product, the following considerations must be taken into account

- Cure cycle desired for the available vulcanization method, the temperature, and the
- The curing method used (.e.g. injection, compression, or transfer molding)
- The interaction of the ultra/secondary accelerators with the primary accelerators
- The interaction of the ultra/secondary accelerators with the polymer systems
- Faster cure rate for economical production of the rubber product
- Easy to handle and dust suppressed physical form
- Non-staining dithiocarbamates are versatile accelerators that can be used in IIR stocks. They are paired with thiazole or sulfenamide accelerators to adjust the cure rate of a stock. For instance, with SBR stocks the system might be 0.6 ZMDC, 0.75 parts of thiazole, 1.8 parts of sulfur.

Dithiocarbamate

Dithiocarbamate. In latex it is less likely...

Ultra/Secondary

Primary

Factor

Ultra/Secondary

Primary

Factor

U L T R A / S E C O N D A R Y  A C C E L E R A T O R S : c o n t i n u e d

ZBED is a typical ultra-accelerator at...

ZDEC is an active form of Zinc...
Part II: Ultra/Secondary Accelerators

In this section the ultra/secondary accelerator review for the manufacture of particular rubber products the following considerations must be taken into account:

- Cure cycle desired for the available vulcanization method, the temperature, and the number of processing stages the compound must undergo
- Maximum vulcanization temperature available
- The number of processing stages the compound must undergo
- Cure time and cure state required for the rubber product
- Molecular weight and cure induction requirements
- Nature of the ultraviolet absorber and curing system
- Nature of the rubber vulcanizate
- Other factors to be considered are the rate of cure of the compound, synergistic effects, and the natural cure rate of the rubber vulcanizate

Selection of ultra/secondary accelerator systems

Selection of ultra/secondary accelerators can be divided into five major classes: the dithiocarbamates, the thiuram disulfides, thiazoles, aminothiazoles, and the benzothiazoles.

The dithiocarbamates are the most popular and effective of the ultra/secondary accelerators. They are used extensively in rubber vulcanization. The cure rate of the rubber vulcanizate is a function of the ultraviolet absorber and the curing system. The nature of the rubber vulcanizate and the curing system affect other properties in a compound.

The choice of the proper ultra/secondary accelerator is very important to a compound and is affected by the number of cycle times for the rubber product.

Dithiocarbamate types

Dithiocarbamates are so powerful that they are rarely used alone except in such specialty applications as spread goods (fabric covered with a rubber coating: e.g., butyl). They are used in combination with other accelerators and are classified into five different types. The choice of the proper ultra/secondary accelerator is very important to a compound and is affected by the number of cycle times for the rubber product.

- 2. Sulfenamides
- 3. Dithiocarbamates
- 4. Thiurams
- 5. Specialty accelerators

Scorch Rates of Some Commonly used Accelerators

<table>
<thead>
<tr>
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<td>F 6</td>
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<tr>
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<td>F 7</td>
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</tr>
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</tr>
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Thiuram Types
Like the thioacetates, thiurams are ultra accelerators. They are made from secondary amines and sulfur disulfides. The most common use is as a secondary accelerator in NR and SBR applications. In modified CR, TBzTD is a retarder for sulfur cured, low unsaturated content rubbers like butyl and EPDM. It contains nitrosoamines is of concern. It gives off dibenzylnitrosoamine which is not carcinogenic, but it is a mutagen. Thiurams 1.0 phr

TMTD is trimethyl thiuram disulfide and is a sulfur bearing accelerator and sulfur donor. It is used extensively in heat resistant compounds. For example EPDM stock might be used with sulfur to provide good curing of sulfur bearing ultra accelerator and sulfur cross-linking. Therefore it can be used in low sulfur systems because of its high activity, and it has a lower scorch rate than TMTD and TETD.

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For ultra/secondary accelerators, the primary accelerator has been chosen, more adjustments of the cure system may be necessary. This is when a specialty accelerator may be needed. The topic of specialty accelerators will be covered in Part III.

summary
The paper evaluates the ultra/secondary accelerator with the primary accelerator in order to the optimization of a cure system. Fortunately there are enough ultra/secondary accelerators to meet most compound needs. Many factors, such as primary accelerator, cure rate, cure method and temperature, multiple processing steps, and target physical properties can limit the type and amount of ultra/secondary accelerators that can be used. Sometimes after a primary and an ultra/secondary accelerator has been chosen, more adjustments of the cure system may be necessary. This is when a specialty accelerator may be needed. The topic of specialty accelerators will be covered in Part III.

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Thiurams Types
Like the dithiocarbamates, thiurams are ultra accelerators. They are made from secondary amine and sulfur. The most common use of thiuram is as a secondary accelerator to sulfur to provide cross linking, therefore it can be used in low sulfur as compared to other accelerators.

TMTD (2,2′-thiobis(6-methylthiocarbamide) tetrahydrodiphenylmethane) is a fast cure accelerator for natural rubber, SBR, and BR. It has a low scorch rate compared to TMTD and TETD. TMTD is too scorchy to be used alone. The cure rate is approximately 13% available sulfur for cross linking, therefore it can be used in low sulfur as compared to other accelerators.

TETD (2,2′-thiobis(6-ethylthiocarbamide) tetrahydrodiphenylmethane) is about the same, but TETD can be used with care. TETD is used in a combination with TMTD or TMTQ, as it is too scorchy to be used alone. Like the thiuram sulfides, the thiuram thioimidates can be used in light colored stocks without staining.

The thiurams are especially useful in cure systems containing low or no elemental sulfur. This is because mix milling is sometimes necessary without added sulfur. The most common use of thiurams is as a secondary accelerator to sulfur in sulfurless accelerated compounds. For example, EPDM stock might use a combination of 1% of sulfur, 2.5 parts of thiuram, and 1.5 parts of TMTD.

TBzTD (2,2′-thiobis(5-tetrabenzylthio carbamide) tetrahydrodiphenylmethane) is a fast curing primary or secondary accelerator. It has 25% available sulfur for vulcanization as compared to 13% and 11% respectively for TMTD and TETD. DPTT (3,3′-dipentamethylene dithiocarbamic acid) is a sulfur bearing accelerator that finds special compounding applications. It has 25% available sulfur, and it has a lower scorch rate compared to TMTD and TETD.

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DPTT (dipentamethylene thiodithiocarbamate) is a sulfur bearing accelerator. It is used especially in compounding applications. In theory, DPTT can be used as a sulfur booster to increase heat resistance in NR and SBR compounds. It also functions as an accelerator for EPDM.

TBzTD (tetrabenzylthiuram disulfide) is a fast curing primary or secondary accelerator. It was developed to replace thiuram such as TMTD, where the presence of harmful information is limited. It is used in combination with thiuram to achieve the desired physical properties of the compound. TBzTD has a lower scorch rate compared to TMTD and TETD.

Ultraviolet (UV) and photooxidation accelerators are used in combination with thiurams to achieve the desired physical properties of the compound. TBzTD has a lower scorch rate compared to TMTD and TETD.
**Thiurams Types**

Like the thiuram disulfides, thiurams are ultra accelerators. They are made from mercaptanamines and carbon disulfide. The most common application of thiuram is as a secondary accelerator in SBR and NBR. Thiuram is one of the best secondary accelerators in NBR and highly unsaturated rubbers. It is the most preferred primary accelerator for EPDM. In modified CR, TBzTD is a retarder or TETD has a pot life 1.5 times that of TMTD.

The proper combination of ultra/secondary accelerators with the primary accelerators is essential to the optimization of a cure system. Fortunately there are enough ultra/secondary accelerator types to meet most compound needs. A balance, such as primary accelerator cure time, temperature, multiple processing steps, and target physical properties can limit the type and amount of ultra/secondary accelerators that can be used. Sometimes cure time is primary and an ultra/secondary accelerator has been chosen, even adjustments of the cure system may be necessary. This is where a specially accelerated cure must be selected. The type of secondary accelerator will be covered in Part II.

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**Thiurams**

<table>
<thead>
<tr>
<th>Compound</th>
<th>SBR 100.0 phr</th>
<th>SBR 100.0 phr</th>
<th>SBR 100.0 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMTD</td>
<td>1.0 phr</td>
<td>1.0 phr</td>
<td>1.0 phr</td>
</tr>
<tr>
<td>TETD</td>
<td>1.0 phr</td>
<td>1.0 phr</td>
<td>1.0 phr</td>
</tr>
<tr>
<td>TBzTD</td>
<td>1.0 phr</td>
<td>1.0 phr</td>
<td>1.0 phr</td>
</tr>
</tbody>
</table>

**Summary**

The proper combination of ultrasecondary accelerators with the primary accelerators is essential to the optimization of a cure system. Fortunately there are enough ultrasecondary accelerator types to meet most compound needs. A balance, such as primary accelerator cure time, temperature, multiple processing steps, and target physical properties can limit the type and amount of ultrasecondary accelerators that can be used. Sometimes cure time is primary and an ultrasecondary accelerator has been chosen, even adjustments of the cure system may be necessary. This is where a specially accelerated cure must be selected. The type of secondary accelerator will be covered in Part II.
Thiazoles are effective in sulfur cures at levels as low as 0.2 phr for curing NR, SBR, and BR. However, for PSBR or EPDM, higher levels are necessary to achieve full cure. Figure 1a shows the cure rate comparison of different dithiocarbamates, where the sulfur and ZnO content is held constant. Figure 1b compares the cure rate of dithiocarbamates with different sulfur contents, demonstrating the importance of sulfur dosage in achieving optimal cure rates.

**Figure 1a**

- Cure Rate of Dithiocarbamates
- **X-axis**: Time (minutes)
- **Y-axis**: Cure Rate (%)
- Comparison of Dithiocarbamates (DPT, TMTD, TBzTD, TETD, DPTT)

**Figure 1b**

- Cure Rate of Dithiocarbamates
- **X-axis**: Time (minutes)
- **Y-axis**: Cure Rate (%)
- Comparison of Dithiocarbamates (Sulfur 1.8 phr, ZnO 5.0 phr)

**Conclusion**

The use of ultra/secondary accelerators in rubber compounding is crucial for achieving optimal cure rates. Selection of the appropriate ultra/secondary accelerator depends on the specific needs of the rubber type, polymer structure, and processing conditions. Comprehensive testing and optimization are necessary to achieve the desired cure rate and mechanical properties.
Thiurams Types

Like the disulfides, the thiuram-type accelerators are ultra accelerators. They are made from secondary amines and carbon disulfide. The most commonly used members of this class are the diethylthiocarbamates (TMTD), dibenzothiazyl disulfides (MBTS), and thiazole disulfides (TETD). The strength of these three accelerators is in the order of TMTD, MBTS, and then TETD. Because of higher scorch resistance, TMTD is the most commonly used secondary accelerator. It has a cure system of 1.5 parts of sulfur, 1.25 parts of thiazole, and 1.5 parts of TMTD. Based on the different sulfur levels, the cure times can be varied from one to three hours.

Thiuram maches, the thiuram sulfides can be used in light colored stocks without staining. It is applicable to replace thiurams such as TMTD, where the presence of harmful mercaptans is not desirable.

NBR and highly unsaturated rubbers. It is the most preferred primary accelerator for sulfur cured, low unsaturated content rubbers like butyl and EPDM. It contains approximately 1% available sulfur for cross linking, therefore it can be used in low sulfur formulations of these polymers.

TMTD is the most susceptible to aging; it is a sulfur donor to increase heat resistance in NBR and SBR compounds. It is also used for a sulfur donor to increase heat resistance in sulfur cures. It also activates the thiazoles and accelerates the cure rate by 10% and 11% respectively for TMTD and TETD. DPTT is used as an accelerator in NR, SBR and NBR applications. It is also used as a sulfur donor to increase heat resistance in NR and SBR compounds. In sulfur cures, TMTD is used as a sulfur donor to increase heat resistance.

The proper combination of ultra/secondary accelerators with the primary accelerators is essential to the optimization of a cure system. Fortunately there are enough ultra/secondary accelerators that can be used to form a cure system that is suitable for a wide variety of rubbers. The presence of harmful mercaptans is not desirable. The thiuram sulfides can be used in light colored stocks without staining. 

TMTD is the most preferred primary accelerator for sulfur cured, low unsaturated content rubbers like butyl and EPDM. It is the most preferred primary accelerator for sulfur cured, low unsaturated content rubbers like butyl and EPDM. It contains approximately 1% available sulfur for cross linking, therefore it can be used in low sulfur formulations of these polymers.

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