accelerators and accelerator systems

Part II: Ultra/Secondary Accelerators

The designation "ultra" is applied to accelerators that speed the rate of vulcanization to the greatest degree. Generally, smaller quantities of sulfur can be used in ultra accelerated compounds to produce optimum physical properties in a shorter curing time than can be obtained with other classes of accelerators such as thiazoles or sulfenamides.

Quite frequently the ultra accelerators are used in combination with primary accelerators at which time they are sometimes called "secondary" accelerators. In Part II the two classes of ultra accelerators that will be discussed are dithiocarbamates and thiurams.

introduction

Accelerators and Accelerator Systems Part I covered the meaning of vulcanization with respect to rheology, selection of accelerators, polymer accelerator interaction and the primary accelerators. The focus here will be on two types of ultra/secondary accelerators, the dithiocarbamates and thiurams and their role in rubber curing systems.

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

1. Thiazoles (Mercapto)

2. Sulfenamides

3. Guanidines

4. Dithiocarbamates

5. Thiurams

6. Specialty Accelerators.

Other ways to classify accelerators are (a) organic or inorganic, (b) acidic or basic, (c) chemical type, (d) by acceleration speed such as slow, medium, semi-ultra and ultra.

selection of ultra/secondary accelerator system

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

- Expected shelf life of the compound
- Ultra/secondary accelerator's solubility in rubber
- The interaction of the ultra/secondary accelerators with the primary accelerators
- The number of processing stages the compound must undergo
- The level of scorch safety the compound needs
- Faster cure rate for economical production of the rubber product
- Determination of sulfur levels needed and its effect on the levels of ultra accelerators
- The curing method used (.e.g. injection, compression, or transfer molding)
- Maximum vulcanization temperature available
- Cure cycle desired for the available vulcanization method, the temperature, and the vulcanizate properties required
- The interaction of the ultra/secondary accelerators with the polymer systems
- The ultra/secondary accelerators effect on other ingredients in a compound
- No known health hazards upon usage of 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.)
- Easy to handle and dust suppressed physical form

Selection of the proper ultra/secondary accelerator is very important to a compounder. It can affect the number of cycle times one can run. The ultra/secondary levels in a compound can determine the amount of storage time (shelf-life) a compound can withstand. The correct selection of ultra/secondary accelerators in combination with a delayed action accelerator (e.g. sulfenamide) will allow sufficient scorch delay before the onset of vulcanization and high torque after the start of vulcanization. One must select ultra/secondary accelerators that work in a synergistic manner with other ingredients in a compound. The next section will give you important information on each type of ultra/secondary accelerator and some applications where they are utilized.

Scorch Rates of Some Commonly used Accelerators

Ultra/Secondary "Kickers"		Primary
SAA-30	Faster	MBT
CuDD		MBTS
DPTT		ZMBT
TMTD		CBTS
ZDMC		BBTS
TM/ETD		Cure-Rite 18
ZDEC		OMTS
DPG		OBTS
TETD		DCBS
DOTG		
TDEC		
TMTM		
TBzTD		
ZDBC	Slower	

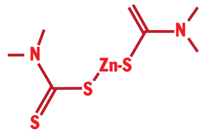
Note: red denotes the dithiocarbamates and blue the thiuram accelerators

By far the most popular ultra/secondary accelerators are the dithiocarbamates and thiurams. The ultra/secondary accelerators often produce scorchy, very fast curing compounds. Their major functions are that they produce increased cure rate (i.e. raise the modulus) and shorten scorch times. Quite frequently they are paired with a primary accelerator to derive maximum levels of processing safety and vulcanization rates.

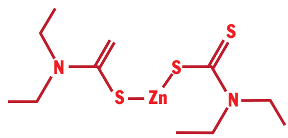
Dithiocarbamate Types

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. hospital sheeting) cured in air at or slightly above room temperature. Usually they are paired with thiazole or sulfenamide accelerators to adjust the cure rate of a stock. A typical curing system with natural rubber might be 0.5 parts of zinc dimethyldithiocarbamate (ZMDC), 0.75 parts of thiazole accelerator, and 2.0 parts of sulfur. With SBR stocks the system might be 0.6 ZMDC, 0.75 parts of thiazole, 1.8 parts of sulfur. Non-staining dithiocarbamates are versatile accelerators that can be used in IIR (butyl), and EPDM. Dithiocarbamates have good tensile and resiliency. They have slightly lower modulus than the thiurams. Popular members of this class are the zinc methyl, ethyl and butyl dithiocarbamates. Salts of bismuth, copper, and tellurium also are used.

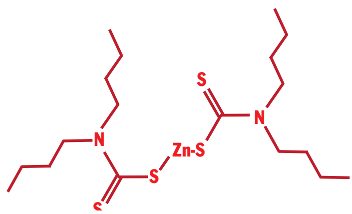
ZDMC or Zinc dimethyldithiocarbamate is an ultra /secondary accelerator for natural and synthetic based compounds that also find uses as a primary or secondary in sulfur based latex compounds. ZDMC is very active at temperatures above 100°C. As a primary accelerator ZDMC gives a faster cure rate and higher modulus, but shorter scorch times which find uses in continuous cure based products such as cables, tubings and profiles. Low unsaturation content rubbers such as butyl and EPDM can be cured using ZDMC as a secondary accelerator. It can be used at a higher dosage to achieve faster cure rates for high temperature curing (CV curing for wire insulation), as well as for curing thicker molded parts. ZDMC with MBT provides good curing activity in EPDM formulations.



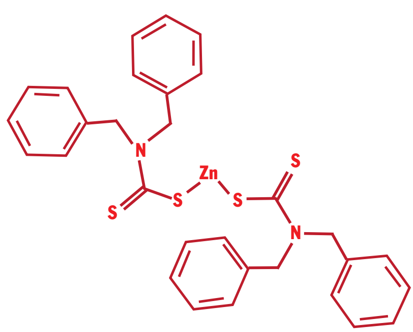
ZDEC or Zinc diethyldithiocarbamate can be used in the same manner as ZDMC, except that quantities should be increased 10% to obtain comparable results.



ZDBC or Zinc dibutyldithiocarbamate is used in adhesives as a stabilizer and as an antioxidant in uncured rubbers. It is also used in combination with other accelerators to produce low compression set, good heat aging, and lower bloom in EPDM compounds. It is recommended as a stabilizer in hot melts.



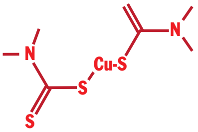
ZBED or Zinc Dibenzyl Dithiocarbamate is an active form of Zinc Dithiocarbamate, which can be modified by MBT or MBTS, etc. It is non-staining, non-discoloring and achieves safer processing than Zinc Dibutyl Dithiocarbamate. In latex it is less likely to cause pre-cure at room temperature than other dithiocarbamates. However, ZBED is a typical ultra-accelerator at normal curing temperatures. It is also useful as a secondary accelerator for the continuous vulcanization of butyl rubber extrusions.



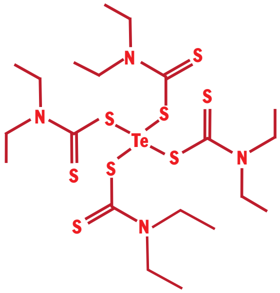
ZDBCX or zinc N, N-di-n-butyldithiocarbamate/di-n-butylamine complex is an ultra-accelerator which is active at room temperature. It can be further activated by Z.I.X., and may also be used as a booster for thiazoles. It may be used in natural rubber and SBR for dry mixes, cements, and latex. It is of particular value for the preparation of transparent and translucent articles from both latex and dry rubber.

+ dibutylamine complex

CuDD or Copper dimethyldithiocarbamate is especially recommended for SBR, EPDM, and Butyl. It is a powerful secondary accelerator. It is possible by using CuDD with MBTS to increase cure rate while holding scorch rate constant, or even reducing it slightly in some compounds. It usually results in higher modulus, tensile strength, lower compression set, and a marked plateau effect on over-cures. CuDD shows a distinct advantage in curing thick items. Compounds designed with CuDD should contain octylated diphenylamine antioxidant to obtain maximum aging, especially in mineral filled compounds.



TDEC or Tellurium diethyldithiocarbamate is the fastest for EPDM and butyl rubber vulcanization. TDEC or TDEC/Thiuram combinations with MBT are used extensively in butyl innerliner tube production and other applications requiring rapid cures.



SAA-30 or 2, 2'-dithiodiethylammonium-bis-dibenzyldithiocarbamate is an ultra-fast accelerator in a polymeric binder that is nitrosamine safe. For reference sake picture ZBED, but instead of a Zn salt, the dithiocarbamate is strongly activated by a thioamine. SAA-30 gives powerful acceleration at low levels. EPDM bloom is not a problem as it is with many accelerators. SAA-30 utilizes sulfur very efficiently to create good cures in formulas with lower levels of sulfur.

$$\left[(C_6H_5CH_2)_2N-\overset{\overset{S}{\|}}{C}-S^- \;\; NH_3^+-CH_2-CH_2-S-\right]_2$$

Fi ures 19a:69b: compares the cure rate of dithiocarbamates4 The formula is SBR based4

SBR	100	phr
ZnO	5	phr
SA	2	phr
Sulfur	1.8	phr
Dithiocarbamate	1.0	phr

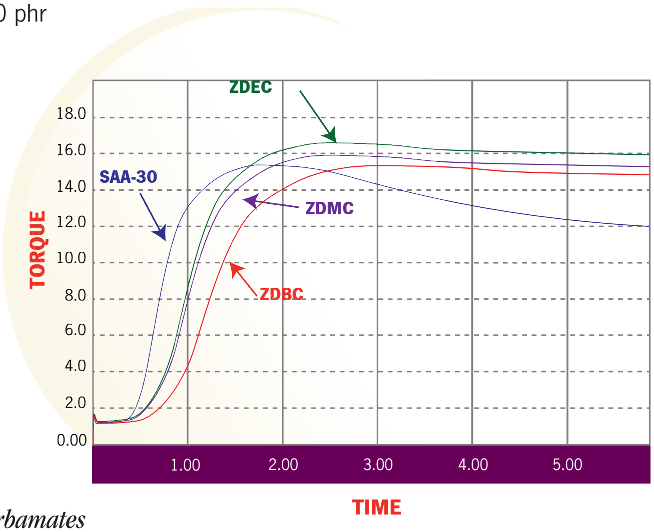


Figure 1a:
Cure Rate of Dithiocarbamates

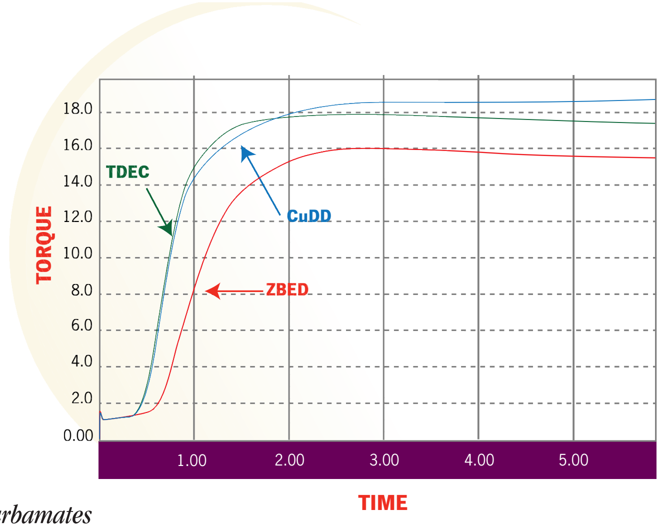


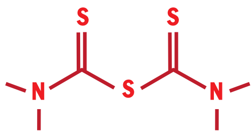
Figure 1b:
Cure Rate of Dithiocarbamates

Thiurams Types

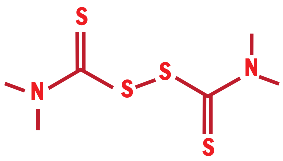
Like the dithiocarbamates, thiuram are ultra-accelerators. They are made from secondary amines and carbon disulfide. The most commonly used members of this class are probably tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide (TETD), and tetramethylthiuram monosulfide (TMTM). The strongest of these three is the TMTD, followed by TETD and then TMTM. TMTD is too scorchy to be used alone. TETD is about the same, but TMTM can be used with care. If TETD is substituted for TMTD, about 10% more TETD should be used. Like the dithiocarbamates, the thiuram sulfides can be used in light colored stocks without staining.

The thiurams are especially useful in cure systems containing low or no elemental sulfur. However, the monosulfide is not strong enough to cure satisfactorily without added sulfur. The most common use of the thiuram is as a secondary accelerator to thiazole or sulfenamide accelerated compounds. For example EPDM stock might have a cure system of 1.5 parts of sulfur, 1.25 parts of thiazole, and 1.5 parts of TMTD.

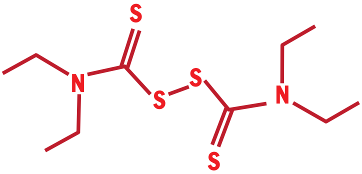
TMTM or Tetramethylthiuram monosulfide is not a sulfur donor. It must be used with sulfur to provide good curing activity, and it has a lower scorch rate than TMTD and TETD.



TMTD or Tetramethylthiuram disulfide is an ultra fast accelerator for NR, SBR, BR, 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 13% available sulfur for cross linking, therefore it can be used in low sulfur /sulfurless EV cures of diene polymers.

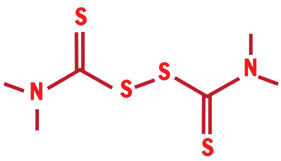


TETD or Tetraethylthiuram disulfide is a sulfur bearing ultra accelerator and sulfur donor. It is used extensively in heat resistant compound design for sulfurless and low sulfur cures. It also activates the thiazoles and sulfenamides.

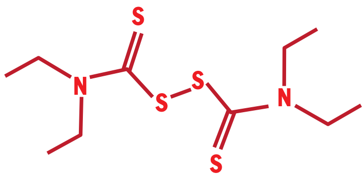


TM/ETD is a combination of Tetramethylthiuram disulfide/Tetraethylthiuram disulfide and is often used for single weighing purposes and is less liable to bloom than TMTD alone in comparable amounts.

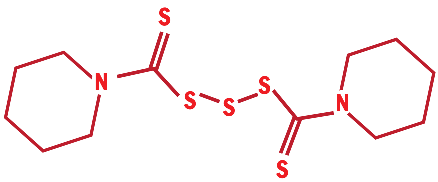
60%



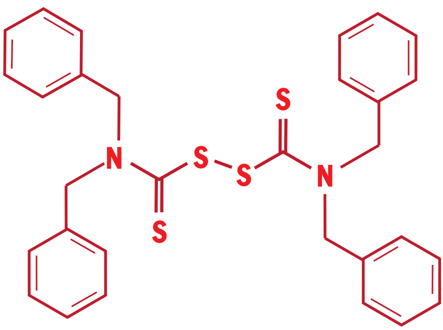
40%



DPTT or Dipentamethylene thiuram tetrahexasulfide is a sulfur bearing accelerator that finds special compounding applications. It has 25% available sulfur for vulcanization as compared to 13% and 11 % respectively for TMTD and TETD. DPTT is used as a sulfur donor to increase heat resistance in NR and SBR compounds. It also functions as an acelerator for Hypalon.



TBzTD or Tetrabenzylthiuram disulfide is a safe secondary amine accelerator. It was developed to replace thiurams such as TMTD, where the presence of harmful nitrosoamines is of concern. It gives off dibenzylnitrosoamine which is not carcinogenic, according to published literature. TBzTD is a fast curing primary or secondary accelerator in NR, SBR and NBR applications. In modified CR, TBzTD is a retarder when used with ETU. Compared with TMTD, TBzTD is safer processing and has longer scorch resistance.



Fi ure 29a:69b: compares the cure rate of thiurams4The formula is SBR based4

SBR	100.0 phr
ZnO	5.0 phr
SA	2.0 phr
Sulfur	1.8 phr
Thiurams	1.0 phr

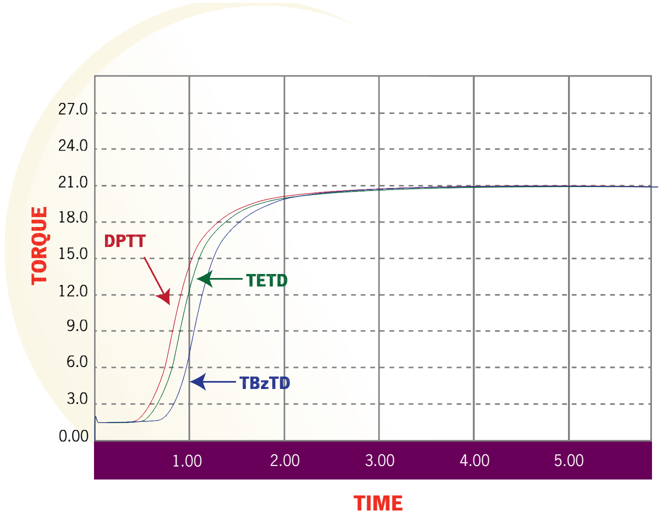


Figure 2a:
Cure Rate of Thiurams

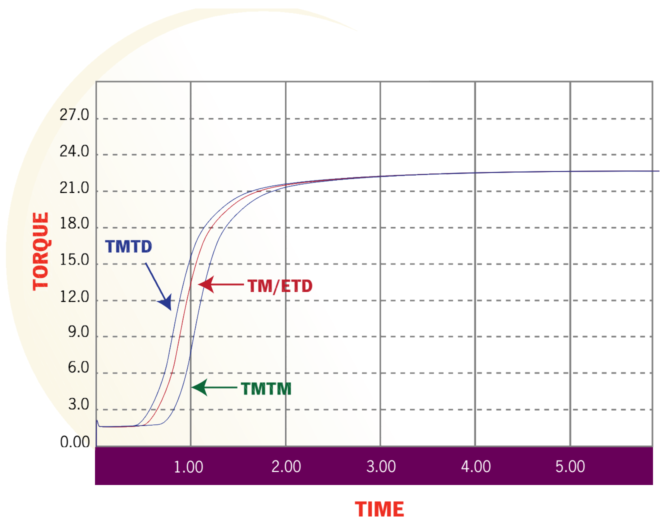


Figure 2b:
Cure Rate of Thiurams

summary

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 grades to meet most compound needs. Many factors, such as primary accelerator, cure rate, temperature, multiple processing steps, and target physical properties can limit the type and amount of ultra/secondary accelerator that can be utilized. 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 acceleratorL may be used. The topic of specialty accelerators will be covered in Part III.