



Designation: D4818 – 21

Standard Classification for Rubber Compounding Materials—Vulcanization Accelerators¹

This standard is issued under the fixed designation D4818; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This classification covers vulcanization accelerators and defines their important chemical and physical characteristics. The properties outlined herein are useful for quality control; they can frequently be directly or indirectly related to the performance characteristics in rubber compounds.

1.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1519 Test Methods for Rubber Chemicals—Determination of Melting Range

D1991 Test Method for Rubber Chemicals—2-Mercaptobenzothiazole (MBT)—Assay

D4571 Test Methods for Rubber Compounding Materials—Determination of Volatile Material

D4574 Test Methods for Rubber Compounding Materials—Determination of Ash Content

D4936 Test Method for Mercaptobenzothiazole Sulfenamide Assay by Reduction/Titration

D5044 Test Method for Rubber Compounding Materials—Free 2-Mercaptobenzothiazole (MBT) in Benzothiazyl Disulfide (MBTS)

¹ This classification is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.20 on Compounding Materials and Procedures.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D5051 Test Method for Rubber Compounding Materials—Benzothiazyl Disulfide (MBTS)—Assay

3. Significance and Use

3.1 *Class 1, Sulfenamides:*

3.1.1 As a group, the 2-benzothiazyl sulfenamides are the principle sulfur vulcanization accelerators used in the rubber industry today. The role of these materials in vulcanization is dual. They provide scorch time (delay period) in the crosslinking or vulcanization operation at processing temperatures. The delay avoids premature crosslinking during the processing, for example, mixing, extrusion, etc. Once the mixed rubber is at the curing temperature, these materials promote a rapid rate of curing (crosslinking, vulcanization).

3.1.2 The presence of certain impurities in this class of materials can affect their performance characteristics.

3.1.3 The 2-benzothiazyl sulfenamides are subject to degradation on extended storage. Significant degradation can affect their performance characteristics. In particular, the quality of the material is a function of storage time, temperature, relative humidity, and the impurity profile of the material; for example, free amines, salts of 2-mercaptobenzothiazole, etc. Since sulfenamide degradation in storage is an autocatalytic process (degradation products accelerate further degradation), significant degradation may only occur after a long induction period.

3.2 *Class 2, Thiazoles*—Thiazole derivatives are versatile vulcanization accelerators that are widely used in the rubber industry either alone or in combination with other accelerators.

3.3 *Class 3, Guanidines*—The guanidines have little importance as primary vulcanization accelerators, except for thick-sectioned goods, because of a typically slow vulcanization rate. As secondary accelerators they are used with other accelerators of the thiazole class. These resulting combinations vulcanize faster and give higher levels of vulcanization than do their individual constituents when used separately. The thiazole-guanidine combinations are frequently used for technical rubber goods.

3.4 *Class 4, Dithiocarbamates*—Vulcanization with dithiocarbamates is faster than with thiurams. Dithiocarbamates are used as ultra accelerators with normal sulfur levels. They are also employed as secondaries or activators for other accelerators.

3.5 *Class 5, Thiurams (disulfides)*—Thiuram disulfide accelerators are used for vulcanization without elemental sulfur to produce rubber compounds that show essentially no reversion and that have low compression set and good aging characteristics. For low sulfur vulcanization, thiurams are normally used in combination with sulfenamides. With a normal amount of sulfur, thiurams act as ultra accelerators.

3.6 *Class 6, Thiurams (other than disulfides)*—This class contains other thiuram types that are not disulfides. They are used as ultra accelerators with normal amounts of sulfur. Di, tetra, and hexasulfides can be employed without sulfur or with low sulfur levels to obtain rubber compounds with much reduced reversion tendencies.

3.7 The chemical or physical characteristics, or both, of these materials may affect their use as vulcanization accelerators.

4. Basis of Classification

4.1 The accelerators are divided into six classes according to their chemical structure and application in the rubber industry. They are as follows:

- 4.1.1 *Class 1*—Sulfenamides,
- 4.1.2 *Class 2*—Thiazoles,
- 4.1.3 *Class 3*—Guanidines,
- 4.1.4 *Class 4*—Dithiocarbamates,
- 4.1.5 *Class 5*—Thiurams (disulfides), and
- 4.1.6 *Class 6*—Thiurams (other than disulfides).

5. Basic Description of Accelerators

5.1 *Sulfenamides*—Compounds designated as 2-benzothiazyl sulfenamides vary in chemical nature and general performance characteristics depending on the nature of substitution around the sulfenamide nitrogen. The sulfenamide nitrogen is the nitrogen atom that is outside of the ring in the structures given below. There are three fundamental types in common use, as follows:

5.1.1 *Sulfenamides of Primary Amines (Type I)*—These compounds have one hydrogen on the sulfenamide nitrogen, in addition to the generic R group. In general, this type, as a group, exhibits a somewhat shorter scorch time and higher cure rate than the other sulfenamides (see Fig. 1).

5.1.2 *Sulfenamides of Unhindered Secondary Amines (Type II)*—These compounds have two primary carbon attachments, each with at least two hydrogens on the carbon bonded to the

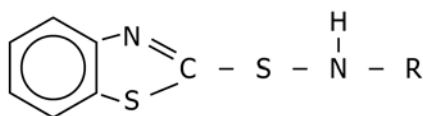


FIG. 1 Sulfenamides of Primary Amines

sulfenamide nitrogen. In this case, X can be one or two. This type, as a group, exhibits an intermediate scorch time and cure rate (see Fig. 2).

5.1.3 *Sulfenamides of Hindered Secondary Amines (Type III)*—These compounds have two secondary carbon attachments to the sulfenamide nitrogen. This type, as a group, exhibits a longer scorch time and lower cure rate than the other sulfenamides (see Fig. 3).

5.2 *Thiazoles*—There are three different thiazoles in common use. They all show a similar vulcanization effect.

5.2.1 *2-Mercaptobenzothiazole (MBT)*—See Fig. 4.

5.2.2 *Zinc Salt of 2-Mercaptobenzothiazole (ZMBT)*—This zinc salt may consist of different substances, but it is generally characterized as illustrated in Fig. 5.

5.2.3 *Dibenzothiazyl disulfide (MBTS)*—See Fig. 6.

5.3 *Guanidines*—There are two different types of guanidines in common use. They both show a similar vulcanization efficiency.

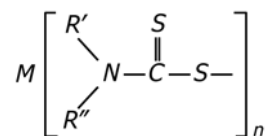
5.3.1 *Symmetric (Type I)*:

5.3.1.1 *Diphenylguanidine (DPG)*—See Fig. 7.

5.3.1.2 *Di-Ortho-Tolylguanidine (DOTG)*—See Fig. 8.

5.3.2 *Asymmetric (Type II), Ortho-Tolylbignanidine (OTBG)*—See Fig. 9.

5.4 *Dithiocarbamates*:



where:

- R' = alkyl groups such as amyl, butyl, ethyl or methyl, or aryl groups such as phenyl or benzyl;
- R'' = alkyl groups such as amyl, butyl, ethyl or methyl, or aryl groups such as phenyl or benzyl;
- M = metals such as zinc, tellurium, copper, cadmium, tellurium, nickel, bismuth, or lead; and
- n = 2 in the case of zinc, copper, cadmium, nickel, and lead;
3 in the case of bismuth; and
4 in the case of tellurium or selenium.

5.5 *Thiuram Disulfides*:

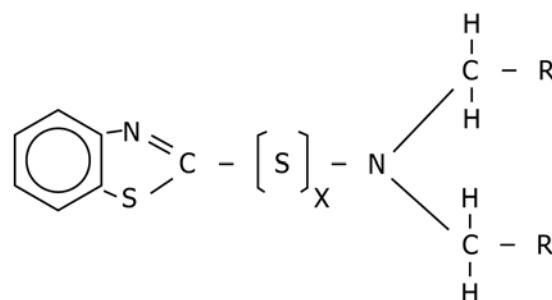


FIG. 2 Sulfenamides of Unhindered Secondary Amines