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.

Designation: D4818 – 89 (Reapproved 2017)

Standard Classification for Rubber Compounding Materials—Vulcanization Accelerators[1]

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 Test Methods D1519, D4571, D4572 and D4574, for measurement of these properties, are not yet adapted for the vulcanization accelerators. Draft methods are being developed and will be submitted through Subcommittee D11.11 for processing and approval. A discussion of the reasons for determining these properties is contained in Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1519 Test Methods for Rubber Chemicals—Determination of Melting Range

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

D4572 Test Method for Rubber Chemicals—Wet Sieve Analysis of Sulfur

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

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. Significance 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

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[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.

Current edition approved Feb. 1, 2017. Published March 2017. Originally approved in 1988. Last previous edition approved in 2012 as D4818 – 89 (2012). DOI: 10.1520/D4818-89R17.

[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.

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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 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 *Dibenzothiazyldisulfide (MBTS)*—See Fig. 6.

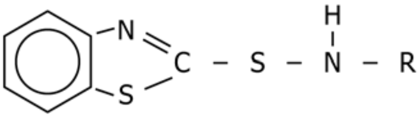


FIG. 1 Sulfenamides of Primary Amines

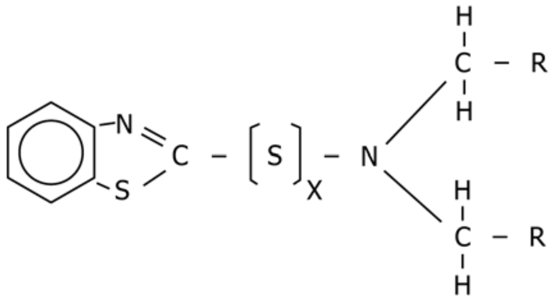


FIG. 2 Sulfenamides of Unhindered Secondary Amines

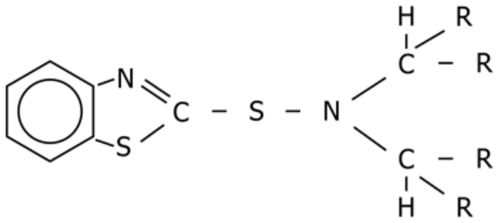


FIG. 3 Sulfenamides of Hindered Secondary Amines

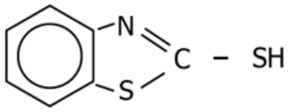


FIG. 4 2-Mercaptobenzothiazole (MBT)

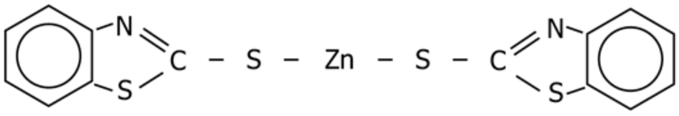


FIG. 5 Zinc Salt of 2-Mercaptobenzothiazole (ZMBT)

FIG. 6 Dibenzothiazyldisulfide (MBTS)

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

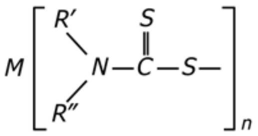
5.3.1 *Symmetric (Type I):*

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:*



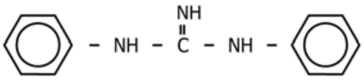


FIG. 7 Diphenyl Guanidine (DPG)

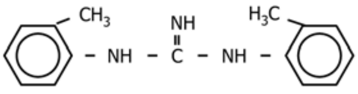


FIG. 8 Di-Ortho-Tolyl Guanidine (DOTG)

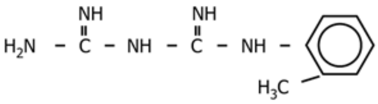


FIG. 9 Ortho-Tolyl Biguanidine (OTBG)

where:

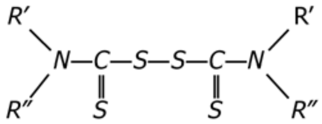
R' = alkyl groups such as amyl, butyl, ethyl or methyl, or aryl groups such as phenyl or benzyl;

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:*



where:

R' = R" = alkyl group,

R' = alkyl group,

R'' = aryl group, and

$R'R''$ = cyclic group.

R' = R" methyl: tetramethyl thiuram disulphide (TMTD),

R' = R" = ethyl: tetraethyl thiuram disulphide (TETD),

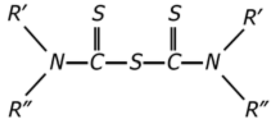
R' = R" = butyl: tetrabutyl thiuram disulphide (TBTD), and

R' = methyl R" = phenyl: dimethyl diphenyl thiuram sulphide (DMPTD).

5.5.1 *Dipentamethylene Thiuram Disulphide (DPTD)*—See Fig. 10.

5.6 *Thiurams (Monosulfides and Polysulfides):*

5.6.1 *Monosulfides:*



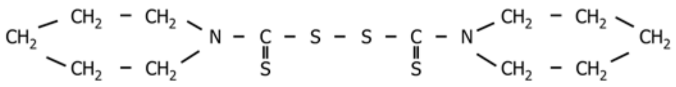
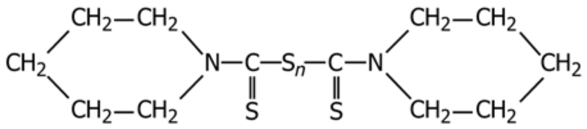


FIG. 10 Dipentamethylene Thiuram Disulphide (DPTD)

where:

$R' = R''$ = methyl: tetramethyl thiuram monosulphide (TMTM).

5.6.2 *Polysulfides:*



where:

n = 1: dipentamethylene thiuram monosulphide (DPTM),

n = 2: dipentamethylene thiuram tetrasulphide (DPTT), and

n = 6: dipentamethylene thiuram hexasulphide (DPTH).

6. Composition and Properties

6.1 The following properties of the accelerators are judged to be most significant in terms of their performance in rubber. The control of these properties is important in maintaining consistent end-product performance.

6.2 *Initial Melting Point*—A determination of the initial melting point shall be done in accordance with Test Method D1519. The initial melting point can be an indication of relative purity of the accelerator. If the accelerator contains significant levels of other materials that are mutually soluble in the accelerator, a significant lowering of the melting point occurs. For example, this occurs when the sulfenamide has undergone appreciable degradation, as discussed in 4.1.3. Many inorganic impurities and certain high molecular weight, highly crystalline, or polar organic molecules, or both, may not depress the initial melting point significantly. Consequently, the melting point is not an absolute indicator of purity (not applicable to all dithiocarbamates since some of them melt at temperatures over 300°C).

6.3 *Wet Sieve Test*—This test is only important for materials with melting points that are higher than the rubber compound mixing temperatures. To efficiently accelerate vulcanization, the accelerator must disperse uniformly in the rubber during mixing and dissolve at vulcanization temperatures. For high melting accelerators, this requires a relatively fine and easily dispersed physical form. A wet screen test is an indication of this property. The test cannot be used, however, with physical forms other than powders.

6.4 *Percent Ash*—A determination of the amount of non-combustibles shall be conducted in accordance with a modification of Test Method D4574. Inorganic materials (ash) are occasional contaminants in vulcanization accelerators, and they may cause problems since they ordinarily will not dissolve in rubbers. Transition metals such as iron, copper, and manganese, especially in soluble form, may have a detrimental effect on the oxidative stability of the rubber (not applicable to dithiocarbamates, which are metal salts).

6.5 *Percent Loss on Heating*—A measure of the amount of heat loss of the accelerator shall be conducted in accordance with a modification of Test Method D4571. The heat loss of the accelerators (except sulfenamides) is nearly identical with the moisture content. Excess moisture in a rubber mixture may cause problems during vulcanization since water is vaporized, which may produce porosity in the cured vulcanizate.

6.6 *Percent Moisture in Sulfenamides*—A determination of moisture content in sulfenamides is essential, since the degradation of sulfenamides in storage, as discussed in 4.1.3, can be caused by hydrolysis reactions.

6.7 *Percent Insolubles in Sulfenamides*—A determination of insolubles in sulfenamides is important, since 2-benzothiazyl disulfide (MBTS) may be present in benzothiazole sulfenamide accelerators as a by-product of the manufacturing process or as a result of benzothiazole sulfenamide degradation as described in 4.1.3. MBTS is also a vulcanization accelerator. However, it has much less delay than the sulfenamides, and appreciable levels of MBTS can cause scorch problems in rubber manufacturing operations. MBTS is much less soluble in some organic solvents than the sulfenamides, and it can consequently be detected by measuring the amount of material that does not dissolve in an appropriate solvent.

6.8 *Assay*—A measurement of the amount of the specified chemical entity in the accelerator by an assay is required, since the purity of the accelerator can affect vulcanization performance characteristics, such as scorch time and cure efficiency, as well as storage stability. Not all impurities have equal detrimental effects on the performance of the accelerator. At the present time, there is no single test that measures all of the impurities.

6.8.1 Assay for sulfenamides and free amine.

6.8.2 Assay for MBT.

6.8.3 Assay for MBTS.

6.8.4 Assay for guanidines.

6.8.5 Assay for dithiocarbamates.

6.8.6 Assay for thiurams (disulfides).

6.8.7 Assay for thiurams (other than disulfides).

6.9 *Percent Free MBT*—A determination of free 2-mercaptobenzothiazole in dibenzothiazyl disulfide (MBTS) is important because of the effect of MBT on scorch safety.

6.10 *Percent Metal Content*—A determination of the metal content in ZMBT and dithiocarbamates is important. It gives only a relative indication of the content of active matter, since small quantities of free metal salts are invariably present as impurities in the accelerator.

6.11 *Dispersibility*—A determination of the dispersibility in a rubber compound is essential, since the accelerators, both in powder or pellet form, must disperse uniformly in a rubber compound to achieve optimal vulcanization.

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