INTERNATIONAL STANDARD

ISO 11235

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1999-04-01

Rubber compounding ingredients — Sulfenamide accelerators — Test methods

Ingrédients de mélange du caoutchouc — Accélérateurs du type sulfénamide — Méthodes d'essai

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11235 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

Annex A forms an integral part of this International Standard.

Rubber compounding ingredients — Sulfenamide accelerators — Test methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

1.1 This International Standard specifies the methods to be used for the evaluation of sulfenamide accelerators.

1.2 The analytical methods are applicable for most commercial sulfenamide accelerators:

— Sulfenamides of primary amines (type I)

— Sulfenamides of unhindered secondary amines (type II)

— Sulfenamides of hindered secondary amines (type III)

1.2.1 MBTS: Benzothiazyl disulfide

NOTE Although MBTS is not a sulfenamide, it is the primary decomposition product of these accelerators and quantitatively determined by the method specified in 4.2.

1.2.2 CBS: *N*-cyclohexylbenzothiazole-2-sulfenamide

1.2.3 TBBS: *N*-*tert*-butylbenzothiazole-2-sulfenamide

1.2.4 DIBS: *N*,*N*'-diisopropylbenzothiazole-2-sulfenamide

1.2.5 DCBS: *N*,*N*'-dicyclohexylbenzothiazole-2-sulfenamide

1.2.6 MBS: *N*-oxydiethylenebenzothiazole-2-sulfenamide

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 1772:1975, *Laboratory crucibles in porcelain and silica*.

ISO 3819:1985, *Laboratory glassware — Beakers*.

ISO 4788:1980, *Laboratory glassware — Graduated measuring cylinders*.

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*.

ISO 6556:1981, *Laboratory glassware — Filter flasks*.

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards*.

ISO 15528:—[1)], *Paints and varnishes — Sampling*.

3 Determination of physical and chemical properties

3.1 Sampling

The sampling of the product shall be performed in accordance with ISO 15528.

To ensure homogeneity, thoroughly blend at least 250 g of the lot sample before removing the test portion.

3.2 Test methods

Property	Clause or subclause
Purity	4
— by reduction with MBT and titration	4.1
— by high performance liquid chromatography (HPLC)	4.2
Insoluble material	5
Melting range	6
— by capillary tube	6.1
— by differential scanning calorimetry (DSC)	6.2
Volatile material	7
Wet sieve analysis	8
Ash	9

3.3 Limit of acceptance

The difference between the results of duplicate determinations shall not exceed the repeatability of the test, if it is defined; otherwise, it is necessary to repeat the test. When the repeatability is not defined, the results of both determinations shall be reported.

1) To be published. (Revision of ISO 842:1984 and ISO 1512:1991)

4 Test methods for purity

4.1 Method to determine purity by reduction with MBT and titration

4.1.1 Scope

The following method is suitable for determining the purity and free amine in sulfenamides commonly used in the rubber industry and is applicable to CBS, DCBS, MBS and TBBS.

4.1.2 Principle

After neutralization of the free amine, the sulfenamide is reduced by means of a solution of mercaptobenzothiazole (MBT). An excess of hydrochloric acid is added and the unreacted hydrochloric acid is then titrated with sodium hydroxide using one of the two following methods:

— method A: potentiometric titration;

— method B: titration using an indicator.

4.1.3 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1.3.1 Basic reagents for methods A and B

4.1.3.1.1 Mercaptobenzothiazole (MBT), min. assay 99,0 %.

4.1.3.1.2 Absolute ethanol.

4.1.3.1.3 Toluene.

4.1.3.1.4 Hydrochloric acid, standard volumetric solution, c(HCl) = 0,1 mol/dm^3.

4.1.3.1.5 Hydrochloric acid, standard volumetric solution, c(HCl) = 0,5 mol/dm^3.

4.1.3.1.6 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/dm^3, carbonate free.

4.1.3.1.7 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,5 mol/dm^3, carbonate free.

4.1.3.1.8 Bromophenol blue, 10 g/dm^3 solution.

Dissolve 1 g of bromophenol blue with a small volume of ethanol (4.1.3.1.2). Transfer to a 100 cm^3 volumetric flask and neutralize with the sodium hydroxide solution (4.1.3.1.6) to a green colour. Dilute to the mark with ethanol (4.1.3.1.2).

4.1.3.2 Prepared reagent for method A

4.1.3.2.1 Mercaptobenzothiazole, 40 g/dm^3 solution, freshly prepared.

Weigh a suitable quantity of MBT (4.1.3.1.1) to the nearest 0,1 g and dissolve in absolute ethanol (4.1.3.1.2). If the MBT does not dissolve completely, heat the solution to a temperature no higher than (55 ± 2) °C (not exceeding 57 °C) to ensure complete dissolution. Cool to room temperature and dilute to the mark of a suitable volumetric flask with absolute ethanol.

4.1.3.3 Prepared reagent for method B

4.1.3.3.1 Ethanol (4.1.3.1.2)/**toluene** (4.1.3.1.3) solution, 5:3 (V:V)

4.1.3.3.2 Mercaptobenzothiazole, 40 g/dm^3 solution, freshly prepared.

Weigh a suitable quantity of MBT (4.1.3.1.1) to the nearest 0,1 g and dissolve in the ethanol/toluene solution (4.1.3.3.1). If the MBT does not dissolve completely, heat the solution to a temperature no higher than (55 ± 2) °C (not exceeding 57 °C) to ensure complete dissolution. Cool to room temperature and dilute to the mark of a suitable volumetric flask with the ethanol/toluene solution (4.1.3.3.1).

4.1.4 Apparatus

4.1.4.1 Mortar and pestle or other appropriate **grinding device**.

4.1.4.2 Pipette, 25 cm^3 capacity, in accordance with the specifications given in ISO 648.

4.1.4.3 Burette, 25 cm^3 capacity, graduated in 0,05 cm^3, in accordance with the general specifications given in ISO 385-1.

4.1.4.4 Beaker, 250 cm^3 capacity, in accordance with the specifications given in ISO 3819.

4.1.4.5 Temperature-controlled bath, capable of being maintained at (55 ± 2) °C.

4.1.4.6 Stop-watch.

4.1.4.7 Magnetic stirrer.

4.1.4.8 pH-meter, with a resolution of 0,1 unit or better.

4.1.4.9 Analytical balance, accurate to within ± 0,1 mg.

4.1.5 Procedure

4.1.5.1 Method A

4.1.5.1.1 Grind a sample and weigh a test portion of approximately 2 g of the blended powder to the nearest 0,1 mg. For TBBS, weigh approximately 1,6 g of the test sample. Transfer it to the beaker (4.1.4.4).

4.1.5.1.2 Add 50 cm^3 of ethanol (4.1.3.1.2) and stir until dissolved. If needed, heat the solution to a temperature no higher than 55 °C. A slight turbidity may remain.

4.1.5.1.3 Cool to room temperature. Add 3 drops of indicator (4.1.3.1.8) and titrate the free amine with 0,1 mol/dm^3 hydrochloric acid (4.1.3.1.4) to the blue-green-colour end point (V_1).

4.1.5.1.4 Add 50 cm^3 of the MBT solution (4.1.3.2.1) and immediately pipette 25 cm^3 of 0,5 mol/dm^3 hydrochloric acid (4.1.3.1.5), exactly measured.

4.1.5.1.5 Stir the solution in a temperature-controlled bath (4.1.4.5) maintained at (55 ± 2) °C for exactly 5 min, timed with the stop-watch (4.1.4.6).

4.1.5.1.6 Titrate potentiometrically the unreacted hydrochloric acid with the 0,5 mol/dm^3 sodium hydroxide (4.1.3.1.7). With continued stirring, add the sodium hydroxide stepwise in increments of 1 cm^3, and record the resultant equilibrium potential (mV) after each addition. Approaching the end point, add titrant in increments of 0,1 cm^3, recording the potential (mV) 20 s after each addition until the end point has been passed.

The end point of the titration is the point of inflection of the titration curve, plotted automatically or manually as the measured potential (mV) against the volume in cubic centimetres of sodium hydroxide solution. At this point, the first derivative curve reaches a maximum whilst the second derivative curve is zero (falling from a positive to a negative value). The end point shall be calculated from the second derivative on the assumption that the change from a positive to a negative value bears a linear relationship with the addition of sodium hydroxide in the 0,1 cm^3 interval (V_3) passing through the inflection point.

4.1.5.2 Method B

4.1.5.2.1 Grind a test sample and weigh approximately 2 g of the blended powder to the nearest 0,1 mg. For TBBS, weigh approximately 1,6 g of the test sample. Transfer it to the beaker (4.1.4.4).

4.1.5.2.2 Add 50 cm^3 of the ethanol/toluene solution (4.1.3.3.1) and stir until dissolved. If needed, heat the solution to a temperature no higher than 55 °C. A slight turbidity may remain.

4.1.5.2.3 Cool to room temperature. Add 3 drops of indicator (4.1.3.1.8) and titrate the free amine with 0,1 mol/dm^3 hydrochloric acid (4.1.3.1.4) to the blue-green-colour end point (V_1).

4.1.5.2.4 Add 50 cm^3 of the MBT solution (4.1.3.3.2) and immediately pipette 25 cm^3 of 0,5 mol/dm^3 hydrochloric acid (4.1.3.1.5), exactly measured.

4.1.5.2.5 Stir the solution in a temperature-controlled bath (4.1.4.5) maintained at (55 ± 2) °C for exactly 5 min, timed by the stop-watch (4.1.4.6).

4.1.5.2.6 Add 3 drops of bromophenol blue indicator (4.1.3.1.8) and titrate the unreacted hydrochloric acid with 0,5 mol/dm^3 sodium hydroxide (4.1.3.1.7) to the green-blue-colour end point. Then continue, drop by drop, to a blue colour (V_3).

4.1.6 Expression of results (methods A and B)

4.1.6.1 Free amine

Calculate the free amine content, expressed as a percentage by mass to the nearest 0,1 % (m/m), by the following equation:

$$\text{Free amine, \%} = \frac{V_1 \times c_1}{10 \times m} \times M_1 \qquad \ldots(1)$$

where

V_1 is the volume, in cubic centimetres, of hydrochloric acid (4.1.3.1.4) used for the titration;

c_1 is the concentration, in moles per cubic decimetre, of the hydrochloric acid (4.1.3.1.4);

m is the mass, in grams, of the test portion;

M_1 is the molecular mass of the corresponding amine (see table 1).

Table 1

Sulfenamide	Molecular mass of the corresponding amine
CBS	99,18
DCBS	181,32
MBS	87,12
TBBS	73,14

4.1.6.2 Purity

Calculate the purity of the sulfenamide, expressed as a percentage by mass to the nearest 0,1 % (m/m), by the following equation:

$$\text{Purity, \%} = \frac{(25 \times c_2) - (V_3 \times c_3)}{10 \times m} \times M_2 \qquad \ldots(2)$$

where:

c_2 is the concentration, in moles per cubic decimetre, of the hydrochloric acid (4.1.3.1.5);

c_3 is the concentration, in moles per cubic decimetre, of the sodium hydroxide (4.1.3.1.7);

V_3 is the volume, in cubic centimetres, of the sodium hydroxide (4.1.3.1.7);

m is the mass, in grams, of the test portion;

M_2 is the molecular mass of the sulfenamide (see table 2).

Table 2

Sulfenamide	Molecular mass
CBS	264,41
DCBS	346,58
MBS	252,30
TBBS	238,37

4.2 Method to determine purity by high performance liquid chromatography (HPLC)

4.2.1 Scope

4.2.1.1 The following test method is suitable for determining the purity of commercially available benzothiazole sulfenamide accelerators, when present in the range from 80 % to 100 %. Determination is carried out by high performance liquid chromatography using ultraviolet detection with the use of an external standard. It is applicable to MBTS, MBS, CBS, TBBS, DIBS, and DCBS.

4.2.1.2 In order to carry out this test method correctly, it is necessary to have expertise in high performance liquid chromatography (HPLC).

4.2.2 Definitions

4.2.2.1
external standard calculation
method of calculating the analyte content by measuring the area of the analyte peak, multiplying it by a response factor, and dividing it by the sample concentration

NOTE All components are assumed to be resolved from the component of interest.

4.2.2.2
lot sample
a sample from production representative of a standard production unit, normally referred to as “the sample”

4.2.2.3
test portion
the actual material, representative of the lot sample, used for a particular determination

4.2.3 Principle

A test portion is dissolved in acetonitrile and a filled-loop volume is analyzed by isocratic HPLC using a temperature-controlled C18 reversed-phase column and an ultraviolet (UV) detector. Peak areas are determined using a chromatographic integrator or laboratory data system with the quantity of analyte being determined by external calibration.

4.2.4 Significance and use

4.2.4.1 This test method is designed to determine the purity of industrially produced and used benzothiazole sulfenamides.

4.2.4.2 Since the results of this test method are based on an integrated peak area, it is assumed that all analytes of interest are resolved from interfering peaks.

4.2.5 Interferences

Components co-eluting with the analyte of interest will cause erroneous results; thus it is required that the column used have a theoretical plate number of at least 10 000.

4.2.6 Reagents and materials

4.2.6.1 Acetic acid, glacial.

4.2.6.2 Acetonitrile, HPLC grade.

4.2.6.3 Methanol, HPLC grade.

4.2.6.4 Water, HPLC grade.

4.2.7 Apparatus

4.2.7.1 Liquid chromatograph, consisting of the following:

4.2.7.1.1 Precision chromatographic pump.

4.2.7.1.2 UV detector, of variable wavelength.

4.2.7.1.3 Column temperature-controller, capable of maintaining the temperature at (35 ± 1) °C, for example a column oven or water jacket.

4.2.7.1.4 Filled-loop injector, with a nominal volume of 10 mm^3 (10 µl) or less.

4.2.7.2 HPLC column, consisting of C18 (ODS) reversed-phase material with spherical, totally porous monomolecular 5 µm particles capable of providing 40 000 theoretical plates per metre (a minimum of 10 000 plates is required for this analysis).

4.2.7.3 Integrator/data system, capable of determining absolute quantities of analyte of interest by means of integration of detector output versus time.

4.2.7.4 Analytical balance, accurate to within ± 0,1 mg.

4.2.8 Calibration and standardization

A primary standard of known purity is used to determine the response factor for each analyte.

4.2.9 Procedure

4.2.9.1 Chromatographic conditions

4.2.9.1.1 Determine the mobile phase composition and the flow rate by adjusting the chromatographic parameters for the particular column chosen. The mobile phase consists of an approximate mixture of HPLC grade acetonitrile (4.2.6.2) and HPLC grade or equivalent water (4.2.6.4), both containing 0,001 mol of glacial acetic acid (4.2.6.1) per cubic decimetre or less depending on the particular column chosen. [HPLC grade methanol (4.2.6.3) may be added to the acetonitrile/water eluent to achieve the necessary separation for DIBS and MBTS.]

4.2.9.1.2 For the analysis of the sulfenamides, adjust the flow rate and mobile phase composition to provide a capacity factor, k', between 4 and 6 for the analyte of interest, and a minimum resolution, R_S, of 2 between the MBTS impurity and the analyte of interest.

Different liquid chromatography columns may exhibit different elution characteristics. Suggested chromatographic starting parameters for analysis are indicated in table 3.

Table 3

Sulfenamide	Water[a] %	Acetonitrile[a] %	Methanol[a] %	Flow rate cm^3/min
DCBS	5	95	0	2,5
CBS	20	80	0	2,0
TBBS	30	70	0	1,7
MBS	45	55	0	1,4
DIBS	15	0	85	1,0

[a] Containing 0,001 mol glacial acetic acid per cubic decimetre (4.2.6.1).

4.2.9.1.3 The capacity factor, k', is defined as the retention time of the analyte, t_A, minus the retention time of an unretained solute (solvent peak), t_0, divided by t_0:

$$k' = \frac{t_A - t_0}{t_0} \quad \ldots(3)$$

4.2.9.1.4 The resolution, R_S, is a function of the capacity factor, selectivity, and the theoretical plates of the column:

$$R_S = 2 \times \frac{t_2 - t_1}{b_2 + b_1} \quad \ldots(4)$$

where

t_1, t_2 are the retention times of the analytes;

b_1, b_2 are the peak widths at 10 % of the peak height.

4.2.9.2 Detector

Monitor the absorbance of all components at 275 nm. Set the detector sensitivity to one absorbance unit full scale (AUFS).

4.2.9.3 Integrator/data system

Adjust the integrator settings to give a full-scale response to one absorbance unit (AU).

4.2.9.4 Preparation of standards

The standard reference materials are purified, if necessary, by multiple recrystallization of the sulfenamides. Dissolve 100 g of the sulfenamide in 200 cm^3 of analytical reagent (AR) grade toluene with slight warming (50 °C). Add 2 g of activated carbon and stir for 30 min. Filter the hot solution by gravity and cool in an ice/acetone bath. Vacuum filter the crystals. Repeat this crystallization. Dissolve the analyte crystals from the second toluene crystallization in hot (50 °C) methanol, cool in an ice/acetone bath, and vacuum filter. Repeat the alcohol recrystallization and dry in a vacuum oven at 50 °C overnight. Repeat the procedure until the desired purity is obtained. Estimate the purity of the standard by gradient HPLC analysis of the impurities and differential thermal analysis (DTA).

Weigh at least 20 mg to the nearest 0,1 mg of the sulfenamide standard reference material in a 100 cm^3 volumetric flask and dilute to volume with acetonitrile. Adjust the standard concentration if necessary by serial dilution with acetonitrile to give a maximum absorbance (peak height) between 0,4 AU and 0,8 AU (the linear range of the chromatographic system). Analyze the standard within 4 h of being diluted. Evaluate the purity of the standard by HPLC analysis of the impurities every 90 days. Store the standard at 5 °C or lower.

4.2.10 Sample analysis

Weigh at least a 20 mg test portion of the well-blended lot sample, to the nearest 0,1 mg, into a 100 cm^3 volumetric flask. Dissolve this test portion in acetonitrile (an ultrasonic bath is recommended) and dilute to volume with acetonitrile. Adjust the concentration, if necessary, by serial dilution with acetonitrile to give a maximum absorbance within 10 % of the standard absorbance. Filter the solution with a chemically resistant filter with a nominal pore size less than or equal to 0,5 µm. Analyze the solution within 4 h of being diluted. Obtain a chromatogram of the standard and measure the area.

4.2.11 Expression of results

4.2.11.1 Response factor

Calculate the response factor for the standard by dividing the concentration of the standard by the measured area count and multiplying this by the purity of the standard:

$$\text{RF} = (\text{concentration of the standard/area count}) \times \text{purity, \%} \quad \ldots(5)$$

Throughout the calculation the units of concentration shall be consistent (i.e. mg/cm^3).

4.2.11.2 Product purity

To determine the purity of the product, multiply the response factor by the measured area count of the analyte and divide by the sample concentration:

$$\text{Purity, \%} = \text{RF} \times \text{area count/sample concentration} \quad \ldots(6)$$

Express the percentage purity of the sulfenamide to the nearest 0,1 % (*m/m*).

4.2.12 Precision and bias

4.2.12.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (accelerators) used in the particular interlaboratory program described below. It is not recommended to use precision parameters for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

4.2.12.2 A type 1 interlaboratory precision program (see ISO/TR 9272) was conducted. Both repeatability and reproducibility are short term. A period of a few days separates replicate test results. Eight laboratories participated and four materials were used. Therefore, $p = 8$, $q = 4$, $n = 4$. A test result is the value obtained from a single determination. Each material was analyzed twice on each of two separate days using the provided standards.

4.2.12.3 Outliers: Two cell results were identified to be cell variance outliers based on Cochran's maximum variance test. These results, for CBS and MBS from one laboratory, were eliminated from the calculations in table 4.

4.2.12.4 Precision parameters: see table 4.

4.2.12.5 Repeatability: The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for a particular test will exceed the repeatability, r, as given in table 4, on an average of not more than once in twenty cases in the normal and correct operation of the test method.

4.2.12.6 Reproducibility: The difference between two single and independent test results found by two operators working under prescribed reproducibility conditions in different laboratories on identical test material will exceed the reproducibility, R, as given in table 4, on an average of not more than once in twenty cases in the normal and correct performance of the test method.

4.2.12.7 Bias: Sample impurities that are not resolved from the analyte of interest will produce a false result. There may be other undetermined sources of bias.

Table 4 — Precision (type 1) — Sulfenamide purity determination

Material	Mean purity	Within laboratory			Between laboratories		
		s_r	r	(r)	s_R	R	(R)
CBS	98,6	0,265	0,74	0,75	0,269	0,75	0,75
DCBS	97,0	0,460	1,29	1,33	1,194	3,34	3,45
TBBS	96,0	0,632	1,77	1,84	1,208	3,38	3,52
MBS	92,5	0,419	1,17	1,27	1,769	4,95	5,36
Pooled or average values		0,444	1,24	1,30	1,110	3,11	3,27

s_r = within laboratory standard deviation
r = repeatability (in measurement units)
(r) = repeatability (in percent)
s_R = between laboratory standard deviation
R = reproducibility (in measurement units)
(R) = reproducibility (in percent)

NOTE The standards utilized in the preparation of this precision statement were individually prepared within each participating laboratory.

5 Test method for insoluble material

5.1 Scope

This test method is suitable for determining the quantity of materials in sulfenamides which are insoluble in suitable organic solvents.

5.2 Principle

A test portion of sulfenamide is dissolved in a prescribed solvent, stirred, and filtered through a crucible. The insoluble content is calculated from the quantity of residue.

5.3 Significance and use

5.3.1 Sulfenamides can degrade in chemical purity and functional performance, usually characterized by a drop in assay, a release of free amine, and an increase in insolubles.

5.3.2 Insolubles are a means of determining the benzothiazyl disulfide (MBTS) content of the sulfenamide; MBTS is a primary degradation product of sulfenamides. Amine salts of mercaptobenzothiazole (MBT) may also be insoluble. However, certain soluble species may also be generated during sulfenamide degradation. Consequently, insolubles are not an absolute measure of purity and can actually decrease with sulfenamide degradation.

5.3.3 This test method may be used as an indication of degradation, for quality control and research and development work.

5.4 Reagents

Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.4.1 **Methanol**, analytical reagent used for testing samples of

N-cyclohexylbenzothiazole-2-sulfenamide (CBS),

N,*N*'-diisopropylbenzothiazole-2-sulfenamide (DIBS),

N-oxydiethylenebenzothiazole-2-sulfenamide (MBS),

N-*tert*-butylbenzothiazole-2-sulfenamide (TBBS).

5.4.2 **Cyclohexane**, analytical reagent used for testing samples of *N*,*N*'-dicyclohexylbenzothiazole-2-sulfenamide (DCBS).

5.5 Apparatus

5.5.1 **Conical flask**, 300 cm^3 capacity.

5.5.2 **Sintered glass crucible**, G4 porosity or equivalent, in accordance with specifications given in ISO 4793.

5.5.3 **Graduated measuring cylinder**, 250 cm^3 capacity, in accordance with specifications given in ISO 4788.

5.5.4 **Magnetic stirrer**.

5.5.5 **Watch glass**.

5.5.6 **Suction flask**, 500 cm^3 capacity, in accordance with specifications given in ISO 6556.

5.5.7 **Forced-air convection oven**, capable of maintaining the temperature at (70 ± 2) °C.

5.5.8 **Analytical balance**, accurate to within ± 0,1 mg.

5.5.9 **Wash bottle**.

5.5.10 **Sieve**, mesh size 0,6 mm (30 mesh US) or equivalent.

5.6 Procedure

5.6.1 If necessary, grind approximately 10 g of the well-mixed lot sample so that the material passes through a 0,6 mm (30 mesh) sieve (5.5.10).

5.6.2 Transfer a 5 g test portion of the sieved material, weighed to the nearest 0,1 mg, to a 300 cm^3 conical flask (5.5.1). Using a graduated measuring cylinder (5.5.3), add 250 cm^3 of methanol (5.4.1). In the case of DCBS, use cyclohexane (5.4.2) instead of methanol. Cover the flask with a watch glass (5.5.5) and stir on a unheated magnetic stirrer, for 30 min at (25 ± 5) °C.

5.6.3 Filter the solution through a clean, dry, preweighed sintered glass crucible (5.5.2). It is important that during the vacuum filtration, the crucible be only half-filled. Wash the conical flask with three 8 cm^3 portions of methanol or, in the case of DCBS, with three 8 cm^3 portions of cyclohexane. Filter the washings as well.

5.6.4 At the end of the filtration, remove the vacuum and wash the crucible two times with 25 cm^3 of methanol or, in the case of DCBS, with 25 cm^3 of cyclohexane. Allow to stand for 2 min, then apply vacuum suction immediately. When this has been done, the walls of the crucible should be free from residue.

5.6.5 Dry the crucible for 60 min in an oven (5.5.7) maintained at (70 ± 2) °C.

5.6.6 Cool to room temperature in a desiccator and obtain the mass of the crucible plus insolubles to the nearest milligram.

5.6.7 Repeat the procedure on a second test portion.

5.7 Expression of results

Calculate the percent insoluble material, expressed as a percentage by mass to the nearest 0,1 % (*m/m*), as follows:

$$\text{Insoluble material, \%} = \frac{(m_3 - m_2)}{m_1} \times 100 \qquad \ldots(7)$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in grams, of the empty crucible;

m_3 is the mass, in grams, of the crucible and insoluble material.

6 Test methods for melting range

6.1 Melting range by capillary tube

6.1.1 Scope

This test method is suitable for determining the melting range of various rubber accelerators.

6.1.2 Significance and use

This test method may be used for research and development. It may also be used for quality assurance, provided agreement between producer and user has been obtained for a standard reference material.

6.1.3 Limitations

The melting range, as determined by this test method, is not recommended as a criterion of purity of a rubber chemical.

6.1.4 Apparatus

6.1.4.1 Melting apparatus.

The apparatus shall consist of a device for heating the sample uniformly at a predetermined rate. A suitable device consists of a glass H-type melting apparatus, usually called a Hershberg tube. One side-tube contains an agitator blade and an internal heater, both controlled by a variable transformer. The thermometer and capillary tubes are placed in the other side-tube. The apparatus shall be shielded from drafts. A good light source and magnifying glass shall be used. A heating medium such as DC-550 silicone fluid shall be used as the bath liquid. The liquid shall cover the bridge of the apparatus at room temperature. Other types of melting point tubes (Thiele, Thiele-Dennis)

and other types of melting-point apparatus, several of which can be found in chemical supply house catalogues, may be used for this test. The repeatability and reproducibility may vary if other types of equipment are used.

6.1.4.2 Capillary tube, glass, approximately 150 mm long and 1,2 mm to 1,4 mm internal diameter with walls 0,2 mm to 0,3 mm thick and closed at one end to contain the sample.

6.1.4.3 Thermometer, partial immersion type and of suitable range.

Its scale shall be graduated in divisions of 0,5 °C or less. Corrections for the thermometer shall be determined by calibration against a certified thermometer.

6.1.4.4 Sieve, 150 µm mesh size (No. 100) for screening the sample.

6.1.5 Preparation of test sample

If necessary, grind approximately 1 g of the well-blended lot sample to pass completely through a 150 µm (No. 100) sieve (6.1.4.4).

6.1.6 Procedure

6.1.6.1 Select the thermometer (6.1.4.3) for the proper range and support it so that it is immersed to the immersion mark in the liquid of the bath (see 6.1.4.1).

NOTE Sulfenamide accelerators cited in this International Standard have melting points ranging from 50 °C to 110 °C.

6.1.6.2 Place sufficient sieved material (6.1.5) into the capillary glass tube (6.1.4.2) to form a column in the bottom of the tube approximately 3 mm to 6 mm high when packed down as closely as possible by moderate tapping on a solid surface.

6.1.6.3 Heat the bath to a temperature approximately 25 °C below the expected melting range. Adjust the heat regulator to a rate increase of approximately 3 °C/min for the remainder of the determination except within the actual melting range. In this range, adjust the temperature rate to (1 ± 0,2) °C/min. When the bath attains the temperature approximately 10 °C below the expected melting range, insert the capillary into the bath. Adjust the height of the tube so that the material in the capillary is beside the centre of the thermometer bulb. The capillary tube is not placed in the bath earlier, since many materials undergo decomposition from prolonged heating. Avoid making any major adjustments to the heat regulator within the actual melting range.

6.1.6.4 Record the melting range as the temperature range between which liquefaction first becomes evident and the temperature at which no further visual change is observed in the mass.

NOTE 1 The initial melting temperature is the temperature at which the first actual formation of liquid occurs, either as a minute drop or as a film. It is not a preliminary contraction, sintering, or darkening. It occurs well before the formation of a meniscus. The liquefaction may occur at the top, bottom, or sides of the sample in the capillary, as well as the rear. When the latter occurs, the point may be missed, unless care is taken to watch the rear of the tube; a mirror is a convenient aid for this purpose.

NOTE 2 The final melting temperature is the temperature at which no further liquefaction is observed.

6.2 Melting range by differential scanning calorimetry (DSC)

6.2.1 Scope

This method is suitable for determining the melting range of various rubber accelerators.

6.2.2 Significance and use

6.2.2.1 This test method may be used for research and development. It may also be used for quality assurance, provided agreement between producer and user has been obtained for a standard reference material.

6.2.2.2 Differential scanning calorimeters are used to determine transition temperatures of materials. For absolute information, temperature calibration of the apparatus or comparison of the resulting data with that of standard reference materials is required.

6.2.3 Limitations

The melting range, as determined by this test method, is not recommended as a criterion of purity of a rubber chemical.

6.2.4 Apparatus

6.2.4.1 Differential scanning calorimeter, capable of heating a test specimen and a reference material at a controlled rate and of automatically recording the differential heat flow between the sample and the reference material to the required sensitivity and precision.

6.2.4.2 Specimen pans, with covers composed of clean aluminium or of other material with a high thermal conductivity.

6.2.4.3 Purge gas, dry and inert (helium or nitrogen).

6.2.4.4 Analytical balance, accurate to within ± 0,1 mg.

6.2.5 Preparation of test sample

If necessary, grind a sufficient quantity of the well-blended lot sample to pass completely through a 150 µm sieve. Use this sieved material for the DSC test.

6.2.6 Procedure

6.2.6.1 Weigh approximately 10 mg to 20 mg of the sieved sample (see 6.2.5) into a DSC specimen pan (6.2.4.2). Cover and seal the specimen pan and place it into the DSC chamber (see 6.2.4.1).

6.2.6.2 Place a covered empty specimen pan in the DSC reference chamber.

6.2.6.3 Close the DSC sample chamber and set the purge-gas (6.2.4.3) flow through the sample chamber at 10 cm^3/min to 20 cm^3/min.

6.2.6.4 Turn on the recording and heating units and programme the temperature for a heating rate of 5 °C/min. Record the DSC curve (see figure 1) from ambient temperature to 25 °C above the expected melting point.

6.2.6.5 From the resultant DSC curve, measure the temperatures for the desired points on the curve, T_e and T_p (figure 1), to the required precision, where:

T_e = extrapolated onset temperature for fusion

T_p = melting peak temperature

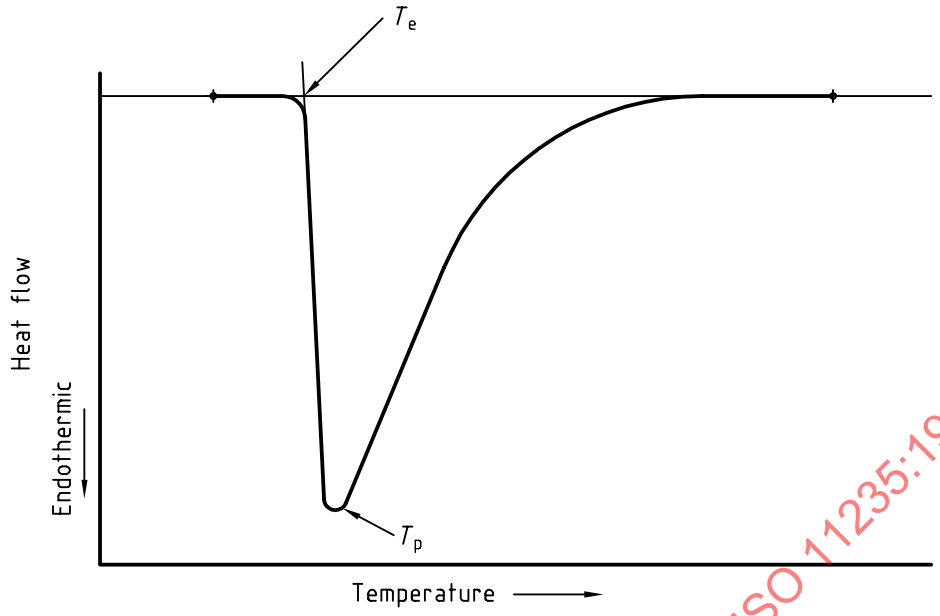

Figure 1 — Transition temperatures (T_e and T_p) on a DSC curve

7 Test method for volatile material

7.1 Scope

This test method is suitable for determining the loss of volatile materials in various rubber accelerators based on the mass loss upon heating at 70 °C.

7.2 Definitions

7.2.1
lot sample
a sample from production representative of a standard production unit, normally referred to as “the sample”

7.2.2
test portion
the actual material, representative of the lot sample, used for a particular determination

7.3 Principle

A test portion is weighed before and after heating at 70 °C.

7.4 Apparatus

7.4.1 Weighing bottle, low form.

7.4.2 Forced-air convection oven, capable of maintaining the temperature at (70 ± 2) °C.

7.4.3 Analytical balance, accurate to within ± 0,1 mg.

7.4.4 Desiccator.

7.5 Procedure

7.5.1 Dry a clean weighing bottle (7.4.1) and stopper (stopper removed) for 30 min in an oven (7.4.2) maintained at (70 ± 2) °C. Place the bottle and stopper in the desiccator (7.4.4) and allow them to cool to room temperature. Weigh the bottle with the stopper to the nearest 0,1 mg (m_1).

7.5.2 Weigh approximately a 20 g test portion into the weighing bottle, stopper and weigh to the nearest 0,1 mg (m_2).

7.5.3 Place the weighing bottle, containing the test portion, and the stopper (with the stopper removed) in the oven, which has been equilibrated at 70 °C, for 3 h.

7.5.4 After heating, stopper the weighing bottle and transfer it to the desiccator. Allow sufficient time for the assembly to reach equilibrium at room temperature. Reweigh the bottle to the nearest 0,1 mg (m_3).

7.5.5 Repeat the procedure on a second test portion.

7.6 Expression of results

Calculate the percent volatile material, expressed as a percentage by mass to the nearest 0,1 % (m/m), as follows:

$$\text{Volatile material, \%} = \frac{(m_2 - m_3)}{(m_2 - m_1)} \times 100 \qquad \ldots(8)$$

where

m_1 is the mass, in grams, of weighing bottle and stopper;

m_2 is the mass, in grams, of weighing bottle, stopper, and test portion before heating;

m_3 is the mass, in grams, of weighing bottle, stopper, and test portion after heating.

8 Test method for wet sieve analysis

8.1 Scope

This test method is suitable for evaluating the particle size distribution of the coarse fraction of sulfenamide accelerator powders. It is limited to the measurement of particles greater than 45 µm.

8.2 Significance and use

This test method is used to evaluate sulfenamide accelerators for their suitability as rubber vulcanizing agents. Accelerator particles must be sufficiently small to be readily dissolved or dispersed in rubber during curing and to produce a uniform crosslinked network. This test method is used for quality control to ensure that no excessively large particles are present and to determine whether the product has a typical size distribution pattern.

8.3 Materials

8.3.1 Liquid detergent.

8.4 Apparatus

8.4.1 Standard sieves, stainless steel, 76 mm diameter, containing stainless steel wire cloth selected from the range of 45 µm to 250 µm mesh size.

8.4.2 Bristle brush.

8.4.3 Balance, with a minimum capacity of 150 g and accurate to within ± 1 mg.

8.4.4 Forced-air convection oven, capable of maintaining the temperature at (70 ± 2) °C.

8.5 Procedure

8.5.1 Weigh a 10,0 g test portion of the well-blended lot sample into a 250 cm^3 beaker. Wet the accelerator with 25 cm^3 of water. Mix thoroughly with a glass stirring rod to guarantee wetting all the accelerator.

NOTE A 1 % solution of a liquid detergent (8.3.1) may be used if the accelerator does not wet properly.

8.5.2 Weigh each cleaned and dried sieve (8.4.1) to the nearest 1 mg. Assemble preweighed stainless steel sieves in order of decreasing fineness with the coarsest screen on top. Carefully transfer the wetted accelerator to the top screen using additional water to wash all of the accelerator out of the beaker. Wash the accelerator through the top sieve with a gentle stream of water from a nozzle, using detergent as needed. Tap or vibrate the screen while washing. Finally, break up all agglomerated particles using the brush (8.4.2). Clean powder from the bristles of the brush using wash water. Be careful that the wash water does not back up on the finer sieves causing the accelerator slurry to overflow the sieve sides.

8.5.3 Remove the top sieve. Wash off any residual accelerator slurry on the underside of the sieve. Repeat the washing procedure described in 8.5.2 for each sieve, ensuring total transport of the fine particles through each successive sieve.

8.5.4 Carefully dry the sides of the sieves with a lint-free towel, and place each sieve separately in a drying oven (8.4.4) maintained at (70 ± 2) °C for 1 h or until the accelerator is dry. Remove the sieves and cool at least half an hour in a desiccator. If the sieved material shows evidence of melting, repeat the test and dry it at 40 °C for 2 h or until constant mass has been reached.

8.5.5 Weigh each sieve to the nearest 1 mg. When the quantity of accelerator on the coarser sieves is very small (a few particles), it may be appropriate to brush the particles onto a preweighed glassine weighing paper and weigh the accelerator directly.

8.6 Expression of results

8.6.1 Calculate the percentage by mass retained on each sieve, P, as follows:

$$P = \frac{m_1}{m_2} \times 100 \qquad \ldots(9)$$

where

m_1 is the mass, in grams, of residue;

m_2 is the mass, in grams, of the test portion.

In order to determine how much would be retained on a fine sieve, it is necessary to sum the mass of material retained on all the coarser sieves and add it to the mass of material from the selected sieve.

8.6.2 The quantity of material passing through each sieve is determined by subtracting the percent of the material retained on the sieve from 100.

9 Test method for the determination of ash

9.1 Scope

This test method is suitable for determining the non-combustible content of rubber chemicals as ash.

9.2 Definitions

9.2.1
lot sample
a sample from production representative of a standard production unit, normally referred to as “the sample”

9.2.2
test portion
the actual material, representative of the lot sample, used for a particular determination

9.3 Principle

The ash content is determined by heating a known quantity of rubber chemical on a hot plate or over a gas burner to volatilize the sample and then heating it in a muffle furnace to complete the ashing process.

9.4 Significance and use

This test method is suitable for the determination of ash from rubber accelerators. This test method may be used for quality control, product acceptance, or research and development. For the purposes of this International Standard, percent ash is considered as an important characteristic of rubber accelerators.

9.5 Apparatus

9.5.1 **Muffle furnace**, capable of maintaining the temperature at ± 25 °C between 500 °C and 800 °C.

9.5.2 **Hot plate**, or **laboratory gas burner**.

9.5.3 **Laboratory fume hood**.

9.5.4 **Porcelain crucible**, high form, size 0, 15 cm^3 capacity, in accordance with specifications given in ISO 1772.

9.5.5 **Clay triangle**.

9.5.6 **Steel crucible tongs**.

9.5.7 **Heat-resistant gloves**.

9.5.8 **Desiccator**.

9.5.9 **Analytical balance**, accurate to within ± 0,1 mg.

9.5.10 **Forced-air convection oven**, capable of maintaining the temperature at (70 ± 2) °C.

9.6 Procedure

9.6.1 Heat the 15 cm^3 crucible (9.5.4) in the muffle furnace (9.5.1) maintained at (750 ± 25) °C for 30 min.

9.6.2 Transfer the crucible to the desiccator (9.5.8), cool to room temperature, and weigh to the nearest 0,1 mg (m_1).

9.6.3 Weigh approximately a 5 g test portion into the previously prepared (heated) crucible and weigh to the nearest 0,01 g. Place the crucible in the clay triangle (9.5.5), and carefully heat the crucible and contents with the gas burner (9.5.2) until all volatile material and pyrolysis products have been removed (gases may flame) and the residue has been carbonized.

9.6.4 Transfer the crucible to the muffle furnace at (750 ± 25) °C and heat for 2 h.

9.6.5 Carefully transfer the crucible containing the ash to the desiccator, cool to room temperature, and reweigh to the nearest 0,1 mg (m_3).

9.6.6 Repeat the procedure on a second test portion.