INTERNATIONAL STANDARD

ISO 11235

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Rubber compounding ingredients — Sulfenamide accelerators — Test methods

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

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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.

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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)

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1.2.1 MBTS: Benzothiazyl disulfide

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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

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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

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

4.1.3.1.2 Absolute ethanol.

4.1.3.1.3 Toluene.

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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.

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4.1.5 Procedure

4.1.5.1 Method A

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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

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

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

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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

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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.

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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.