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Rubber compounding ingredients — Sulfenamide accelerators — Test methods

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

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document 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*.

This third edition cancels and replaces the second edition (ISO 11235:2016), which has been technically revised.

The main changes are as follows:

— errors in Formula (1) and Formula (2) have been corrected;

— the CAS Registry Number®[1)] has been added for each chemical;

— the usage of auto titrator with electrode has been added in Clause 5;

— Annex A has been changed from “normative” to “informative”.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Rubber compounding ingredients — Sulfenamide accelerators — Test methods

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 determine the applicability of any other restrictions.

1 Scope

This document specifies the methods to be used for the evaluation of sulfenamide accelerators:

— MBTS: benzothiazyl disulphide;

— CBS: *N*-cyclohexylbenzothiazole-2-sulfenamide;

— TBBS: *N*-*tert*-butylbenzothiazole-2-sulfenamide;

— DIBS: *N*,*N*'-diisopropylbenzothiazole-2-sulfenamide;

— DCBS: *N*,*N*'-dicyclohexylbenzothiazole-2-sulfenamide;

— MBS: *N*-oxydiethylenebenzothiazole-2-sulfenamide.

NOTE 1 Although MBTS is not a sulfenamide, it is the primary decomposition product of these accelerators and quantitatively determined by the method specified in 5.2.

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).

NOTE 2 Classification and key properties of sulfenamide accelerators are described in Annex A.

The method (5.2) to determine purity by high performance liquid chromatography (HPLC) is the preferred method.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1772, *Laboratory crucibles in porcelain and silica*

ISO 3819, *Laboratory glassware — Beakers*

ISO 4788, *Laboratory glassware — Graduated measuring cylinders*

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

ISO 6556, *Laboratory glassware — Filter flasks*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
lot sample
sample from production representative of a standard production unit, normally referred to as "the sample"

3.2
test portion
actual material, representative of the lot sample, used for a particular determination

4 Determination of physical and chemical properties

4.1 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.

4.2 Test methods

The test methods list of sulfenamide accelerators is shown in Table 1.

Table 1 — List of the test methods

Property	Clause or subclause of this document
Purity by reduction with MBT and titration	5.1
Purity by high performance liquid chromatography (HPLC)	5.2
Insoluble material	6
Melting range by capillary tube	7.1
Melting range by differential scanning calorimetry (DSC)	7.2
Volatile material	8
Wet sieve analysis	9
Ash	10

4.3 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.

5 Test methods for purity

5.1 Method to determine purity by reduction with MBT and titration

5.1.1 Purpose

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.

5.1.2 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.

5.1.3 Reagents

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

5.1.3.1 Basic reagents for methods A and B

5.1.3.1.1 2-Mercaptobenzothiazole (MBT) (CAS 149-30-4), min. assay 99,0 %.

5.1.3.1.2 Absolute ethanol (CAS 64-17-5).

5.1.3.1.3 Toluene (CAS 108-88-3).

5.1.3.1.4 Hydrochloric acid (CAS 7647-01-0), standard volumetric solution, c(HCl) = 0,1 mol/dm^3.

5.1.3.1.5 Hydrochloric acid (CAS 7647-01-0), standard volumetric solution, c(HCl) = 0,5 mol/dm^3.

5.1.3.1.6 Sodium hydroxide (CAS 1310-73-2), standard volumetric solution, c(NaOH) = 0,1 mol/dm^3, carbonate free.

5.1.3.1.7 Sodium hydroxide (CAS 1310-73-2), standard volumetric solution, c(NaOH) = 0,5 mol/dm^3, carbonate free.

5.1.3.1.8 Bromophenol blue (CAS 115-39-9), 10 g/dm^3 solution.

Dissolve 1 g of bromophenol blue with a small volume of ethanol (5.1.3.1.2). Transfer to a 100 cm^3 volumetric flask and neutralize with the sodium hydroxide solution (5.1.3.1.6) to a green colour. Dilute to the mark with ethanol (5.1.3.1.2).

5.1.3.2 Prepared reagent for method A

5.1.3.2.1 2-Mercaptobenzothiazole, 40 g/dm^3 solution, freshly prepared.

Weigh a suitable quantity of MBT (5.1.3.1.1) to the nearest 0,1 g and dissolve in absolute ethanol (5.1.3.1.2). 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.

5.1.3.3 Prepared reagent for method B

5.1.3.3.1 Ethanol (5.1.3.1.2)/**toluene** (5.1.3.1.3) solution, 5:3 (V:V).

5.1.3.3.2 2-Mercaptobenzothiazole, 40 g/dm^3 solution, freshly prepared.

Weigh a suitable quantity of MBT (5.1.3.1.1) to the nearest 0,1 g and dissolve in the ethanol/toluene solution (5.1.3.3.1). 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 (5.1.3.3.1).

5.1.4 Apparatus

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

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

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

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

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

5.1.4.6 Stop-watch.

5.1.4.7 Magnetic stirrer.

5.1.4.8 pH-meter, with a resolution of 0,1 unit or better (or auto titrator with electrode, in the case that 5.1.5.1.6 is automatically tested).

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

5.1.5 Procedure

5.1.5.1 Method A

5.1.5.1.1 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 (5.1.4.4).

5.1.5.1.2 Add 50 cm^3 of ethanol (5.1.3.1.2) and stir until dissolved. If needed, heat the solution to a temperature no higher than 55 °C. A slight turbidity can remain.

5.1.5.1.3 Cool to room temperature. Add 3 drops of indicator (5.1.3.1.8) and titrate the free amine with 0,1 mol/dm^3 hydrochloric acid (5.1.3.1.4) to the blue-green-colour end point (V_1).

5.1.5.1.4 Add 50 cm^3 of the MBT solution (5.1.3.2.1) and immediately pipette 25 cm^3 of 0,5 mol/dm^3 hydrochloric acid (5.1.3.1.5), exactly measured.

5.1.5.1.5 Stir the solution in a temperature-controlled bath (5.1.4.5) maintained at (55 ± 2) °C for exactly 5 min, timed with the stop-watch (5.1.4.6).

5.1.5.1.6 Titrate potentiometrically the unreacted hydrochloric acid with the 0,5 mol/dm^3 sodium hydroxide (5.1.3.1.7). 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 while 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.

The above steps can be tested automatically using an auto titrator with electrode.

5.1.5.2 Method B

5.1.5.2.1 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 (5.1.4.4).

5.1.5.2.2 Add 50 cm^3 of the ethanol/toluene solution (5.1.3.3.1) and stir until dissolved. If needed, heat the solution to a temperature no higher than 55 °C. A slight turbidity can remain.

5.1.5.2.3 Cool to room temperature. Add 3 drops of indicator (5.1.3.1.8) and titrate the free amine with 0,1 mol/dm^3 hydrochloric acid (5.1.3.1.4) to the blue-green-colour end point (V_1).

5.1.5.2.4 Add 50 cm^3 of the MBT solution (5.1.3.3.2) and immediately pipette 25 cm^3 of 0,5 mol/dm^3 hydrochloric acid (5.1.3.1.5), exactly measured.

5.1.5.2.5 Stir the solution in a temperature-controlled bath (5.1.4.5) maintained at (55 ± 2) °C for exactly 5 min, timed by the stop-watch (5.1.4.6).

5.1.5.2.6 Add 3 drops of bromophenol blue indicator (5.1.3.1.8) and titrate the unreacted hydrochloric acid with 0,5 mol/dm^3 sodium hydroxide (5.1.3.1.7) to the green-blue-colour end point. Then continue, drop by drop, to a blue colour (V_3).

5.1.6 Expression of results (methods A and B)

5.1.6.1 Free amine

Calculate the mass fraction of free amine content, F, expressed in per cent to the nearest 0,1 with Formula (1):

$$F = \frac{V_1 \times c_1}{10 \times m} \times M_1 \quad (1)$$

where

V_1 is the volume, in cubic centimetres, of hydrochloric acid (5.1.3.1.4) used for the titration;

c_1 is the concentration, in moles per cubic decimetre, of the hydrochloric acid (5.1.3.1.4);

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

M_1 is the molecular mass of the corresponding amine (see Table 2).

Table 2 — Molecular mass of the corresponding amine

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

5.1.6.2 Purity

Calculate the mass fraction of purity of the sulfenamide, P, expressed in per cent to the nearest 0,1 with Formula (2):

$$P = \frac{(25 \times c_2) - (V_3 \times c_3)}{10 \times m} \times M_2 \quad (2)$$

where

c_2 is the concentration, in moles per cubic decimetre, of the hydrochloric acid (5.1.3.1.5);

c_3 is the concentration, in moles per cubic decimetre, of the sodium hydroxide (5.1.3.1.7);

V_3 is the volume, in cubic centimetres, of the sodium hydroxide (5.1.3.1.7);

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

M_2 is the molecular mass of the sulfenamide (see Table 3).

Table 3 — Molecular mass of the sulfenamide

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

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

5.2.1 Purpose

5.2.1.1 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.