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Rubber compounding ingredients — Sulfenamide accelerators — Test methods

Ingrédients de mélange du caoutchouc — Accélérateurs de 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.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This second edition cancels and replaces the first edition (ISO 11235:1999), which have been technically revised:

- the method to determine purity by high performance liquid chromatography (HPLC) is stated as the preferred method in the scope and in the new 5.2.1.3;
- the normative references in Clause 2 and in the text have been updated;
- precision data in 4.2.12 have been moved in an informative Annex B and a Bibliography has been added.

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

This International Standard 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 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).

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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.

3.1
external standard calculation
<high performance liquid chromatography> 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 1 to entry: All components are assumed to be resolved from the component of interest.

3.2
lot sample
sample from production representative of a standard production unit, normally referred to as "the sample"

3.3
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

Table 1 — List of the test methods

Property	Clause or subclause of this International Standard
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 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.

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

5.1.3.1.2 Absolute ethanol.

5.1.3.1.3 Toluene.

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

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

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

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

5.1.3.1.8 Bromophenol blue, 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 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.

4.1.3.3 Prepared reagent for method B

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

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

Weigh a suitable quantity of MBT (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.

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 may 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.

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

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

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).