Designation: D4934 – 02 (Reapproved 2012)

Standard Test Method for Rubber Compounding Materials: 2-Benzothiazyl Sulfenamide Accelerators—Insolubles[1]

This standard is issued under the fixed designation D4934; 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 test method covers a general procedure for the determination of insoluble impurities of sulfenamides in suitable organic solvents.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

3. Summary of Test Method

3.1 A specimen of sulfenamide is dissolved in a prescribed solvent, stirred, and filtered through a crucible. The insoluble content is calculated from the amount of residue.

4. Significance and Use

4.1 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. This test method may be used as an indication of such degradation.

4.2 Since MBTS (mercaptobenzothiazole disulfide) is a primary degradation product of sulfenamides, the determination of MBTS is a means of assessing possible degradation of sulfenamides. Insolubles are a means of mercaptobenzothiazyl 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. Apparatus

5.1 *Erlenmeyer Flask,* 300 cm^3.

5.2 *Sintered Glass Crucible,* G4.

5.3 *Measuring Cylinder,* 250 cm^3.

5.4 *Magnetic Stirrer.*

5.5 *Watch Glass.*

5.6 *Vacuum Flask.*

5.7 *Explosion-proof, Vented Air Circulating Oven,* capable of temperature regulation of 70 ± 2°C.

5.8 *Balance,* analytical, with a sensitivity of ±0.01 g.

5.9 *Washing Bottle.*

5.10 *Sieve,* 30 Mesh (U.S. Standard), or equivalent (for example, 0.6 mm).

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] 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.

6.2 *Methanol,* analytical reagent.

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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[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.

[3] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

6.3 *Cyclohexane,* analytical reagent.

7. Hazards

7.1 Methanol and cyclohexane, with threshold limit values (TLVs) of 200 cm^3/m^3 and 300 cm^3/m^3, respectively, and high flammability, should be handled with appropriate caution.

7.2 Good laboratory safety practices should be followed in handling all chemicals and carrying out manipulations.

8. Sampling

8.1 Sampling shall be at the discretion of the analyst to obtain as representative a sample as possible of the lot to be tested.

9. Procedure

9.1 *Solvents:*

9.1.1 *Methanol*—Use for testing specimens of *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), *N,N*-diisopropyl-2-benzothiazyl sulfenamide (DIBS), 2(morpholinothio)benzothiazole (MBS), and *N-tert*-butyl-benzothiazole sulfenamide (TBBS).

9.1.2 *Cyclohexane*—Use for testing DCBS specimens.

9.2 Grind approximately 10 g of a well-mixed lot sample so that material passes through a 30-mesh (0.6-mm) sieve.

9.3 Transfer 5 g of the specimen (W_1), weighed to the nearest 0.01 g, to a 300-cm^3 Erlenmeyer flask. Using a graduated cylinder, add 250 cm^3 of methanol. In the case of DCBS, use cyclohexane instead of methanol. Cover the flask with a watch glass and stir cold, on a magnetic stirrer, for 30 min at 25 ± 5°C.

9.4 Filter the solution, with suction, through a clean, dry, preweighed (W_2) sintered glass crucible. It is important that during filtration, the crucible is only half filled. Wash the Erlenmeyer flask with 25 cm^3 of methanol, or in the case of DCBS, with 25 cm^3 of cyclohexane. Filter the washings.

9.5 At the end of the filtration, remove the suction 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 and then suck the washings through quickly. When this has been done, the walls of the crucible should be free from residue.

9.6 Dry the crucible for 60 min in an oven maintained at 70°C.

9.7 Cool to room temperature in a desiccator and obtain the mass of the crucible plus insolubles to the nearest milligram (W_3).

10. Calculation

10.1 Calculate the percent insoluble content, *C*, in percent as follows:

$$C = [(W_3 - W_2)/W_1] \times 100 \quad (1)$$

where:

W_1 = mass of sample, g,
W_2 = mass of empty crucible, g, and
W_3 = mass of crucible and insoluble material, g.

11. Report

11.1 Report the following information:

11.1.1 The proper identification of the sample, and

11.1.2 The results obtained from two individual determinations and their average reported to the nearest 0.01 %.

12. Precision and Bias

12.1 This precision and bias section has been prepared in accordance with Practice D4483. Refer to Practice D4483 for terminology and other statistical calculation details.

12.1.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (rubbers) used in the particular interlaboratory programs as described below. The precision parameters should not be used for acceptance/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.

12.2 A somewhat limited Type 1 (interlaboratory) precision with three laboratories on two different days was evaluated in 1988. The results are given in Table 1. Both repeatability and reproducibility are short term. A period of a few days separates replicate test results. A test result is the mean value, as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

TABLE 1 Type 1 Precision Percent Insolubles

Material	Average	Within Laboratory			Between Laboratory		
		S_r[A]	*r*	(*r*)	S_R	*R*	(*R*)
CBS	0.43	0.045	0.129	30.1	0.161	0.456	106.0
MBS	0.52	0.024	0.068	13.1	0.057	0.163	31.4
DCBS	0.82	0.040	0.115	14.0	0.128	0.363	44.1
Pooled values[B]	0.59	0.038	0.107	18.2	0.123	0.349	59.1

[A] S_r = repeatability standard deviation.
r = repeatability = 2.83 times the square root of the repeatability variance.
(r) = repeatability (as a percent of material average).
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 times the square root of the reproducibility variance.
(R) = reproducibility (as a percent of material average).
[B] No values omitted.

12.3 The precision of this test method may be expressed in the format of the following statements which use what is called an "appropriate value'' of *r, R*, (*r*), or (*R*), that is, that value to be used in decisions about test results (obtained with the test method). The *appropriate value* is that value of *r* or *R* associated with a mean level in Table 1 closest to the mean level under consideration at any given time, for any given material, analysis procedure, and test method in routine testing operations.

12.4 *Repeatability*—The repeatability, *r*, of this test method has been established as the *appropriate value* tabulated in Table 1. Two single test results, obtained under normal test procedures, that differ by more than this tabulated *r* (for any given level) must be considered as derived from different or nonidentical sample populations.

12.5 *Reproducibility*—The reproducibility, *R*, of this test method has been established as the *appropriate value* tabulated in Table 1. Two single test results obtained in two different laboratories, under normal test procedures, that differ by more than the tabulated *R* (for any given level) must be considered to have come from different or nonidentical sample populations.

12.6 Repeatability and reproducibility expressed as a percent of the mean level, (*r*) and (*R*), have equivalent application statements as above for *r* and *R*. For the (*r*) and (*R*) statements, the difference in the two single test results is expressed as a percent of the arithmetic mean of the two test results.

13. Keywords

13.1 insolubles; mercaptobenzothiazole (MBT); mercaptobenzothiazole disulfide (MBTS); rubber accelerators; rubber chemicals; 2-benzothiazole sulfenamides