Designation: D1519 – 95 (Reapproved 2014)

Standard Test Methods for Rubber Chemicals—Determination of Melting Range[1]

This standard is issued under the fixed designation D1519; 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 These test methods cover the determination of the melting range of commercial rubber processing chemicals either by use of capillary melting point tubes or by differential scanning calorimetry (DSC).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

E1 Specification for ASTM Liquid-in-Glass Thermometers

E324 Test Method for Relative Initial and Final Melting Points and the Melting Range of Organic Chemicals (Discontinued 2001) (Withdrawn 2001)[3]

E473 Terminology Relating to Thermal Analysis and Rheology

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 *differential scanning calorimetry*—see Terminology E473.

4. Significance and Use

4.1 This test method may be used for research and development. It also may be used for quality assurance, provided a standard has been agreed upon between a producer and a user.

4.2 For identification purposes, melting range should be supplemented by measurements of a more specific physical and chemical property.

4.3 This test method is not recommended for rubber chemicals that decompose at their melting ranges.

4.4 The melting range as determined by Test Method A—Capillary Tube Melting Range is not recommended as a criterion of purity of a rubber chemical.

5. Sampling

5.1 Grind a representative sample of the chemical to be tested with a mortar and pestle, if necessary, to pass completely through a 150-µm (No. 100) sieve. Use the sample without further treatment.

TEST METHOD A—CAPILLARY TUBE MELTING RANGE

6. Apparatus

6.1 *Melting Apparatus*—Any electric melting apparatus that satisfies the requirements of Test Method E324 may be used or any suitable manually heated oil bath such as Hershberg tube.

6.2 *Capillary Tube*—The capillary tube to contain the sample shall be a glass tube approximately 150 mm long and 1.2 to 1.4 mm in internal diameter with walls 0.2 to 0.3 mm thick and closed at one end.

6.3 *Thermometer*—The thermometer shall be of the partial immersion type and of suitable range selected from Specification E1, or of an equivalent range as specified by the Chemical Manufacturers Association. It shall be divided into subdivisions of 0.5°C (1°F) or less. Corrections for the thermometer shall be determined by calibration against a thermometer certified by National Institute of Standards and Technology.

6.4 *Sieve*—A150-µm (No. 100) sieve for screening the sample shall be provided.

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[1] These test methods are 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] The last approved version of this historical standard is referenced on www.astm.org.

7. Procedure

7.1 Select the thermometer of the proper range and support it so that it is immersed to the immersion mark in the liquid of the bath.

7.2 Charge the capillary glass tube with sufficient powder to form a column in the bottom of the tube about 3 to 6-mm high when packed down as closely as possible by moderate tapping on a solid surface.

7.3 Heat the bath until a temperature approximately 25°C below the expected melting range is reached. Then regulate the rate of rise so that it averages about 3°C/min for the rest of the determination except that the rate of rise is 1 ± 0.2°C/min during the actual melting of the sample. When the temperature has risen to about 10°C below the expected melting range, insert the capillary in the bath and adjust the height of the tube so that the material in the capillary is beside the center of the thermometer bulb. The capillary tube is not placed in the bath previously, since many materials undergo decomposition upon prolonged heating. Major adjustments of the heat source should be avoided during the actual melting range.

7.4 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 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.

8. Report

8.1 Report the results to the nearest division on the thermometer, after applying necessary calibration corrections.

9. Precision and Bias[4]

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

9.2 The results in this precision and bias section give an estimate of the precision of the test method with the materials used in the particular interlaboratory program as described in 9.3. 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.

9.3 A Type 1 interlaboratory precision program was conducted. Repeatability is short term and reproducibility is short term. Seven laboratories participated and three materials were used. A test result is the value obtained from one determination. Two determinations were run on each material, and this protocol was repeated on each of three days. The analysis for precision followed the general procedure as set forth in Annex 5 of Practice D4483. Each cell of Practice D4483 Table 1 basic data format contained six values (three test days, two test results each day). The estimates for the repeatability parameters therefore contain two undifferentiated sources of variation, that is, replicates within days and between days. The final precision parameters are given in Table 1 of this test method.

9.4 The results of the precision calculations for the initial melting point and the final melting point are arranged in ascending "mean level" order, and given in Table 1.

9.5 *Repeatability*—The pooled repeatability, *r*, of this test method has been established as 1.58°C, as given in Table 1. Two single test results obtained under normal test method procedures that differ by more than 1.58°C must be considered as suspect, that is, having been derived from different or nonidentical sample populations. If this is the case, appropriate corrective action should be taken.

9.6 *Reproducibility*—The pooled reproducibility, *R*, of this test method has been established as 3.40°C, as given in Table 1. Two single test results obtained under normal test method procedures that differ by more than 3.40°C must be considered as suspect, that is, having been derived from different or nonidentical sample populations. If this is the case, appropriate corrective action should be taken.

9.7 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value of the melting point is exclusively defined by the test method. Bias, therefore, cannot be determined.

TABLE 1 ASTM Test Method Precision—Type 1: Test Method D1519 Capillary Melting Range

NOTE 1—This is short-term precision (days).

NOTE 2—These are the same chemicals used for the DSC.

Material	Mean Level, ° C	Within Laboratories[A]			Between Laboratories[A]		
		Sr	*r*	(*r*)	*SR*	*R*	(*R*)
Initial A	47.3	0.681	1.91	4.02	1.07	3.00	6.34
Initial B	98.8	0.491	1.38	1.39	1.26	3.52	3.57
Initial C	176.4	0.671	1.88	1.07	1.25	3.49	1.98
Final A	49.4	0.376	1.05	2.13	0.55	1.53	3.10
Final B	101.4	0.426	1.19	1.18	1.43	3.99	3.94
Final C	179.7	0.663	1.86	1.03	1.50	4.19	2.33
Pooled		0.565	1.58	1.80	1.22	3.40	3.54

[A] *Sr* = within laboratory, standard deviation.
r = repeatability in measurement units.
(*r*) = repeatability (in percent).
SR = between laboratory, standard deviation.
R = reproducibility in measurement units.
(*R*) = reproducibility (in percent).

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1070.

TEST METHOD B—DIFFERENTIAL SCANNING CALORIMETRY

10. Apparatus

10.1 *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 samples and the reference material to the required sensitivity and precision.

10.2 *Specimen Pans,* composed of aluminum or other metal of high thermal conductivity. The specimen pans must not react with the sample and must not melt under the temperatures of the test.

10.3 *Nitrogen,* or other inert purge gas supply.

10.4 *Analytical Balance,* with a capacity greater than 20 mg, capable of weighing to the nearest 0.01 mg.

11. Calibration

11.1 Using the same heating rate, purge gas, and flow rate to be used for the specimen, calibrate the temperature axis of the instrument using the procedure in Test Method E967.

12. Procedure

12.1 Weigh about 10 to 20 mg of the sieved specimen into a DSC specimen pan. Cover and seal the specimen pan and place into the DSC sample holder.

12.2 Place an empty sealed pan into the reference sample holder.

12.3 Close the sample chamber and ensure that the purge gas flow matches that used for the calibration.

12.4 Heat the specimen rapidly to 50°C below the melting temperature and allow to equilibrate.

12.5 Heat the specimen through the endotherm until baseline is re-established above the melting endotherm. Heating rate must be the same as that used for the calibration of the instrument. Ten degrees Celsius is a commonly used rate. Record the accompanying thermal curve.

12.6 Reweigh the specimen after completion of scanning, and discard. Report any mass loss observed.

NOTE 3—Mass loss is only one indication of suspected sample degradation or decomposition. Other decomposition indicators, such as color change, may be noted if the specimen pan is opened.

12.7 From the resultant curve, measure the temperatures for the desired points on the curve, T_e, T_p (see Fig. 1) to the required precision,

where:

T_e = extrapolated onset temperature for fusion, °C, and
T_p = melting peak temperature, °C.

13. Report

13.1 Report T_e and T_p, as well as heating rate used.

13.2 Any side reaction (for example, thermal degradation or oxidation) also should be reported and the reaction identified, if possible.

14. Precision and Bias[4]

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

14.2 The results in this precision and bias section give an estimate of the precision of the test method with the materials used in the particular interlaboratory program as described in 14.3. The precision parameters should not be used for acceptance/rejection testing of any group of materials without

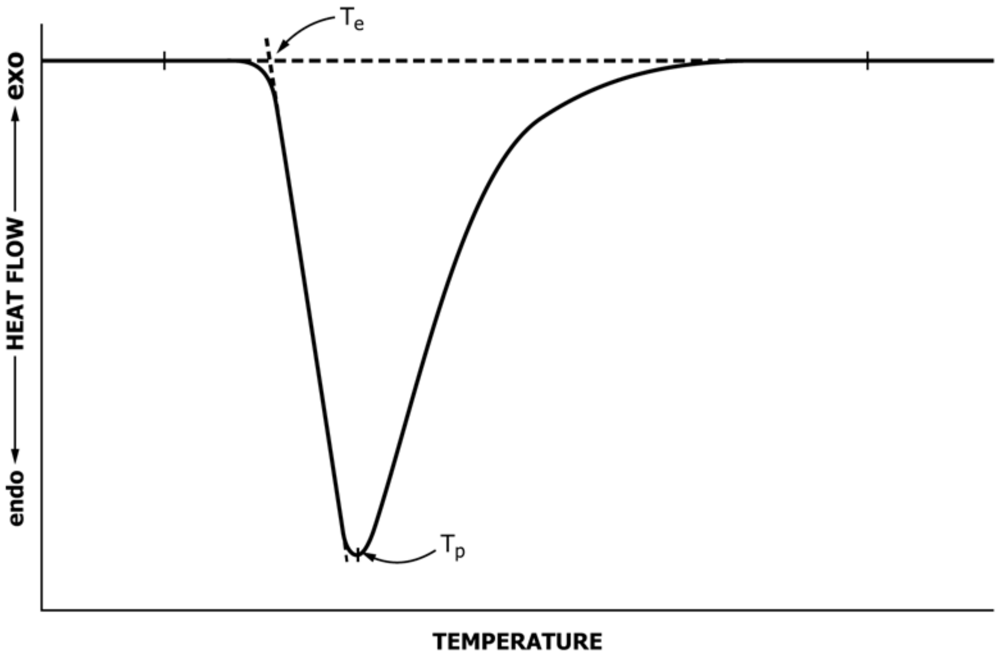

FIG. 1 Sample Melting Endotherm

documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

14.3 A Type 1 interlaboratory precision program was conducted. Repeatability is short term and reproducibility is short term. Eleven laboratories participated and three materials were used. A test result is the value obtained from one determination. Two determinations were run on each material, and this protocol was repeated on each of three days. The analysis for precision followed the general procedure as set forth in Annex 5 of Practice D4483. Each cell of Practice D4483 Table 1 basic data format contained six values (three test days, two test results each day). The estimates for the repeatability parameters therefore contain two undifferentiated sources of variation, that is, replicates within days and between days. The final precision parameters are given in Table 2 of this test method.

14.4 The results of the precision calculations for the onset and the peak are arranged in ascending "mean level" order, and given in Table 2.

14.5 *Repeatability*—The pooled repeatability, *r*, of this test method has been established as 1.40°C, as given in Table 2. Two single test results obtained under normal test method procedures that differ by more than 1.40°C must be considered as suspect, that is, having been derived from different or nonidentical sample populations. If this is the case, appropriate corrective action should be taken.

14.6 *Reproducibility*—The pooled reproducibility, *R*, of this test method has been established as 3.75°C, as given in Table 2. Two single test results obtained under normal test method procedures that differ by more than 3.75°C must be considered as suspect, that is, having been derived from different or nonidentical sample populations. If this is the case, appropriate corrective action should be taken.

TABLE 2 ASTM Test Method Precision—Type 1: Test Method D1519 DSC

NOTE 1—This is short-term precision (days).

NOTE 2—These are the same chemicals used for the DSC.

Material	Mean Level, ° C	Within Laboratories[A]			Between Laboratories[A]		
		Sr	*r*	(*r*)	*SR*	*R*	(*R*)
Onset A	47.0	0.575	1.61	3.43	1.90	5.31	11.30
Onset B	99.0	0.469	1.31	1.33	1.24	3.46	3.50
Onset C	176.8	0.376	1.05	0.59	1.15	3.21	1.82
Peak A	50.7	0.682	1.91	3.77	2.15	6.02	11.88
Peak B	102.4	0.445	1.25	1.22	1.20	3.37	3.29
Peak C	180.9	0.370	1.04	0.57	1.37	3.84	2.12
Pooled		0.499	1.40	1.82	1.34	3.75	5.65

[A] *Sr* = within laboratory, standard deviation.
r = repeatability in measurement units.
(r) = repeatability (in percent).
SR = between laboratory, standard deviation.
R = reproducibility in measurement units.
(R) = reproducibility (in percent).

14.7 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value of the melting point is exclusively defined by the test method. Bias, therefore, cannot be determined.

15. Keywords

15.1 capillary; differential scanning calorimetry (DSC); melting range; rubber chemicals