Designation: D 6493 – 99

Standard Test Methods for Softening Point of Hydrocarbon Resins by Automated Ring and Ball Apparatus[1]

This standard is issued under the fixed designation D 6493; 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 are intended for determining the softening point of hydrocarbon resins and similar materials by means of an automated ring-and-ball apparatus.

1.1.1 The ring and ball softening point of a hydrocarbon resin may be run with lower precision using the manual ring and ball softening point in Test Method E 28.

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 method 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:*

E 1 Specification for ASTM Thermometers[2]

E 28 Test Methods for Softening Point of Resins Derived from Naval Stores by Ring-and-Ball Apparatus[3]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]

3. Significance and Use

3.1 In general, with materials of these types, softening does not take place at a definite temperature. As the temperature rises, these materials gradually change from brittle or exceedingly thick and slow-flowing materials to softer and less viscous liquids. For this reason, the determination of the softening point must be made by a fixed, arbitrary, and closely defined method if the results obtained are to be comparable.

3.2 In these test methods, the softening point is defined as the temperature at which a disk of the sample held within a horizontal ring is forced downward a distance of 25.4 mm (1 in.) under the weight of a steel ball as the sample is heated at 5°C/min in a water, glycerin, silicone oil, ethylene glycol/water or glycerin/water bath.

4. Sample Preparation

4.1 *Preparation of Sample by the Pour Method*:

4.1.1 This procedure is suitable for materials that can be heated and poured without adverse effects on the softening point.

4.1.2 Select a sample representative of the material to be tested. The sample should consist of flakes, pastilles, or freshly broken lumps. Avoid inclusion of finely divided material or dust.

4.1.3 Select a quantity at least twice that necessary to fill the desired number of rings, and melt it in a clean container, using an oven, hot plate, sand bath or oil bath to prevent local overheating. Take care to avoid incorporating air bubbles in the sample. Melt the sample completely, but do not heat it above a temperature necessary to pour the material readily. The time from the beginning of heating to the pouring of the sample should not exceed 15 min.

4.1.4 For materials that tend to crack or shrink in the ring on cooling, immediately before filling the ring, preheat the ring to approximately the temperature at which the material is to be poured. The ring, while being filled, should rest **bottom down** on a suitable metal surface. Pour the sample into the ring so as to leave an excess on cooling. After cooling a minimum of 30 min, trim off the excess resin on the periphery of the ring. To remove excess resin from the top, cut the excess material off cleanly with a slightly heated knife or spatula, or grasp the ring in a pair of tongs and draw the top surface quickly and firmly over the surface of a heated metal plate. In case the test is repeated, use a clean container and fresh sample.

4.2 *Preparation of Sample by the Powder Method*:

4.2.1 See Appendix X1.1, Alternate Sample Preparation Procedures.

4.3 *Preparation of Samples Having a Low Softening Point (up to 35°C (95°F))*:

4.3.1 Place a ring on a piece of aluminum foil. Pour the material to be tested into the ring, then place the foil and the filled ring on dry ice or in a freezer to cool. The material in the ring must be free of bubbles.

4.3.2 After cooling, cut and scrape off any excess material using a slightly heated spatula, then slide the ring gently from

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[2] *Annual Book of ASTM Standards*, Vol 14.03.

[3] *Annual Book of ASTM Standards*, Vol 06.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

the foil. Place the ring in the supporting apparatus, and perform the softening point analysis according to Section 11.

5. Apparatus

5.1 *Automated Ring and Ball Softening Point Instrument with Control Unit*, test units, and test inserts.

5.2 *Ring*—A brass, shouldered ring conforming to the dimensions shown in Fig. 1(a).

5.3 *Ball*—A steel ball, 9.53 ± 0.1 mm (⅜in.) in diameter, weighing between 3.45 and 3.55 g.

5.4 *Beaker*, 600 mL. Ensure that the dimensions will properly fit the heating unit.

5.5 *Stir Bar*—The dimensions must be such that the bar spins freely under the test stand.

6. Reagents and Materials

6.1 *Bath Liquids*:

6.1.1 *Distilled or Deionized Water, Freshly Boiled*—For softening points between 35°C (95°F) and 80°C (176°F).

6.1.1.1 Use distilled or deionized water that has been cooled to at least 27°C (81°F) below the anticipated softening point, but in no case lower than 5°C (41°F).

6.1.2 *USP Glycerin*—For softening points between 80°C (176°F) and 150°C (302°F). Repeated use of glycerin will increase the moisture content over time and may affect results. Replace with fresh glycerin if any change in appearance is noted.

NOTE 1—Glycerin should not be used for softening points greater than 150°C (302°F) due to the 160°C (320°F) flash point of glycerin.

6.1.3 *Silicone Oil (Polydimethylsiloxane)*—For softening points above 80°C (176°F). The oil must have a temperature range of 200°C+ (392°F+), remain clear within the temperature range, have no apparent effect or reactivity with the test specimen, have a high water repellency, and maintain a uniform viscosity and stirring rate within the temperature range.[5]

NOTE 2—Replace with fresh silicone oil if any change in appearance is noted. Do not use silicone oil that contains any gels; gels are an indicator that degradation has occurred.

[5] Supporting data are available from ASTM Headquarters. Request RR:D01–1113.

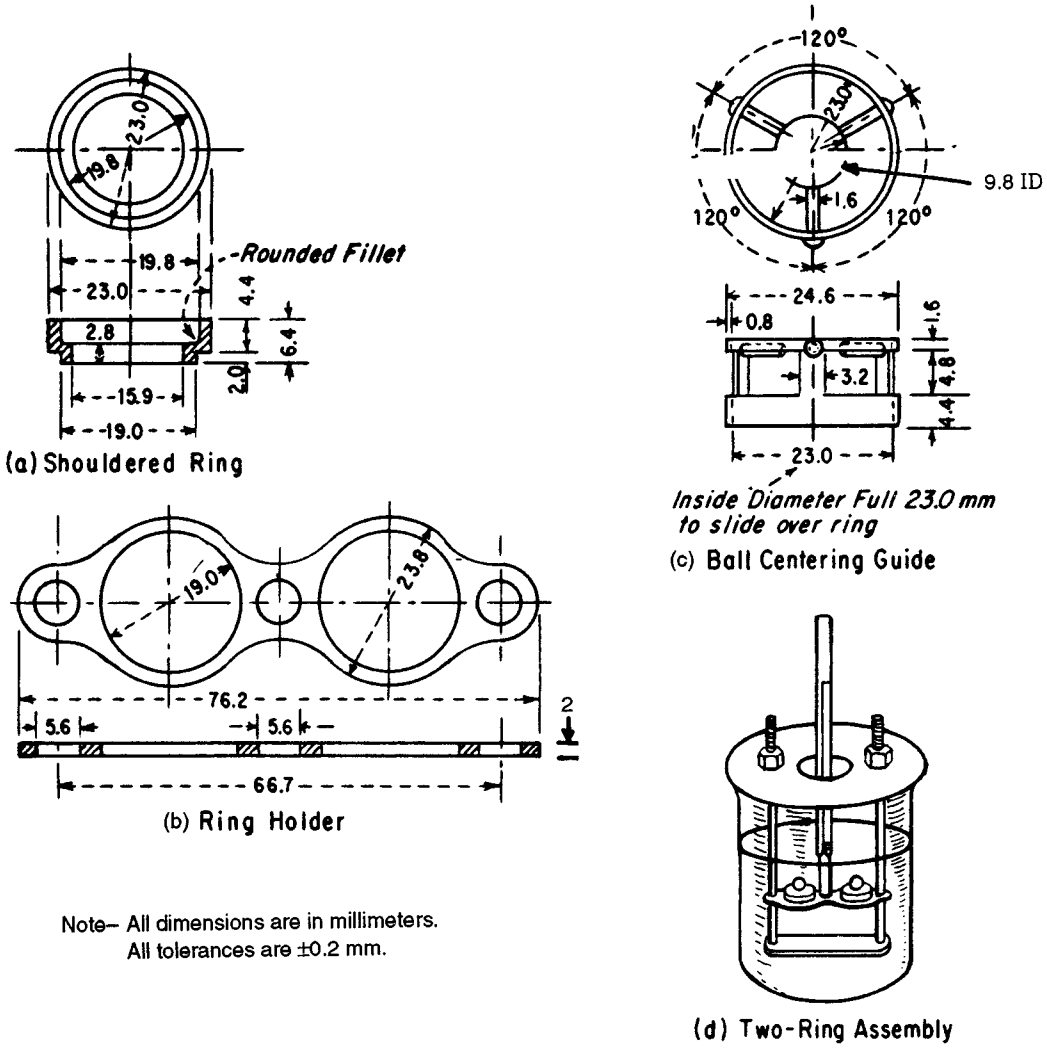

FIG. 1 Shouldered Ring, Ring Holder, Ball-Centering Guide, and Assembly of Apparatus Showing Two Rings

6.1.4 *Ethylene Glycol*—For softening points up to 35°C (95°F).

6.1.4.1 Prepare a fresh 50/50 (volume/volume) mixture of distilled water and ethylene glycol prior to sample analysis. For softening points between 0°C and 35°C, a 50/50 (v/v) mixture of glycerin and water may be used.

7. Calibration

7.1 The calibration of any automated ring and ball softening point apparatus must be performed on a regular basis, since accurate temperature control is required. Follow the manufacturer's instructions for calibration of the instrument.

8. Procedure for Materials Having a Softening Point Between 35°C (95°F) and <80°C (176°F)

8.1 Add a stir bar to the 600-mL beaker and fill with approximately 500 mL of distilled or deionized water, conforming to the requirements in 6.1.1. Ensure that the beaker is properly positioned on the heater in the test unit. Place the prepared sample rings in the test insert. Place the ball-centering guide and ball on top of the sample ring. Place the test insert in the beaker of water, suspending it from the support pins. Place the temperature measuring device in the test insert. Verify that the control unit is set for the correct bath liquid.

8.2 *Heating*—Heat the bath so that the temperature of the water is raised uniformly at a rate of 5°C (10°F)/min. Protect the bath from drafts, using shields if necessary. The maximum permissible variation for any 1-min period after the first three minutes is ±0.5°C (±1°F). Reject any test in which the rate of temperature rise does not fall within these limits. The test is complete when the light beam has been interrupted by the falling ball and material.

NOTE 3—Rigid adherence to the prescribed rate of heating is absolutely essential for reproducibility of results.

8.3 *Softening Point*—Record as the softening point the temperature displayed on the unit after the light beam has been interrupted by the falling ball and material.

8.4 Start the cooling process in the instrument. **Remove** the temperature measuring device from the test insert, then remove the test insert from the beakers. Thoroughly clean the test insert, ball, and ring in a suitable solvent.

9. Procedure for Materials Having Softening Points Between 80°C (176°F) and 150°C (302°F)

9.1 Use the same procedure as described in Section 8, except fill the bath with glycerin or silicone oil.

NOTE 4—For materials softening around 80°C (176°F) report the bath liquid, since a glycerin or silicone oil bath will yield a slightly higher result than a water bath.

10. Procedure for Materials Having Softening Points Above 150°C (302°F)

10.1 Use the same procedure as described in Section 8, except fill the bath with silicone oil (Note 2).

11. Procedure for Materials Having Softening Points Below 35°C (95°F)

11.1 *Apparatus*:

11.1.1 *Isopropyl Alcohol Dry Ice Bath*.

11.2 *Procedure*:

11.2.1 Cool the bath, described in 6.1.4.1, to –25°C (–13°F) in an isopropyl alcohol dry ice bath.

11.2.2 Use the same procedure as in Section 8 except for the bath liquid, and begin heating as directed once the test specimen in the ring has been placed in the bath.

12. Report

12.1 Report the softening point to the nearest 1.0°C.

12.2 Report the bath liquid used in the test.

13. Precision and Bias [5]

13.1 *Automatic Method Precision*—An interlaboratory study of the ring and ball softening point of three hydrocarbon resins was run in 1998 by 23 laboratories. The design of the experiment, similar to that of Practice E 691, and an analysis of the data are given in ASTM Research Report No. D01-1113.

13.1.1 *Test Result*—The precision information given for ring and ball softening point of a hydrocarbon resin at the 70°C level in a water bath, and for hydrocarbon resins at the 100° to 135°C level in a glycerin or silicone oil bath, respectively, is for the comparison of two test results.

13.1.2 *Precision*:

13.1.2.1 For a material having a 70°C ring and ball softening point run in a water bath:

(*1*) *Repeatability Limit 95 %* (within laboratory) = 0.7°.

(*2*) *Reproducibility Limit 95 %* (between laboratories) = 3.8°.

13.1.2.2 For a material having a 100° to 135°C ring and ball softening point run in a glycerin or silicone oil bath:

(*1*) *Repeatability Limit 95 %* (within laboratory) = 1.8°.

(*2*) *Reproducibility Limit 95 %* (between laboratories) = 4.6°.

13.1.2.3 These terms (repeatability limit and reproducibility limit) are used as specified in Practice E 177. The respective standard deviations among test results, related to the above numbers by the factor 2.8, are:

13.1.2.4 For a material having a 70°C ring and ball softening point run in a water bath:

(*1*) *Repeatability Standard Deviation* = 0.3°.

(*2*) *Reproducibility Standard Deviation* = 1.4°.

13.1.2.5 For a material having a 100° to 135° ring and ball softening point run in a glycerin or silicone oil bath:

(*1*) *Repeatability Standard Deviation* = 0.7°.

(*2*) *Reproducibility Standard Deviation* = 1.7°.

13.2 *Bias*—Since there is no accepted reference material, method or laboratory suitable for determining the bias for the procedure in these test methods for measuring the ring and ball softening point, no statement on bias is being made.

14. Keywords

14.1 hydrocarbon resin; ring and ball; softening point

APPENDIX

(Nonmandatory Information)

X1. ALTERNATIVE SAMPLE PREPARATION PROCEDURE

X1.1 *Preparation of Sample by the Powder Method*:

X1.1.1 This sample preparation procedure is suitable for materials that cannot be melted and poured without altering the softening point.

X1.1.2 *Apparatus*—For the powder method of sample preparation the following additional apparatus is required:

X1.1.2.1 *Ring*—A brass, shouldered ring conforming to the dimensions shown in Fig. 1(a); alternatively, a ring made of steel may be used to minimize the possibility of its deformation during the compacting operation.

X1.1.2.2 *Mortar and Pestle*—A steel mortar and pestle with sleeve, knock-out-button, and ring support conforming to the dimensions shown in Fig. X1.1.

X1.1.2.3 *Press*—A hydraulic press or any other suitable press capable of maintaining sustained pressures up to 55 MPa (8000 psi).

X1.1.3 *Procedure*:

X1.1.3.1 Select the sample as described in 4.1.2 and break up the lumps until there are no particles larger than 3.175 mm (⅛ in.). Mix the material thoroughly, and quarter down until a suitable quantity (approximately 50 to 75 g) is obtained for powdering.

X1.1.3.2 Pulverize the quartered sample in a porcelain mortar or by other suitable means, and fractionate by screening through a No. 50 sieve. Immediately use the material passing the No. 50 sieve for preparation of the ring.

X1.1.3.3 Assemble the ring with the ring support, the mortar, and the knock-out button, together with the sleeve, as shown in Fig. X1.1. Take care to ensure that the ring is properly centered and seated in the cut-out section of the sleeve.

X1.1.3.4 Pour the pulverized material into the sleeve until it is about 12.7 mm (0.5 in.) above the top of the ring (approximately 3 g required). Place the pestle in the sleeve and compact the material by applying a pressure of 48 to 51 MPa (7000 to 7500 psi) in a suitable press, and holding this pressure for 3 to 5 min. Remove the ring from the mortar and sleeve.

X1.1.3.5 Carefully and cleanly scrape off the excess of material remaining on the top surface of the ring until the top

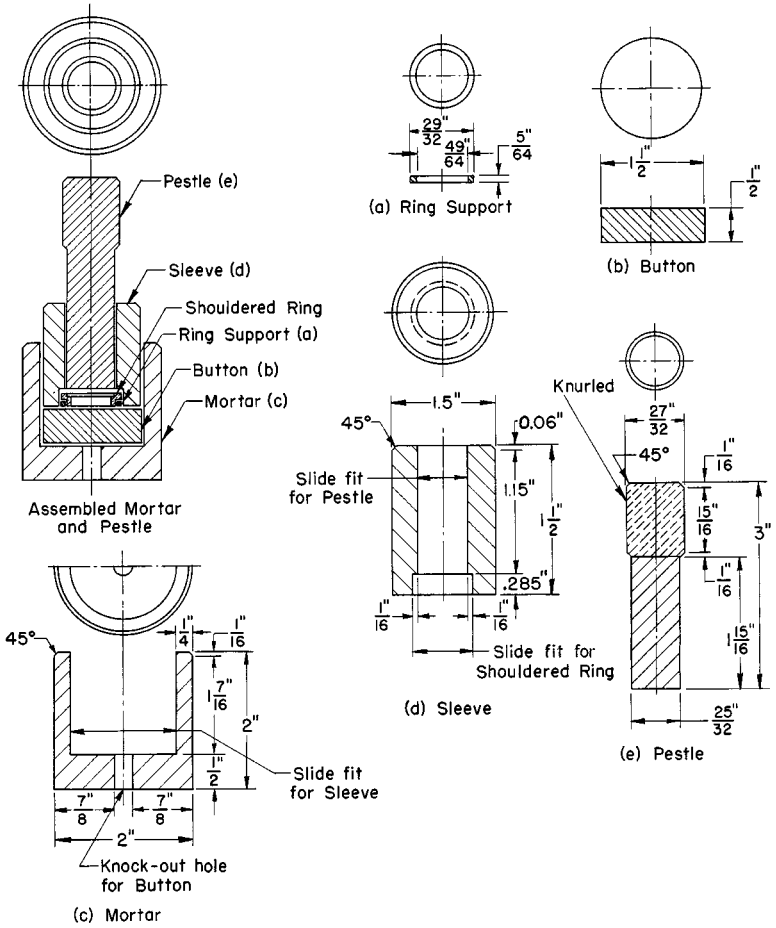

FIG. X1.1 Mortar and Pestle

of the sample is level with the ring. If the top and bottom surfaces of the sample in the ring are not smooth and level with the ring, discard, and repeat the compacting operation, using a clean ring and freshly pulverized material.