



Designation: D 1601 – 99

## Standard Test Method for Dilute Solution Viscosity of Ethylene Polymers<sup>1</sup>

This standard is issued under the fixed designation D 1601; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope \*

1.1 This test method covers the determination of the dilute solution viscosity of ethylene polymers at 135°C. It is applicable to a reasonably wide spectrum of ethylene polymers having densities from 0.910 to 0.970 g/cm<sup>3</sup>. Directions are given for the determination of relative viscosity (viscosity ratio), inherent viscosity (logarithmic viscosity number), and intrinsic viscosity (limiting viscosity number) (see Appendix X4).

1.2 The values as stated in SI units are to be regarded as the 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.*

NOTE 1—This test method is technically equivalent to ISO 1628-3.

NOTE 2—Appendix X1-Appendix X3 contain material from the previous version of Test Method D 1601 and are included for information only.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 86 Method for Distillation of Petroleum Products at Atmospheric Pressure<sup>2</sup>
- D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids<sup>2</sup>
- D 883 Terminology Relating to Plastics<sup>3</sup>
- D 1600 Terminology for Abbreviated Terms Relating to Plastics<sup>3</sup>
- D 4020 Specification for Ultra-High-Molecular Weight Polyethylene Molding and Extrusion Materials<sup>4</sup>
- E 1 Specification for ASTM Thermometers<sup>5</sup>
- IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System<sup>6</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.05).

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<sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 08.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 08.03.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.03.

<sup>6</sup> Annual Book of ASTM Standards, Vol 14.04.

#### 2.2 ISO Standards:<sup>7</sup>

ISO 1628-3 Plastics—Determination of Viscosity Number and Limiting Viscosity Number—Part 3: Polyethylenes and Polypropylenes

### 3. Terminology

3.1 Units, symbols, and abbreviations used in this test method are those recommended in IEEE/ASTM SI 10 and Terminologies D 883 and D 1600 (see also Appendix X4).

### 4. Significance and Use

4.1 The knowledge of dilute solution viscosity serves as an additional tool in characterizing ethylene polymers. Viscosity data alone may be of limited value in predicting the processing behavior of the polymer. However, when used in conjunction with other flow and physical property values, the solution viscosity of ethylene polymers may contribute to their characterizations.

4.2 Satisfactory correlation between solution viscosity and certain other properties is possible from polymers of a single manufacturing process. The solution viscosity test is not sensitive to some molecular configurational patterns that may occur among polymers from different manufacturing processes. Hence, its correlation with other properties of polymers produced by different processes, by even one manufacturer, may be limited.

4.3 The viscosity of polymer solutions may be drastically affected by the presence of known or unknown additives in the sample. The use of solution viscosity may be of questionable value where ethylene polymers are known or suspected to contain colorants, carbon black, low molecular weight hydrocarbons, fillers, or other additives.

4.4 The measurement of dilute solution viscosity of ethylene polymers presents problems not ordinarily encountered in viscosimetry. Ethylene polymers are not soluble at room temperature in any known solvent. Some of the higher density materials are insoluble below 100°C. Extreme care must be exercised in transferring the solution to the viscometer for the test if the correct solution concentration is to be maintained. This test has no significance unless the sample is completely soluble.

<sup>7</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

\*A Summary of Changes section appears at the end of this standard.

4.5 The solution viscosity is a function of the root-mean-square size of the polymer molecules in solution. It is known that the solvent selected and the temperature of the determination have an effect on the root-mean-square size of the particles. Hence, where a viscometer, solvent, or temperature other than specified is used, data may not be comparable to that obtained by this procedure.

## 5. Apparatus

5.1 *Volumetric Flasks*, 100-mL, grade EXAX or better.<sup>8</sup>

5.2 *Transfer Pipets*, Grade EXAX or better.<sup>8</sup>

5.3 *Constant Temperature Bath*, capable of maintaining  $135 \pm 10.1^\circ\text{C}$ .

5.4 *Viscometer*, Ubbelohde No. 1, calibrated for kinetic energy correction constant.

NOTE 3—Other types of viscometers may be used provided they can be shown to agree with the type specified.

5.5 *Oven*, maintained at  $140 \pm 5^\circ\text{C}$ .

5.6 *Timer*, as specified in 4.5 of Test Method D 445.

5.7 *Thermometer*—An ASTM High Softening Point Thermometer having a range from 30 to  $200^\circ\text{C}$ , and conforming to the requirements for Thermometer 16C in Specification E 1.

## 6. Reagents and Materials

6.1 *Solvent*—Decahydronaphthalene, practical grade, purified and redistilled, as follows:

6.1.1 The solvent shall be purified by percolation through 100 to 200 mesh commercial grade silica gel. This treatment removes naphthalene, tetrahydronaphthalene, and oxy compounds, particularly peroxides.

6.1.2 The redistilled product shall conform to the following requirements when tested in accordance with Method D 86:

| Standard Distillation | ASTM        |
|-----------------------|-------------|
| Initial boiling point | Method D 86 |
| 10 mL                 | 190°C min   |
| 20 mL                 | 191°C min   |
| 80 mL                 | 192°C min   |
| 90 mL                 | 194°C max   |
| Dry point             | 195°C max   |
|                       | 196°C max   |

NOTE 4—While use of other solvents, such as tetrahydronaphthalene or xylene, may sometimes be advantageous, they will generally yield different values for solution viscosities.

6.1.3 Immediately after redistillation of the decahydronaphthalene, add 0.2 % Tetrakis [methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate] methane to inhibit oxidation during the viscosity determination.

6.2 *Heat Transfer Medium*—Any liquid heat transfer medium that will not appreciably affect the accuracy of the test may be used. Care should be exercised in using fluids that discolor or smoke with prolonged heating.

NOTE 5—Silicone heat-transfer fluids are adequate for this use<sup>9</sup>.

## 7. Procedure

7.1 *Decahydronaphthalene Preparation*—Add 0.2 % weight/volume stabilizer (Irganox 1010 or equivalent), to the decahydronaphthalene, stir to dissolve, filter through fast filter paper, and store in a clean amber bottle.

7.2 *Cleaning the Viscometer*—Clean the viscometer thoroughly as follows: fill with cleaning solution, let stand overnight, empty and rinse several times with distilled water, then rinse with acetone and purge with dry nitrogen.

7.3 *Solution Preparation*—Weigh 20 to 30 mg of the UHMWPE (see Note 6) into the Erlenmeyer flask. Add the decahydronaphthalene at room temperature, using a burette to measure in milliliters a volume equal to 4.5 times the UHMWPE weight in milligrams (for example, 26 mg of UHMWPE and 117 ml of decahydronaphthalene). Heat the flask, with stirring, to  $150^\circ\text{C} \pm 2^\circ\text{C}$ . Continue stirring at  $150^\circ\text{C} \pm 2^\circ\text{C}$  for 1 h, with the flask lightly stoppered. Examine the flask to see if undissolved UHMWPE remains. If so, heat an additional 15 min and reexamine. Heat for an additional 15 min, if necessary, but do not heat longer than 2 h total.

7.4 *Viscosity Measurement:*

7.4.1 Place the clean viscometer into the constant-temperature bath. Fill the viscometer with decahydronaphthalene, and allow it and the solvent to equilibrate at  $135 \pm 0.1^\circ\text{C}$ . Measure the flow time of the solvent,  $t_0$ , three times, and average the results. The viscometer may have to be cleaned if replicate measurements of flow time differ by more than 0.3 s (see 7.4.3). Remove the decahydronaphthalene from the viscometer with vacuum and thoroughly rinse the viscometer with xylene at 110 to  $120^\circ\text{C}$  or decahydronaphthalene at  $135^\circ\text{C}$ . Remove the xylene or decahydronaphthalene with vacuum and aspirate dry air or nitrogen to dry the viscometer (2 or 3 min). It is essential that the viscometer be completely dry.

7.4.2 Transfer the hot ( $150^\circ\text{C}$ ) polymer solution to the viscometer with sufficient quantity to fill to the mark (see Note 7), allow to equilibrate at  $135^\circ\text{C} \pm 0.1^\circ\text{C}$ , and measure the flow time of the solution,  $t_s$ , in triplicate, and average the results.

7.4.3 Between uses, clean the viscometer by rinsing with hot xylene or decahydronaphthalene, drying with air or nitrogen, and storing filled with hot decahydronaphthalene. If solvent flow time changes by more than 0.3 s, or if difficulty is encountered in obtaining reproducible flow times with any solution or solvent, clean the viscometer with cleaning solution as described in 7.2.

NOTE 6—If the UHMWPE is suspected to contain moisture or other volatiles, it shall first be dried in a vacuum oven at  $60^\circ\text{C}$  for 2 h.

NOTE 7—Filling of the viscometer is made easier by the use of a glass funnel warmed with a heating mantle. This helps to prevent the UHMWPE solution from precipitating.

<sup>8</sup> Glassware used in this test method should be tested in accordance with the procedures described in the National Institute of Standards and Technology Circular No. C-434, "Testing of Glass Volumetric Apparatus," and should not exceed the limits of accuracy set forth in the circular.

<sup>9</sup> The silicone fluids available from the Dow Corning Corp., Midland, MI, or from the Union Carbide Corp., Linde Silicones Div., New York, NY, have been found satisfactory for this purpose.

## 8. Calculation

8.1 Calculate the relative solution viscosity as follows:

$$\eta_r = (t_s - k/t_s)/(t_o - k/t_o) \quad (1)$$

where:

$k$  = kinetic energy correction constant for the particular viscometer used,

$t_s$  = flow time of solution at 135°C (average of three measurements), and

$t_o$  = flow time of pure solvent at 135°C (average of three measurements).

## 9. Report

9.1 Report the following information:

9.1.1 Complete identification of the material tested including type, source, manufacturer's code numbers, and trade name.

9.1.2 Conditioning procedure used, if any.

9.1.3 The relative viscosity (viscosity ratio) of one or more concentrations, depending on whether it is desired to obtain relative, inherent, or intrinsic viscosity (viscosity ratio, logarithmic viscosity number, or limiting viscosity number) (see Appendix X4).

9.1.4 The intrinsic viscosity (limiting viscosity number), when desired, to three significant figures (see Appendix X4).

## 10. Precision and Bias

10.1 Table 1 is based on a round robin conducted in 1997 in

**TABLE 1 Relative Solution Viscosity**

| Material     | Average | $S_r^A$ | $S_R^B$ | $r^C$ | $R^D$ |
|--------------|---------|---------|---------|-------|-------|
| UHMWPE No. 1 | 1.454   | 0.015   | 0.049   | 0.042 | 0.136 |
| UHMWPE No. 2 | 1.653   | 0.017   | 0.048   | 0.047 | 0.136 |

<sup>A</sup> $S_r$  = within-laboratory standard deviation for the indicated material. It is obtained by first pooling the within-laboratory standard deviations of the test results from all of the participating laboratories.

$$S_r = [ \{ (s_1)^2 + (s_2)^2 + \dots + (s_n)^2 \} / n ]^{1/2}$$

<sup>B</sup> $S_R$  = between-laboratory reproducibility, expressed as standard deviation:

$$S_R = [ S^2 + S_L^2 ]^{1/2}$$

where  $S_L$  = standard deviation of laboratory means.

<sup>C</sup> $r$  = within-laboratory critical interval between two test results =  $2.8 \times S_r$ .

<sup>D</sup> $R$  = between laboratories critical interval between two test results =  $2.8 \times S_R$ .

accordance with Practice E 691, involving two materials tested by six laboratories. One laboratory distributed the two commercial UHMWPE samples chosen for the evaluation. Each laboratory obtained six test results for each material.

**NOTE 8—Caution:** The explanations of  $r$  and  $R$  (10.1.1-10.1.4) are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be applied to acceptance or rejection of materials, as these data apply only to the materials tested in the round robin and are unlikely to be representative of other lots, formulations, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their materials and laboratory (or between laboratories). The principles of 10.1.1-10.1.4 would then be valid for such data.

10.1.1 *Concept of  $r$  and  $R$  in Table 1*—If  $S_r$  and  $S_R$  have been calculated from a large enough body of data, and for test results from testing one sample for each test result, then the following applies:

10.1.2 *Repeatability*— $r$  is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory. Two test results shall be judged not equivalent if they differ by more than the  $r$  value for the material.

10.1.3 *Reproducibility*— $R$  is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories, not necessarily on the same day. Two test results shall be judged not equivalent if they differ by more than the  $R$  value for that material.

10.1.4 Any judgement in accordance with 10.1.2 and 10.1.3 would have an approximate 95 % (0.95) probability of being correct.

10.2 *Bias*—There are no recognized standards by which to estimate bias of this method.

## 11. Keywords

11.1 dilute solution viscosity; ethylene polymers; inherent viscosity (logarithmic viscosity number); intrinsic viscosity (limiting viscosity number); reduced viscosity (viscosity number); relative viscosity; specific viscosity; viscosity ratio

## APPENDIXES

### (Nonmandatory Information)

#### X1. PROCEDURE FROM PREVIOUS VERSION (D 1601 – 86 (1991)<sup>e1</sup>) DATING BACK TO 1957

X1.1 If it is desired to determine only the relative viscosity (viscosity ratio) or the inherent viscosity (logarithmic viscosity number), weigh one specimen of 0.18 to 0.22 ± 0.0002 g and transfer it quantitatively to a 100-mL volumetric flask which has been purged with nitrogen.

**NOTE X1.1**—Usually the determination of relative or inherent viscosity (viscosity ratio or logarithmic viscosity number) may suffice.

X1.2 To determine the intrinsic viscosity (limiting viscosity number), weigh four specimens of the following approximate

weights to ± 0.0002 g:

|            |                |
|------------|----------------|
| Specimen 1 | 0.09 to 0.11 g |
| Specimen 2 | 0.18 to 0.22 g |
| Specimen 3 | 0.28 to 0.32 g |
| Specimen 4 | 0.38 to 0.42 g |

**NOTE X1.2**—The intrinsic viscosity (limiting viscosity number) may also be measured using successive dilutions of only one, or duplicate, solutions. This has the advantage of requiring that only one polymer specimen be weighed. Dilutions to the solution of this specimen in the viscometer are a time-saving device. The technique is as follows: Weigh one, or a duplicate, specimen of 0.38 to 0.42 g to an accuracy of ±0.0002