Designation: ~~D1601 – 12~~ D1601 – 18

Standard Test Method for Dilute Solution Viscosity of Ethylene Polymers[1]

This standard is issued under the fixed designation D1601; 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 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^2. Directions are given for the determination of relative viscosity (viscosity ratio), inherent viscosity (logarithmic viscosity number), and intrinsic viscosity (limiting viscosity ~~number) (see~~ number).~~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.*~~

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.3.1 **Warning—***Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.*

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

NOTE 2—Appendix X1 – Appendix X3 contain material from the previous version of Test Method D1601 and are included for information only.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

~~D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure~~

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)

D446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers

D883 Terminology Relating to Plastics

D1600 Terminology for Abbreviated Terms Relating to Plastics

D4020 Specification for Ultra-High-Molecular-Weight Polyethylene Molding and Extrusion Materials

~~E1~~E2251 Specification for ~~ASTM Liquid-in-Glass Thermometers~~Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

E2935 Practice for Conducting Equivalence Testing in Laboratory Applications

IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System

2.2 *ISO Standards:*[3]

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

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.05).

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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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

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

3. Terminology

3.1 Units, symbols, and abbreviations used in this test method are those recommended in IEEE/ASTM SI-10 and Terminologies D883 and D1600~~ (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~~is potentially a 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.~~contributes to characterizing the material.

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.~~is limited without structural characterization.

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

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.

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 in this standard is used, the data ~~may~~ is likely not ~~be~~ comparable to that obtained by this procedure.

5. Apparatus

5.1 ~~*Volumetric Flasks,*~~ *Burets,* ~~100-mL, grade EXAX or better.~~(specifications).

5.2 ~~*Transfer Pipets,*~~*Erlenmeyer flask,* ~~Grade EXAX or better.~~250 mL with stopper.

5.3 *Constant Temperature Bath,* capable of maintaining 135 ± l0.1°C.

5.4 *Viscometer,* Ubbelohde Size 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 ± 5°C.

5.6 *Timer,* as specified in 4.5 of Test Method D445.

5.7 *Thermometer*—An ASTM High Softening Point Thermometer having a range from 30 to 200°C, and conforming to the requirements for Thermometer 16C in Specification ~~E1~~E2251. Thermometric devices such as resistance temperature detectors (RTDs), having accuracies equal to or better than Thermometer 16C in the specified temperature range are also appropriate for use.

6. Reagents and Materials

6.1 *Solvent*—~~*Decahydronaphthalene,*~~*Decahydronaphthalene (Decalin) CAS # 97-17-8,* 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 D86:~~

~~Standard Distillation~~	~~ASTM Method D86~~
~~Initial boiling point~~	~~190°C min~~
~~10 mL~~	~~191°C min~~
~~20 mL~~	~~192°C min~~
~~80 mL~~	~~194°C max~~
~~90 mL~~	~~195°C max~~
~~Dry point~~	~~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.~~

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.

6.1.2 Immediately after redistillation of the decahydronaphthalene, add 0.2 % Tetrakis [methylene 3-(3',5'-di-tert-butyl-4'-hydroxphenyl) 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~~ is recommended. Use caution when using fluids that discolor or smoke with prolonged heating.

NOTE 5—Silicone heat-transfer fluids are adequate for this use[4].

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,~~ before use, and store in a clean amber bottle.

7.2 *Cleaning the Viscometer*—Clean the viscometer thoroughly as follows: fill with appropriate 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—~~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°C ± 2°C. Continue stirring at 150°C ± 2°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.~~

7.3.1 *Polyolefins other than UHMWPE*—The polymer concentration that gives a relative viscosity of the solution between 1.2 and 2.0. Weigh an appropriate amount of polymer to the nearest 0.0001 g into the Erlenmeyer flask. Typically an appropriate weight is between 0.1 and 0.5 g, depending on the molecular weight Add 100 mL of decahydronaphthalene at room temperature. Heat the flask, with stirring, to 150°C ± 2°C. Continue stirring at 150°C ± 2°C for 1 h, with the flask lightly stoppered. Examine the flask to see if undissolved polyolefin 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.

7.3.2 *UHMWPE*—Weigh 20 to 30 mg of the UHMWPE (see Note 6) into an appropriate 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°C ± 2°C. Continue stirring at 150°C ± 2°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 ± 0.1°C. Measure the flow time of the solvent, t_o, three times, and average the results. The viscometer ~~may have~~ needs 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°C or decahydronaphthalene at 135°C. Remove the xylene or decahydronaphthalene ~~with vacuum~~ and aspirate dry air or nitrogen to dry the viscometer (2 or 3 min). If needed, rinse the viscometer with a lower boiling nonpolar solvent to enhance drying. It is essential that the viscometer be completely dry.

7.4.2 Transfer the hot (150°C) polymer solution to the viscometer with sufficient quantity to fill to the mark (see Note 7), allow to equilibrate at 135°C ± 0.1°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°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. Stainless steel mesh folded into a cone may be used to filter the solutions during loading.

8. Calculation

8.1 Calculate the relative solution viscosity as follows:

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

$$\eta_r = (t_s - k/t_s^2)/(t_o - k/t_o^2) \qquad (1)$$

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

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[4] 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.

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~~ number).~~Appendix X4).~~

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

10. Precision and Bias

10.1 Table 1 is based on a round robin conducted in 1997 in accordance with Practice E691, 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. (**Warning—**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 E691 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.)

~~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 E691 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*—~~*Repeatability Limit, r*—~~r~~The ~~is the interval representing the critical~~ value below which the absolute difference between two individual 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~~ obtained under repeatability conditions may be expected to occur with a probability of approximately 0.95 (95 %).~~r value for the material.~~

10.1.3 ~~*Reproducibility*—~~*Reproducibility Limit, R*—~~R~~The ~~is the interval representing the critical~~ value below which the absolute difference between two individual 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~~ obtained under reproducibility conditions may be expected to occur with a probability of approximately 0.95 (95 %).~~R value for that material.~~

10.1.4 ~~Any judgement~~ When required, conducting equivalence testing on numerical data from two sources shall be conducted in accordance with ~~10.1.2~~E2935 ~~and~~or ~~10.1.3 would have an approximate 95 % (0.95) probability of being correct.~~any known method for judging the equivalence of two means, for example, a t-test.

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

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

[A] 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.

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

[B] S_R = between-laboratory reproducibility, expressed as standard deviation:

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

where S_L = standard deviation of laboratory means.

[C] r = within-laboratory critical interval between two test results = 2.8 × S_r.

[D] R = between laboratories critical interval between two test results = 2.8 × S_R.