Designation: D6703 – 19

Standard Test Method for Automated Heithaus Titrimetry[1]

This standard is issued under the fixed designation D6703; 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 describes a procedure for quantifying three Heithaus compatibility parameters that quantify the colloidal stability of asphalts and asphalt cross blends and aged asphalts.

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

1.3 The text of this standard references notes and footnotes which provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered as requirements of the standard.

1.4 *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.*

1.5 *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]

D8 Terminology Relating to Materials for Roads and Pavements

D3279 Test Method for *n*-Heptane Insolubles

D3666 Specification for Minimum Requirements for Agencies Testing and Inspecting Road and Paving Materials

D4124 Test Method for Separation of Asphalt into Four Fractions

D8055 Guide for Selecting an Appropriate Electronic Thermometer for Replacing Mercury Thermometers in D04 Road and Paving Standards

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

E563 Practice for Preparation and Use of an Ice-Point Bath as a Reference Temperature

E644 Test Methods for Testing Industrial Resistance Thermometers

3. Terminology

3.1 Refer to Terminology D8 for definitions of terms relating to materials for roads and pavements.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *asphaltene peptizability, n*—the tendency of asphaltenes to exist as a stable dispersion in a maltene solvent, measured by the Heithaus parameter p_a.

3.2.2 *asphalt state of peptization, n*—a measure of the ability of the combination of a maltene solvent and dispersed asphaltenes to form a stable dispersed system.

3.2.3 *colloidal suspension, n*—an intimate mixture of two substances, one of which, called the dispersed phase (or colloid), is uniformly distributed in a finely divided state through the second substance, called the dispersion medium (or dispersing medium).

3.2.4 *compatibility, n*—the state of peptization of an asphalt, which is measured quantitatively by the Heithaus parameter *P*.

3.2.5 *dispersed phase, n*—one phase of a dispersion consisting of particles or droplets of one substance distributed through a second phase.

3.2.6 *dispersing medium, n*—one phase of a dispersion that distributes particles or droplets of another substance, the disperse phase.

3.2.7 *flocculation, n*—the process of aggregation and coalescence into a flocculent mass. See Test Method D3279.

3.2.8 *Heithaus compatibility parameters, n*—three parameters: asphaltene peptizability (p_a), maltene peptizing power (p_o), and asphalt state of peptization (P), measured using Heithaus titration methods.

3.2.9 *maltene peptizing power, n*—the ability of a maltene solvent to disperse asphaltenes, measured by the Heithaus parameter p_o.

[1] This test method is under the jurisdiction of ASTM Committee D04 on Road and Paving Materials and is the direct responsibility of Subcommittee D04.47 on Miscellaneous Asphalt Tests.

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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.

4. Summary of Test Method

4.1 Three 40-mL reaction vials shall be tared (Fig. 1). Three samples of asphalt of weights 0.400 g, 0.600 g, and 0.800 g shall be transferred to each of three reaction vials. Toluene (3.000 mL) shall be added to each reaction vial to dissolve the asphalt constituting three solutions which differ by concentration. Each solution is titrated with isooctane (2,2,4-trimethyl pentane) to promote onset of flocculation of the solution.

4.2 Titrations are performed by placing reaction vials separately in the apparatus illustrated in Fig. 2. Each reaction vial is separately placed into a 250-mL water-jacketed reaction vessel. A sample circulation loop is made by pumping the solution through a short path length quartz flow cell housed in an ultraviolet-visible spectrophotometer then back to the reaction vial with high flow rate metering pump. A titration loop is made by pumping titrant into the sample reaction vial at a constant flow rate using a low flow rate metering pump, thus a second reaction vessel containing titrant is placed into a second 250-mL water-jacketed reaction vessel. During a titration the output signal from a spectrophotometer is recorded using a data acquisition system (computer) to record the change in percent transmittance $\%T$ of detected radiation at 740 nm plotted as a function of time t (Fig. 3), as the titrated solution passes through a quartz flow cell.

4.3 The spectrophotometer output signal measures turbidity of the sample solution as a titration experiment proceeds to a flocculation onset point, corresponding to the onset of flocculating asphaltene phase separating from the solution. Fig. 3 illustrates a plot of $\%T$ versus t for three test solutions. Values of $\%T$ increase with time up to the flocculation onset point, after which values of $\%T$ decrease with time. The time required to reach flocculation onset t_f multiplied by the titrant flow rate gives the titrant flocculation volume V_T.

4.4 The measured weight of each asphalt sample, W_a, the volume of toluene initially used to dissolve each sample, V_S, and the volume of titrant at onset of flocculation, V_T, shall be used as the input data required to calculate compatibility parameters.

5. Significance and Use

5.1 This test method is intended as a laboratory diagnostic tool for estimating the colloidal stability of bitumen asphalt,

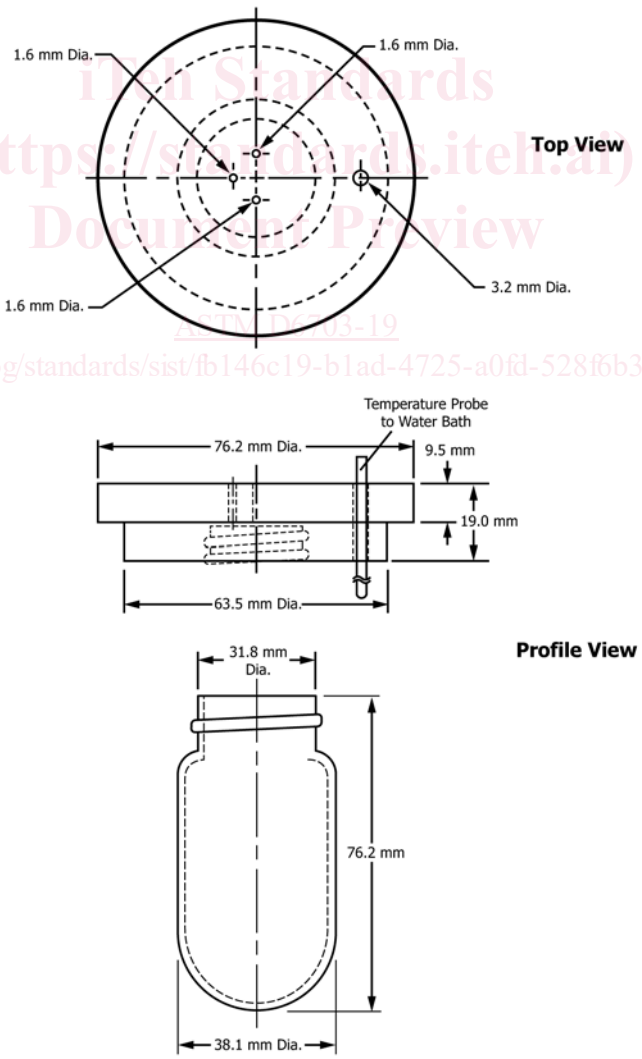

FIG. 1 Reaction Vial (40 mL) with TFE-fluorocarbon Cover and Temperature Probe

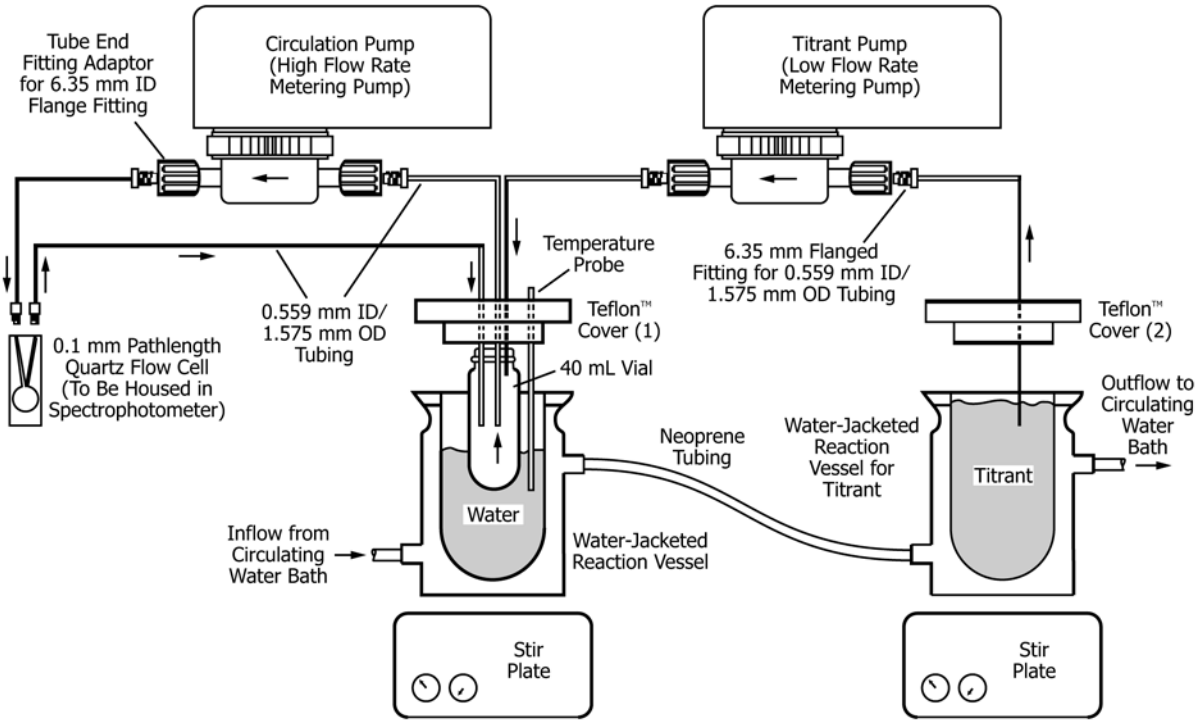

FIG. 2 Automated Titration Apparatus

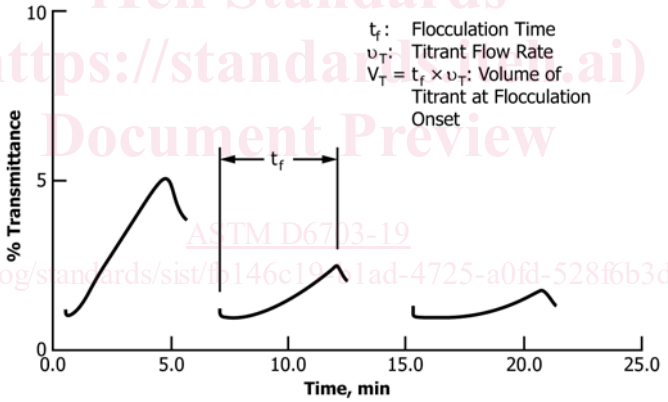

FIG. 3 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

asphalt cross blends, aged asphalt, and heavy oil residuum. Historically, bituminous asphalt and heavy oil residua have been modeled as colloidal suspensions in which a polar associated asphaltene moiety (the dispersed phase) is suspended in a maltene solvent moiety (the dispersing medium) (refer to Test Methods D3279 and D4124 for further definition of asphalt fraction materials). The extent to which these two moieties remain in state of peptization is a measure of the compatibility (colloidal stability) of the suspension. Compatibility may influence the physical properties of these materials, including rheological properties, for example, phase angle and viscosity. This test method and other similar test methods, along with the classical Heithaus test, may be recommended as a measure of the overall compatibility of a colloidal system by determining a parameter referred to as the state of peptization, *P*. The value of *P* commonly varies between 2.5 to 10 for unmodified or neat asphalts. Materials calculated to have low values of *P* are designated incompatible. Materials calculated to have high *P* values are designated compatible. Values in *P* are calculated as a function of two parameters that relate to the peptizability of the asphaltene moiety (the asphaltene peptizability parameter, p_a) and the solvent power of the maltene moiety (the maltene peptizing power parameter, p_o). Values of p_a and p_o are calculated as functions of the quantities C_{min} and FR_{max}. Values of C_{min} and FR_{max} are determined from experimental variables, the weight of asphalt (W_a), the volume of solvent (V_S) to dissolve the weight of asphalt, and the volume of titrant (V_T) added to initiate flocculation.

6. Apparatus

6.1 *UV-Visible Spectrophotometer,* shall have a wavelength scanning range from 200 to 1000 nm, with adjustable aperture or attenuator.

6.2 *Digital Acquisition System (computer).*

6.3 *Water-Jacketed Reaction Vessel,* shall be of volume: 250 mL, two.

6.4 *TFE-Fluorocarbon Covers,* two.

6.4.1 *TFE-Fluorocarbon Cover No. 1,* (see Fig. 1), shall be threaded to hold a 40-mL reaction vial. Three holes, 1.5-mm diameter, concentric to the cover's center shall be tapped to set within the inside diameter of the vial when attached to the TFE-fluorocarbon cover. One additional hole, 3.0 mm, shall be tapped off center, positioned just to the outside of where the reaction vial is positioned in the TFE-fluorocarbon cover. This hole shall allow for a temperature probe (refer to Guide D8055, Practice E563, and Test Methods E644) to be inserted into the water-filled reaction vessel.

6.4.2 *TFE-Fluorocarbon Cover No. 2,* may be used as a lid for the second 200-mL water-jacketed reaction vessel, containing titrant. Dimensions: thickness, 2.0 mm; diameter, 70 mm. One hole 1.5 mm in diameter tapped through the cover's center. This cover shall be identical to the cover described in 6.4.1 except for the number of holes, and should be threaded to hold a second 40-mL reaction vial as a titration reservoir.

6.5 *High Flow Rate Metering Pump,* shall have a flow rate range from 0.5 to 10.0 mL/min; flow rate consistency, ±0.1 mL/min; and piston chamber resistant to damage from solvent contact.

6.6 *Low Flow Rate Metering Pump,* shall have a flow rate range from 0.100 to 1.000 mL/min; flow rate consistency, ±0.002 mL/min; and piston chamber resistant to damage from solvent contact.

6.7 *Magnetic Stirring Plates,* two.

6.8 *Refrigerated Water Bath Circulator,* shall have a temperature variation of ±0.1 °C and temperature range from 0 °C to 100 °C.

6.9 *Quartz Flow Cell,* shall have a 0.20-mm path length[3] with 6.35-mm flanged fittings.

6.10 *TFE-Fluorocarbon Tubing,* shall have a 0.559-mm inside diameter/1.575-mm outside diameter.

6.11 *Reaction Vials,* shall be of a 40-mL volume capacity.

6.12 *"4-hole" TFE-Fluorocarbon Cover and "1-hole" TFE-Fluorocarbon Cover.*

6.13 *TFE-fluorocarbon-Coated Magnetic Stir Bars.*

6.14 *Stopwatch.*

6.15 *Syringe,* shall be 5.000 mL, glass, gas-sealed, and resistant to solvents toluene and n-heptane.

6.16 *TFE-Fluorocarbon Tube Fittings (4),* which shall include standard 6.35-mm flanged fittings for 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing.

6.17 *Neoprene Tubing,* shall be 13 mm inside diameter.

6.18 *Tubing Clamps,* shall be sized to fit 13-mm inside diameter tubing.

6.19 *Thermometer,* shall be a platinum resistance thermometer (PRT) readable to the nearest 0.1 °C, with a Pt 100 Class AA tolerance rating with probe length >80 mm, and probe diameter 3.0 mm. Standardize the PRT system (probe and readout device) in accordance with Test Methods E644. Corrections shall be applied to ensure accurate measurements within 0.1 °C (shall be calibrated to ±0.1 °C, and shall conform to Guide D8055, Practice E563, and Test Methods E644).

6.20 *Graduated Cylinders,* two. Shall be of volumes: 1.000 ± 0.001 mL and 10.0 ± 0.1 mL.

6.21 *Argon Gas Supply.*

6.22 *Laboratory Jacks*—Laboratory jacks may be used as stands for metering pumps.

6.23 *Beakers,* two. Shall be of volume: 500 mL.

6.24 *Polypropylene Rinse Bottles,* two. Shall be of volume: 200 mL.

6.25 *TFE-Fluorocarbon Lined Caps,* shall be 40-mL reaction vials.

7. Reagents

7.1 *Purity of Reagents*—HPLC-grade chemicals should be used in all sample preparations and 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.[4] 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.

7.2 *Isooctane* (2,2,4-trimethylpentane), HPLC grade.

7.3 *Toluene,* HPLC grade.

7.4 *Toluene,* reagent grade.

8. Assembly

8.1 *Installation Requirements:*

8.1.1 The following assembly should be conducted in a fume hood. The fume hood should be of sufficient size to accommodate all pieces of the apparatus and supplies needed to perform the test method.

8.1.2 The fume hood should be equipped with a pump or house vacuum line for the assembly of a vacuum trap, used during the procedural cleanup step (see 10.2.8).

8.2 *Assembly* (Fig. 2):

8.2.1 *Circulation Loop Assembly*—A sample (circulation loop) is assembled using a high flow rate metering pump

[3] The sole source of supply of the apparatus known to the committee at this time is Starna Cells, Inc. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[4] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.