Designation: D6703 – 13

StandardTest 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 *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]

D3279 Test Method for*n*-Heptane Insolubles

D4124 Test Method for Separation of Asphalt into Four Fractions

D5546 Test Method for Solubility of Asphalt Binders in Toluene by Centrifuge

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *asphalt binder, n*—asphalt which may or may not contain an asphalt modifier (see **asphalt modifier**).

3.1.1.1 *Discussion*—This term is often used in the Performance Graded Binder system.

3.1.2 *asphalt cross-blend, n*—any mixture of two or more asphalts blended together to form a consistent material.

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

3.1.4 *asphaltene, n*—insoluble fractions of asphalt that are precipitated by use of selected solvents, such as n-heptane.

3.1.5 *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.

3.1.6 *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).

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

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

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

3.1.10 *flocculation, n*—the process of aggregation and coalescence into a flocculent mass.

3.1.11 *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.

3.1.12 *maltene, n*—soluble fractions of asphalt that are recovered from an eluate by use of selected solvents, such as n-heptane.

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

4. Summary of Test Method

4.1 Three 40 mL reaction vials are tared. Three samples of asphalt of weights 0.400 g, 0.600 g and 0.800 g are transferred to each of three reaction vials. Toluene (3.000 mL) is added to each reaction vial to dissolve the asphalt constituting three solutions which differ by concentration. Each solution is

[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.

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. 1. Each reaction vial is separately placed into a 250 mL water-jacketed reaction vessel (Fig. 1) to provide temperature control of the system. The 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 second reaction vessel is filled with titrant is placed into a second 250 mL water-jacketed reaction vessel. 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. During a titration the output signal from the spectrophotometer is recorded using a Data acquisition system (computer) to record the change in percent transmittance (*%T*) of detected radiation at 740 nm passing through the quartz cell plotted versus time, *t*, during which the titrant.

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. 2 illustrates a plot of *%T* versus *t* for three test solutions. Values of *%T* are observed to increase with time to the flocculation onset point, after which values of *%T* are observed to decrease. The time required to reach flocculation onset t_f multiplied by the titrant flow rate gives the titrant flocculation volume V_T.

4.4 Given the weights 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, values of *C* referred to as the dilution concentration and *FR* referred to as the flocculation ratio are calculated as $C = W_a/(V_S + V_T)$ and $FR = V_S/(V_S + V_T)$. Values of *C* plotted along an *x*-axis versus *FR* plotted along a *y*-axis result in a linear regression line (Fig. 3). This line is extrapolated to both axes. The point at which the line intercepts the *x*-axis is defined as C_{min}. The point at which the line intercepts the *y*-axis is defined as FR_{max}. These two values are used to calculate the three Heithaus compatibility parameters, designated p_a, p_o, and *P*. The parameter p_a, the peptizability of asphaltenes, is defined as the quantity $(1 - FR_{max})$. The parameter p_o, the peptizing power of maltenes, is defined as the quantity FR_{max} $[(1/C_{min}) + 1]$. The parameter *P*, the overall compatibility of the system, is defined as $[p_o/(1 - p_a)]$, or $(1/C_{min} + 1)$.

5. Significance and Use

5.1 This test method is intended primarily as a laboratory diagnostic tool for estimating the colloidal stability of bitumen asphalt, 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, D4124, and D5546 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 influences 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, measures the overall compatibility of a colloidal system by determining a

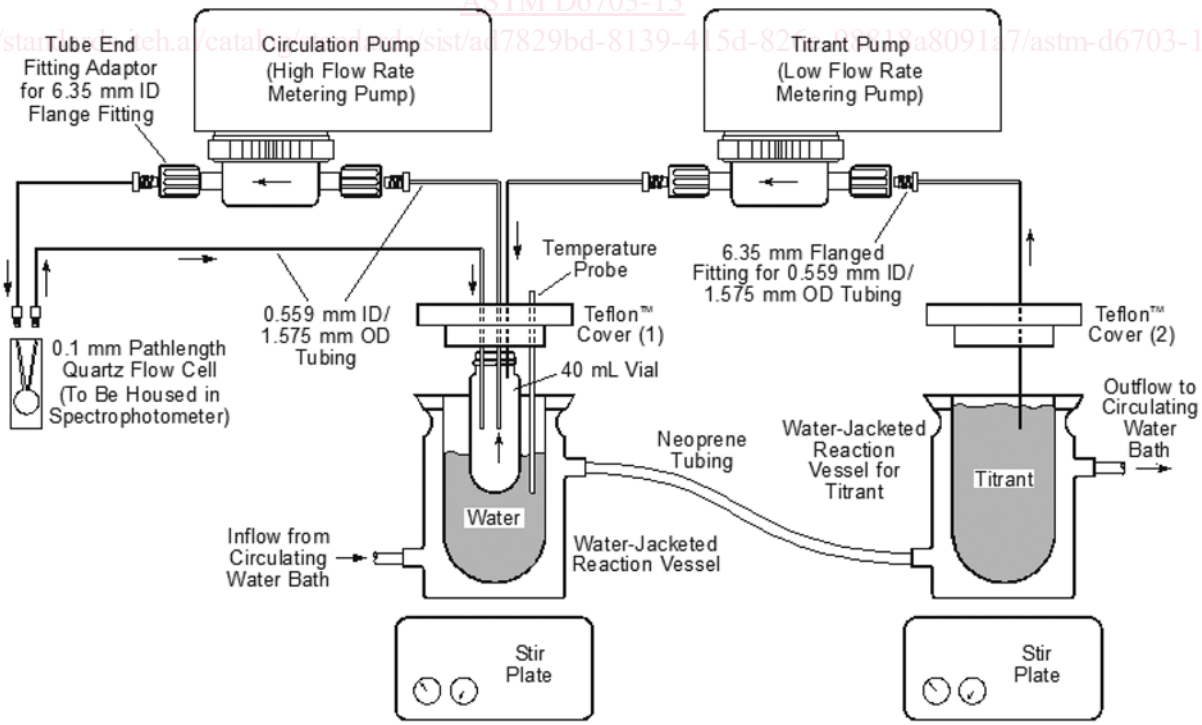

FIG. 1 Automated Titration Apparatus

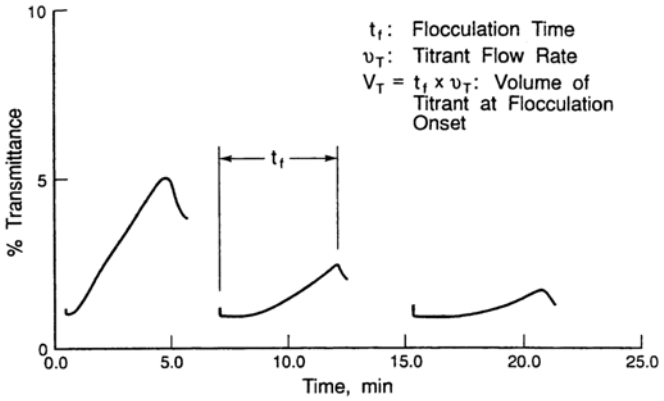

FIG. 2 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

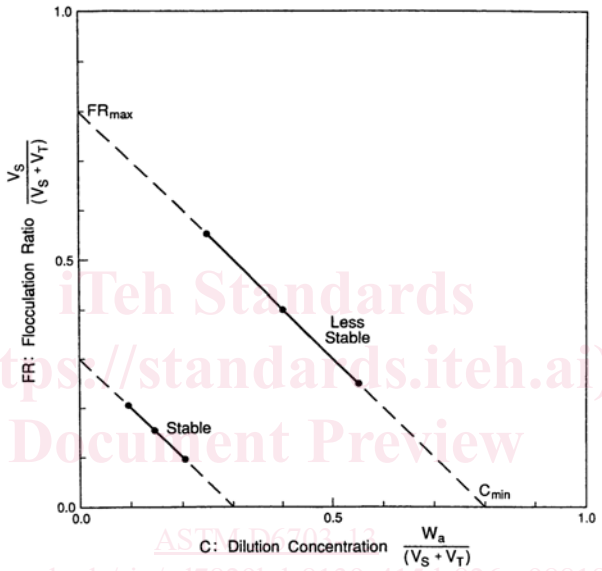

FIG. 3 Flocculation Ratio Versus Dilution Concentration for One Stable Asphalt and One Less Stable Asphalt

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,* 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,* 250-mL, two.

6.4 *TFE-fluorocarbon Covers,* two.

6.4.1 *TFE-fluorocarbon Cover No. 1,* (see Fig. 4), threaded to hold a 40 mL reaction vial. Three holes, 1.5 mm diameter, concentric to the cover's center are tapped to set within the inside diameter of the vial when attached to the TFE-fluorocarbon cover,. One additional hole, 3.0 mm, is tapped off center, positioned just to the outside of where the reaction vial is positioned in the TFE-fluorocarbon cover. This hole allows the temperature probe to be inserted into the water-filled reaction vessel.

6.4.2 *TFE-fluorocarbon Cover No. 2,* 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 is identical to the cover described in 6.4.1 except for the number of holes, and is not threaded.

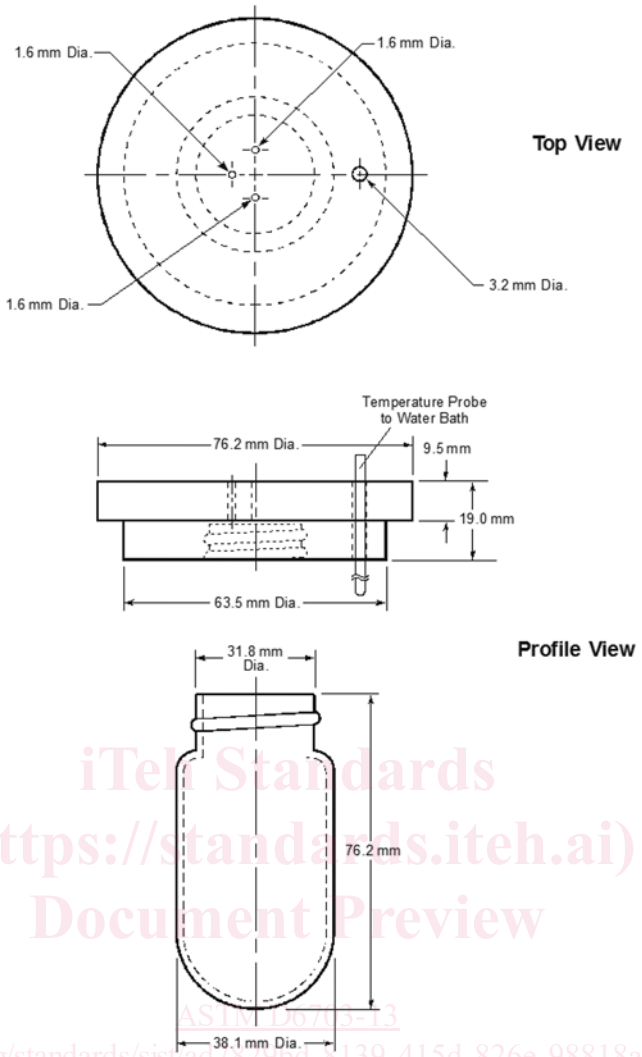

FIG. 4 Reaction Vial (30 mL) with TFE-fluorocarbon Cover and Temperature Probe

6.5 *High Flow Rate Metering Pump*—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*—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*—Temperature variation, ±0.1°C; temperature range from 0 to 100°C.

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

6.10 *TFE-fluorocarbon Tubing,* 0.559 mm inside diameter/1.575 mm outside diameter.

6.11 *Reaction Vials,* 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,* 5.000 cc, glass, gas-sealed, and resistant to solvents that it will be used to sample.

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

6.17 *Neoprene Tubing,* 13 mm inside diameter.

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

6.19 *Digital Probe Thermometer,* °C (calibrated to ±0.2°C). Probe length, >80-mm, probe diameter, 3.0 mm.

[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.