Designation: D 6556 – 03

Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption[1]

This standard is issued under the fixed designation D 6556; 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 total surface area by the Brunauer, Emmett, and Teller (B.E.T. NSA) theory of multilayer gas adsorption behavior using multipoint determinations and the external surface area based on the statistical thickness surface area method.

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 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.* (The minimum safety equipment should include protective gloves, sturdy eye and face protection).

2. Referenced Documents

2.1 *ASTM Standards:*

D 1799 Practice for Carbon Black—Sampling Packaged Shipments[2]

D 1900 Practice for Carbon Black—Sampling Bulk Shipments[2]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

3. Summary of Test Method

3.1 The total and external surface areas are measured by evaluating the amount of nitrogen adsorbed, at liquid nitrogen temperature, by a carbon black at several partial pressures of nitrogen. The adsorption data is used to calculate the NSA and STSA values.

4. Significance and Use

4.1 This test method is used to measure the total and external surface area of carbon blacks based on multipoint nitrogen adsorption. The NSA measurement is based on the B.E.T. theory and it includes the total surface area, inclusive of micropores, pore diameters less than 2 nm (20 Å). The external surface area, based on the statistical thickness method (STSA), is defined as the specific surface area that is accessible to rubber.

5. Apparatus

5.1 *Multipoint Static-Volumetric Gas Adsorption Apparatus*, with Dewar flasks and all other accessories required for operation.

5.2 *Sample Cells* that, when attached to the adsorption apparatus, will maintain isolation of the sample from the atmosphere equivalent to a helium leak rate of $<10^{-5}$ cm^3/min, per atmosphere of pressure difference.

5.3 *Balance, Analytical*, with 0.1 mg sensitivity.

5.4 *Heating Mantle or Equivalent*, capable of maintaining a temperature of 300 ± 10°C.

5.5 *Oven, Gravity Convection*, capable of maintaining a temperature of 125 ± 10°C.

6. Reagents

6.1 *Liquid nitrogen*, 98 % or higher purity.

6.2 *Ultra-high purity nitrogen gas*, cylinder or other source of prepurified nitrogen gas.

6.3 *Ultra-high purity helium gas*, cylinder or other source of prepurified helium gas.

7. Sampling

7.1 Samples may be taken in accordance with Practice D 1799 and Practice D 1900.

8. Sample Preparation Procedure

8.1 Dry a portion of carbon black at 125°C for 1 h. If the carbon black is known to be substantially free of moisture, or subsequent preparation steps are known to be adequate for moisture removal, then this step may be omitted.

8.2 Condition an empty sample cell for a minimum of 10 minutes at the same conditions intended for degassing the sample. Weigh the empty sample cell to the nearest 0.1 mg and record the mass.

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[1] This test method is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.21 on Adsorptive Properties of Carbon Black.

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[2] *Annual Book of ASTM Standards*, Vol 09.01.

8.3 Weigh approximately 0.4 g of the carbon black into the sample cell.

NOTE 1—For carbon black powder samples, add enough carbon black to give a depth of approximately 2 in. in straight wall sample tubes, or approximately 0.4 g for bulb-type sample cells.

8.4 *Flow Degassing*:

8.4.1 Open the gas control valve and insert the delivery tube into the sample tube, and allow purging with either helium or nitrogen for a minimum of 1 min.

8.4.2 Place a heating mantle or other source of heat around the sample cell and degas the sample at 300 ± 10°C for ½ h or longer to ensure that all traces of moisture condensing in the top of the tube are absent. The minimum degassing time that gives a stable surface area (that is, a surface area that does not increase with additional degassing) may be used for degassing.

8.4.3 Once the typical degassing times have been determined, future samples can be degassed on the basis of time alone, if desired, allowing a reasonable margin of excess time. Some samples will be found to require less than ½ h, especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for degassing.

8.4.4 After degassing, the sample tube may be moved directly to the analyzer. Otherwise, remove the sample tube from the heat source and continue the flow of purging gas until it is ready for analysis.

8.4.5 Go directly to Section 9 and continue the remaining steps of the procedure.

8.5 *Vacuum Degassing*:

8.5.1 With the apparatus at atmospheric pressure, place the sample cell containing the carbon black onto the degassing apparatus.

8.5.2 Begin the degassing procedure as appropriate for the apparatus.

8.5.3 Place a heating mantle or other source of heat around the sample cell and degas the sample at 300 ± 10°C for ½ h or longer as required to obtain and hold a pressure less than 1.4 Pa (10 µm Hg).

8.5.4 Once the typical degassing times have been determined, future samples can be degassed on the basis of time alone, if desired, allowing a reasonable margin of excess time. Some samples will be found to require less than ½ h, especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for degassing.

8.5.5 Go directly to Section 9 and continue the remaining steps of the procedure.

9. Measurement Procedure

9.1 Refer to the user's manual or specific instructions for the multipoint gas adsorption analyzer to be used, and become thoroughly familiar with the procedures.

9.2 Fill the Dewar with liquid nitrogen and allow it to reach temperature equilibrium, preferably 0.5 to 1 h.

9.3 Accurately determine the saturation pressure of the liquid nitrogen bath by running replicate determinations until two consecutive saturation pressure values agree within 0.13 kPa (1 mm Hg).

9.4 Determine the free space of the sample cell by measurement with helium or by calculation using an assumed carbon black density of 1.9 g/cm^3.

9.5 Obtain a minimum of five data points evenly spaced in the 0.1 to 0.5 relative pressure (P/P_o) range. For some tread carbon blacks, particularly N100 and N200 series, it is necessary to measure two additional data points, 0.05 and 0.075, in order to increase the accuracy of the NSA measurement. A data point consists of the relative pressure of equilibrium and the total amount of nitrogen gas adsorbed by the sample at that relative pressure.

9.6 Determine the mass of the cell with dry sample to the nearest 0.1 mg. This may be done before or after measuring nitrogen adsorption. Avoid inconsistent use of helium, as a buoyancy error of 1 mg/cm^3 of cell volume can occur. As an alternative, the carbon black mass may be determined directly by pouring it from the sample cell into a tared weighing pan, taking care to remove all of the carbon black.

10. Calculation

10.1 Most automated instruments will perform the following computations at the completion of the analysis. The user must verify that the internal computations conform to the following method.

10.2 *Sample Mass*:

$$\text{sample mass (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell}) \tag{1}$$

Record masses to nearest 0.1 mg.

10.3 *Volume of Nitrogen Adsorbed*

10.3.1 Calculate total volume of nitrogen adsorbed per gram of sample to the nearest 0.0001 cm^3/g as follows:

$$V_a = \frac{\textit{Volume of Nitrogen for each dosing in cm}^3}{\textit{sample mass in g}} \tag{2}$$

10.4 *Nitrogen Surface Area*:

10.4.1 Determine the nitrogen surface area (NSA) using a B.E.T. plot from the Brunauer, Emmett, and Teller[3] equation as follows:

$$\frac{P}{V_a\,(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{P}{P_o} \tag{3}$$

where:

P = manometer pressure in kPa,

P_o = saturation vapor pressure of nitrogen in kPa,

V_m = volume of nitrogen per gram that covers one monomolecular layer in standard cm^3/g, and

C = B.E.T. constant. Its numerical value depends on the heat of adsorption of the monomolecular layer.

10.4.2 Plot P/P_o on the X-axis versus $\frac{P}{V_a\,(P_o - P)}$ on the Y-axis, for data sets having P/P_o in the range of 0.05 to 0.30 (linear region of B.E.T. equation).

10.4.3 The data points (three or more) that give the best straight line are used to calculate the slope and y-intercept. The

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[3] Brunuaer, Emmett and Teller, Journal of the American Chemical Society, Volume 60, 1938, p. 309.