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# Standard Test Method for Carbon Black—Morphological Characterization of Carbon Black Using Electron Microscopy[1]

This standard is issued under the fixed designation D3849; 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 *(1)* the morphological (for example, size and shape) characterization of carbon black from transmission electron microscope images which are used to derive the mean particle and aggregate size of carbon black in the dry (as manufactured) state, from CAB chip dispersion or removed from a rubber compound and *(2)* the certification of mean particle size using a correlation based on statistical thickness surface area measurements.

1.2 The values stated in SI units are to be regarded as the standard. The values 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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]

D3349 Test Method for Absorption Coefficient of Ethylene Polymer Material Pigmented with Carbon Black

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

D6556 Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption

## 3. Terminology

3.1 *Definitions:*

3.1.1 *General:*

3.1.1.1 *carbon black particle*—a small spheroidally shaped, paracrystalline, non-discrete component of an aggregate; it can only be separated from the aggregate by fracturing; carbon black particle size is a distributional property; therefore, the term particle size implies the mean value from multiple measurements.

3.1.1.2 *carbon black aggregate*—a discrete, rigid colloidal entity that is the smallest dispersible unit; it is composed of extensively coalesced particles; carbon black aggregate size is a distributional property; therefore, the term aggregate size implies the mean value from multiple measurements.

3.1.1.3 *statistical thickness surface area (STSA)*—the external specific surface area of carbon black that is calculated from nitrogen adsorption data using the de Boer theory and a carbon black-specific model.

3.1.1.4 *glow discharge*—a plasma of ionized gas that is formed in a high-voltage field at pressures of about 3 to 20 Pa (25 to 150 × $10^{-3}$ torr); an alternating current (a-c) glow discharge using air is effective in cleaning and oxidizing the surface of carbon substrates to improve the wetting characteristics of polar vehicles containing pigment dispersions.

3.1.1.5 *substrate*—a thin film that is used to support electron microscope specimens; evaporated carbon films are commonly used because of relatively good mechanical strength, stability, and conductivity.

3.1.2 *Aggregate Dimensional Properties from Image Analysis:*

3.1.2.1 *area (A)*—the two-dimensional projected area of the carbon black aggregate image.

3.1.2.2 *perimeter (P)*—the total boundary length of an aggregate.

3.1.2.3 *volume (V)*—an estimate of the volume of the carbon black aggregate using stereological principles.

3.1.3 *Image Analysis:*

3.1.3.1 *dilation*—the converse of erosion; this process is accomplished by changing any OFF pixel to ON if it has greater than a preset minimum of ON neighbors, causing image

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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.

features to grow in size, which fills in small breaks in features, internal voids, or small indentations along the feature surface.

3.1.3.2 *erosion*—the process by which image features are reduced in size by selectively removing pixels from their periphery; it consists of examining each binary pixel and changing it from ON to OFF if it has greater than a preset minimum of neighbors that are OFF; it serves a number of useful functions, such as smoothing feature outlines and separating features touching each other.

3.1.3.3 *feature*—areas within a single continuous boundary that have gray-level ranges that allow them to be distinguished from the background area outside the feature via thresholding.

3.1.3.4 *thresholding*—selecting a range of brightness such that discrimination is possible between the feature and the background; the gray levels within carbon black images become lower with decreasing particle size.

## 4. Significance and Use

4.1 Carbon black morphology significantly affects the transient and end-use properties of carbon black loaded polymer systems. A carbon black's particle size distribution is its single most important property, and it relates to degree of blackness, rubber reinforcement, and ability to impart UV protection. For a given loading of carbon black, blackness, reinforcement, and UV protection increase with smaller particle size. Aggregate size and shape (structure) also affect a carbon black's end-use performance, as higher carbon black structure increases viscosity and improves dispersion. The stiffness (modulus) of elastomer systems becomes significantly higher with increasing structure. The preferred method for measuring carbon black morphology (for example, size and shape) is transmission electron microscopy (TEM), but due to the semi-quantitative nature of TEM, it is not suited for mean particle size (MPS) certification. While useful morphological information can be obtained from TEM measurements within a laboratory, due to their inherent between-laboratory variability, TEM generated values should not be used for specification purposes.

4.2 Certification of carbon blacks for UV protection (weatherability) in certain plastics applications has historically been performed using TEM generated mean particle size values. ASTM Committee D24 has demonstrated that due to challenges with obtaining quantitative primary particle size data, particularly between laboratories, a qualification test based on surface area has been implemented, as detailed in Test Method B.

4.3 Carbon black aggregate dimensional and shape properties are dependent upon the nature of the system in which the sample is dispersed, as well as the mixing procedure.

## Test Method A – Morphological Evaluation (Semi-Quantitative) Via Transmission Electron Microscopy

## 5. Summary of Test Method

5.1 Transmission electron microscopy (TEM) is utilized to measure the morphological properties of carbon black. A variety of dispersion methods are offered depending upon the sample type. Both dry black and CAB chip dispersions are used for measuring the morphology of bulk carbon black. A pyrolysis technique is included that facilitates the removal of carbon black from vulcanized rubber. This aforementioned technique can be employed to identify the carbon black type from an end use product. It should be noted that the accuracy and precision of Method A is insufficient for generating quantitative data as required in the case of MPS certification. Please refer to Method B for MPS certification.

## 6. Apparatus

6.1 *Electron Microscope,* transmission-type, with a point-to-point resolution of 1.0 nm or better. Operating voltages should be high enough to provide the desired resolution and low enough to produce images of sufficient contrast. Recommended voltages can be in the 60 to 120 kV range. The microscope column should contain a liquid nitrogen-cooled anti-contamination device or a "cold finger" to reduce sample contamination and to maintain column cleanliness. For image acquisition, the microscope should include a charge-coupled device (CCD) camera mounted either above or below the instrument's viewing chamber.

6.2 *Image Analysis System,* consisting at minimum of a TEM-interfaced camera capable of 640 × 480 pixel or better resolution, a computer equipped with frame grabbing hardware to capture TEM images digitally, and software to perform morphological operations and measurements on image features and store resulting data. Operations must include background/noise elimination, thresholding, and edge smoothing. Area and perimeter are then measured on features in the processed images.

6.3 *Two-Roll Mill.*

6.4 *Vacuum Evaporator,* standard-type, for preparing carbon films to be used as substrates for electron microscopy. The evaporator should be capable of reducing the absolute pressure to 1.3 mPa ($1 \times 10^{-5}$ torr) and should also contain the necessary apparatus for a-c glow discharge.

6.5 *Ultrasonic Generator,* variable power tank-type or probe that provides sufficient energy to give acceptable dispersion.

6.6 *Dry Box,* capable of maintaining a relative humidity level of no greater than 30 %.

6.7 *Analytical Balance,* with an accuracy of about 0.5 mg.

6.8 *Electrically Heated Tube Furnace,* capable of being heated to 800 to 900°C under an inert environment, with the ability to introduce and remove the sample boat to the heated zone without allowing oxygen intrusion.

6.9 *Pyroprobe,* capable of being heated from 150 to 1000°C in an inert environment.

6.10 *Carbon Rods,* approximately 3.1 mm in diameter.

6.11 *Carbon Rod Sharpener.*

6.12 *Glass Microscope Slides,* 25 by 75-mm.

6.13 *Test Tubes,* 75 by 10-mm, 4-$cm^3$ capacity, 0.5-mm wall thickness, with corks.