Designation: D 3849 – 04

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

This standard is issued under the fixed designation D 3849; 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 morphological characterization of carbon black primary aggregates from transmission electron microscope images. These measurements 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.

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

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 3182 Practice for Rubber—Materials, Equipment, and Procedures for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets

D 3191 Test Methods for Carbon Black in SBR (Styrene-Butadiene Rubber)—Recipe and Evaluation Procedures

D 3192 Test Methods for Carbon Black Evaluation in NR (Natural Rubber)

D 6556 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 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.

3.1.1.2 *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.

3.1.1.3 *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.

3.1.1.4 *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. This process causes image 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.

[1] This test method is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.81 on Carbon Black Microscopy and Morphology.

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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.

3.1.3.3 *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 and rubber reinforcement. For a given loading of carbon black, blackness and reinforcement 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 these properties is transmission electron microscopy.

4.2 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.

5. Apparatus

5.1 *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.

5.2 *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.

5.3 *Two-Roll Mill*:

5.4 *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 (1×10^{-5} torr) and should also contain the necessary apparatus for a-c glow discharge.

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

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

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

5.8 *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.

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

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

5.11 *Carbon Rod Sharpener.*

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

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

5.14 *Transfer Pipets*, disposable Pasteur-type, 225 mm long, 1-mm inside diameter at tip.

5.15 *Rubber Bulbs*, for pipets.

5.16 *Glass Vials*, 40-cm^3 capacity, with solvent-resistant tops.

5.17 *Büchner Funnel*, No. 3, 111-mm inside diameter.

5.18 *Filter Paper*, general purpose.

5.19 *Carbon Coated Electron Microscope Specimen Grids*, 3-mm diameter, 200 to 300 mesh. Commercially available or can be prepared as described in Annex A1.

5.20 *Wire Screening*, with openings approximately 1 mm^2.

5.21 *Tweezers*, fine-tipped.

5.22 *Spatulas*, micro-type with V-shaped spoon that is approximately 2 mm wide at top and 12.5 mm long.

5.23 *Fluorocarbon Duster.*

5.24 *Lens Tissue,* lint-free.

5.25 *Porcelain Boats*, for pyrolysis, 98 mm long, 15 mm wide at top.

5.26 *Centrifuge*, high speed (15 000 to 20 000 r/min) with head for 75 by 10 mm test tubes.

5.27 *Beakers*, 2000-cm^3 capacity.

6. Reagents and Materials

6.1 *Chloroform*, reagent grade.

6.2 *Tetrahydrofuran (THF)*, reagent grade.

6.3 *1,2-Dichloroethane*, reagent grade.

6.4 *Ethyl Acetate*, reagent grade.

6.5 *Poly (Vinyl Formal) Resin*, Grade 15/95.

6.6 *Cellulose Acetate Butyrate Resin (CAB).*

6.7 *Phthalate-Type Plasticizer (such as santicizer).*

7. Sample Preparation—Dispersion Procedures

7.1 *Dry Carbon Black (Sonic Bath)*:

7.1.1 Weigh 8 to 10 mg of carbon black into a test tube containing 1 cm^3 of solvent (typically chloroform or THF).

NOTE 1—With experience, it may not be necessary to weigh each carbon black sample, as an estimated amount from the microspatula may be sufficient. There is considerable latitude in the amount of carbon black used. The finer N100 and N200 blacks may require somewhat less carbon black than the coarser semi-reinforcing types.

7.1.2 Adjust the power of the ultrasonic bath for maximum agitation; this may require that the water level be adjusted. As the ultrasonic energy heats the water in the bath, ice should be added to control the temperature in order to maintain maximum dispersive capability.

7.1.3 Place the stoppered test tube containing the carbon black and solvent mixture into the most intense part of the

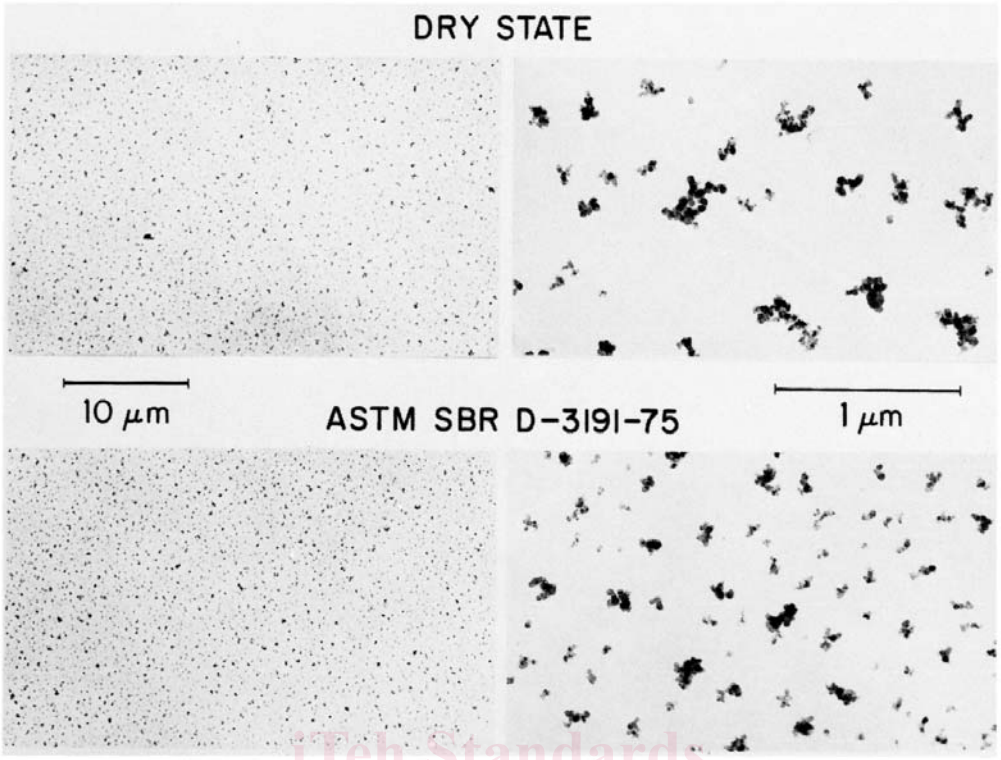

FIG. 1 Ultrasonic Dispersions of N-220 Carbon Black

ultrasonic field and allow the mixture to agitate for 3 to 5 min. The test tube should be held with tongs or mounted in a simple wire holder.

7.1.4 Transfer a small portion of the concentrated carbon black-solvent mixture into another test tube containing 1 cm^3 of fresh solvent. The amount of concentrate required increases with particle size. Blend the mixture by repeatedly transferring the sample between the transfer pipet and the test tube, then cork the test tube and repeat the ultrasonic dispersion procedure.

7.1.5 Check the concentration of the diluted dispersion by extracting a small amount into the tip of the pipet and viewing against a white background. For tread grade carbon blacks, the dispersions should be relatively transparent, becoming somewhat darker with increasing particle size. The diluted dispersions for very coarse carbon blacks such as N700 to N900 series will be on the threshold of complete opacity. If necessary, adjust the concentration by adding more concentrate or solvent as required, then repeat the ultrasonic agitation. The volume of the carbon black-solvent mixture should be maintained at approximately 1 cm^3. If considerable dilution is required, the excess volume above 1 cm^3 should be discarded.

NOTE 2—A reasonable degree of latitude exists for achieving the proper concentration levels in the final dispersions for different grades of carbon black. Concentration and overall dispersion quality are best determined by screening the actual specimens in the electron microscope and then making the necessary adjustments.

7.1.6 Place a specimen grid with carbon substrate (film side up) on a piece of filter paper. Remove a small amount of the final diluted dispersion using a fresh pipet and place one drop on the grid as close to the center as possible, from a height of about 12 mm. Allow the specimen to dry for about 1 min on a piece of filter paper. This specimen preparation procedure should be performed in a dry box if the relative humidity in the room exceeds 30 %.

7.1.7 For TEM grids that contain formvar or residual CAB (CAB chip dispersions), place the TEM grid in an appropriate sample holder, place in the pyrolysis chamber and allow adequate time for the chamber to be purged by an inert gas to prevent oxidation of the sample. Pyrolize the specimen grid at a sufficient temperature (typically greater than 550°C) to remove the poly (vinyl formal) film or CAB, or both.

7.1.8 Acceptable dispersions of a carbon black in the dry state and removed from a rubber compound (SBR) are illustrated for N-220 and N-774 carbon blacks in Figs. 1 and 2.

7.2 *Dry Carbon Black (Ultrasonic Probe)*:

7.2.1 Weigh 5 to 10 mg of carbon black into a 30-cm^3 glass vial and add approximately 20 cm^3 of solvent (typically chloroform).

NOTE 3—With experience, it may not be necessary to weigh each carbon black sample, as an estimated amount from the microspatula may be sufficient. There is considerable latitude in the amount of carbon black used. The finer N100 and N200 blacks may require somewhat less carbon black than the coarser semi-reinforcing types.

7.2.2 Place the vial containing the carbon black and solvent into an ice-water bath.

7.2.3 Insert the probe to a depth of approximately 2.5 cm into the vial and ultrasonicate at 40 to 50 watts for 10 min.

NOTE 4—The ultrasonic probe and ice-water bath containing the