Designation: D3849 – 13

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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 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.

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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.

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.

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 (1×10^{-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.

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

6.15 *Rubber Bulbs,* for pipets.

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

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

6.18 *Filter Paper,* general purpose.

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

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

6.21 *Tweezers,* fine-tipped.

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

6.23 *Fluorocarbon Duster.*

6.24 *Lens Tissue,* lint-free.

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

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

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

7. Reagents and Materials

7.1 *Chloroform,* reagent grade.

7.2 *Tetrahydrofuran (THF),* reagent grade.

7.3 *1,2-Dichloroethane,* reagent grade.

7.4 *Ethyl Acetate,* reagent grade.

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

7.6 *Cellulose Acetate Butyrate Resin (CAB).*

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

8. Sample Preparation—Dispersion Procedures

8.1 *Dry Carbon Black (Sonic Bath):*

8.1.1 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.

8.1.2 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.

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

8.1.4 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.

8.1.5 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.

8.1.6 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 %.

8.1.7 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.

8.1.8 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.

8.2 *Dry Carbon Black (Ultrasonic Probe):*

8.2.1 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.

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

8.2.3 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 sample vial should be housed in an acoustic enclosure to reduce cavitation noise.

8.2.4 Transfer a small portion (approximately 2 to 4 cm^3) of the concentrated carbon black/solvent mixture into another vial and add 20 cm^3 of fresh solvent. An additional three-minute sonication is recommended.

8.2.5 Check the concentration of the diluted dispersion by extracting a small amount into a pipet and then placing 1 drop on a white filter paper. For tread grade carbon blacks, the dispersions should be relatively transparent, becoming somewhat darker with increasing particle size. The dispersion for very coarse carbon blacks, such as N700 to N900 series, will be on the threshold of complete opacity.

8.2.6 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 20 cm^3. Repeat 8.2.5.

Note 5—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.

8.2.7 When the final dispersion drop on the filter paper is in an acceptable color range, place a specimen grid with a thin carbon substrate (film side up) on a piece of filter paper. Using a fresh pipet, remove a small amount of the final dispersion and
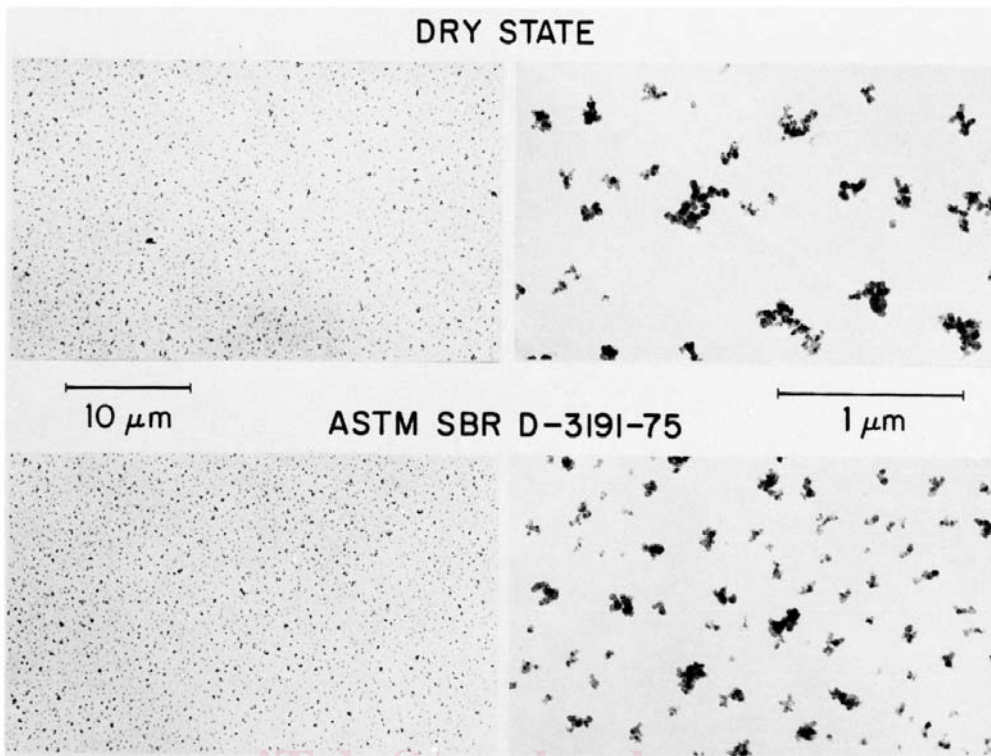
DRY STATE

10 μm   ASTM SBR D-3191-75   1 μm

FIG. 1 Ultrasonic Dispersions of N-220 Carbon Black

DRY STATE

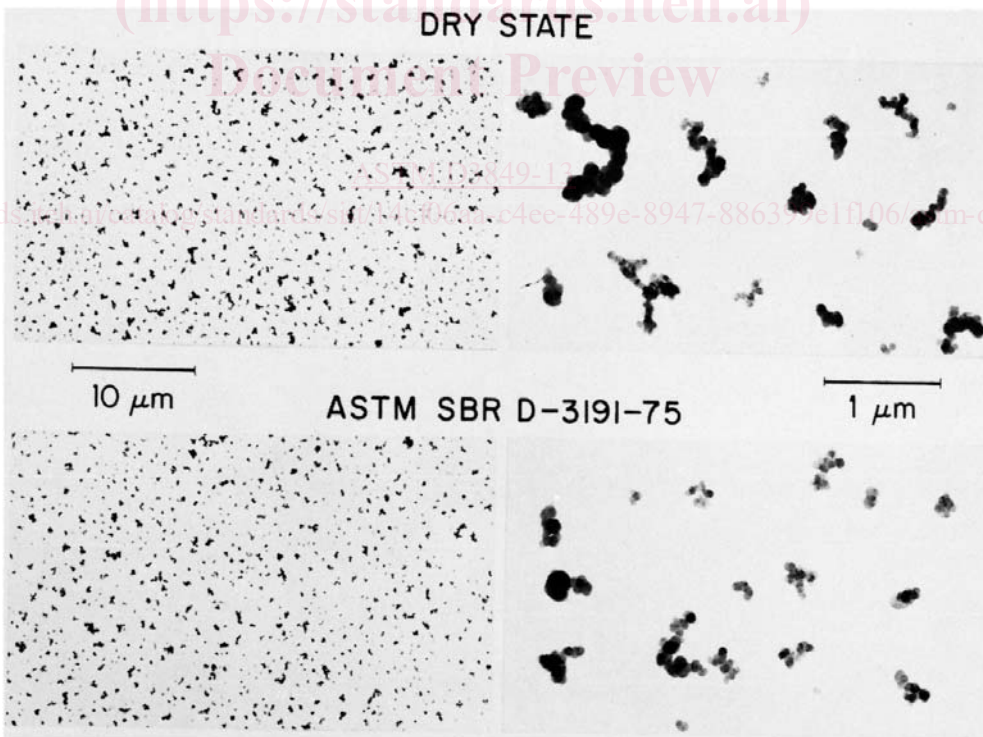10 μm   ASTM SBR D-3191-75   1 μm

FIG. 2 Ultrasonic Dispersions of N-774 Carbon Black

place one drop on the grid as close to the center as possible, from a height of about 12 mm. Allow the specimen grid to dry for approximately 1 min on the filter paper. (If the relative humidity is greater than 35 %, purge ultra-high purity nitrogen over the specimen grid retaining the sample.)

8.2.8 Place the grid into the microscope and examine the dispersion for visual separation of discrete aggregates. If the dispersion shows a high concentration (overlap of aggregates, agglomeration, and so forth), adjust the concentration of the dispersion by following 8.2.6 and prepare a new specimen grid by following 8.2.7.

8.3 *Carbon Blacks Removed from Vulcanized Rubber Compounds:*

8.3.1 Cut thin sections (about approximately 1 mm^3) of the rubber compound using a razor blade.

8.3.2 Place 5 to 10 sections 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. Heat the sample at a temperature in excess of the decomposition temperature of the polymer.

8.3.3 It should be noted that heteroatom polymers, such as neoprene and nitrile rubber, will not pyrolyze cleanly and often carbonize and sinter the aggregates together, resulting in poor dispersion. These samples cannot be analyzed with any degree of confidence; therefore, caution must be used when these polymers are encountered. Additionally, rubber compounds containing 5 % or more silica typically result in higher sintered aggregate dispersions with agglomerated silica. Advanced techniques for removal of the silica must be employed in order to get reliable results.

8.3.4 Allow the sample to cool to room temperature before removing it from the pyrolysis chamber. Place the sample in a test tube containing 1 cm^3 of solvent (typically chloroform or THF).

8.3.5 Disperse the residual carbon black sample as described in 8.1.2 – 8.1.8.

8.4 *Carbon Black in CAB (Cellulose Acetate Butyrate):*

8.4.1 The preparation of the CAB chip utilizes high shear mixing on a two-roll mill, which greatly reduces the level of aggregation; therefore, the aggregate size measurements then become more directly related to particle size, thus reducing shape-related corrections.

8.4.2 *Preparation of CAB Chip:*

8.4.2.1 The following conditions were defined for a Farrel Tecno Lab Polymill 110P. Slight adjustments may be necessary depending on the size of the 2-roll mill used.

8.4.2.2 Preheat the 2-roll mill to give a temperature on the front roll of the mill at 76°C and the rear roll at 66°C, noting that rolls should be in motion while heating.

8.4.2.3 Set the roll gap to 0.2 mm and roll rate of 20 r/min.

8.4.2.4 Weigh out the following ingredients depending on the carbon black type being analyzed:

	Weight (g)		
	Carbon Black	CAB	Phthalate-Type Plasticizer
N100-N300 (25 % CB Loading)	37.5	82.5	30.0
N500-N900 (40 % CB Loading)	60.0	66.0	24.0

8.4.2.5 Mix the carbon black and CAB resin in a container, then add the Phthalate-type plasticizer, taking care not to let the Phthalate-type plasticizer touch the sides of the container.

8.4.2.6 Stop the rolls, then evenly distribute the mixture across the roll gap and allow it to heat for 2 min.

8.4.2.7 Initiate the rollers, noting that it may be necessary to intermittently turn off the mill heaters to control the temperature, as the energy of mixing will generate additional heat. For the 25 % carbon black loading, the temperature may increase up to 10°C above the starting conditions, and up to 20°C for the 40 % carbon black loading.

8.4.2.8 Any material that passes through the mill gap must be collected and added back to the mixture.

8.4.2.9 After the material has completely banded (uniform sheet), cut the band and fold it together, then replace it in the gap for a total mix time of 10 min. During the 10 min of mixing, the material is to be removed from the rollers, folded together, then placed back in the gap at 1-min intervals.

8.4.2.10 Remove the material from the mill, cut it into approximately eight equal parts and allow it to cool mix to room temperature.

8.4.2.11 Slowly add material back to mill for an additional 5 min of mixing. During the mixing cycle, the material is to be removed from the rollers, folded together, then placed back in the gap at 1-min intervals.

8.4.2.12 Remove the material from the mill, cut it into approximately eight equal parts and allow it to cool mix to room temperature.

8.4.2.13 Repeat 8.4.2.11 for an additional 5-min mixing cycle for a total flux time of 20 min.

8.4.2.14 Remove the material from the mill and allow it to cool to room temperature.

8.4.3 Cut approximately a 25-mg section of the chip and place in a glass test tube containing 1 cm^3 of solvent (chloroform or tetrahydrofuran is suitable). There is considerable latitude in the mass of the sample. With experience, this can be estimated satisfactorily.

8.4.4 Disperse the carbon black in the CAB chip as described in 8.1 (bath) or 8.2 (probe).

9. Calibration and Standardization

9.1 Prepare the electron microscope/image analysis system for operation according to the manufacturer's recommendation.

9.2 Set the microscope to a suitable operating magnification. This depends on both the type of carbon black sample and the image analysis system. Select a magnification such that the field of view is larger than the largest aggregate while still having enough resolution such that the primary particles in the smallest aggregates are discernable and the smallest aggregates are distinguishable from noise (for example, anomalous particles or dust). The following resolution guidelines are offered as an example for cameras having 2K × 2K resolution or better.

Particle Size Range (nm)	Resolution (nm/pixel)
14 to 21	1.5 to 2.0
22 to 26	2.0 to 2.5
27 to 37	2.5 to 3.0
38 to 49	3.0 to 4.0
50 to 62	4.0 to 5.0
63 to 100	5.0 to 6.0
101 to 199	6.0 to 12.0
200 to 400	12.0 to 20.0

9.2.1 Another optional guideline for selecting a suitable resolution is to determine the magnification that will yield EMSA values similar to STSA values. (See Test Method D6556.)

9.2.2 These guidelines do not address samples that have multi-modal primary particle sizes.

9.3 Confirm the instrument resolution using a calibration grating at the center of the specimen stage in the eucentric position, for example, 2160 lines/mm.

9.4 Determine the magnification factor in nm/pixel, and its square in nm^2/(square pixel), for use in converting raw pixel data to dimensional properties.

10. TEM Analysis Procedure

10.1 With the specimen removed, set the beam intensity to the proper level for the image analysis system.

10.2 Correct for any shading in the blank image and reset the brightness level.

10.3 Insert the first carbon black specimen into the electron microscope, locate it at the center of the microscope stage, and adjust to eucentric height. Focusing and stigmating the images at higher magnification than used to acquire the images is recommended in accordance with good microscopy practices.

10.4 Start the measurements on a field near one side of a grid opening. Continue to select and measure adjoining fields of carbon black aggregates in a straight line tracking pattern toward the center of the grid opening, until the far edge of the opening has been reached. Repeat if necessary until data for about 2000 aggregates have been recorded.

10.5 *Image Analysis:*

10.5.1 Each image analysis system will have its own proprietary means for processing the images it receives from the camera. However, some general comments and guidelines are in order.

10.5.2 Thresholding can be accomplished via an automated process, manually for each field, or even using a preset threshold if carbon film thickness and morphology are consistent and other imaging conditions are not altered.

10.5.3 The image analysis software should be configured to perform edge smoothing and noise reduction. An example of edge smoothing is, but is not limited to, erosion followed by dilation (1 pixel depth and minimum number of cycles—typically 1 to 2 cycles.) This can smooth "noise" associated with particle boundaries without significantly altering the "real" data. Noise reduction attempts to eliminate measurement of objects that are not carbon black. For example, if images are acquired using the table in 9.2, the software may be configured to reject objects smaller than 50 pixels in area. These features are smaller than a single particle having the mean primary particle size, and are probably noise.

10.5.4 A "guard frame" should be employed to selectively deal with partial aggregate images (aggregates that touch image boundaries). Rejecting all aggregates that touch image or guard frame boundaries, or setting the relative size of the guard frame too small or too large, will tend to bias the results. Appropriate magnification/resolution selection will help minimize these effects.

10.6 Repeat the analysis for a standard carbon black sample with a similar particle size suitable for the appropriate magnification. This analysis verifies that the microscope, camera and image processing system are functioning properly.

10.7 At a minimum, area (A) and perimeter (P) of the aggregate projections must be measured for use in the following morphological property calculations.

11. Calculations

11.1 *Single Aggregate:*

11.1.1 *Measured Parameters:* [3]
A = aggregate area (nm^2), and
P = aggregate perimeter (nm).

11.1.2 *Derived Parameters:*
D = area-equivalent aggregate diameter (nm) = $(4A/\pi)^{1/2}$,
α = aggregation factor = $13.092 \ (P^2/A)^{-0.92}$ (however, if this yields $\alpha < 0.4$, use $\alpha = 0.4$),
d_p = average particle size for a single aggregate (nm) = $\alpha\pi A/P$,
V_A = aggregate volume (nm^3) = $(8/3) \ A^2/P$,
V_P = particle volume (nm^3) = $\pi d_p^3/6$, and
n = number of particles in the aggregate = V_A/ V_P.

11.2 *Distributional Properties for Particles and Aggregates:*

11.2.1 *Derived Parameters:*
$n_t = \Sigma n$ for all of the aggregates measured, or total number of all particles,
m = mean particle size (nm) = $[\Sigma(n*d_p)] / n_t$,
sd = particle size standard deviation (nm) = $[\Sigma n(d_p - m)^2 / (n_t - 1)]^{1/2}$,
wm = weight mean particle size (nm) = $[\Sigma (n * d_p^4)] / [\Sigma (n * d_p^3)]$,
hi = particle size heterogeneity index = wm/m,
d_{sm} = particle size surface mean diameter (nm) = $[\Sigma (n * d_p^3)] / [\Sigma (n * d_p^2)]$,
EMSA = electron microscope surface area (m^2/g) = $6000 / (\rho * d_{sm})$ (where: $\rho = 1.8 \ g/cm^3$; assume density of carbon black),
N_t = number of aggregates measured,
M = mean aggregate size (nm) = $\Sigma D / N_t$,
SD = aggregate size standard deviation (nm) = $[\Sigma(D - M)^2 / (N_t - 1)]^{1/2}$,
WM = weight mean aggregate size (nm) = $\Sigma D^4 / \Sigma D^3$, and
HI = aggregate size heterogeneity index = WM/M.

12. Report

12.1 Report the following information for particle size distributional properties:

12.1.1 Dispersion method (CAB, DB, or removed from rubber compound),

12.1.2 Number of aggregates measured,

12.1.3 Mean particle size, m (nm),

12.1.4 Weight mean, wm (nm),

12.1.5 Heterogeneity index, hi, and

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[3] If not done automatically in the image analysis software, the measured parameters must be converted from pixels and square pixels to nm and nm^2 before use in subsequent calculations.