Designation: D 3849 – 95a (Reapproved 2000)

Standard Test Method for Carbon Black — Primary Aggregate Dimensions from Electron Microscope Image Analysis[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. The measurements are applicable to carbon blacks in the dry (as manufactured) state, extracted from unvulcanized rubber compounds and in a cellulose acetate butyrate paint chip dispersion.

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:*

D 297 Test Methods for Rubber Products—Chemical Analysis[2]

D 1416 Test Methods for Rubber from Synthetic Sources—Chemical Analysis[2]

D 3182 Practice for Rubber—Materials, Equipment, and Procedures for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets[2]

D 3191 Test Methods for Carbon Black in SBR (Styrene-Butadiene Rubber)—Recipe and Evaluation Procedures[2]

D 3192 Test Methods for Carbon Black Evaluation in NR (Natural Rubber)[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *Aggregate Dimensional Properties from Image Analysis:*

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

3.1.1.2 *chord*—the length of a scanning intercept across an aggregate in a given direction. The *mean chord* (π *A/P*) is the average width of an aggregate in all directions.

3.1.1.3 *Feret's diameter*—the maximum spacing between parallel tangents to an aggregate in a given direction. The average Feret (*L*) is derived from an average of multiple measurements at specific angular increments.

3.1.1.4 *length (L_1)*—the longest Feret's diameter of an aggregate.

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

3.1.1.6 *projected length (L_2)*—the total length of an aggregate in a given direction, including the contribution of multiple entrants. The projected length is equal to the number of scan lines multiplied by a calibration factor that is equal to the scan line spacing in the proper dimensional units (usually nanometres for carbon blacks).

3.1.1.7 *volume*—the volume of carbon black aggregates may be measured directly by well-calibrated scanning microdensitometry (*V*) or geometrically (V_1) as follows:

$$V_1 = 8A^2/3P \quad (1)$$

3.1.1.8 *width*—the width of a carbon black aggregate may be described in terms of either the mean chord or Feret's diameter. The average width (*W*) is defined as the mean chord measured in a direction that is perpendicular to the longest projection. *W* is equal to the projected area divided by the longest projection. The average nondirectional width (W_1) is equal to the mean chord (π *A/P*). The shortest width (W_2) is equal to the shortest chord length and is derived from chord sizing. The longest width (W_3) is the shortest Feret's diameter from multiple measurements in different directions.

3.1.2 *Aggregate Nondimensional Shape Parameters*

3.1.2.1 *circularity factor (C.F.)*—the amount of deviation of the two-dimensional projected aggregate area from a circle expressed as follows:

$$C.F. = P^2/4\pi A \quad (2)$$

3.1.2.2 *form factor*—the length/width ratio of the aggregate. Some of the more commonly used ratios are as follows:

$$F_1 = L_1/W_1 \quad (3)$$

$$F_2 = L/W_1 \quad (4)$$

[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.

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

$$F_3 = L_1/W_3 \quad (5)$$

3.1.2.3 *sphericity factor (S.F.)*—The amount of deviation of the projected aggregate image from a sphere expressed as follows:

$$S.F. = P^3/6\pi^2V \quad (6)$$

3.1.3 *carbon black aggregate*—a discrete, rigid colloidal entity that is the smallest dispersible unit; it is composed of extensively coalesced particles.

3.1.4 *carbon black particle*—a small spheroidally shaped, paracrystalline, non-discrete component of an aggregate; it is separable from the aggregate only by fracturing.

3.1.5 *chord sizing*—an operation in which a specified length increment (ΔL) is cut off each detected chord in an image. All chords shorter than ΔL are completely eliminated from the image and all chords larger than ΔL are shortened by ΔL. The operation is repeated over a range that eventually eliminates all of the chords in the image and thereby provides a chord size distribution.

3.1.6 *detected image*—an electronic monitor display of the chords across the features in a given field. The detected image should match the actual image as closely as possible.

3.1.7 *epidiascope*—a device for projecting images of photographic prints, negatives, or transparencies on the scanner tube.

3.1.8 *feature*—areas within a single continuous boundary (for example, an aggregate image) that have an optical-density value (gray-level range) that is distinct from the background area outside the feature.

3.1.8.1 *feature cropping*—the splitting of features at the boundaries of the measuring frame that, if uncorrected, results in erroneously small size values for these features.

3.1.9 *fiber optics coupling*—bundles of small-diameter light-channeling fibers that transmit the optical image from the fluorescent viewing screen within an electron microscope to the scanner of the image analysis system with a minimal loss of brightness.

3.1.10 *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.

3.1.11 *gray level*—variations in the intensity of images in terms of the electrical output of the scanner. The brightest region in an image gives the highest electrical output and is defined as“ white,” while the complete absence of light in a field is“ black.” The tone of detected features usually ranges between these extremes and the electrical output signal is known as the gray level.

3.1.11.1 *gray-level discrimination*—the ability to distinguish between different gray levels within features or between different features in a field. The gray levels within carbon black images in the electron microscope become lower with diminishing aggregate size.

3.1.12 *image analysis*—measurement of the size, shape, and distributional parameters of feature images by electronic scanning methods.

3.1.12.1 *feature specific*—image analysis data output that provides individual measurements on each separate feature. A multiparameter feature specific system enables the linking of different type measurements for each separate feature, thus enabling direct calculation of multivariate functions such as F, P^2/A, etc.

3.1.12.2 *field specific*—an image analysis data output that provides only field totals for each measured parameter. Number average measurements are obtained by dividing the total measured parameter by the feature count.

3.1.12.3 *off-line*—this type of image analysis system is based on scanning of negatives, transparencies, or photographic prints of the features utilizing an epidiascope or similar optical device.

3.1.12.4 *on-line*—a type of image analysis system in which the scanner is a part of the microscope or directly coupled to the microscope.

3.1.13 *microdensitometer*—an image analysis device for resolving gray-level differences within or between features and for integrating the optical density across scanned images of irregularly shaped objects. The latter provides three-dimensional size measurements (volume) of the particles or aggregates of noncrystalline materials such as silicas, or poorly crystallized materials such as carbon black.

3.1.14 *shading*—variation in the electrical output from the scanner from areas of identical gray level in different parts of the image. Shading can be due to optical effects, scanner deficiencies, or to artefacts in the specimen. A shading compensator is employed to correct any instrumental deficiencies.

3.1.15 *specimen anticontamination device*—a cold trap (cooled by liquid nitrogen) that is located in the vicinity of the specimen in an electron microscope in order to prevent the deposition of contaminants, such as diffusion pump oil vapor from the vacuum system, on the specimen.

3.1.16 *specimen grid*—a specimen mount in the form of a thin circular mesh about 3 mm in diameter that fits the standard specimen holders of transmission electron microscopes. Grids are used to support the thin substrates required for electron microscopy and are made most commonly of copper. Tungsten grids are used when the specimen must be heated at elevated temperatures.

3.1.17 *substrate*—a thin cast or vacuum-evaporated film that is used to support electron microscope specimens. Evaporated carbon films are a commonly used substrate because of relatively good mechanical strength, stability, and conductivity.

4. Significance and Use

4.1 Carbon black primary aggregate morphology significantly affects the transient and end-use properties of black loaded polymer systems. Vulcanizate hysteresis and strength properties (tear, tensile, and abrasion resistance) increase with diminishing aggregate size. Extrusion die swell diminishes and vulcanizate modulus increases with increasing aggregate irregularity (for example, the amount of deviation from a spherical shape).

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 resolving power of 1.0 nm or better. Operating voltages (electron beam) should include settings of 40 and 60 kV. The specimen chamber should contain an anticontamination device.

5.2 *Image Analysis System*, television scanner-type. The system shall also include a television monitor for viewing the specimens, a well-defined measuring frame that is visible on the monitor and has the capability of correcting for the effects of feature cropping at the borders, a compensator for eliminating shading effects, a detector for discerning the boundaries of the carbon black aggregates at different gray levels, and one or more computer modules for converting the output of the detector into dimensional information. Minimum requirements for dimensional output are area, perimeter, average Feret's diameter, and feature count. Desirable additional outputs are volume by microdensitometry and Feret's diameters in different directions. The system shall contain one or more devices for automated data recording, processing, averaging, and printing of results. Acceptable recorder-processing systems include an on-line computer, desk-top calculator, or a magnetic tape recorder-computer combination. The image analysis system may be field or feature specific, the latter being preferred. The system may be off-line or on-line. For the latter, a fiber optics coupling between the scanner and electron microscope is recommended.

5.3 *Vacuum Evaporator*, [3] 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.

5.4 *Ultrasonic Generator*:

5.4.1 *Dispersion Procedures A and C*—Variable power tank-type ultrasonic cleaning unit,[4] 80 kHz, 100 W.

5.4.2 *Dispersion Procedure B*—Probe-type ultrasonic generator,[5] 20 kHz, 150 W.

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

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

5.7 *Combustion Furnace and Tube*—meeting the requirements described in Methods D 1416 or D 297.

5.8 *Carbon Rods*, [6] approximately 3.1 mm in diameter.

5.9 *Carbon Rod Sharpener*. [7]

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

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

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

5.13 *Rubber Bulbs*, for pipets.

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

5.15 *Glass Tubes*, straight wall, flat bottom, 90 mm in height, 26 to 27-mm inside diameter.

5.16 *Glass Jars*, 30-cm^3 capacity, wide-mouth with solvent-resistant caps, height and outside diameter approximately 43 mm.

5.17 *Glass Dishes*, two 185 mm in diameter, 100 mm in height.

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

5.19 *Vinyl Tubing*, approximately 50 mm long, 12.5-mm inside diameter.

5.20 *Clamp*, hose cock, open-jaw type.

5.21 *Filter Paper*, 125-mm diameter, fast.

5.22 *Electron Microscope Specimen Grids*, 3-mm diameter, 300-mesh copper.

5.23 *Electron Microscope Specimen Grids*, 3-mm diameter, 200-mesh tungsten.

5.24 *Specimen Grid Holders*. [8]

5.25 *Test Tube Holders*, for 48 tubes up to 16 mm in outside diameter.

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

5.27 *Forceps*, fine-tipped, locking-type.

5.28 *Tweezers*, fine-tipped.

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

5.30 *Solvent Dispenser*, portable high-speed type.

5.31 *Fluorocarbon Duster*. [9]

5.32 *Lens Tissue*, [10] lint-free.

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

5.34 *Centrifuge*, 2094 rad/s (20 000 r/min) with head for 75 by 10 mm test tubes.

5.35 *Test Tubes*, polypropylene, 75 by 10 mm, 5 cm^3 capacity, 0.5 mm wall thickness with caps.

5.36 *Beakers*, 2000 cm^3 capacity.

6. Reagents and Materials

6.1 *Castor Oil*, laboratory grade.

6.2 *Chloroform*, reagent grade.

6.3 *Collodion*, typical commercial grade, U.S.P.

6.4 *1,2-Dichloroethane*, reagent grade.

6.5 *Ethyl Acetate*, reagent grade.

6.6 *Poly (Vinyl Formal) Resin*,[11] Grade 15/95.

6.7 *Cellulose Acetate Butyrate Resin*. [12]

6.8 *Phthalate Type Plasticizer*. [13]

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[3] The following vacuum evaporator systems have been found to be acceptable: Denton Model DV-515, available from Denton Vacuum, Inc., Cherry Hill Industrial Center, Cherry Hill, NJ 08034; Ladd Vacuum Evaporator, Catalog No. 40000, Ladd Research Industries, Inc., P.O. Box 901, Burlington, VT 05401.

[4] Ladd Research Industries, Inc., P.O. Box 901, Burlington, VT 05401, Catalog No. 12400, is satisfactory.

[5] Branson Instruments, Inc., Model No. 185E, is satisfactory.

[6] Denton Vacuum Inc., Cherry Hill Industrial Center, Cherry Hill, NJ 08034, Catalog No. 5095-002, is satisfactory.

[7] Ernest F. Fullam, Inc., P.O. Box 444, Schenectady, NY 12301, Catalog No. 1204, is satisfactory.

[8] L.K.B. Instruments Co., 12221 Parktown Dr., Rockville, MD 20852, Catalog No. 4828B, is satisfactory.

[9] Ernest F. Fullam, Inc., P.O. Box 444 Schenectady, NY 12301, Catalog No. 1180-1, is satisfactory.

[10] Ladd Research Industries, Inc., P. O. Box 901, Burlington, VT 05401, Catalog No. 12700, is satisfactory.

[11] Formvar, a registered trademark of Monsanto, also available as Catalog No. 18050 and 18060, Ladd Research Industries, Inc., P.O. Box 901, Burlington, VT 05401.

[12] Eastman CAB 381-2 is satisfactory.

[13] Monsanto Santicizer 160 is satisfactory.

7. Sampling

7.1 *Dry Carbon Blacks*—Select vial size samples at random from larger size lots. The samples may be in either pelletized or nonpelletized form. Cap and label the vials for storage.

7.2 *Carbon Black in SBR* (*Styrene-Butadiene Rubber*) *and NR* (*Natural Rubber*)—Prepare the rubber compounds in accordance with the formulations and mixing procedures described in Test Methods D 3191 or D 3192. Sheet out in accordance with Practice D 3182 but do not vulcanize. Label the slabs and store at or below room temperature. A freezer (0°C) is recommended for long-term storage of unvulcanized rubber compounds.

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

7.3.1 Weigh 160 g of carbon black, 176 g of CAB, and 64 g of plasticizer and blend by stirring in a beaker until the mixture becomes a uniform, free flowing powder.

7.3.1.1 The 160 g loading range (40 % by weight) is applicable for the majority of rubber grade carbon blacks but is not a critical aspect of the procedure.

7.3.1.2 Lower loadings in the range of 80 g (25 % by weight) generally provide easier mixing for the finer N100 and N200 grades or conductive types such as N472.

7.3.2 Mix the carbon black into the CAB resin by milling on a two-roll mill (200 by 460 mm) with a nip setting of 0.28 mm.

7.3.3 Regulate the temperature of the front roll of the mill at 82°C and the rear roll at 62°C.

7.3.4 Fuse the CAB-carbon black powder together on the mill (<1 min) and mix for a total of 10 min.

7.3.5 Cool the mix to room temperature and remix for 5 min. Repeat this procedure and sheet out the mix into thin slabs. Label the slabs and store at room temperature.

8. Samples and Test Specimens

8.1 *Samples*:

8.1.1 *Dry Carbon Blacks—Dispersion Procedure A*—Weigh 8 to 10 mg of black, place in a test tube containing 1 cm^3 of chloroform (from dispenser), and cork. Repeat this procedure for two more different samples from the same vial of black.

NOTE 1—With experience, it is not necessary to weigh each black sample. One full scoop with the microspatula provides a satisfactory amount of black for all samples.

8.1.2 *Dry Carbon Blacks—Dispersion Procedure B*—Weigh 7 mg of black and place in a vial containing 30 cm^3 of collodion solution prepared by mixing 1 cm^3 of collodion, 45 cm^3 of ethyl acetate, and 0.05 cm^3 (1 drop) of castor oil. Repeat the sampling procedure for two more samples from the same vial of black.

8.1.2.1 There is considerable latitude in the amount of black used. The 7-mg figure is based on the average rubber reinforcing-type black. The finer N100 and N200 blacks require somewhat less black and the coarser semireinforcing types require considerably more. Coarse blacks in the N700 to N900 classes require about 40 to 50 mg per 30 cm^3 of vehicle. Also, high DBP (dibutyl phthalate) absorption blacks require somewhat more sample and low DBP absorption blacks somewhat less sample.

8.1.3 *Carbon Blacks in SBR and NR, Dispersion Procedure C*—Cut an elongated thin section (about 4 mm^2 in cross-sectional area) of the unvulcanized rubber compound using a razor blade. From this, weigh a 75-mg sample and cut into small fragments that are approximately 1 mm.[3] Repeat this procedure for two more samples from different parts of the same rubber compound.

NOTE 2—With experience, it is not necessary to weigh the rubber sample. A20-mm long sample with a cross-sectional area of approximately 4 mm^2 is adequate.

NOTE 3—This is the recommended procedure for a large batch of rubber compound containing the same carbon black. Ideally, each of the three samples should be selected from a different slab. For small test batches, however, one sample from a single slab is considered adequate.

8.1.4 *Carbon Black in CAB, Dispersion Procedure D*—Cut an elongated thin section from the CAB compound in accordance with 8.1.3. From this, weigh a 25 mg sample and place in a glass test tube containing 1 cm^3 of ethyl acetate and cork.

8.1.4.1 There is considerable latitude in the mass of the sample. With experience, this can be estimated satisfactorily.

8.2 *Test Specimens*:

8.2.1 *Substrate Preparation*—Prepare thin backing films by wiping a clean glass slide with lint-free lens tissue. Wipe three times with one sheet of lens tissue and then repeat with a fresh sheet. Dip the slide into a 0.25 % solution of poly (vinyl formal) in 1,2-dichloroethane (Fig. 1(*a*)). Drain the dipped slide vertically on lens tissue until the film dries (about 1 to 2 min). Then, score all the edges of the film by rubbing a razor blade around the top edges of the slide. Blow away all film fragments using the fluorocarbon duster.

8.2.1.1 Carefully float the poly (vinyl formal) film on to a distilled water surface in the Büchner funnel (Fig. 1(*b*)). The water is held in the funnel by means of a small piece of vinyl tubing and clamp at the bottom. Place the 300-mesh copper specimen grids (shiny side up) one at a time on the top of the floating poly (vinyl formal) film (Fig. 1(*c*)). Generally, a total of 70 or more grids are prepared in a single operation.

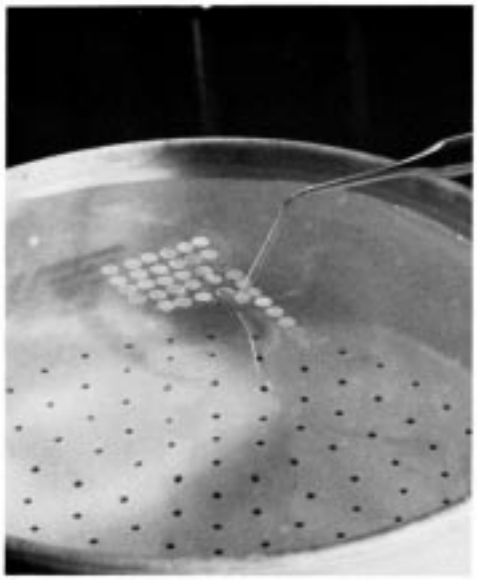
8.2.1.2 Prepare a small screen platform and place face down on the grids as shown in Fig. 1(*d*). Remove the grids and poly (vinyl formal) film from the water by depressing the screen platform and rotating it 180° through the water (Fig. 2(*a*)). An alternative procedure, used for the heavier tungsten grids, requires that the screen platform be placed under the water at the bottom of the Büchner funnel. The grids are deposited on the platform, shiny side down. Next, the poly (vinyl formal) film is positioned over the grids and allowed to settle on them by removing the water from the funnel. This procedure is applicable to either tungsten or copper grids, but the surface deposition and inversion method is simpler and considerably quicker. Allow the coated grids on the screen platform to dry at least 3 to 4 h before using them. Preferably, prepare the films in the afternoon and allow to dry overnight.

NOTE 4—In preparing poly (vinyl formal) films on 200-mesh tungsten grids, it is preferable to make them somewhat thicker so that they do not sag into the larger grid openings. A solution of 0.5 % poly (vinyl formal) in 1,2-dichloroethane is satisfactory for 200-mesh grids. Prior to use, the uncoated tungsten grids should be heated to 800°C, in accordance with Methods D 1416 or D 297, to remove any contaminants.

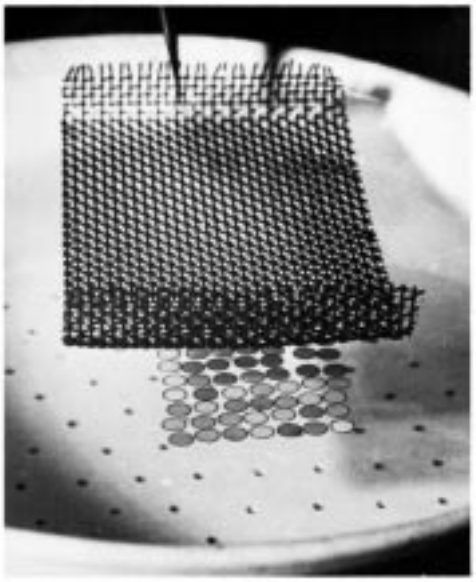
8.2.1.3 Place the screen platform containing the poly (vinyl formal) coated grids in a vacuum evaporator that has been set

(*a*) Dipping Slide in Poly (Vinyl Formal) Solution

(*b*) Floating Film onto a Water Surface



(*c*) Placing Specimen Grids on Film with Vacuum Pipet



(*d*) Placing Screen Platform on Floating Film with Grids

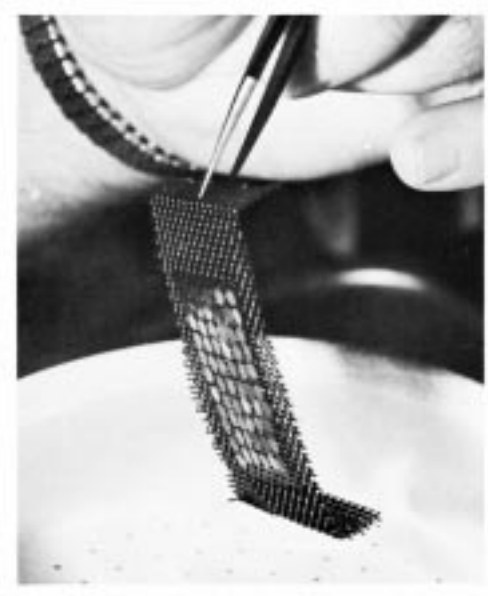
FIG. 1 The Preparation of Poly (Vinyl Formal) Backing Films for Evaporated Carbon Substrates

up for carbon evaporation. Pare down one carbon rod using the sharpener to provide a 1-mm diameter, 3-mm long, cylindrical tip. Set this up to make contact in the center of the flat surface of the second carbon rod, which has not been pared down (Fig. 2(*b*)). Center the grids on the screen platform in the evaporator under the a-c glow loop at a distance 100 mm away from the evaporation tip of the carbon rods.

8.2.1.4 Place the bell jar on the evaporator stage and evacuate to an absolute pressure of about 2.7 mPa (2×10^{-5}torr). Apply current to the carbon rods until the tip glows with a red color. Allow the carbon tip to degas at this setting until the pressure remains stable at 2.7 mPa or below.

8.2.1.5 Increase the current through the carbon rods until the tip starts to evaporate (Fig. 2(*c*)). Continue to increase the current slowly until the entire tip evaporates. This should take about 30 to 40 s.

8.2.1.6 Turn off the current through the carbon rods and allow the system to cool for about 10 min. Close the valve connecting the oil diffusion pump to the specimen chamber under the evaporator bell jar. Allow air to enter the bell jar until an absolute pressure of 20 Pa (150×10^{-3} torr) is achieved. Activate the a-c glow discharge system at approximately 1500 V. Dim the room lights and inspect the glow pattern. There should be a discernible pinkish glow around the loop, while the region around the specimens (on the grounded stage) is dark (Fig. 2(*d*)). The specimens are in the zone of maximum ion bombardment. Maintain the glow discharge at a pressure of 13 to 20 Pa (100 to 150×10^{-3}torr) for a period of 3 min. Turn off



(*a*) Removal of Poly (Vinyl Formal) Coated Grids from the Water

(*b*) Pared-Down Carbon Rod Tip for Evaporator

(*c*) Evaporation of Carbon on to Poly (Vinyl Formal) Coated Grids

(*d*) a-c Glow Discharge Treatment of Carbon Substrates

FIG. 2 The Preparation of Carbon Substrates for Carbon Black Chloroform Dispersions

the glow discharge and bring the bell jar to atmospheric pressure. Remove the coated specimen grids and store in a dry atmosphere.

NOTE 5—There are other acceptable methods for preparing evaporated carbon substrates. The method described here is necessary for good testing with Dispersion Procedures A and C. The carbon substrates for Dispersion Procedure B are less critical because the carbon black aggregates are suspended in a dried nitrocellulose film at the time they are deposited on the carbon surface. An active hydrophilic carbon film surface is required for the carbon black-chloroform dispersions utilized for Procedures A and C. This is the purpose of the a-c glow discharge treatment. It is further recommended that the air used in the glow treatment have a relatively low moisture content (for room air, a relative humidity no greater than 30 %). Under summertime conditions where the relative humidity of a laboratory often exceeds 30 %, dry air from a tank should be bled into the bell jar for the glow procedure.

For Dispersion Procedure B, it is recommended that the poly (vinyl formal) backing film be removed from the carbon substrates by washing the grids in 1,2-dichloroethane or chloroform. This procedure is also acceptable for Procedures A and C but is not necessary. The deposition of the carbon black-chloroform dispersion removes any large fragments of the poly (vinyl formal) backing film around the edges of the grid, which might contaminate the specimen chamber of the electron microscope over the course of analyzing many specimens. The extra thickness of the backing film has not been found detrimental in obtaining suitable contrast and intensity for electron microscope image analysis procedures.

8.2.2 *Dry Carbon Blacks—Dispersion Procedure A*:

8.2.2.1 Adjust the water level in the tank-type ultrasonic

generator for maximum agitation with 1 cm^3 of the carbon black-chloroform mixture in a corked test tube. A water level of about 55 mm has been found satisfactory for the specific ultrasonic system in accordance with 5.4.1. Set the power level at the highest possible setting that does not cause breakage of the test tube (about 80 W).

8.2.2.2 Place the corked test tube containing the 9-mg sample of carbon black in 1 cm^3 of chloroform into the most intense part of the ultrasonic field and allow the mixture to agitate for 3 min (Fig. 3(*b*)). The test tube may be held with tongs or mounted in a simple wire holder as shown.

8.2.2.3 Place 1 cm^3 of fresh chloroform in another test tube. Using a transfer pipet, remove a small amount of the concentrated carbon black-chloroform mixture that has been agitated for 3 min. The amount of concentrate is measured in the elongated tip of the pipet and increases with increasing black aggregate size. For optimum dilution, typical heights of 9-mg carbon black-1-cm^3 chloroform dispersions in the 1-mm inside diameter tips of the transfer pipet are as follows:

Carbon Black Type	Amount in Pipet Tip, mm
N110	10 to 15
N330	20 to 25
N550	35 to 40
N774	60 to 65
N990	80 to 85

8.2.2.4 Place the tip of the pipet with the concentrate into the test tube of fresh chloroform and thoroughly blend the mixture by repeatedly transferring the sample between the pipet and the test tube (Fig. 3(*c*)). After blending, cork the test tube and repeat the ultrasonic dispersion procedure for 2 min.

8.2.2.5 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 aggregate size. The diluted dispersions for very coarse blacks such as N761 or N990 will be on the threshold of complete opacity. If necessary, adjust the concentration by adding more concentrate or chloroform as required and repeat the ultrasonic agitation for about 20 s. The volume of the carbon black-chloroform mixture should always be maintained at approximately 1 cm^3 during the dispersion process. If considerable further dilution is required, the excess volume above 1 cm^3 should be discarded.

NOTE 6—There is a judgment factor in achieving the proper concentration levels in the final dispersions for different grades of carbon black, although a reasonable degree of latitude exists for acceptable specimens. Concentration and overall dispersion quality are best checked by screening the actual specimens (on grids) in the electron microscope and then making the necessary adjustments. For a given study containing similar carbon blacks, this can generally be done for a single sample and the observed concentration criteria will then apply to all others. Sealed 1-mm inside diameter capillaries containing acceptable final dispersions for different grades of carbon black can also be utilized as concentration standards. These may require occasional ultrasonic agitation.

8.2.2.6 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 (Fig. 3(*d*)). Allow the specimen to dry for about 1 min. Then, store in a specimen grid holder and list the holder location and carbon black identification in a sample catalog.

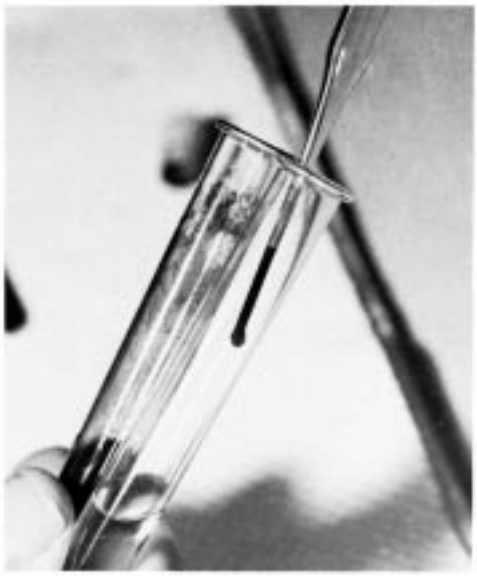
NOTE 7—This specimen preparation procedure should be performed in a dry box if the relative humidity in the room exceeds 30 %.

8.2.2.7 Repeat the entire dispersion procedure for the remaining two samples of the same carbon black, again preparing one specimen from each concentrate.

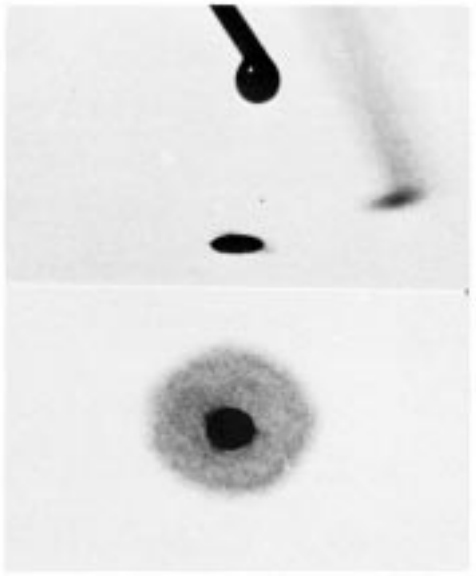
8.2.2.8 Prepare all other unknown carbon blacks in the study, along with the appropriate standards, in triplicate, employing the same procedures. It is recommended that two standard blacks be employed in each study, if possible. These should be selected on the basis of dimensional properties that

(*a*) Sampling of Dry Black with Microspatula

(*b*) Ultrasonic Agitation of Black-Chloroform Concentrate



(*c*) Dilution of Black Dispersion with Transfer Pipet



(*d*) Deposition of Diluted Dispersion on Carbon Substrate on Filter Paper

FIG. 3 Dispersion of Carbon Black Sample in Chloroform

are similar to those observed for the unknown blacks during visual screening of the specimens in the electron microscope.

NOTE 8—The ASTM D-24 Standard Reference Blacks[14] are suitable as industry-wide standards for electron microscope image analysis.

8.2.3 *Dry Carbon Blacks—Dispersion Procedure B*:

8.2.3.1 Place the vial containing the carbon blackcollodion solution into a water-ice bath in one of the large glass dishes. Immerse the ultrasonic probe into the vial and subject to maximum power for 10 min. Hold the vial and probe in position by means of clamps connected to a suitable support.

8.2.3.2 Remove the vial from the clamp and dip a clean microscope slide into the carbon black dispersion. Lift the slide vertically from the vial, allow to drain briefly and then place on hot plate (low setting) and allow to dry. Use a support to elevate the top of the slide so that only one end is in contact with the hot plate at an angle of about 45°.

8.2.3.3 When dry, score the edges of the cast film on one side of the slide with a razor blade in accordance with 8.2.1. Also, make a single cut across the center of the film on the face of the slide.

8.2.3.4 Prepare a water bath (distilled water) in the second

[14] Standard Reference Blacks, SRB-2, are available from Cities Service Co., Columbian Div. Drawer 4887, Monroe, LA 71201, in 4-lb (1.81-kg) or 50-lb (22.7-kg) quantities.

large dish, the outside of which has been coated with black tape. Position a lamp to reflect light off the water surface. Also prepare a flat grid platform from the wire mesh screening. Fold the edges of the screening over slightly to hold a piece of blotting paper in position on top of the mesh platform. Attach wire hooks to one end of the platform and immerse completely under the water bath, allowing the ends of the hooks to protrude over the side of the dish.

8.2.3.5 Place two or three grids with carbon substrates (film side up) on the submerged grid platform.

8.2.3.6 Breathe moist breath on the dispersion slide (as in cleaning eye glasses) and slowly float the film on to the water surface of the dish (Fig. 1(*b*)). The film will split into two sections at the center score mark.

8.2.3.7 Carefully raise the grid platform under one of the floating films until it comes to rest on the specimen grids. Remove the platform from the water bath and allow the grids to air dry on the blotting paper. The second floating film may be used in case of accidental loss of the first one.

8.2.3.8 When dry, transfer one of the specimen grids (film side up) to a small (about 12 mm^2) piece of blotting paper. Clamp the edge of the grid to the blotting paper with locking forceps and then immerse for at least 2 h (preferably overnight) in a vial of ethyl acetate.

8.2.3.9 Remove the specimen grid from the ethyl acetate and allow it to dry on a fresh piece of blotting paper. When dry, store in a specimen holder and catalog the location and black identification.

8.2.3.10 Repeat the specimen preparation procedures for the remaining two samples of the same black. Also prepare all other unknown samples of carbon black in the study, along with the appropriate standards, in triplicate. In actual practice, it is more efficient to prepare several samples at one time and allow them to wash overnight concurrently.

8.2.4 *Carbon Black in SBR and NR—Dispersion Procedure C*:

8.2.4.1 Insert the rubber fragments prepared in 8.1.3 into three wide-mouth jars containing 25 cm^3 of chloroform. Cap and allow to stand overnight (16 h). Drain the liquid from the jar containing the swollen bits of unvulcanized rubber compound. Add about 10 cm^3 of fresh chloroform and agitate gently. Again, pour off the liquid completely and add 5 cm^3 of fresh chloroform.

8.2.4.2 Cap the jar and immerse in the water bath of the tank-type ultrasonic agitator. Set the unit for maximum power and agitate in the most intense part of the field for 10 min.

NOTE 9—Breakdown of the carbon-rubber gel is generally fairly complete during the initial 10-min ultrasonic agitation in the jar. However, complete breakdown is not necessary to obtain a representative carbon black sample. Samples of black removed at different agitation times have not indicated significant morphological differences. The coarse, semireinforcing grades of black sometimes present a problem in that they do not form a coherent gel, that is, the black diffuses throughout the solvent in the jar without ultrasonic agitation. Under these conditions, one cannot effectively remove the dissolved polymer in the jar by decanting the clear liquid. Although the excess of soluble rubber polymer does not affect the final dispersion quality, a more dilute suspension of black is produced. This requires either the addition of more concentrate in the final dispersion or the use of less chloroform in the initial jar preparation.

8.2.4.3 Remove 1 cm^3 of the black dispersion from the jar, place in a test tube, and cork. Treat this sample in the same manner as the concentrate in 8.2.2.2 and continue with all of the remaining steps for Procedure A. The one exception pertains to the carbon substrates. These should be prepared on tungsten grids.

8.2.4.4 Place the specimens (film side up) along the bottom of one or more porcelain boats and record their positions.

8.2.4.5 Place the porcelain boats containing the specimens in a combustion tube furnace and pyrolytically remove any residual rubber polymer in accordance with either Methods D 1416 or D 297. It is advisable to use a clean combustion tube if the equipment has been used extensively for bulk pyrolysis of rubber samples.

8.2.4.6 Remove the porcelain boats from the furnace and cool them to room temperature before exposing them to air. Store the grids in a specimen holder, in accordance with 8.2.2.6 and 8.2.3.8. Acceptable dispersions in the dry state and SBR are illustrated for N-220 and N-774 carbon blacks in Fig. 4 and Fig. 5.

8.2.5 *Carbon Black in CAB—Dispersion Procedure D*:

8.2.5.1 Place the corked test tube containing the 25 mg sample of the CAB-carbon black mixture in 1 cm^3 of ethyl acetate into the ultrasonic disperser and agitate for 3 min in accordance with 8.2.2.2.

8.2.5.2 Add an additional 3 cm^3 of ethyl acetate to the test tube and transfer the contents to a polypropylene test tube with cap. Centrifuge at 1571 to 2094 rad/s (15 000 to 20 000 r/min) until the carbon black has been separated from the mixture. The centrifugation step requires about 30–40 min. For efficiency, several samples are generally centrifuged simultaneously.

8.2.5.3 Drain the clear liquid from above the carbon black sediment in the test tube and add 1 cm^3 of fresh chloroform.

8.2.5.4 Agitate the mixture ultrasonically for 30 s in accordance with 8.2.2.2.

8.2.5.5 Place 1 cm^3 of fresh chloroform in a glass test tube and add 2 to 7 drops of the carbon black suspension and blend in accordance with 8.2.2.3 and 8.2.2.4. The N100–N400 type carbon blacks generally require 2 to 3 drops from the original CAB dispersion concentrate while the coarser N500–N900 grades require about 5 to 7 drops.

8.2.5.6 Agitate the diluted mixture for 3 min in accordance with 8.2.2.2 and continue with all of the remaining steps for Procedure A. The one exception pertains to the carbon substrates. These should be prepared on tungsten grids as in 8.2.4.

8.2.5.7 Place the specimens in porcelain boats in accordance with 8.2.4.4 and continue with the remaining steps of Procedure C.

9. Calibration and Standardization

9.1 Prepare the electron microscope and image analysis systems for operation.

9.2 When the absolute pressure within the microscope is at a suitable operating level, for example, 1.3 mPa (1×10^{-5} torr), fill the reservoir of the specimen anticontamination system with liquid nitrogen. Refill when necessary during operation.

9.3 Select the desired electron beam energy, turn on the high voltage, and saturate the filament. Select and align the proper

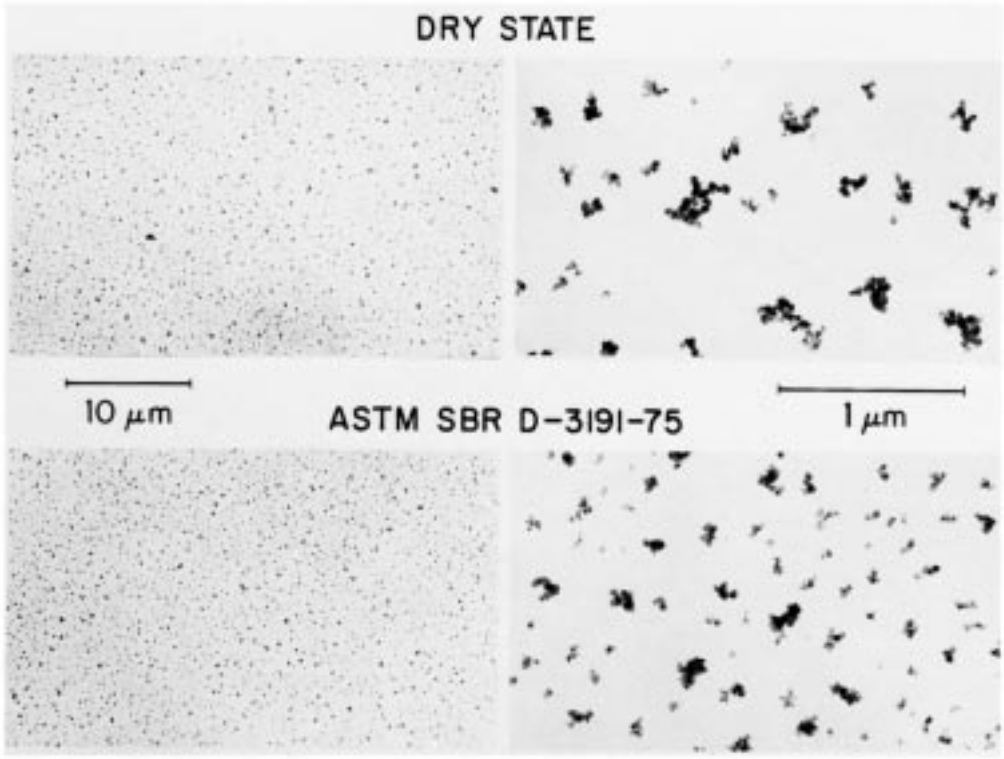


FIG. 4 Ultrasonic Dispersions of N-220 Carbon Black

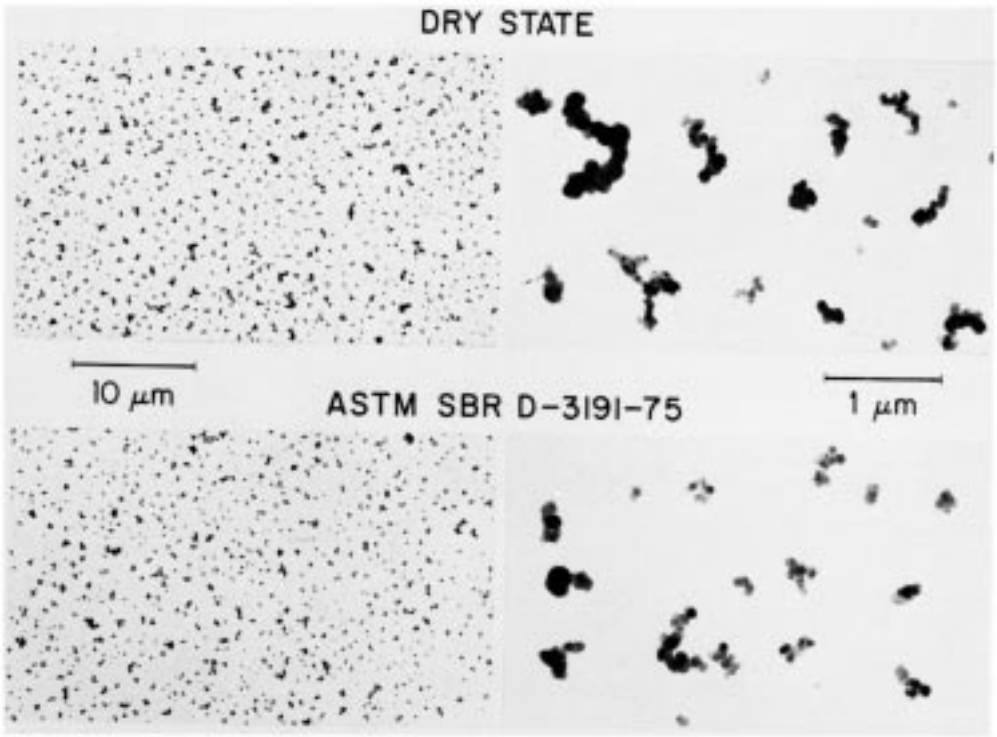


FIG. 5 Ultrasonic Dispersions of N-774 Carbon Black

size objective aperture. There is considerable latitude in the operating voltage and aperture size, depending on the type of image analysis system and carbon black.

NOTE 10—For on-line systems with fiber optics couplings to Plumbicon type scanners, 40-kV and 20-μm apertures are recommended for tread-grade carbon blacks. For the coarser, semireinforcing blacks, 60-kV and 30-μm apertures are recommended. Image contrast in an electron microscope increases with decreasing electron beam energy and diminishing objective aperture size. Maximum contrast is suitable for image analysis

systems not utilizing microdensitometry. The latter requires an intermediate level of contrast to distinguish different gray levels. Very low operating voltages in the range from 20 to 30 kV are applicable to off-line image analysis systems using film, in order to provide the best possible boundary detection at low magnifications. Images recorded on film are not recommended for microdensitometry because of the difficulty in controlling optical density.

9.4 Set the microscope at the proper operating magnification. This again depends on both the type of carbon black sample and the image analysis system. Magnification should be as high as possible for good resolution but low enough to permit reasonably efficient sampling. A suitable guideline to magnification selection may be based on the number of carbon black aggregates in the measuring frame during operation. An average of about 30 appears to be optimum, and is applicable to both on-line and off-line systems. For this reason, group the blacks of a similar size range in any given study, along with the appropriate standards.

9.4.1 Some typical operating magnifications (monitor) for an on-line image analysis system for carbon blacks in the dry state are listed as follows:

Carbon Black Type	Magnification
N110, N220, N231	140 000
N375, N339	115 000
N330, N347, N351	95 000
N550, N774	50 000
N990	40 000

NOTE 11—There is considerable latitude in these listed magnification levels. Intermediate magnifications are often utilized when a range of blacks are included in a given study. Magnification levels can be increased somewhat for blacks in rubber because of aggregate breakdown during mixing.

9.5 Calibrate the magnification of the microscope (for example, replica of 113 000 lines/metre (28 800 lines per inch) diffraction replica) at the center of the specimen stage.

10. Procedure

10.1 *On-Line System*:

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

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

10.1.3 Insert the first carbon black specimen into the electron microscope and locate at the center of the microscope stage.

10.1.4 Set the image for the proper illumination and detection.

NOTE 12—Because of the relatively low contrast, in the electron microscope, of certain carbon blacks (for example, small aggregate size types), auto detection based on the rise time of the video signal will give erroneous (underdetected) data compared to data collected by manual detection techniques, especially analog/digital visual comparison. Therefore results from the auto detected mode (usually underdetected) are not always comparable to results from the manually detected mode (usually nearly correct).

10.1.5 Adjust the image focus as required. Start the measurements on a field at one side of a grid opening.

10.1.6 Continue to select and measure adjoining fields of carbon black aggregates in a straight line tracking pattern toward the center of the grid opening. Continue until data on about 225 aggregate images have been recorded. Other objective field selection methods are also acceptable.

10.1.7 Move to the next adjoining grid opening and repeat the measuring process. Make occasional checks on the detected image if the system is not automated in this respect. (See Note 12.)

10.1.8 Continue the measurements on a third grid opening until data on a total of 675 to 700 aggregate images have been recorded.

10.1.9 Remove the specimen and return it to its proper location in the holder. Record any necessary sample identification information required for data processing (for example, coding and sequencing for punch cards if these are employed with a magnetic tape or on-line computer recording system).

10.1.10 Insert the first specimen of the next carbon black sample and carry out the measurements in the same manner. Continue until one specimen has been measured for each of the unknown carbon black samples and standards. Then proceed to the second and third specimens of each carbon black until all samples have been measured in triplicate.

10.1.11 Recheck the magnification of the microscope and use the average of the initial and final values for calculating the final dimensional parameters for all carbon black samples.

10.2 *Off-Line System*:

10.2.1 Insert the first carbon black specimen into the electron microscope and locate at the center of the electron microscope stage.

10.2.2 Set the microscope image for the proper focus and illumination for photomicrography.

10.2.3 Photograph enough fields to provide images of at least 675 to 700 aggregates. The micrographs should represent at least three different grid openings. Field selection may be based on straight line tracking as in 10.1.6 or by random selection of different openings. For the latter sampling procedure, take one micrograph at the center of grid openings that have been selected from a random number table. Sample enough grid openings to provide the necessary 675 to 700 aggregate images on the final micrographs. Remove the specimen from the microscope and return it to its position in the specimen holder.

10.2.4 Repeat the procedure in 10.2.1 to 10.2.3 for the first specimen of all other unknown carbon blacks. Then proceed to the second and third specimens of each carbon black until all samples have been recorded in triplicate.

10.2.5 Process the photographic film or plates on which the aggregate images have been recorded. Image analysis measurements can be performed directly on the negatives or on positive enlargements at the desired final magnification.

10.2.6 Mount the first micrograph in position for image analysis and set for the proper illumination and image detection.

10.2.7 Measure the aggregate images in a stepwise pattern. Measure all of the micrographs of each carbon black specimen. Carry out the sampling to provide a similar aggregate count on each micrograph with the total count being in the range from 675 to 700.

10.2.8 Measure the micrographs of all specimens in accordance with 10.2.6 and 10.2.7.

11. Calculation

11.1 *Aggregate Dimensions*:

11.1.1 Accumulate data on the three specimens of each carbon black sample that was measured.

11.1.2 Calculate the number average linear dimensional parameters (for example, aggregate perimeter) as follows:

$$\bar{P} = \frac{\Sigma P}{N} \times \frac{k}{M} \tag{7}$$

where:

P = aggregate perimeter, nm,
N = total aggregate count,
k = factor required to convert the instrumental aggregate dimensions to nanometres, and
M = linear magnification factor.

11.1.3 Calculate $\bar{L}$ and $\bar{W}$ values in a similar manner.

11.1.4 Calculate the number average area functions (for example, projected aggregate area) as follows:

$$\bar{A} = \frac{\Sigma A}{N} \times \left(\frac{k}{M}\right)^2 \tag{8}$$

11.1.5 Calculate the number average volumetric functions (for example, aggregate volume) as follows:

$$\bar{V} = \frac{\Sigma V}{N} \times \left(\frac{k}{M}\right)^3 \tag{9}$$

11.1.6 Normalize all results for unknown blacks by multiplying the measured parameter by a factor that is obtained by dividing the established value for the particular control black by its measured value. This applies to each measured parameter (for example, $\bar{A}$, $\bar{P}$, and $\bar{L}_1$) which should be normalized separately. If two or more controls are employed (the recommended procedure), use the average factor for normalization. The current industrywide number average values (dry state) for the aggregate area (A), perimeter (P), and longest dimension (L_1) of the four ASTM D-24 Standard Reference Blacks are listed as follows:

Reference Black	$\bar{A}$, nm^2	$\bar{P}$, nm	$\bar{L}_1$, nm
A-2	5657	371	117
B-2	10667	586	165
C-2	6819	472	134
D-2	65400	1332	412

NOTE 13—This step does not appear to be necessary when collecting data within a single laboratory; however, if interlaboratory comparisons are to be made, this step is required.

11.2 *Particle Size*:

11.2.1 Accumulate feature specific aggregate dimensional measurements on three carbon black specimens using preparation Procedure D.

11.2.2 Calculate an average particle size for each measured carbon black aggregate as follows:

$$d = \alpha \, \Pi \, A/P \tag{10}$$

where:

d = the number average particle diameter for each aggregate, nm,
A = projected aggregate area, nm^2,
P = aggregate perimeter, nm, and
α = a non-dimensional particle aggregation factor.

11.2.2.1 Calculate α for each measured carbon black aggregate as follows:

$$\alpha = C_2 (P^2/A)^{C_1} \tag{11}$$

$$C_1 = -0.92 \text{ and } C_2 = 13.092 \tag{12}$$

11.2.2.2 If the calculated value of $\alpha \leq 0.4$ use a value of 0.4 for that aggregate.

11.2.3 Calculate the volume, V_1, of each measured carbon black aggregate as follows:

$$V_1 = 8A^2/3P \tag{13}$$

11.2.4 Calculate the average particle volume, V_P, for each measured carbon black aggregate as follows:

$$V_P = \frac{\Pi d^3}{6} \tag{14}$$

11.2.5 Calculate the number of particles, n, in each measured carbon black aggregate as follows:

$$n = V_1/V_P \tag{15}$$

11.2.6 Calculate the number average particle diameter, as follows:

$$\bar{d} = \Sigma \, nd/n_t \tag{16}$$

where:

d = the number average particle diameter for all aggregates, nm, and
n_t = Σ n for all of the measured carbon black aggregates.

11.2.7 Calculate the standard deviation for the particle size distribution as follows:

$$SD = [\Sigma n(d-\bar{d})^2/(n_t-1)]^{1/2} \tag{17}$$

11.2.8 Calculate the coefficient of variation for the particle size distribution as follows:

$$COV = SD/\bar{d} \tag{18}$$

11.2.9 Calculate the surface mean particle diameter, d_{sm}, as follows:

$$d_{sm} = \Sigma \, nd^3/\Sigma \, nd^2 \tag{19}$$

11.2.10 Calculate the specific surface area as follows:

$$S = \frac{6000}{\rho \, d_{sm}} \tag{20}$$

where:

S = surface area, 10^3m^2/kg (m^2/g), and
ρ = the density of the carbon black, kg/m^3(9/cm^3).

11.2.11 Normalize the particle size values for unknown carbon blacks by using the established values for one or more of the ASTM D-24 Standard Reference Blacks. The Standard Reference Blacks closest to the particle size of the unknowns should be analyzed as controls. Normalize d and d_{sm} in accordance with the procedure described in 11.1.6. Normalize the standard deviation value with the same normalization factor used for d. Do not normalize the coefficient of variation value. Typical d, SD, COV, and d_{sm} values for four ASTM D-24 Standard Reference Blacks are listed as follows:

Reference Black	$\bar{d}$, nm	SD, nm	COV	d_{sm}, nm
A-3	97.1	48.1	0.50	144.9
B-3	30.5	11.9	0.39	41.6
C-3	20.6	9.3	0.45	28.0

D-3	53.5	28.4	0.53	84.8

(See Note 13 on normalization under 11.1.6.)

12. Report

12.1 *Aggregate Dimensional Properties*:

12.1.1 Identify the morphological state of the black (dry black, SBR, or NR), the manner in which the specimens were prepared (Procedure A, B, or C), and the type of data output (feature or field specific).

12.1.2 List the number of specimens (N_s) and the total aggregate count (N).

12.1.3 Report the normalized values for $\bar{A}$ to the nearest 1.0 nm,[2] $\bar{P}$ to the nearest 1.0 nm, and $\bar{L}$ to the nearest 0.1 nm. Also identify the ASTM D-24 standard that was employed as a control.

12.1.4 List any other $\bar{L}$ or $\bar{W}$ values to the nearest 0.1 nm.

12.1.5 Report $\bar{V}$ values to the nearest 100 nm.[3]

12.1.6 Report any nondimensional aggregate shape factors to the nearest hundredth. Examples of shape factor calculations (F_1, *C.F.*, and *S.F.*) are listed as follows:

Feature Specific

$$\bar{F}_1 = \frac{\Sigma(L_1/W_1)}{N} \tag{21}$$

$$C.F. = \frac{\Sigma(P^2/4\pi A)}{N} \tag{22}$$

$$S.F. = \frac{\Sigma(P^3/6\pi^2 V)}{N} \tag{23}$$

Field Specific

$$\bar{F}_1 = \bar{L}_1/\bar{W}_1 \tag{24}$$

$$C.F. = \bar{P}^2/4\pi\bar{A} \tag{25}$$

$$S.F. = \bar{P}^3/6\pi^2\bar{V} \tag{26}$$

12.1.6.1 The field specific parameters should not be used interchangeably with feature specific parameters.

12.2 *Particle Size*:

12.2.1 Report the normalized values for d, SD, and d_{sm} to the nearest 0.1 nm.

12.2.2 Report the COV value to the nearest 0.01.

13. Precision and Bias

13.1 Based on cumulative three-specimen results (N = 2000) in a single laboratory across the full range of rubber grade carbon blacks (dry state), the average coefficients of variation for aggregate area, perimeter, and longest Feret's diameter are as follows:

$$\bar{A} = 4.4 \tag{27}$$

$$\bar{P} = 2.8 \tag{28}$$

$$\bar{L}_1 = 2.5 \tag{29}$$

NOTE 14—The standard deviation of average aggregate dimensions from electron microscope image analysis increases with increasing aggregate size. Therefore, test precision over a wide range of carbon blacks is best stated on a percentage basis.

14. Keywords

14.1 carbon black; electron microscopy; image analysis; primary aggregate dimensions