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Standard Test Method for Carbon Black—Morphological Characterization of Carbon Black — Primary Aggregate Dimensions from Using Electron Microscope Image Analysis 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] 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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1. Scope

1.1 This test method covers the morphological characterization of carbon black primary aggregates from transmission electron microscope images. These measurements are applicable used to derive the mean particle and aggregate size of carbon blacks in the dry (as manufactured) state, extracted from unvulcanized rubber compounds and in a cellulose acetate butyrate paint 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:*

D 297 Test Methods 3182 Practice for Rubber Products—Chemical Analysis Rubber—Materials, Equipment, and Procedures for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets[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]

D 6556 Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *Aggregate Dimensional Properties from Image Analysis:General*

3.1.1.1 *area (A)*—the two-dimensional projected area of the carboncarbon 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 pagrticle size implies the mean value from multiple measurements.

3.1.1.2 *chord*—the length of a scanning intercept across ancarbon black aggregate in a given direction. The *mean chord* ($\pi A/P$)—a discrete, rigid colloidal entity that is the average width smallest dispersible unit; it is composed of extensively coalesced particles. Carbon black aggregate sinze is all distributional propeerty; therefore, the term aggregate size implies the mean value from multiple measurements.

3.1.1.3 *Feret's diameter*—the maximum spacing between parallel tangents to an aggregateglow discharge—a plasma of ionized gas that is formed in a given direction. The average Feret (*L*) high-voltage field at pressures of about 3 to 20 Pa (25 to 150 $\times$ 10^{-3} torr). An alternating current (a-c) glow discharge using air is derived from an average effective in cleaning and oxidizing the surface of multiple measurements at specific angular increments. carbon substrates to improve the wetting characteristics of polar vehicles containing pigment dispersions.

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

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

3.1.1.6 *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).

3.1.2.3 *volume (V)*—an estimate of the volume of the 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:

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

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

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

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

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

using stereological principles.

3.1.3 *carbon black aggregate Image Analysis*—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

3.1.3.1 *erosion*—the process by fracturing.

3.1.5 *chord sizing*—an operation in which a specified length increment (ΔL) is cut off each detected chord image features are reduced in an image. All chords shorter than ΔL are completely eliminated size by selectively removing pixels from theimr periphery. It consists of examining each binary pixel and all chords larger changing it from ON to OFF if it has greater than ΔL are shortened by ΔL. The operation is repeated over a range preset minimum of neighbors that eventually eliminates all are OFF. It serves a number of the chords in the image useful functions such as smoothing feature outlines and separating features touching each other.

3.1.3.2 *dilation*—theby converse of erosion. This provcess is accomplished by changing any OFF pixel to ON if it has greater than a chord size distribution.

3.1.6 *detected image*—an electronic monitor display preset minimum of the chords across the ON neighbors. This process causes image features to grow 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, size, which fills in small breaks in features, internal voids, or transparencies on small indentations along the scanner tube.

3.1.8 feature surface.

3.1.3.3 *feature*—areas within a single continuous boundary (for example, an aggregate image) that have an optical-density value (gray-level range) gray-level ranges that is distinct allow them to be distinguished 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 feature via thresholding.

3.1.3.4 *thresholding*—selecting a minimal loss range of brightness.

3.1.10 *glow discharge*—a plasma of ionized gas brightness such that discrimination 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 possible between 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 figure and is defined as" white," while the complete absence of light in a field is" black." background. 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 decreasing particle 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 carbon black loaded polymer systems. Vulcanizate hysteresis A carbon black's particle size distribution is its single most important property, and strength properties (tear, tensile, it relates to degree of blackness and abrasion resistance) rubber reinforcement. For a given loading of carbon black, blackness and reinforcement increase with diminishing aggregate smaller particle size. Extrusion die swell diminishes Aggregate size and vulcanizate modulus 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 aggregate irregularity (for example, the amount of deviation from a spherical shape). 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 resolving power resolution of 1.0 nm or better. Operating voltages (electron beam) should include settings of 40 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 specimen chamber 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*, 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~~ consisting at ~~the borders,~~ minimum of a ~~compensator for eliminating shading effects, a detector for discerning the boundaries~~ TEM-interfaced camera capable of ~~the carbon black aggregates at different gray levels, and one~~ 640 × 480 pixel or ~~more~~ better resolution, a computer ~~modules for converting the output of the detector into dimensional information. Minimum requirements for dimensional output are area, perimeter, average Feret's diameter,~~ equipped with frame grabbing hardware to capture TEM images digitally, and ~~feature count. Desirable additional outputs are volume by microdensitometry~~ computer software to perform morphological operations and ~~Feret's diameters in different directions. The system shall contain one or more devices for automated data recording, processing, averaging,~~ measurements on image features and ~~printing of results. Acceptable recorder-processing systems~~ store resulting data. Operations must 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~~ background/noise elimination, thresholding, erosion and ~~electron microscope is recommended.~~ dilation on thresholded (binary) images, and measurements must include area, perimeter and a minimum of 16 Feret diameters at angular spacings of 11.25°.

5.3 *Two-roll Mill*:

5.4 *Vacuum Evaporator*,~~[3]~~,[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}~~ $(1 \times 10^{-5}$ 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.~~

~~[3] The following vacuum evaporator systems have been found to be acceptable: Denton Model DV-515,~~

[3] Formvar, a registered trademark of Monsanto, also available ~~from Denton Vacuum, Inc., Cherry Hill Industrial Center, Cherry Hill, NJ 08034; Ladd Vacuum Evaporator,~~ as Catalog No. ~~4~~ 18050 and 18060, 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.~~

[4] 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.

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

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 %.

5.67 *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 RodsElectrically Heated Tube Furnace*, approximately 3.1 mm in diameter. 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 *Carbon Rod Sharpener*. [5]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.

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

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

5.135 *Rubber Bulbs*, for pipets.

5.146 *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.

5.18 *Filter Paper*, general purpose.

5.19 *Vinyl TubingCarbon Coated Electron Microscope Specimen Grids*, approximately 50 mm long, 12.5-mm inside diameter. 3-mm diameter, 200 to 300 mesh. Commercially available or can be prepared as described in Annex A1.

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*. [5]

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

5.21 *Tweezers*, fine-tipped.

5.292 *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

5.23 *Fluorocarbon Duster.*

5.324 *Lens Tissue*, lint-free.

5.33

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

5.34

5.26 *Centrifuge*, 2094 rad/s (20 000 high speed (15 000 to 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

5.27 *Beakers*, 2000 cm^3 capacity.

6. Reagents and Materials

6.1 *Castor Oil*, laboratory grade.

6.2 *Chloroform*, reagent grade.

6.2 *Tetrahydrofuran (THF)*, reagent grade.

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

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

6.54 *Ethyl Acetate*, reagent grade.

6.65 *Poly (Vinyl Formal) Resin,*[3] *Resin,*[6] Grade 15/95.

6.6 *Cellulose Acetate Butyrate Resin (CAB).*

6.7 *Cellulose Acetate Butyrate Resin*. [5]

6.8 *PhthalatePhthalate Type Plasticizer.*

7. Sample Preparationg—Dispersion Procedures

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 (Sonic Bath)*:

8.1.1 *Dry Carbon Blacks—Dispersion Procedure A*—Weigh

7.1.1 Weigh 8 to 10 mg of black, place in carbon black into a test tube containing 1 cm^3 of solvent (typically chloroform (from dispenser), and cork. Repeat this procedure for two more different samples from the same vial of black. or THF).

NOTE 1—With experience, it is may not be necessary to weigh each carbon black sample. One full scoop with sample, as an estimated amount from the microspatula provides a satisfactory may be sufficient. There is considerable latitude in the amount of carbon black for all samples.

8.1.2 *Dry Carbon Blacks—Dispersion Procedure B*—Weigh 7 mg 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 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 v simple wire holder.

7.1.4 Transfer a small portion of the concentrated carbon black-solvent mixture into another test tube containing 30 1 cm^3 of collodion solution prepared 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 of collodion, 45. If considerable dilution is required, the excess volume above 1 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. should be discarded.

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

NOTE 3—This is latitude exists for achieving the recommended procedure proper concentration levels in the final dispersions for a large batch different grades of rubber compound containing the same carbon black. Ideally, each of Concentration and overall dispersion quality are best determined by screening the three samples should be selected from actual specimens in the electron microscope and then making the necessary adjustments.

7.1.6 Place a ~~different slab. For~~ specimen grid with carbon substrate (film side up) on a piece of filter paper. Remove a small ~~test batches, however,~~ amount of the final diluted dispersion using a fresh pipet and place one drop on the grid as close to the center a~~m~~s possible, from a ~~single slab is considered adequate.~~

~~8.1.4 *Carbon Black*~~ *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* ~~*CAB, Dispersion Procedure D*—Cut an elongated thin section from~~ a dry box if the relative humidity in the room exceeds 30 %.

7.1.7 For TEM grids that contain formvar or residual CAB ~~compound~~ (CAB chip dispersions), place the TEM grid in ~~accordance with 8.1.3. From this, weigh a 25 mg~~ an appropriate sample ~~and~~ holder, place in ~~a glass test tube containing 1 cm^3 of ethyl acetate~~ the pyrolysis chamber and ~~cork.~~

~~8.1.4.1 There is considerable latitude in~~ allow adequate time for the ~~mass of the sample. With experience, this can~~ chamber to be ~~estimated satisfactorily.~~

~~8.2 *Test Specimens*:~~

~~8.2.1 *Substrate Preparation*—Prepare thin backing films~~ purged by ~~wiping a clean glass slide with lint-free lens tissue. Wipe three times with one sheet~~ an inert gas to prevent oxidation of ~~lens tissue and then repeat with a fresh sheet. Dip~~ the sample. Pyrolid~~z~~e the specimen grid at~~o~~ a ~~0.25 % solution of~~ 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 ~~1,2-dichloroethane (Fig.~~ the dry state and removed from a rubber compound (SBR) are illustrated for N-220 and N-774 carbon blacks in Figs. 1 and ~~(*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~~

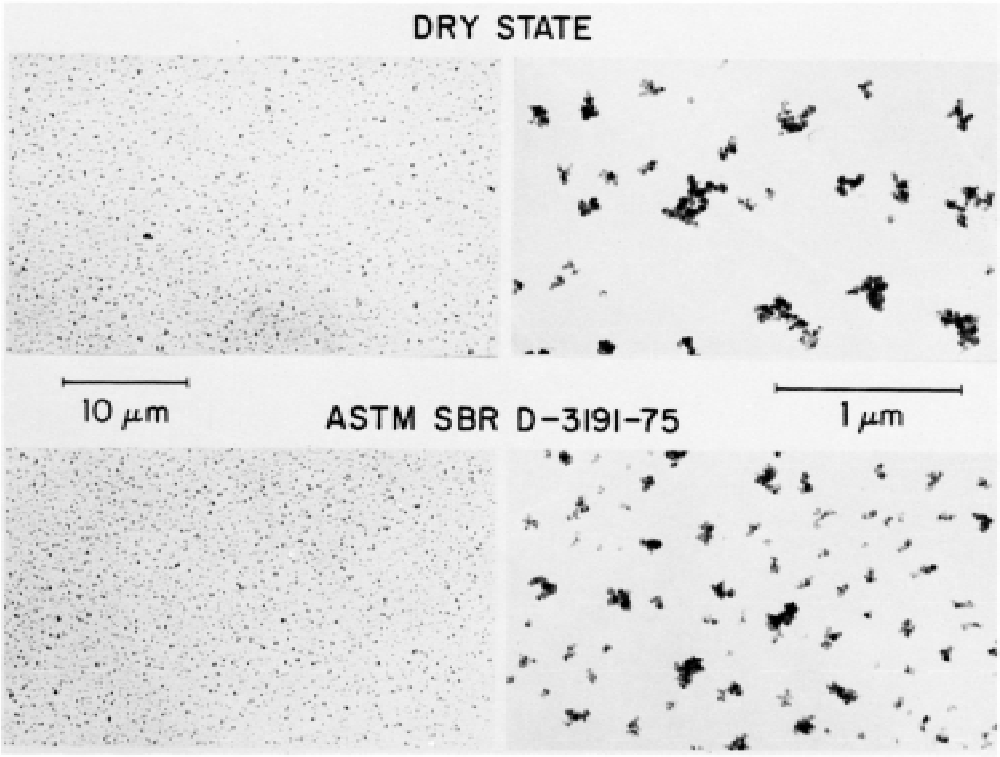

FIG. 1 Ultrasonic Dispersions of N-220 Carbon Black

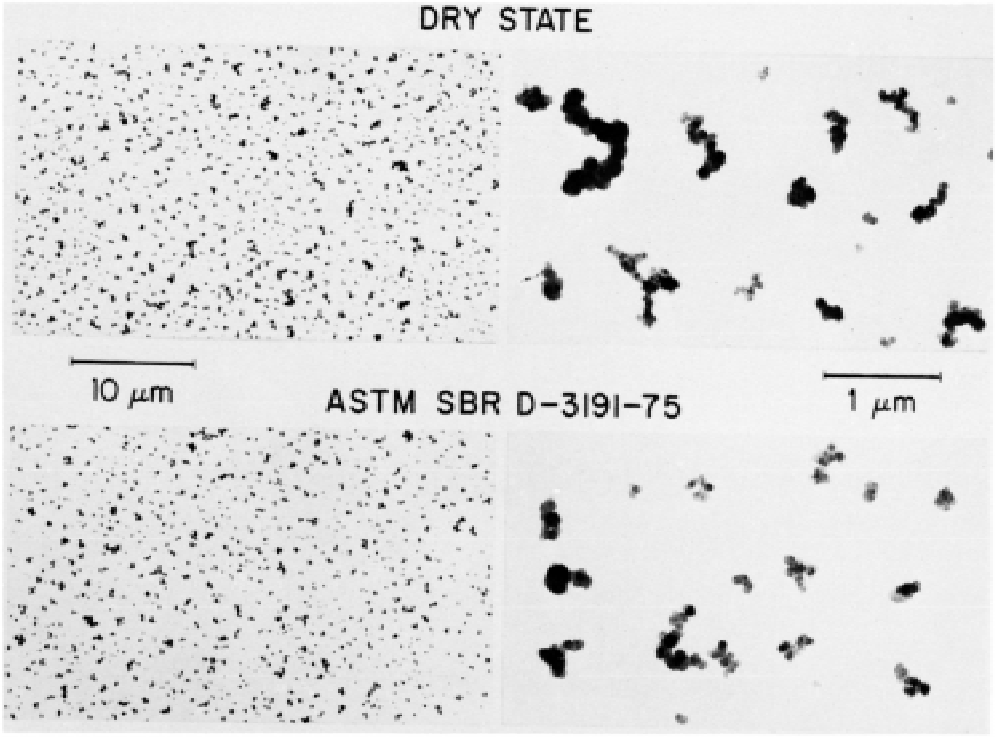

FIG. 2 Ultrasonic Dispersions of N-774 Carbon Black

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 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 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 2.

7.2 *Dry Carbon Blacks—Dispersion Procedure A Black (Ultrasonic Probe)*:

8.2.2.1 Adjust the water level in the tank-type ultrasonic generator for maximum agitation with 1

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

NOTE 63—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 a judgment factor considerable latitude in achieving the proper concentration levels in the final dispersions for different grades amount of carbon black, although a reasonable degree of latitude exists for acceptable specimens. Concentration black used. The finer N100 and overall dispersion quality are best checked by screening N200 blacks may require somewhat less carbon black than the actual specimens (on grids) in coarser semi-reinforcing types.

7.2.2 Place the electron microscope and then making the necessary adjustments. For a given study vial 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 solvent into an ice-water bath.

7.2.3 Insert the grid as close probe to the center as possible, from a height depth of about 12 mm (Fig. 3(*d*)). Allow approximately 2.5 cm into the specimen vial and ultrasonicate at 40 to dry 50 watts for about 1 min. Then, store in a specimen grid holder and list the holder location and carbon black identification in a sample catalog. 10 min.

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 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[5] 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 4—The ultrasonic probe into the vial and subject to maximum power for 10 min. Hold ice-water bath containing the sample vial and probe should be housed 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 large dish, the outside of which has been coated with black tape. Position a lamp acoutic enclosure to reflect light off the water surface. Also prepare reduce cavitation noise.

7.2.4 Transfer 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 portion (approximately 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 4 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 concentrated carbon black/solvent mixture into another vial and add 20 cm^3 of fresh chloroform and agitate gently. Again, pour off solvent.

7.2.5 Check the liquid completely 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 5 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.

7.2.6 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 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. . Repeat 7.2.5.

NOTE 9—Breakdown 5—A reasonable degree of latitude exists for achieving the carbon-rubber gel is generally fairly complete during the initial 10-min ultrasonic agitation proper concentration levels in the jar. However, complete breakdown is not necessary to obtain a representative carbon black sample. Samples of black removed at final dispersions for 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, carbon black. Concentration and overall dispersion quality are best determined by screening the black diffuses throughout the solvent actual specimens in the jar without ultrasonic agitation. Under these conditions, one cannot effectively remove electron microscope and then making the dissolved polymer in necessary adjustments.

7.2.7 When the jar by decanting the clear liquid. Although the excess of soluble rubber polymer does not affect the final dispersion quality, drop on the filter paper is in an acceptable color range, place a more dilute suspension specimen grid with a thin carbon substrate (film side up) on a piece of black is produced. This requires either the addition filter paper. Using a fresh pipet, remove a small amount 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 place one drop on the same manner grid as close to the concentrate in 8.2.2.2 and continue with all center as possible, from a height of about 12 mm. Allow the remaining steps for Procedure A. The one exception pertains specimen grid to the carbon substrates. These should be prepared dry for approximately 1 min on tungsten grids.

8.2.4.4 Place the specimens (film side up) along filter paper.

7.2.8 Place the bottom of one or more porcelain boats grid into the microscope and record their positions.

8.2.4.5 Place examine the porcelain boats containing dispersion for visual separation of discrete aggregates. If the specimens in dispersion shows a combustion tube furnace high concentration (overlap of aggregates, agglomeration, 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 so forth), adjust the equipment has been used extensively for bulk pyrolysis concentration of rubber samples.

8.2.4.6 Remove the porcelain boats from the furnace dispersion by following 7.2.6 and cool them to room temperature before exposing them to air. Store the grids in prepare a new 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 grid by following 7.2.7.

7.3 *Carbon ~~Black in CAB—Dispersion Procedure D~~ Blacks Removed from Vulcanized Rubber Compounds*:

~~8.2.5.1 Place the corked test tube containing the 25 mg sample of the CAB-carbon black mixture in~~

7.3.1 Cut thin sections (about approximately 1 ~~cm~~ mm^3) of ~~ethyl acetate into~~ the ~~rul~~rubber compound using a razor blade.

7.3.2 Place 5 to 10 sections i~~c d~~n an appropriate sample holder, place in the pyrolysis chamber and ~~agitate~~ allow adequate time for ~~3~~ 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.

7.3.3 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 ~~8.2.2.2.~~

~~8.2.5.2 Add an additional 3~~ 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.

7.3.4 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).

7.3.5 Disperse the residual carbon black sample as described in 7.1.2-7.1.8.

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

7.4.1 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.

7.4.2 *Preparation of CAB Chip*:

7.4.2.1 The following conditions were defined for a Farrel Tecno Lab Polymill 110P. Slight adjustments may be necessary depending on the ~~test tube and transfer~~ size of the ~~contents~~ 2-roll mill used.

7.4.2.2 Preheat the 2-roll mill to give a ~~polypropylene test tube with cap. Centrifuge~~ temperature on the front roll of the mill at ~~1571~~ 76°C and the rear roll at 66°C, noting that rolls should be in motion while heating.

7.4.2.3 Set the roll gap to ~~2094 rad/s (15 000 to 20 000 r/min) until~~ 0.2 mm and roll rate of 20 r/min.

7.4.2.4 Weigh out the following ingredients depending on the carbon black ~~has been separated from~~ type being analyzed:

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

7.4.2.5 Mix the ~~mixture. The centrifugation step requires about 30–40 min.~~ carbon black and CAB resin in a container, then add the Santicizer, taking care not to let the Santicizer touch the sides of the container.

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

7.4.2.7 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 ~~efficiency, several samples are generally centrifuged simultaneously.~~

~~8.2.5.3 Drain~~ the ~~clear liquid from~~ 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.

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

7.4.2.9 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 t~~t~~he rollers, folded together, then placed back in the gap at 1-min intervals.

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

7.4.2.11 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.

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

7.4.2.13 Repeat step 7.4.2.11 for an additional 5-min mixing cycle for a total flux time of 20 min.

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

7.4.3 Cut approximately a 25 mg section of the chip and place in a glass test tube containing 1 cm^3 of ~~fresh chloroform.~~

~~8.2.5.4 Agitate the mixture ultrasonically for 30 s~~ solvent. There is considerable latitude in ~~accordance with 8.2.2.2.~~

~~8.2.5.5 Place 1 cm^3~~ the mass of ~~fresh chloroform in a glass test tube and add 2 to 7 drops of~~ the sample. With experience, this can be estimated satisfactorily.

7.4.4 Disperse 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~~ chip as described 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. 7.1 (bath) or 7.2 (probe).

8. Calibration and Standardization

98.1 Prepare the electron microscope and/image analysis systems for operation.

9.2 When operation according to the absolute pressure within manufacturer's recommendation.

8.2 Set 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 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 magnification to Plumbicon type scanners, 40-kV and 20-µm apertures obtain EMSA values that 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 similar to distinguish different gray levels. Very low operating voltages in the range from 20 to 30 kV STSA values (see Test Method D 6556). The following resolution guidelines are applicable offered to off-line image analysis systems using film, in order to provide get the best possible boundary detection at low magnifications. Images recorded on film are not recommended for microdensitometry because of the difficulty operator 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 magnification range, but low enough to permit reasonably efficient sampling. A suitable guideline to minor adjustments (±1 magnification selection level) may be based on the number of carbon black aggregates in the measuring frame during operation. An average of about 30 appears necessary to be optimum, and is applicable to both on-line and off-line systems. For this reason, group the blacks of a achieve 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:

EMSA and STSA values:

Carbon Black Type Particle Size Range (nm)	Magnification Resolution (nm/pixel)
N110, N220, N231	140 000
14 to 21	1.5 to 2.0
N375, N339	115 000
22 to 26	2.0 to 2.5
N330, N347, N351	95 000
27 to 37	2.5 to 3.0
N550, N774	50 000
38 to 49	3.0 to 4.0
N990	40 000
50 to 62	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 intensity4.0 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
5.0	56575.0 to 6.0		
A-2	5.0 to 6.0		
A-263 to 100	3716.0 to 12.0		
101 to 199	6.0 to 12.0		
101 to 199	117		
200 to 400			

B-2	10667	586	165
C-2	6819	472	134
D-2	65400	1332	412
D-2	65400	1332	41212.0 to 20.0

NOTE 13—This step does not appear to be necessary when collecting

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

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

9. TEM Analysis Procedure

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

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

9.3 Insert the first carbon black specimen into the electron microscope, locate it at the center of the microscope stage, adjust to eucentric height, and adjust the microscope focus.

9.4 Start the measurements on a single laboratory; however, if interlaboratory comparisons are field near one side of a grid opening. Continue to be made, this step is required.

11.2 *Particle Size* *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.*

9.5 *Image Analysis*:

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:

$$d = \alpha \Pi A/P \quad (10)$$

where:

d = the

9.5.1 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.

9.5.2 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.

9.5.3 Configure the acquisition software to reject aggregates smaller than 50 pixels in area (if resolution is chosen correctly as directed above, this is slightly smaller than a single particle having the mean particle size value). These features are generally attributable to noise in the image. The use of erosion followed by dilation (1 pixel depth and minimum number of cycles—typicavlly 1 to 2 cycles) on each binary image can smooth "noise" associated with particle boundaries without significantly altering "real" data if magnification/resolution are selected optimally (see above).

9.5.4 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. Again, proper magnification/resolution selection will help minimize these effects.

9.6 Repeat the analysis for each aggregate, nm,

A = projected 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.

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

10. Calculations

10.1 *Single Aggregate*:

10.1.1 *Measured Parameters*[4]

A = aggregate area (nm^2), and

P = aggregate perimeter (nm).

10.1.2 *Derived Parameters*

D = area-equivalent aggregate diameter (nm) = $(4A/\pi)^{1/2}$,

P = aggregate perimeter, nm, and

α = a non-dimensional particle

α = aggregation factor.

11.2.2.1 Calculate 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 each measured carbon black a single aggregate as follows:

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

$$C_1 = -0.92 \text{ and } C_2 = 13.092 \quad (12)$$

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

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

$$V_1 = 8A^2/3P \quad (13)$$

11.2.4 Calculate the average particle volume, $V = V_A/V_P$.

10.2 *Distributional Properties* for each measured carbon black aggregate as follows:

$$V_P = \frac{\Pi d^3}{6} \quad (14)$$

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

$$n = V_1/V_P \quad (15)$$

11.2.6 Calculate the number average particle diameter, as follows:

$$\bar{d} = \Sigma nd/n_t \quad (16)$$

Particles and Aggregates:

10.2.1 *Derived Parameters*

where:
$\bar{d}$ = the number average particle diameter for all aggregates, nm, and
n_t = Σ n for all of the measured carbon black aggregates.
= Σn for all of the aggregates measured, or total number of all particles,
m = mean particle size (nm) = $[\Sigma(n*d_p)] / n_t$

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

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

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

$$COV = SD/\bar{d} \quad (18)$$

11.2.9 Calculate the surface standard deviation (nm) = $[\Sigma n(d_p - m)^2/ (n_t - 1)]^{1/2}$,
wm = weight mean particle diameter, $d_{s\ size\ (nm)} = [\ \Sigma\ (n * d_p m$, as follows:

$$d_{sm} = \Sigma nd^3/\Sigma nd^2 \quad (19)$$

11.2.10 Calculate the specific surface area as follows:

$$S = \frac{6000}{\rho\, d_{sm}} \quad (20)$$

where:

S = surface area, 10^4)] / [Σ (n * d_p^3)],
hi = particle size heterogeneity index = wm/m,
d_{sm} = particle size surface mean diameter (nm) = [Σ (n * d_p^3)] / [Σ (n * d_p^2/kg)],
EMSA = electron microscope surface area (m^2/g), and
ρ = the/g) = 6000 / (ρ * d_{sm}); where: ρ = 1.8 g/cm^3 (assume density of the carbon black), k
N_t = number of aggregates measured,
M = mean aggregate size (nm) = Σ D / N_t,
SD = aggregate size standard deviation (nm) = [Σ(D − M)^{32}/ (9N_t − 1)]$^{1/c2}$,
WM= weight mean aggregate size (nm) = ΣD^4/ ΣD^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	— *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. , and

HI = aggregate size heterogeneity index = WM/M.

11. Report

12.1 *Aggregate Dimensional Properties*:
12.1.1 Identify
11.1 Report the morphological state of the black (dry black, SBR, following information for Particle Size Distributional Properties:
11.1.1 Dispersion method (CAB, DB or NR), the manner in which the specimens were prepared (Procedure A, B, or C), and the type removed from rubber compound),
11.1.2 Number 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 *A* to the nearest 1.0 nm, aggregates measured,
11.1.3 Mean particle size, m (nm),
11.1.4 Weight mean, wm (nm),
11.1.5 Heterogeneity index, hi, and
11.1.6 Electron microscope surface area, EMSA ($m^{2\,\bar{p}\,\bar{\omega}}$/g).
11.2 Report 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 *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

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

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

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

Field-Specific

$$\bar{F}_1 = \bar{L}_1/\bar{W}_1 \quad (24)$$

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

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

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 following information 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 Aggregate Size Distributional Properties:
11.2.1 Dispersion method (DB or removed from rubber grade carbon blacks (dry state), the average coefficients compound),
11.2.2 Number of variation for aggregates measured,
11.2.3 Mean aggregate area, perimeter, and longest Feret's diameter are as follows:

$$\bar{A} = 4.4 \quad (27)$$

$$\bar{P} = 2.8 \quad (28)$$

$$\bar{L}_1 = 2.5 \quad (29)$$

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. size, m (nm),

11.2.4 Weight mean, WM (nm), and
11.2.5 Heterogeneity index, HI.

12. Keywords

142.1 aggregate size; automated image analysis; carbon black; electron microscopy; image analysis; primary aggregate dimensions particle size

ANNEX

(Mandatory Information)

A1. PREPARATION OF CARBON COATED TEM GRIDS

A1.1 *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. 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 aerosol duster.

A1.2 Carefully float the poly (vinyl formal) film on to a distilled water surface in the Büchner funnel. Place the specimen grids (shiny side up) one at a time on the top of the floating poly (vinyl formal) film. Generally, a total of 40 or more grids are prepared in a single operation.

A1.3 Prepare a small screen platform and place face down on the grids, then remove the grids and poly (vinyl formal) film from the water by depressing the screen platform and rotating it 180°. An alternative procedure allows placement of the screen platform underneath the water in the Büchner funnel. The grids are deposited on the platform and the poly (vinyl formal) film is positioned over the grids and allowed to settle on them by draining the water from the funnel. Allow the coated grids to dry at least 3 to 4 h before using them.

A1.4 Place the screen platform containing the poly (vinyl formal) coated grids in a vacuum evaporator that has been set 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. Center the grids on the screen platform in the evaporator at a distance 100 mm away from the evaporation tip of the carbon rods. Insure that a-c glow loop is moved to the side during this process. Follow manufacturer's recommendation for carbon evaporation.

A1.5 Turn off the current through the carbon rods and allow the system to cool for about 10 min. Close the vacuum valve and allow air to enter the bell jar so that it can be removed. Place a-c glow loop directly over the screen platform, then replace the bell jar. Apply vacuum to achieve an absolute pressure of 20 Pa (150×10^{-3} torr). 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. 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 the glow discharge and bring the bell jar to atmospheric pressure. Remove the coated specimen grids and store in a dry atmosphere.