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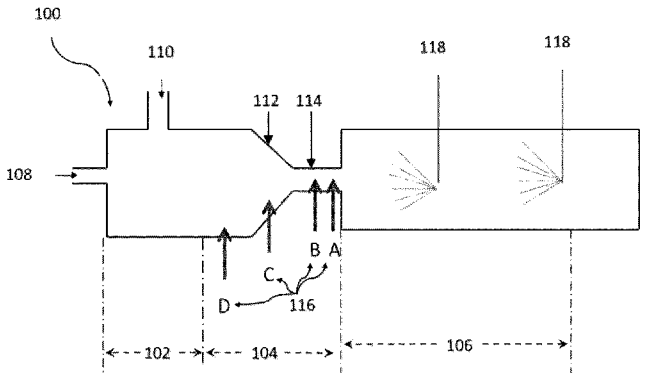

FIG. 1

(57) Abstract: Carbon blacks having broad aggregate size distributions, distinctive morphology and shape distributions, together with rubber compositions and tires containing such carbon blacks.

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CARBON BLACK WITH SHAPE-MODIFIED AGGREGATE DISTRIBUTION, RUBBER PRODUCTS USING THE SAME

BACKGROUND

TECHNICAL FIELD

[0001] The present disclosure relates to carbon blacks, and specifically to carbon blacks with a distinctive morphology and shape-modified aggregates and aggregate size distribution, together with rubber products containing such carbon blacks.

TECHNICAL BACKGROUND

[0002] Carbon black is an engineered, particulate elemental carbon found in countless items used on a daily basis. It is a useful ingredient in, for example, rubber goods, improving their strength, durability, and overall performance. It is also used as a pigment and as a performance-enhancing component in, for example, printing inks, paints, and plastics.

[0003] Carbon black morphology has historically been a rich area for development of new carbon blacks since this property has a significant impact on the properties they impart to various composites, namely rubber goods. Typically, carbon blacks are described in product specifications and in the literature by their colloidal properties, namely surface area, tint and structure.

[0004] In particular, variation of the carbon black aggregate size distribution has been utilized to impart desirable properties to rubber compounds. Typically, this has been achieved by making the aggregate size distribution broader, thereby increasing the average inter-aggregate spacing and reducing the degree of carbon black networking that is primarily responsible for the heat generation in rubber compounds. In rubber compounds, a lower degree of carbon black networking is traditionally associated with lower hysteresis, which is the primary source of rolling resistance in a tire, and therefore it is a strong driver for lower fuel consumptions.

[0005] As such, it has become important to devise ways to further reduce the networking potential of carbon black either through surface modification to improve the carbon black elastomer interaction, or through its morphology. However, practically speaking, the ability to make broader and broader aggregate size distributions has reached a limit. First, from the reactor standpoint, the broadening of conversion oil sprays in the reactor to produce broad

aggregate size carbon blacks has its own limitations, even if considering a wide range of reactor technology. In addition, when one makes the aggregate size broader, it typically results in a broader particle size distribution, hence the aggregate size and particle size distributions are coupled. In other words, conventional technology requires that the particle size distribution must be made broader in conjunction with the aggregate size distribution, which has its own disadvantages.

[0006] For conventional tire tread compounds, the use of broad aggregate size carbon blacks can often result in poor wear performance and lower electrical conductivity.

[0007] Thus, there is a need for improved carbon black materials that can facilitate optimizing the aggregate size distributions, through broadening and control of the shape distribution, to provide for a significantly improved range of and balance of viscoelastic properties such as dynamic stiffness, hysteresis, treadwear and durability, among other properties, while maintaining narrow particle size distribution and compound electrical conductivity.

[0008] This and other needs are met with the carbon black of the invention, the methods for producing it and compositions containing it.

SUMMARY

[0009] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, this disclosure, in one aspect, relates to shape modified carbon blacks, and specifically to carbon blacks having unique shape properties and distributions. In the following description, this carbon black will be named "carbon black of the invention" or "Inventive Carbon Black", the two expressions being synonymous.

[0010] Another aspect of the invention relates to rubber compounds comprising at least one carbon black of the present invention.

[0011] Additional aspects of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or can be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be

understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE FIGURES

[0012] The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention.

[0013] FIG. 1 illustrates an exemplary carbon black reactor, in accordance with various aspects of the present disclosure.

[0014] FIGS. 2A-2D illustrate shape classifications for carbon black aggregates, including Type 1 Spheroidal (FIG. 2A), Type 2 Ellipsoidal (FIG. 2B), Type 3 Linear (FIG. 2C), and Type 4 Branched (FIG. 2D), in accordance with various aspects of the present disclosure.

[0015] FIG. 3A illustrates exemplary carbon black aggregates having a normal aggregate size distribution, together with an exemplary plot of the aggregate size distribution, in accordance with various aspects of the present disclosure.

[0016] FIG. 3B illustrates exemplary carbon black aggregates of the present disclosure having a different distribution of large, higher structured aggregates and small, lower structure aggregates, together with an exemplary plot of the aggregate size distribution illustrating the modified aggregate size distribution, in accordance with various aspects of the present disclosure.

[0017] FIG. 4 illustrates aggregate size distributions for a normal ASD of an ASTM type carbon black (solid line) and an Inventive Carbon Black (dotted line), and also shows morphological descriptors from typical disc centrifuge photosedimentometry, in accordance with various aspects of the present disclosure.

[0018] FIGS. 5A-5E show examples of the ASDs for various Comparative Carbon Blacks versus the Inventive Carbon Blacks of Similar Surface Area and Structure.

[0019] FIGS. 6A and 6B illustrate transmission electron micrographs of aggregates of Comparative Carbon Black A and Inventive Carbon Black 1, in accordance with various aspects of the present disclosure.

[0020] FIGS. 7A and 7B illustrate low and high magnification transmission electron micrographs, respectively, of a very large and higher structure aggregate composed of numerous particles of the Inventive Carbon Black.

DESCRIPTION

[0021] The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

[0022] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0023] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

[0024] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0025] As used herein, unless specifically stated to the contrary, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a filler" or "a solvent" includes mixtures of two or more fillers, or solvents, respectively.

[0026] By "conventional carbon black" it means carbon black materials manufactured without using the processes described herein, such as, for example, ASTM grade carbon blacks as described in ASTM D-1765-19 which have historically been used in the tire and

rubber industry and exhibit the colloidal balance of properties as described in ASTM D-1765-19.

[0027] As used herein, unless specifically stated to the contrary, the term "Heterogeneity Index" or "HI" is intended to refer to a ratio providing a normalized measure of the breadth of distribution or polydispersity. Specifically, the term "HI_{ASD}" refers to the aggregate size heterogeneity index, and the term "HI_{PSD}" refers to the particle size heterogeneity index, both as defined in ASTM D3849-14a ("Morphological Characterization of Carbon Black Using Electron Microscopy-Method A"). The aggregate size heterogeneity index HI_{ASD} is determined by the weight mean aggregate size ("WM_{agg}") divided by the mean aggregate size ("M_{agg}"),

$$HI_{ASD} = WM_{agg} / M_{agg}, \qquad (1)$$

wherein the weight mean aggregate size WM_{agg} is determined by:

$$WM_{agg}\ (nm) = \sum D^4_{agg} / \sum D^3_{agg} \quad (2);$$

wherin $\sum$ for equations 2, 3, 5, 6, 9, and 11 represents the sum over all aggregates measured;

wherein the mean aggregate size M_{agg} is determined by:

$$M_{agg}\ (nm) = \sum D_{agg} / N_t \quad (3);$$

wherein D_{agg} is the area-equivalent aggregate diameter (nm), expressed as $(4A/\pi)^{1/2}$; A is the aggregate area (nm^2) of the two-dimensional projection, as measured by transmission electron microscopy; and N_t is the total number of aggregates measured.

The particle size heterogeneity index HI_{PSD} is determined by the weight mean particle size ("WM_{pt}") divided by the mean particle size ("M_{pt}"):

$$HI_{PSD} = WM_{pt} / M_{pt}, \qquad (4)$$

wherein the weight mean particle size WM_{pt} is determined by:

$$WM_{pt}\ (nm) = [\sum (n * d_p^4)] / [\sum (n * d_p^3)] \quad (5),$$

wherein the mean particle size M_{pt} is determined by:

$$M_{pt}\ (nm) = [\sum (n * d_p)] / n_t \qquad (6),$$

wherein n_t is $\sum n$ for all of the aggregates measured or the total number of all particles; n is the total number of particles in the aggregate, expressed as V_A/V_P; V_A is the aggregate volume, expressed in nm^3 as $(8/3)A^2/P$; V_P is the particle volume, expressed in nm^3 as $\pi d_p^3/6$; A is the aggregate area (nm^2); P is the aggregate perimeter (nm); d_p is the average particle size for a single aggregate, expressed in nm as $\alpha\pi A/P$; and α is the aggregation factor, expressed as $13.092(P^2/A)^{-0.92}$, but α is 0.4 if the calculated value is less than 0.4.

[0028] As used herein, unless specifically stated to the contrary, the term "Divergence Ratio" is intended to refer to a ratio of the aggregate size distribution heterogeneity index HI_{ASD} determined using TEM/AIA, according to ASTM D3849-14A (method A) as explained above over the particle size distribution heterogeneity index HI_{PSD} determined using TEM/AIA, according to ASTM D3849-14A (method A) as explained above:

$$\text{Divergence Ratio} = HI_{ASD} / HI_{PSD} \qquad (7)$$

The Divergence Ratio can be an indicator of decoupling of the aggregate size distribution (ASD) and the particle size distribution (PSD). Low Divergence Ratios, such as, for example, values less than about 1.5-1.7, can indicate either a broad ASD and broad PSD, or a narrow ASD and narrow PSD, such that the ASD and PSD are coupled and move in tandem. Higher Divergence Ratios, such as, for example, values greater than about 1.5-1.7 can indicate a decoupling of ASD and PSD, such as when the ASD is being broadened at a rate faster than the PSD. Such a higher Divergence Ratio can indicate a carbon black grade having a broad ASD and a normal or narrow PSD.

[0029] As used herein, the term "shape distribution" can refer to a method for categorizing carbon black into four shape aggregates categories (i.e., spheroidal (type 1), ellipsoidal (type 2), linear (type 3), branched (type 4)), as illustrated respectively in FIG. 2A, FIG. 2B, FIG 2C and FIG. 2D and described in "Morphology of Carbon-Black aggregates: Fractal versus Euclidian Geometry" by Herd and al., Rubber Chemistry and Technology v.65, p.107-129, and gives direct information regarding the balance of shape types for a shape modified grade of carbon black versus a normal or conventionally manufactured carbon black. The aggregate shape distribution is determined using skeletonization techniques and basic image analysis parameters in conjunction with skeletonization techniques based on the methods described in "The Use of Skeletonization for the Shape Classification of Carbon-Black Aggregates," by

Herd et al., Rubber Chemistry and Technology, v.66, p.491-509. The term "Shape Specific Heterogeneity Index of type Z" or "SSHI of type Z" is intended to refer to a ratio of the weight percent of a particular aggregate shape category named Z to the number percent of that aggregate shape category named Z present in a carbon black material. For example SSHI of type 4 (or SSHI of branched aggregates or SSHI type 4) refers to a ratio of the weight percent of an aggregate branched shape category to the number percent of that aggregate branched shape category present in the carbon black material (SSHI type 4 = Weight % of type 4/ Number % of type 4). For each type of aggregate shape category, the number percent basis (Number %) is determined simply as follows:

[0030] $\text{Number\%}t_Z = N_{tZ} / N_t$ (8)

wherein N_{tZ} represents the total number of aggregates in a given shape category, Z (1, 2, 3 or 4) and N_t represents the total number of aggregates for all shape categories (1, 2, 3 and 4).

[0031] For each aggregate shape category, the weight percent basis (Weight%) is determined simply as follows:

[0032] $\text{Weight\%}t_Z = \Sigma ((1.8*(8/3)*A^2)/P)_{tZ} / \Sigma((1.8*(8/3)*A^2)/P)_t$ (9)

wherein $\Sigma((1.8*(8/3)A^2)/P)_{tZ}$ represents the total weight of aggregates in a given shape category, Z (1, 2, 3 or 4) and $\Sigma((1.86*(8/3)A^2)/P)t$ represents the total weight of aggregates for all shape categories (1, 2, 3 and 4).

[0033] As used herein, unless specifically stated to the contrary, the term "TEM" is intended to refer to transmission electron microscope.

[0034] As used herein, unless specifically stated to the contrary, the term "void volume" is intended to refer to the relative amount of occluded volume of an individual aggregate relative to its volume, expressed as void volume = V'/V_A,

where V' is the amount of occluded volume of an aggregate and V_A is the volume of the aggregate from TEM measurements, expressed as:

$$V' = V_{es} - V_A \quad (10),$$

wherein V_{es} is the volume of a sphere, expressed as $4/3\pi r^3$, with the equivalent diameter of the individual aggregate taken as an average of the average Feret diameter (F_{av}), which is the

average distance between two parallel lines rotated around a two-dimensional object, and the area-equivalent aggregate diameter; V_A is the volume of the aggregate calculated using the two-dimensional image analysis parameters of area and perimeter, expressed in nm^3 as $(4A/\pi)^{1/2}$; A is the area of an aggregate from a two-dimensional TEM projection of the aggregate. Additional information regarding these terms and their relevance to carbon black materials can be found in ASTM D-3849-14a. Void volume, as it pertains to carbon black, can be further described in Journal of Colloid and Interface Science, 32, Issue 1, Jan 1970, pp115-131 and in ASTM Method D7854-21, which are each hereby incorporated by reference in their entirety for the purpose of describing carbon black void volume and its application to vehicle absorption and die swell of filler elastomer compounds.

For a carbon black material measurement via TEM/AIA that is representative of the material's aggregate size and shape distribution and comprises a plurality of aggregates, wherein each aggregate has an individual void volume, the apparent void volume of the carbon black material can be calculated by summing the individual void volume of each individual aggregate relative to its proportion of the total measured volumes that are representative of the aggregate size distribution. Higher apparent void volume V'/V_A values can indicate a higher degree of branching or aggregate complexity. For example, a V'/V_A of 2 means that the carbon black material can occlude up to twice its own volume.

The V'/V_A for a carbon black material can be calculated as:

$$V'/V_A = \Sigma V'/\Sigma V_A \qquad (11),$$

wherein this parameter is summed over all aggregates, with V' and V_A as defined previously.

[0035] Disc centrifuge photosedimentometry can also be used for determination of various aggregate size properties or parameters as related to its distributional nature. This technique utilizes Stoke's Law, modified for centrifugal sedimentation to determine the Stoke's diameters of the Carbon Black aggregates and its aggregate size distributional properties. These various aggregate size distributional (ASD) parameters, as shown in FIG. 4, can include the Mean, Mode, D_{10}, D_{50}, D_{90}, and Delta D50 or full width at half maximum (FWHM). The D_{10} aggregate diameter represents the aggregate diameter where 10% of the volume distribution lies below the D_{10} value, the D_{50} aggregate diameter represents the aggregate diameter where 50% of the volume distribution lies below the D_{50} value, and the D90 aggregate diameter represents the aggregate diameter where 90% of the volume

distribution lies below the D_{90} value. These parameters can also be used to calculate a term called the Span, which is calculated as $(D_{90} - D_{10})/D_{50}$ and can be an indicator of the breadth of an ASD. Other parameters include Delta D_{50}, which is the full width at half maximum of the ASD peak, which may be useful as an indicator of the breadth of the ASD for unimodal ASDs, but can be less useful, if not useful at all, for multimodal ASDs, depending upon the relative magnitude of one of the modes in the multi-modal ASD. Typically, Delta D_{50} is divided by the Mode (Delta D_{50} / Mode) to normalize the parameter and make it comparable between carbon black materials as the Delta D_{50} itself is directly influenced by the particle size, aggregate size and aggregate structure. Unless stated to the contrary, these values can be determined by disc centrifuge photosedimentometry according to the standard ISO 15825:2017.

[0036] References in the specification and concluding claims to parts by weight, of a particular element or component in a composition or article, denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a composition containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the composition.

[0037] References in the specification and concluding claims to phr of a particular element or component in a composition or article, denote the parts per hundred units of mass of rubber of the particular element or component.

[0038] Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0039] As used herein, the terms "optional" or "optionally" means that the subsequently described event or circumstance can or can not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0040] Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds can not be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods of the invention.

[0041] Each of the conventional carbon black materials (or comparative carbon blacks described in the Examples), together with their methods of manufacture are either commercially available and/or the methods for the production thereof are known to those of skill in the art. These conventional carbon blacks may be found from the following suppliers: Birla Carbon, Cabot Corporation, Orion, etc…

[0042] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions, and it is understood that there are a variety of structures that can perform the same function

that are related to the disclosed structures, and that these structures will typically achieve the same result.

[0043] Carbon blacks for rubber applications are typically identified by a four-character "N" or "S" number, e.g., NXXX or SXXX. The category (grade) is determined by ASTM D1765-19. The first character of the category gives some indication of the influence of the carbon black on the rate of cure of a typical rubber formulation containing the black, where "N" is used for normal cure carbon blacks and "S" is used for slow cure carbon blacks. The second character gives information on the average surface area of the carbon black. Thus, carbon blacks with the same second character are grouped into a series ending in "00," e.g., N200 series. The last two characters are assigned arbitrarily.

[0044] The morphological characteristics of carbon black, such as particle size, aggregate size and aggregate structure, can affect various processing characteristics and performance properties, such as, for example, tread wear, rolling resistance, heat buildup, hardness, modulus, and tear resistance, of various end products like tires and mechanical rubber goods. Accordingly, different grades of carbon black are used in different polymeric formulations, depending on the specific service requirements of the tires and rubber goods. For example, different grades of carbon black can also be used in different parts of a tire, N100, N200, and N300 series blacks are often used in treads (i.e., tread grade carbon blacks), while N300, N500, N600, and N700 series blacks are often found in sidewalls and carcass compounds (i.e., carcass grade carbon blacks). In one aspect, the carbon black of the present invention can comprise a furnace carbon black. In another aspect, the carbon black of the present invention can comprise a shape-modified version of an ASTM grade carbon black, such as, for example, an N100, N200, N300, N400, N500, N600, N700, N800, or N900 carbon black. In another aspect, the carbon black of the present invention can comprise a tread grade carbon black, suitable for use in passenger tire tread compounds, truck tire tread compounds, and mining tires. In another aspect, the carbon black of the present invention can comprise a carcass grade carbon black. In yet another aspect, the carbon black of the present invention can comprise a carbon black suitable for use in non-tread or carcass compounds of a tire, such as, for example, a sidewall, innerliner, sub-tread or bead filler compound.

[0045] Morphological characteristics of carbon black include, for example, particle size/fineness, surface area, aggregate size/structure, aggregate size distribution, and aggregate shape. Particle size is a measurement of the diameter of the primary particles of carbon black.

These roughly spherical particles of carbon black have an average diameter in the nanometer size range. Particle size can be measured directly via electron microscopy or indirectly by surface area measurement. Average particle size is an important factor that can determine the dispersibility, tensile strength, tear resistance, hysteresis, and abrasion resistance in a rubber article while in liquids and plastics systems, the average particle size can strongly influence the relative color strength, UV stability, and conductivity of the composite. At equal structure, smaller particle size imparts higher tensile strength, tear resistance, hysteresis and abrasion resistance, stronger color, UV resistance, and increased difficulty of dispersion.

[0046] The surface area of carbon black is a function of particle size and porosity. Surface area is measured by gas and liquid phase adsorption techniques and depends on the amount of adsorbent required to form a surface monolayer. Iodine adsorption number, sometimes referred to as Iodine no. or simply Iodine (Iodine Adsorption No.; ASTM D1510-2017), was historically the primary indicator of surface area for defining different grades. Nitrogen surface area, or NSA (ASTM D6556-2017) and statistical thickness surface area, or STSA, (ASTM D6556-2017) are now used more frequently for surface area measurements. NSA and STSA are better measures of the true surface area than iodine, since NSA and STSA are less influenced by the chemical composition of the carbon black surface. These tests use liquid nitrogen and are based on the original Brunauer, Emmett, and Teller (BET) method. In a final application, surface area, and especially STSA, reflects the area accessible to rubber molecules per unit weight of carbon black. High surface area is associated with a high level of reinforcement in rubber compounds, but at the expense of more difficult dispersion, processing, and increased hysteresis.

[0047] Carbon black particles coalesce to form larger clusters or aggregates, which are the primary dispersible units of carbon black. Measurement of aggregate structure can be obtained from electron microscopy or oil absorption, specifically the oil absorption number, OAN (ASTM D2414-2018). Another measure of structure is the compressed oil absorption number, or COAN (ASTM D3493-2018), where a carbon black sample is mechanically compressed prior to performing the oil absorption measurement. The difference between OAN and COAN values can be an indicator of the stability of the carbon black structure. Carbon blacks with relatively large aggregates with a high number of primary particles can be high structure carbon blacks, with aggregates that have more void space and high oil absorption. High structure carbon black can increase rubber compound viscosity, modulus,

and conductivity. High structure can also reduce die swell, loading capacity, and improve dispersibility. Lower structure carbon blacks can decrease rubber compound viscosity and modulus, increase elongation, die swell and loading capacity, but can also decrease dispersibility. If all other features of a carbon black are kept constant, narrow aggregate size distribution increases difficulty of carbon black dispersion and increases hysteresis and lowers resilience.

[0048] Carbon black aggregates can also vary in shape and can be grouped into one of four traditional shape categories, as illustrated in FIG. 2 and as described in in "Morphology of Carbon-Black aggregates: Fractal versus Euclidian Geometry" by Herd and al., Rubber Chemistry and Technology v.65, p.107-129", including Spheroidal (Type 1, FIG. 2A), Ellipsoidal (Type 2, FIG. 2B), Linear (Type 3, FIG. 2C), and Branched (Type 4, FIG. 2D). It should be understood that shape and aggregate size are distributional properties, and that for any given production sample of carbon black, there can exist a range of individual aggregates having varying shapes and/or sizes. An image analysis technique of skeletonization can be performed using transmission electron microscopy with automated image analysis (TEM/AIA), in conjunction with other aggregate shape parameters (e.g., form factor, circularity, roundness, aspect ratio, solidity, number of particles per aggregate, aggregate absorptivity index, skeleton ends and skeleton branches), to validate shape descriptors and categorize the different aggregate shape types that were initially segregated visually as ideal examples of each shape type. The aggregate parameters can then be used in a discrimination analysis program (e.g., Statistica) to develop and define regression equations for discrimination of aggregates into various shape categories, as it is described in "Morphology of Carbon-Black Aggregates: Fractal versus Euclidian geometry" by Herd and al., Rubber Chemistry and Technology v.65, p.107-129 and in The Use of Skeletonization for the Shape Classification of Carbon-Black Aggregates," by Herd et al., Rubber Chemistry and Technology, v.66, p.491-509".

Manufacture of Conventional Carbon Black Materials

[0049] The basic method for the production of carbon black is well known. Generally, carbon black is produced by the partial oxidation or thermal decomposition of hydrocarbon gases or liquids, where a hydrocarbon raw material (hereinafter called "feedstock hydrocarbon") is injected into a flow of hot gas wherein the feedstock hydrocarbon is pyrolyzed and converted into a smoke before being quenched by a water spray. The hot gas is produced by burning

fuel in a combustion section. The hot gas flows from the combustion section into a reaction section which is in open communication with the combustion section. The feedstock hydrocarbon is introduced into the hot gas as the hot gas flows through the reaction section, thereby forming a reaction mixture comprising particles / aggregates of forming carbon black. The reaction mixture flows from the reactor into a cooling section which is in open communication with the reaction section. At some location in the cooling section, one or more quench sprays of, for example, water, are introduced into the flowing reaction mixture thereby lowering the temperature of the reaction mixture below the temperature necessary for carbon black formation. The carbon black aggregates are then separated from the flow of hot gas. A broad range of carbon black types can be made by controlled manipulation of the reactor conditions.

[0050] Many carbon black reactors normally comprise a cylindrical combustion section axially connected to one end of a cylindrical or frusto-conical reaction section. A reaction choke is often axially connected to the other end of the reaction section. The reaction choke has a diameter substantially less than the diameter of the reaction section and connects the reaction section to the cooling section. The cooling section is normally cylindrical and has a diameter which is substantially larger than the diameter of the reaction choke.

[0051] With reference to FIG. 1, a carbon black reactor 100 is shown comprising a combustion section 102. The combustion section 102 comprises a cylindrical inlet 108 in the upstream end of the combustion section for the introduction of a fuel, such as natural gas or fuel oil, and a second opening 110 in the peripheral wall of the combustion section for the introduction of an oxygen-containing gas, such as air. In the combustion section, the fuel and oxygen-containing gas are combusted.

[0052] The reactor also includes a reaction section 104 axially aligned with the combustion section. The hot gas produced in the combustion section flows substantially axially through the reactor, that is, the hot gas flows substantially parallel to the longitudinal axis of the reactor. The reaction section includes a conical section 112 extending forward from the downstream end of the combustion section. The reaction section is in open communication with the combustion section through the open downstream end of the combustion section. The reaction section has an inner diameter which gradually decreases as the reaction section converges towards a reaction choke 114. The reaction choke extends forward from the

converging end of the reaction section, and the reaction choke is in open communication with the reaction section through an opening in the converging end of the reaction section.

[0053] While the fuel is used to generate hot gases, the feedstock hydrocarbon is converted into carbon black via an incomplete combustion process. The feedstock hydrocarbon, or conversion oil, can comprise a variety of hydrocarbon materials, such as fluidized catalyst cracker (FCC) residuals, fuel oil, or coal tar. The feedstock hydrocarbon can also be a renewable feedstock. One or more hydrocarbon injection nozzles 116 are positioned along the length of the reaction section and/or the reaction choke. In FIG. 1, the position of exemplary injection nozzles are denoted by the letters A, B, C, and D. The feedstock hydrocarbon injection nozzles can extend through the outer walls of the reaction section and the reaction choke and protrude into the interior of the carbon black reactor. It should be noted that any number of injection nozzles can be utilized in a reactor and the position of any one or more nozzles can vary, depending upon the specific reactor design and the desired properties of a resulting carbon black.

[0054] As the hot combustion gas flows axially through the converging reaction section and axially through the reaction choke, feedstock hydrocarbon is injected through the hydrocarbon injection nozzles into the flow of hot combustion gas. The hot oxygen-containing combustion gas pyrolyzes the feedstock hydrocarbon as the feedstock hydrocarbon enters the flow of hot oxygen-containing gas, thereby forming a flowing reaction mixture comprising hot gas and particles of forming carbon black.

[0055] The flowing reaction mixture travels axially through the reaction choke to a cooling section. The cylindrical cooling section 106 with an inner diameter substantially greater than the inner diameter of the reaction choke is mounted to the downstream portion of the reaction choke. The cooling section comprises an annular upstream wall surrounding the reaction choke and a cylindrical outer shell extending forward from the annular upstream wall towards a downstream opening. One or more quench spray nozzles 118 can extend from the outer wall of the cooling section into the interior portion of the cooling section.

[0056] As the flowing reaction mixture enters the cooling section, the reaction mixture is carried by the flow of hot gas towards the one or more quench sprays. The quench spray, normally water, lowers the temperature of the flow of hot gas to a temperature below that required for carbon black formation, thereby halting or "quenching" the carbon formation

process. The cooled gas and the particles/aggregates of formed carbon black then flow from the cooling section to a carbon black recovery system.

[0057] Carbon black recovery systems are well known to those skilled in the art and thus are not discussed here in detail. Additives, such as, for example, potassium containing structure control additives, can optionally be mixed with a feedstock hydrocarbon and/or injected separately into one or more of the feedstock hydrocarbon injection nozzles.

[0058] Although the carbon black reactor illustrated in FIG. 1 is shown having a cylindrical cross-section, it should be understood that carbon black reactors having non-cylindrical cross-sections can also be used to practice the present invention. Accordingly, the present invention is not limited to any particular carbon black reactor design, and one of skill in the art, in possession of this disclosure, could readily determine how to utilize the invention in a given reactor system. It should also be understood that a combustion section which produces tangential flow, as opposed to an axial flow, can be used with the present invention.

Conventional Control of Carbon Black Aggregates, Size and Distribution

[0059] It is well known that carbon black exists as a collection of aciniform aggregates that cover a wide range of particle size, surface area and aggregate size and structure. The mean particle size and particle size distribution of carbon black directly determine its specific surface area, and as mentioned previously, smaller mean particle size increases the specific surface area and vice – versa. The aggregate size is determined by both the mean particle size, number of particles per aggregate and their spatial arrangement, or degree of branching and complexity that defines the aggregate structure.

[0060] The aggregate structure and absorptive capacity manifests itself through its impact on viscosity and modulus development in a rubber compound, with higher structure driving higher viscosity and modulus. More fundamentally and from a morphological standpoint, structure manifests itself through aggregate size and complexity, with lower structure aggregates having a more compact structure, and higher structure aggregates having a more branched and open architecture capable of occluding a significant amount of oil or polymer.

[0061] Historically, variations in carbon black structure were achieved by adding potassium-based compounds into the carbon black reactor. The introduction of such a potassium-based compound directly influences the structure build: the addition of less potassium-based

compound results in higher structure carbon blacks, whereas the addition of more potassium-based compound results in lower structure carbon blacks. While not wishing to be bound by theory, it is believed that this method works by imparting a positive charge on the nascent carbon black particles, and when production of lower structure carbon blacks are desired, the positive charge severely reduces the sticking probability of the nascent, primary particles during collision and during aggregate formation in the reactor, resulting in lowering or preventing substantial growth and branching of aggregates, decreasing its structure or aggregate complexity. Conversely, for production of high structure aggregates, removal of the potassium-based additive eliminates particle charging, allowing the nascent, primary particles to collide and adhere to one another, resulting in the growth and branching of aggregates, increasing its structure or aggregate complexity.

[0062] For various applications, such as, for example, tires and mechanical rubber goods, the morphological properties of carbon black can have a significant impact on the viscoelastic properties of a rubber compound containing the carbon black, such as hardness, modulus, and compression set. ASTM grades of carbon black, along with recently developed narrow or broad aggregate size distribution grades of carbon black have reached an apparent limit in performance and morphological distributional width. Thus, methods for controlling the morphological properties of individual aggregates are becoming necessary as a means to produce distinctive carbon blacks under more controlled and specific dimensions and more controlled and optimized aggregate size distributions.

[0063] In one sense, carbon black morphological properties have historically been controlled in a bulk manner, wherein all of the aggregates in a given production run are modified generally in the same manner. For many decades, there has been a proliferation of low, medium and high structure grades of carbon black for use in many different applications, whether in inks and coatings and plastics, or rubber compounds for tires and mechanical rubber goods. For commercially produced ASTM grades, the approach for controlling structure has been blunt in that potassium-based additives have been charged in as uniform manner as possible. This approach has been successful in yielding materials that provide the generally desired average structure level in line with ASTM D1765-19 target values that provides the tire and rubber goods manufacturers with their desired viscoelastic / rheological properties for the various rubber, liquids, or plastics composites as may be required.

[0064] In terms of the carbon black aggregate size distribution, researchers and carbon black producers have used a variety of techniques to make the aggregate sizes narrower or broader depending upon the targeted application and desired final compound properties.

[0065] For narrow aggregate size distribution, the carbon black reactor is typically a single reactor as described in this patent, with a smaller choke size, generally less than 6 inches (152.4 mm) and a tapered outlet to prevent recirculation of carbon black and creation of larger aggregates that might broaden the ASD. Such a reactor and process are described in US 10,829,613 B2, granted November 10, 2020.

[0066] For broad aggregate size distribution carbon blacks, in practically all of the methods used to produce such materials, it is apparent that the broadening of the carbon black aggregate size distribution is primarily achieved by blending carbon blacks of different particle size or surface area by direct physical blending or by controlling the relative zones of particle and aggregate formation in the reactor (mostly to produce carbon blacks with distinctly and significantly different mean particle size or surface area). The impact of structure on the aggregate size distribution at the same surface area has been purported in the literature, but there has been no practical implementation nor description of such processes in actual production as described in patents, nor any descriptions of said processes such that those skilled in the art could understand and replicate such processes.

[0067] Several earlier papers on broad aggregate size distribution were reported by Janzen and Kroaus in the Proceedings of the International Rubber Conference, Brighton, UK, 1972; also Stacy, Johnson and Kraus, Rubber Chemistry and Technology, 1975, **48**, 538, and also Hess and Klamp, Rubber Chemistry and Technology, 1983, **56**, 390, (full references attached herein). In these academic papers, blends of two or more carbon blacks of different surface area and mean particle size were studied where it was noted that such blends generally give poorer treadwear due to the tail or larger end of the ASD being primarily composed of the carbon black with the larger mean particle size. In the 1972 report of Janzen and Kraus, blends of carbon blacks of similar mean particle size, but with different structure, were reported as another method to broaden the aggregate size distribution. It was found that low and moderate treadwear were not impacted by the ASD, yet high severity treadwear was negatively impacted by about 10%. All of these studies were conducted using laboratory-based physical blends and did not teach anything about the carbon black process to achieve such morphological properties.

[0068] A Japanese patent, filed on September 16, 1982, Application Number S57-159661 and Disclosure Number S59-49267, published March 21, 1984, by Tokai Carbon Company, describes a "Y" shaped reactor with two separate reactors composed of their own air blower, flame and conversion oil injection zones for nascent formation of carbon black particles and aggregates that collide in a single reaction and aggregate formation zone at an intersection angle of 30° to 90°, further downstream. Slightly further downstream of this single formation zone zone was an annulus that could be opened or closed to varying degrees. The goal of this reactor design was to modify the balance of the aggregate structure and raise the COAN for a given level of OAN.

[0069] A US patent, 4,786,677, date granted, November 22, 1988, also by Tokai Carbon Company, disclosed the use of the same type of "Y" reactor for a rubber composition containing a carbon black with two modal diameters satisfying the relationship $20 \leq L \leq 110-0.3*(NSA, m^2/g)$, where L is the distance (in nanometers, nm) between the two modal diameters as determined by DCP. The carbon blacks are produced in a "Y" reactor with two separate reactor lines with their own flame, air blower and conversion oil injection ports arranged such that the forming and formed particle nuclei and carbon black aggregates are colliding in one zone at an angle between 30° and 60°. Each production zone, according to said document, produces materials corresponding to each of the two modal diamters in the aggregate equivalent Stokes diameter distribution that is achieved by controlling the structure and the NSA of each reactor leg in the "Y" reactor. Nothing is taught with regards to how the structure is controlled, rather the NSA is noted as also being varied between the two reactors that form the "Y" by controlling the particle/aggregate formation time to reach the quench. Based on information taught in the patent, the description of the process appears to show that that a difference in mean particle size and surface area (or a broad particle size distribution) is being used to broaden the ASD in addition to any contribution from the structure, of which methods to control and vary along with absolute values of are not taught in any manner in the patent.

[0070] A US Patent 5,254,325, granted October 19, 1993 discloses methods to control and widely vary the particle size and its distribution as coupled to broadening of the aggregate size distribution. This is achieved by injecting additional material hydrocarbon streams at distances along the reactor carbon black formation zones to produce different particle sizes and distributions and hence broaden the ASD.

[0071] A US patent, US 8,258,207 B2, granted on September 4, 2012, reported on the preparation and in-rubber properties of physical blends of carbon black, as prepared in the laboratory, unimodal in nature, perhaps with a shoulder. Such broad ASD materials were prepared with large differences in the STSA (or delta STSA) of blend components ranging from 58 m^2/g up to 182 m^2/g, indicating broad to very broad particle size distributions are also predominantly used to vary the ASD. Further, data for the carbon blacks used in the blends showed that in addition to large variations in STSA being used to broaden the ASD, differences in structure in the blend components was kept constant to varying by as much as 32 ml/100g of Compressed OAN (delta COAN). It was noted and claimed that such blended materials also demonstrated a slightly lower OAN than as predicted from the blend components. Note that differences in PSD were coupled to differences in OAN or COAN to produce, in lab scale, the broad ASD carbon blacks.

[0072] A Chinese patent, CN105647242BB, granted August 22, 2017, discloses an ultra-wide aggregate size distribution carbon black, also made with a "Y" reactor, and in this instance, based on operating conditions of each "Y' reactor as described in the patent, one skilled in the art can determine that the NSA of each reactor in the "Y" produces a carbon black with a much different STSA thus, the broad aggregate size distribution is primarily driven by the wide particle size distribution. No information is disclosed nor claimed around variation of aggregate structure.

[0073] Even with these bulk variations in aggregate properties as described above, there is a need for improved carbon blacks with modified morphological properties that can, for example, exhibit an optimized aggregate size distribution, broadened and controlled by controlling the aggregate shape distribution, with a narrow to normal particle size distribution, while maintaining electrical conductivity and optionally maintaining or improving tread wear properties of a resulting tire compound. The shape modified carbon blacks of the present invention can impart such improved performance properties to elastomer compounds.

Shape Modified Carbon Black Materials and Methods of Manufacture

[0074] As briefly described above, the present disclosure provides, in one aspect, methods for modifying the shape and/or shape distribution of carbon black aggregates. In various aspects, the number and/or weight percent of carbon black aggregates in any one or more

shape categories can be increased or decreased. In another aspect, the methods to change the shape distribution of a carbon black can have little or no impact on the aggregate size distribution and/or particle size distribution of the carbon black. In another aspect, such techniques can alter the aggregate size distribution of a carbon black by, for example, broadening the aggregate size distribution. In another aspect, the aggregate size of a carbon black can be broadened, without broadening the particle size distribution. In yet another aspect, the aggregate size distribution can be broadened to a greater extent than any broadening of the particle size distribution. In one aspect, the aggregate size distribution can be broadened by extending the larger size range of the distribution. In another aspect, the aggregate size distribution can be broadened by extending the smaller size range of the distribution. In yet another aspect, the aggregate size distribution can be broadened by extending both the smaller and larger size ranges of the distribution. In still another aspect, the disclosure provides methods for making broader aggregate size distributions than conventionally possible.

[0075] For example, an Inventive Carbon Black can provide a faster carbon black incorporation and improved carbon black dispersibility in a polymeric (e.g., rubber) matrix. In various aspects, modification of the carbon black aggregate shape and shape distribution can provide benefits when incorporated into an elastomer, such as, for example, an improved reduction in hysteresis while maintaining electrical conductivity. In another aspect, the use of such shape-modified carbon black materials can provide improved hysteresis while maintaining dynamic stiffness, electrical conductivity, and/or failure properties.

[0076] The carbon black material of the present invention can be made using innovative variations of traditional carbon black manufacturing methods. Various methods of making the Inventive Carbon Black are described below and in the Examples. Variations on these methods can be determined by one of skill in the art. In one aspect, the carbon blacks of the present invention can be produced by modifying a carbon black tread reactor, such as those described generally in United States Patents Nos. 4,927,607 and 5,256,388, the disclosure of which are hereby incorporated by reference in their entireties. Other carbon black reactors can be used, and one of skill in the art can determine an appropriate reactor for a particular application. Feedstock, combustion feeds, and quenching materials are well known in the carbon black art. The choice of these feeds is not critical to the carbon blacks of the present invention. One of skill in the art can determine appropriate feeds for a particular application.

The amounts of feedstock, combustion feeds, and quenching materials can also be determined by one of skill in the art which are suitable for a particular application. The feedstock can be a renewable feedstock such as plant-based feedstock, preferably a non-edible plant-based feedstock or a waste material feedstock. The plant-based feedstock may be woods, grass, cellulose, hemicellulose, lignin, tall oil, rubber seed oil, tobacco seed oil, castor oil, tall oil, pongamia oil, crambe oil, neem oil, rice bran oil etc. The waste material feedstock may be cooking oil, distillation residues from biosiel plants, pyrolysis oil, waste material comprising natural rubber or synthetic rubbers obtained from tires, cables sheaths, tubes, conveyor belts, shoes soles, hoses etc. The feedstock may be a mixture or renewable carbon black feedstock and hydrocarbon feedstock. The hydrocarbon feedstock may be aliphatic or aromatic, saturated or unsaturated hydrocarbons or mixtures thereof, coal tar distillates, residuals oils which are produced during the catalytic cracking of petroleum fractions, residual oils which are procduced during olefin production throught cracking of naptha or gas oil, natural gas or mixture or combinaison of any on the foregoing.

[0077] Inventive Carbon Blacks of the present disclosure having an optimized aggregate size distribution, typically broader and optimized through control of the aggregate shape distribution, along with a narrow or normal particle size distribution can decrease the propensity for carbon black network formation and lower the hysteresis in a resulting rubber compound, while the particle size distribution in conjunction with the optimized aggregate shape distribution can maintain a better foundation for tread wear and tear properties and electrical conductivity.

[0078] As described above, these methods have reached a practical limit based on general reactor technology, yet more flexibility in manipulating and controlling the aggregate size distribution is required. As such, carbon blacks with controlled shape distribution have been invented to provide materials with advanced and distinctive morphological properties.

[0079] In one aspect of the present invention, Inventive Carbon Black can be produced by non-uniform injection of a structure control additive, such as a potassium-containing compound, in different reactor zones, in an effort to control the aggrgetae structure in each zone and subsequently the aggregate shape and ultimately the size distribution. Typically a broader aggregate size distribution is the result when implementing the shape-modification process. This method of aggregate shape control provides a means to go beyond normal reactor limitations and provide unique carbon blacks that yield beneficial properties to rubber

compounds, particularly in reduced networking and lowering heat buildup, yet with a good balance of durability.

[0080] In one aspect, the Inventive Carbon Black can be produced in a single reactor via the non-uniform injection of a structure control additive. In another aspect, the Inventive Carbon Black can be produced using two or more reactors.

[0081] In one aspect, the method of the present disclosure provides an Inventive Carbon Black having a modified and/or controllable distribution of aggregate shapes. In such an aspect, the Inventive Carbon Black can have a different distribution of aggregates ranging from low structure to medium structure to high structure, as compared to a conventional carbon black. In a specific aspect, the amount, on a number or weight basis, can be greater for each of the low and high structure aggregates or higher for one class and lower for another class (higher or lower structure aggregates), and in each case with a different shape distribution relative to a conventional carbon black. In another aspect, the modified shape distribution can result in wider aggregate size distribution (hereinafter "ASD") of a carbon black without increasing the particle size distribution (i.e., the size of individual primary particles that make up an aggregate, hereinafter "PSD"). In another aspect, the present invention can provide a multi-modal ASD carbon black. In a specific aspect, the present invention can provide a bi-modal or even a uni-modal ASD carbon black, wherein a greater number of low structure aggregates and a greater number of high structure aggregates are produced, as compared to a conventional carbon black. The techniques of the present invention provide improved methods for precisely controlling different size fractions of the ASD at a given particle size, and also result in control of the shape distributional aspects of the resulting carbon black material and control of the modes, mean and weight mean of the ASD.

[0082] In yet another aspect of this invention, the shape modification process provides for a new method for control of the bulk average structure level, or OAN, of the carbon black material. Normally, and as explained previously, such control is achieved through more or less addition of the potassium-based structure control additive in the oil, equally portioned between one or more conversion oil spray planes, or in a separate water spray, common to all chambers of the reactor past its point of introduction. In the process for shape modification of the present invention, the OAN control may be achieved through variation of the oil split in each of the two or more conversion oil spray planes, holding the flow rate and

concentration of the potassium-based additive constant at zero or a part-per-million (ppm) level, in one or more planes, preferably in a plane located behind the spray plane(s) closet to the choke outlet. By varying the oil rate and potassium flow rate in these planes one can manipulate the amount of very low, medium or very high structure aggregates and control the OAN very precisely to meet production targets.

[0083] In another aspect of this invention, it is possible to make the shape modified carbon black of the present invention by using two reactors converging into a common header, where one reactor produces a carbon black of a given surface area, but with a very low to low structure (OAN >0 ml/100 g but <70 ml/100g), while, in a second reactor, also making a carbon black with a very high structure (OAN >120 ml/100g) similar in surface area to carbon black produced in reactor one. This approach is not limited to two reactors nor three nor four or more reactors. This approach may not be cost effective however, since depending upon the blend ratio of the various aggregate shapes (low, medium and or high structure), one or more reactor(s) may have a diminished production rate that increases cost.

[0084] In another aspect of the present invention, one may also make a shape-modifed carbon black by physically blending two or more carbon blacks, post the reactor either in a carbon black production plant, in a separate blending facility, or even at the customers' mixing facility. This would require production of the individual blend components, packaging and then metering and blending using dedicated blending equipment and processes. This would generally not be cost effective either and can degrade the bead quality and generate fines, which negatively impact dispersion.

[0085] FIG. 3A illustrates example aggregates from a conventional ASTM grade carbon black, having a narrow/normal ASD and narrow/normal PSD. FIG. 3B illustrates example aggregates from the Inventive Carbon Black, having a very broad ASD and a narrow PSD. In FIG. 3B, larger, high structure aggregates (illustrated with gray particles) are formed, together with a number of smaller, low structure aggregates.

[0086] In one aspect, production of Inventive Carbon Blacks can be achieved by utilizing hydrocarbon injection nozzles located at two or more axial planes (i.e., distance from the choke outlet) in the reactor section and/or choke of a reactor. In various aspects, the planes where hydrocarbon injection nozzles are located can depend upon the specific reactor design, but can range, for example, from about 1 inch to about 50 inches (2.54 cm to 127 cm), or

more, from the choke outlet. In one aspect, two planes of hydrocarbon injection nozzles can be used. In another aspect, three planes of hydrocarbon injection nozzles can be used. In yet other aspects, four, five, or more planes of hydrocarbon injection nozzles can be used. In one aspect, each plane of the plurality of hydrocarbon injection nozzle planes can be spaced equally apart, by, for example, about 2 (5.08 cm), 4 (10.16 cm), 6 (15.24 cm), 8 (20.32 cm), 10 (25.40 cm), 12 (30.48 cm), 14 (35.56 cm), 16 (40.64 cm), 18 (45.72 cm), 20 (50.80 cm), 24 (60.96 cm), 26 (66.04 cm), 28 (71.12 cm), 30 (76.20 cm), 32 (81.28 cm), 34 (86.36 cm), 36 (91.44 cm), 38 (96.52 cm), 40 (101.60 cm), 42 (106.68 cm), 44 (111,76 cm), 46 (116.84 cm), 48 (121,92 cm), or 50 inches (127.00 cm), or more. In a specific aspect, at least two planes of hydrocarbon injection nozzles are positioned at least 8 inches (20.32 cm) apart. In other aspects, at least two planes of hydrocarbon injection nozzles are positioned at least 10 (25.4 cm), 12 (30.48 cm), 14 (35.56 cm), 15 (38.1 cm), 16 (40.64 cm), 18 (45.72 cm), 20 (50.8 cm), 24 (60.96 cm), 26 (66.04 cm), 28 (71.12 cm), 30 (76.20 cm), 32 (81.28 cm), 34 (86.36 cm), 36 (91.44 cm), 38 (96.52 cm), 40 (101.60 cm), 42 (106.68 cm), 44 (117.76 cm), 46 (116.84 cm), 48 (116.84 cm), 50 (127.00 cm), or more inches apart.

[0087] In another aspect, each plane of the plurality of hydrocarbon injection nozzle plans can be spaced apart at irregular distances from other planes. In yet another aspect, each plane can comprise two or more individual hydrocarbon injection nozzles, spaced, for example, uniformly, around the periphery of the reactor. If such individual nozzles are spaced uniformly around the periphery of the reactor, the angle between individual nozzles can be described as 360/number of individual nozzles.

[0088] In one aspect, the number of individual hydrocarbon injection nozzles positioned at each plane can be the same. In another aspect, the number of individual hydrocarbon injection nozzles positioned at each plane can vary. In a related aspect, the position and/or arrangement of individual hydrocarbon injection nozzles can vary from one plane to another. In still another aspect, the amount and/or type of feedstock hydrocarbon injected at any given plane or through any individual hydrocarbon injection nozzle can be the same or different from any other plane or individual hydrocarbon injection nozzle.

[0089] In one aspect, the present disclosure provides a method for manufacturing a carbon black, wherein each of a plurality of feedstock hydrocarbon injection nozzles are positioned within planes in a carbon black reactor, and wherein such planes are positioned at least 8 inches (20.32 cm), 10 inches (25.40 cm), 12 inches (30.48 cm), 14 inches (35.56 cm), 16

inches (40.64 cm), 20 inches (50.80 cm), 22 inches (55.88 cm), 24 inches (60.96 cm), 26 inches (66.04 cm), 28 inches (71.12 cm), 30 inches (76.20 cm), 32 inches (81.28 cm), 34 inches (86.36 cm), 36 inches (91.44 cm), 38 inches (96.52 cm), 40 inches (101.60 cm), 42 inches (106.68 cm), 44 inches (117.76 cm), 46 inches (116.84 cm), 48 inches (116.84 cm), 50 inches (127.00 cm), or more from each other. In another aspect, an Inventive Carbon Black can be manufactured in a reactor configured such that any one or more of a plurality of feedstock hydrocarbon injection nozzles are positioned at locations distant from each other, as measured from the end of the reactor choke, and wherein the feedstock hydrocarbon is injected into the reactor in a non-uniform manner. In another aspect, a carbon black can be manufactured in a reactor configured such that any one or more of a plurality of feedstock hydrocarbon injection nozzles are positioned at locations distant from each other, as measured from the end of the reactor choke, and wherein a structure control additive, such as a potassium containing compound is injected, separately or combined with the feedstock hydrocarbon, into the reactor in a non-uniform manner. In one aspect, the feedstock hydrocarbon can be injected into the reactor via injection sprays, wherein a potassium containing compound can be introduced in multiple spray locations positioned, for example, along the choke, and wherein the amount or rate of potassium compound addition can vary between each spray location. In various aspects, the structure control additive can be added in a non-uniform manner. In one aspect, non-uniform structure control addition can be wherein all or a portion of a structure control additive can be added at a location not typically used in carbon black manufacture, either alone or in combination with a feedstock hydrocarbon. In another aspect, non-uniform structure control addition can be wherein all or a portion of a structure control additive can be added at a plurality of locations, and wherein the amount and/or rate of structure control addition at each of the plurality of locations can be the same or can vary. In various aspects, all or a portion of a structure control additive can be mixed with a feedstock hydrocarbon and added through one injection nozzle. In another aspect, more structure control additive can be added through one injection nozzle or the injection nozzles in one plane, than through other injection nozzles.

Properties of Shape Modified Carbon Blacks of the present invention

[0090] It should be noted that the Inventive Carbon Black of the present invention can comprise any grade of carbon black. In one aspect, the Inventive Carbon Black can comprise a furnace carbon black. In another aspect, the Inventive Carbon Black can have colloidal

properties, such as, for example, Iodine number, nitrogen surface area, statistical thickness surface area, oil absorption number, or compressed oil absorption number, described for ASTM grade carbon blacks (ASTM1765-2019), such as, for example, N134, N121, N115, N110, N220, N234, N299, N330, N339, N550, N539, N660, N762, N772, or N990. Various properties and ranges are recited below. It is contemplated that any combination of such recited ranges are part of the invention. For any of the ranges and/or values recited herein, it should be understood that the Inventive Carbon Black can also have a value higher than or lower than any specifically recited ranges, and the disclosure is not intended to be limited to only the specifically recited ranges and/or values.

[0091] In one aspect, the Inventive Carbon Black can have a nitrogen surface area (NSA) measured according to the ASTM standard D6556-2017 of from about 135 m^2/g to about 145 m^2/g, from about 135 m^2/g to about 140 m^2/g, or from about 130 m^2/g to about 140 m^2/g, for example, about 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, or 145 m^2/g. In another aspect, the Inventive Carbon Black can have a nitrogen surface area of from about 110 m^2/g to about 130 m^2/g, or from about 115 m^2/g to about 125 m^2/g, for example, about 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, or 130 m^2/g. In another aspect, the Inventive Carbon Black can have a nitrogen surface area of from about 95 m^2/g to about 110 m^2/g, or from about 80 m^2/g to about 145 m^2/g, for example, about 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 102, 104, 106, 108, 110, 112, 114, 116, 118, 120, 122, 124, 126, 128, 130, 132, 134, 136, 138, 140, 142, 144, or 145 m^2/g. In another aspect, the Inventive Carbon Black can have a nitrogen surface area of from about 75 m^2/g to about 85 m^2/g, from about 80 m^2/g to about 90 m^2/g, or from about 80 m^2/g to about 85 m^2/g, for example, about 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, or 85 m^2/g. In another aspect, the Inventive Carbon Black can have a nitrogen surface area of from about 85 m^2/g to about 95 m^2/g, from about 80 m^2/g to about 95 m^2/g, or from about 90 m^2/g to about 95 m^2/g, for example, about 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, or 95 m^2/g. In still another aspect, the Inventive Carbon Black can have a nitrogen surface area of from about 60 m^2/g to about 70 m^2/g, or from about 65 m^2/g to about 75 m^2/g, for example, about 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, or 75 m^2/g. In another aspect, the Inventive Carbon Black can have a nitrogen surface area of from about 50 m^2/g to about 60 m^2/g, or from about 40 m^2/g to about 75 m^2/g, for example, about 40, 42, 44, 46, 48, 50, 52, 54, 56, 58, 60, 62, 64, 66, 68, 70, 72, 74, or 75 m^2/g. In still another aspect, the Inventive Carbon Black can have a nitrogen surface area of from greater than

about 0.5 m^2/g to about 60 m^2/g, or from about 1 m^2/g to about 50 m^2/g, for example, about 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, or 50 m^2/g. In another aspect, the Inventive Carbon Black can have a nitrogen surface area equivalent to that of an N100 series carbon black. In another aspect, the Inventive Carbon Black can have a nitrogen surface area equivalent to that of an N200 series carbon black. In another aspect, the Inventive Carbon Black can have a nitrogen surface area equivalent to that of an N300 series carbon black. In other aspects, the Inventive Carbon Black can have a nitrogen surface area equivalent to that of an N400 series, N500 series, N600 series, N700 series, N800 series, or N900 series carbon black. In other aspects, the Inventive Carbon Black can have a nitrogen surface area of from about 40 m^2/g to about 250 m^2/g, for example, about 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, 230, 235, 240, 245, or 250 m^2/g.

[0092] In one aspect, the Inventive Carbon Black can have a statistical thickness surface area (STSA) measured according to the ASTM standard 6556-2017 of from about 135 m^2/g to about 145 m^2/g, from about 135 m^2/g to about 140 m^2/g, from about 130 m^2/g to about 140 m^2/g, from about 125 m^2/g to about 135 m^2/g for example, about 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, or 145 m^2/g. In another aspect, the Inventive Carbon Black can have a statistical thickness surface area of from about 105 m^2/g to about 115 m^2/g, from about 110 m^2/g to about 120 m^2/g, or from about 110 m^2/g to about 115 m^2/g, for example, about 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, or 115 m^2/g. In yet another aspect, the Inventive Carbon Black can have a statistical thickness surface area of from about 70 m^2/g to about 80 m^2/g, from about 65 m^2/g to about 80 m^2/g, from about 70 m^2/g to about 85 m^2/g, from about 60 m^2/g to about 70 m^2/g, from about 80 m^2/g to about 85 m^2/g, from about 80 m^2/g to about 90 m^2/g or from about 72 m^2/g to about 78 m^2/g, for example, about 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, or 90 m^2/g. In yet another aspect, the Inventive Carbon Black can have a statistical thickness surface area of from about 120 m^2/g to about 125 m^2/g, or from about 110 m^2/g to about 140 m^2/g, for example, about 110, 112, 114, 116, 118, 120, 121, 122, 123, 124, 125, 126, 128, 130, 132, 134, 136, 138, or 140 m^2/g. In yet another aspect, the Inventive Carbon Black can have a statistical thickness surface area greater than about 120 m^2/g, for example, about 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147,

148, 149, or 150 m^2/g. In another aspect, the Inventive Carbon Black can have a statistical thickness surface area of from about 140 to about 200 m^2/g, for example, about 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, or 200 m^2/g. In still other aspects, the Inventive Carbon Black can have a statistical thickness surface area of from about 1 m^2/g to about 15 m^2/g, from about 5 m^2/g to about 10 m^2/g, from about 25 m^2/g to about 40 m^2/g, from about 40 m^2/g to about 65 m^2/g, from about 65 m^2/g to about 95 m^2/g, from about 95 m^2/g to about 105 m^2/g, from about 95 m^2/g to about 120 m^2/g, from about 100 m^2/g to about 130 m^2/g, or from about 110 to about 160 m^2/g. In other aspects, the Inventive Carbon Black can have a statistical thickness surface area equivalent to that of an N100, N200, N300, N400, N500, N600, N700, N800, or N900 series carbon black.

[0093] In one aspect, the Inventive Carbon Black can have an oil absorption number (OAN) measured according to the ASTM standard D2414-2018 of from about 115 ml/100g to about 135 ml/100g, from about 115 ml/100g to about 125 ml/100g, from about 120 ml/100g to about 125 ml/100g, from about 120 ml/100g to about 130 ml/100g, from about 105 ml/100g to about 125 ml/100g, from about 110 ml/100g to about 125 ml/100g, or from about 125 ml/100g to about 135 ml/100g, for example, about 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, or 135 ml/100g. In another aspect, the Inventive Carbon Black can have an oil absorption number (OAN) of from about 65 ml/100g to about 75 ml/100g, from about 70 ml/100g to about 80 ml/100g, or from about 70 ml/100g to about 75 ml/100g, for example, about 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, or 80 ml/100g. In another aspect, the Inventive Carbon Black can have an oil absorption number (OAN) of from about 90 ml/100g to about 105 ml/100g, from about 95 ml/100g to about 105 ml/100g, from about 100 ml/100g to about 110 ml/100g, or from about 100 ml/100g to about 105 ml/100g, for example, about 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, or 110 ml/100g. In another aspect, the Inventive Carbon Black can have an oil absorption number (OAN) of from about 80 ml/100g to about 90 ml/100g, or from about 65 ml/100g to about 110 ml/100g, for example, about 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, or 110 ml/100g. In another aspect, the Inventive Carbon Black can have an oil absorption number (OAN) of from about 80 ml/100g to about 200 ml/100g, for example, about 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155,

160, 165, 170, 175, 180, 185, 190, 195, or 200 ml/100g. In yet another aspect, the Inventive Carbon Black can have an oil absorption number (OAN) of less than about 170 ml/100g, less than about 150 ml/100g, less than about 130 ml/100g, or less than about 125 ml/100g. In other aspects, the Inventive Carbon Black can have an oil absorption number equivalent to that of an N100, N200, N300, N400, N500, N600, N700, N800, or N900 series carbon black.

[0094] In one aspect, the Inventive Carbon Black can have a compressed oil absorption number (COAN) measured according to the ASTM standard D3493-2018 of from about 60 ml/100g to about 70 ml/100g, from about 65 ml/100g to about 75 ml/100g, or from about 65 ml/100g to about 70 ml/100g, for example, about 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, or 75 ml/100g. In another aspect, the Inventive Carbon Black can have a compressed oil absorption number (COAN) of from about 80 ml/100g to about 95 ml/100g, from about 85 ml/100g to about 95 ml/100g, or from about 85 ml/100g to about 90 ml/100g, for example, about 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, or 95 ml/100g. In another aspect, the Inventive Carbon Black can have a compressed oil absorption number (COAN) of from about 90 ml/100g to about 105 ml/100g, from about 90 ml/100g to about 100 ml/100g, from 95 ml/100g to about 105 ml/100g, or from about 100 ml/100g to about 110 ml/100g, for example, about 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, or 110 ml/100g. In another aspect, the Inventive Carbon Black can have a compressed oil absorption number (COAN) of from about 75 ml/100g to about 80 ml/100g, or from about 65 ml/100g to about 125 ml/100g, for example, about 65, 67, 69, 71, 73, 75, 77, 79, 81, 83, 85, 87, 89, 91, 93, 95, 97, 99, 101, 103, 105, 107, 109, 111, 113, 115, 117, 119, 121, 123, or 125 ml/100g. In another aspect, the Inventive Carbon Black can have a compressed oil absorption number (COAN) of from about 105 ml/100g to about 150 ml/100g, from about 105 ml/100g, to about 145 ml/100g, from about 105 ml/100g to about 140 ml/100g, from about 105 ml/100g to about 135 ml/100g, from about 105 ml/100g to about 130 ml/100g, from about 105 ml/100g to about 125 ml/100g, from about 110 ml/100g to about 125 ml/100g, from about 110 ml/100g to about 120 ml/100g, or from about 115 ml/100g to about 125 ml/100g, for example, about 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, or 150 ml/100g. In other aspects, the Inventive Carbon Black can have a compressed oil absorption number equivalent to that of an N100, N200, N300, N400, N500, N600, N700, N800, or N900 series carbon black.

[0095] In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 2.0. In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 2.2. In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 2.5. In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 2.8. In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 2.7, at least about 2.8, or at least about 2.9. In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 3.0. In one aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), as described herein, of at least about 3.5. In another aspect, the Inventive Carbon Black can have an aggregate size heterogeneity index (HI_{ASD}), of from about 2.0 to about 4.0, from about 2.2 to about 3.8, from about 2.5 to about 4.0, from about 2.5 to about 5, or from about 2.5 to about 3.5, for example, about 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, or 5.0. In another aspect, the Inventive Carbon Black can have an aggregate heterogeneity index (HI_{ASD}), of from about 2 to about 10, from about 2.2 to about 7.0, from about 2.5 to about 3, from about 3 to about 6.0, from about 2.8 to about 9, or from about 4 to about 9, for example, about 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, or more.

[0096] In one aspect, the Inventive Carbon Black can have a particle size heterogeneity index (HI_{PSD}), as described herein, of less than about 1.80. In another aspect, the Inventive Carbon Black can have a HI_{PSD} of less than about 1.75, less than about 1.70, less than about 1.68, or less than about 1.65. In another aspect, the Inventive Carbon Black can have a particle size heterogeneity index (HI_{PSD}), as described herein, of from about 1.30 to about 1.80, from about 1.35 to about 1.80, from about 1.45 to about 1.70, from about 1.45 to about 1.50, from about 1.45 to about 1.55, from about 1.50 to about 1.65, from about 1.50 to about 1.60, from about 1.50 to about 1.70, from about 1.50 to about 1.70, from about 1.55 to about 1.70, from about 1.55 to about 1.60, or from about 1.65 to about 1.70, for example, about 1.30, 1.35, 1.40, 1.45, 1.46, 1.48, 1.50, 1.52, 1.54, 1.56, 1.58, 1.60, 1.62, 1.64, 1.66, 1.68, 1.69, or 1.70, 1.72, 1.74, 1.76, 1.78, or 1.80.

[0097] In one aspect, the Inventive Carbon Black can have a Divergence Ratio, as described herein, of at least about 1.50, at least about 1.60, at least about 1.70, at least about 1.80, at least about 1.90, at least about 2.00, at least about 2.10, at least about 2.20, or at least about 2.30. In another aspect, the Inventive Carbon Black can have a Divergence Ratio of from about 1.50 to about 3.00, from about 1.50 to about 2.70, from about 1.60 to about 2.70, from about 1.70 to about 2.50, from about 1.80 to about 2.50, from about 1.80 to about 2.70, from about 1.70 to about 3.00, or from about 1.70 to about 2.70, for example, about 1.50, 1.60, 1.70, 1.80, 1.90, 2.00, 2.10, 2.20, 2.30, 2.40, 2.50, 2.60, 2.70, 2.80, 2.90, or 3.00. In another aspect, the Inventive Carbon Black can have a Divergence Ratio of from about 2.00 to about 4.00, from about 2.00 to about 6.00, from about 2.50 to about 5.00, from about 3.00 to about 7.00, or from about 3.50 to about 9.00, for example, about 2.00, 2.50, 3.00, 3.50, 4.00, 4.50, 5.00, 5.50, 6.00, 6.50, 7.00, 7.50, 8.00, 8.50, or 9.00.

[0098] In another aspect, the Inventive Carbon Black has a shape specific heterogeneity index (SSHI), as described herein, for Type 4 branched aggregates of at least 2.1, at least 2.2, at least 2.3, at least 2.4, at least 2.5, at least 2.6, at least 2.7, at least 2.8, at least 2.9, at least 3.0, at least 3.1, at least 3.2, at least 3.3, at least 3.4, at least 3.5, or at least 3.6. In another aspect, the Inventive Carbon Black has a shape specific heterogeneity index (SSHI), as described herein, for Type 4 branched aggregates of from about 2.1 to about 4.0, from about 2.1 to about 2.5, from about 2.3 to about 3.8, from about, 2.2 to about 2.5, from about 2.3 to about 2.5, from about 2.5 to about 4.0, from about 2.7 to about 3.3, from about 2.8 to about 3.2, from about 2.7 to about 3.8, from about 2.8 to about 3.8, from about 2.7 to about 3, from about 2.8 to about 3.0, from about 3.0 to about 4.0, from about 3.2 to about 3.8, from about 3.3 to about 3.8, from about 3.5 to about 3.7, or from about 3.5 to about 4.0, for example, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9 or 4.0.

[0099] In one aspect, the Inventive Carbon Black can have an NSA of from about 132 m^2/g to about 142 m^2/g, from about 134 m^2/g to about 140 m^2/g, or about 137 m^2/g; an STSA of from about 128 m^2/g to about 138 m^2/g, from about 130 m^2/g to about 136 m^2/g, or about 133 m^2/g; an OAN of from about 116 ml/100g to about 126 ml/100g, from about 118 ml/100g to about 124 ml/100g, or about 121 ml/100g; a COAN of from about 94 ml/100g to about 104 ml/100g, from about 96 ml/100g to about 102 ml/100g, or about 99 ml/100g; a HI_{ASD} of from about 3.2 to about 4.2, from about 3.4 to about 4.0, or about 3.7; a HI_{PSD} of from about 1.53 to about 1.63, from about 1.56 to about 1.60, or about 1.58; a Divergence Ratio of from about

1.84 to about 2.84, from about 2.04 to about 2.64, or about 2.34; and a SSHI (Type 4) of from about 3.10 to about 4.10, from about 3.30 to about 3.90, or about 3.60. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 3.10 to about 4.10, together with any one or more other properties recited in this paragraph.

[00100] In one aspect, the Inventive Carbon Black can have an NSA of from about 134 m^2/g to about 144 m^2/g, from about 136 m^2/g to about 142 m^2/g, or about 139 m^2/g; an STSA of from about 128 m^2/g to about 138 m^2/g, from about 130 m^2/g to about 136 m^2/g, or about 133 m^2/g; an OAN of from about 137 ml/100g to about 147 ml/100g, from about 139 ml/100g to about 145 ml/100g, or about 142 ml/100g; a COAN of from about 100 ml/100g to about 110 ml/100g, from about 102 ml/100g to about 108 ml/100g, or about 105 ml/100g; a HI_{ASD} of from about 3.7 to about 4.8, from about 3.9 to about 4.6, or about 4.3; a HI_{PSD} of from about 1.47 to about 1.57, from about 1.49 to about 1.55, or about 1.52; a Divergence Ratio of from about 2.36 to about 3.36, from about 2.56 to about 3.16, or about 2.86; and a SSHI (Type 4) of from about 3.01 to about 4.01, from about 3.26 to about 3.86, or about 3.51. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 3.01 to about 4.01, together with any one or more other properties recited in this paragraph.

[00101] In one aspect, the Inventive Carbon Black can have an NSA of from about 135 m^2/g to about 145 m^2/g, from about 137 m^2/g to about 143 m^2/g, or about 140 m^2/g; an STSA of from about 125 m^2/g to about 135 m^2/g, from about 127 m^2/g to about 133 m^2/g, or about 130 m^2/g; an OAN of from about 148 ml/100g to about 158 ml/100g, from about 150 ml/100g to about 156 ml/100g, or about 153 ml/100g; a COAN of from about 112 ml/100g to about 122 ml/100g, from about 114 ml/100g to about 120 ml/100g, or about 117 ml/100g; a HI_{ASD} of from about 3.5 to about 4.5, from about 3.7 to about 4.3, or about 4.0; a HI_{PSD} of from about 1.68 to about 1.79, from about 1.69 to about 1.76, or about 1.74; a Divergence Ratio of from about 1.80 to about 2.80, from about 2.00 to about 2.50, or about 2.30; and a SSHI (Type 4) of from about 2.91 to about 3.91, from about 3.11 to about 3.71, or about 3.41. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 2.91 to about 3.91, together with any one or more other properties recited in this paragraph.

[00102] In one aspect, the Inventive Carbon Black can have an NSA of from about 130 m^2/g to about 140 m^2/g, from about 132 m^2/g to about 138 m^2/g, or about 135 m^2/g; an STSA of from about 129 m^2/g to about 139 m^2/g, from about 131 m^2/g to about 137 m^2/g, or about 134 m^2/g; an OAN of from about 93 ml/100g to about 103 ml/100g, from about 95 ml/100g to

about 101 ml/100g, or about 99 ml/100g; a COAN of from about 76 ml/100g to about 86 ml/100g, from about 78 ml/100g to about 84 ml/100g, or about 81 ml/100g; a HI_{ASD} of from about 4.1 to about 5.1, from about 4.3 to about 4.9, or about 4.6; a HI_{PSD} of from about 1.56 to about 1.66, from about 1.58 to about 1.64, or about 1.61; a Divergence Ratio of from about 2.35 to about 3.35, from about 2.55 to about 3.15, or about 2.85; and a SSHI (Type 4) of from about 3.52 to about 4.22, from about 3.72 to about 4.02, or about 3.82. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 3.52 to about 4.22, together with any one or more other properties recited in this paragraph.

[00103] In one aspect, the Inventive Carbon Black can have an NSA of from about 130 m^2/g to about 140 m^2/g, from about 132 m^2/g to about 138 m^2/g, or about 135 m^2/g; an STSA of from about 123 m^2/g to about 133 m^2/g, from about 125 m^2/g to about 131 m^2/g, or about 128 m^2/g; an OAN of from about 179 ml/100g to about 189 ml/100g, from about 181 ml/100g to about 187 ml/100g, or about 184 ml/100g; a COAN of from about 119 ml/100g to about 129 ml/100g, from about 121 ml/100g to about 127 ml/100g, or about 124 ml/100g; a HI_{ASD} of from about 3.3 to about 4.3, from about 3.5 to about 4.1, or about 3.8; a HI_{PSD} of from about 1.55 to about 1.65, from about 1.57 to about 1.63, or about 1.60; a Divergence Ratio of from about 1.87 to about 2.87, from about 2.07 to about 2.67, or about 2.37; and a SSHI (Type 4) of from about 2.39 to about 3.39, from about 2.59 to about 3.19, or about 2.89. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 2.39 to about 3.39, together with any one or more other properties recited in this paragraph.

[00104] In one aspect, the Inventive Carbon Black can have an NSA of from about 71 m^2/g to about 81 m^2/g, from about 73 m^2/g to about 79 m^2/g, or about 76 m^2/g; an STSA of from about 71 m^2/g to about 81 m^2/g, from about 73 m^2/g to about 79 m^2/g, or about 76 m^2/g; an OAN of from about 117 ml/100g to about 127 ml/100g, from about 119 ml/100g to about 125 ml/100g, or about 122 ml/100g; a COAN of from about 97 ml/100g to about 107 ml/100g, from about 99 ml/100g to about 105 ml/100g, or about 102 ml/100g; a HI_{ASD} of from about 3.0 to about 4.0, from about 3.2 to about 3.8, or about 3.5; a HI_{PSD} of from about 1.41 to about 1.51, from about 1.43 to about 1.49, or about 1.46; a Divergence Ratio of from about 1.89 to about 2.89, from about 2.09 to about 2.69, or about 2.39; and a SSHI (Type 4) of from about 3.69 to about 4.69, from about 3.89 to about 4.49, or about 4.19. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 3.69 to about 4.49, together with any one or more other properties recited in this paragraph.

[00105] In one aspect, the Inventive Carbon Black can have an NSA of from about 76 m^2/g to about 86 m^2/g, from about 78 m^2/g to about 84 m^2/g, or about 81 m^2/g; an STSA of from about 75 m^2/g to about 85 m^2/g, from about 77 m^2/g to about 83 m^2/g, or about 80 m^2/g; an OAN of from about 128 ml/100g to about 138 ml/100g, from about 130 ml/100g to about 136 ml/100g, or about 133 ml/100g; a COAN of from about 105 ml/100g to about 115 ml/100g, from about 107 ml/100g to about 113 ml/100g, or about 110 ml/100g; a HI_{ASD} of from about 2.5 to about 3.5, from about 2.7 to about 3.3, or about 3.0; a HI_{PSD} of from about 1.56 to about 1.66, from about 1.58 to about 1.64, or about 1.61; a Divergence Ratio of from about 1.60 to about 2.39, from about 1.70 to about 2.19, or about 1.89; and a SSHI (Type 4) of from about 2.59 to about 3.59, from about 2.79 to about 3.39, or about 3.09. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 2.59 to about 3.59, together with any one or more other properties recited in this paragraph.

[00106] In one aspect, the Inventive Carbon Black can have an NSA of from about 73 m^2/g to about 83 m^2/g, from about 75 m^2/g to about 81 m^2/g, or about 78 m^2/g; an STSA of from about 73 m^2/g to about 83 m^2/g, from about 75 m^2/g to about 81 m^2/g, or about 78 m^2/g; an OAN of from about 126 ml/100g to about 136 ml/100g, from about 128 ml/100g to about 134 ml/100g, or about 131 ml/100g; a COAN of from about 96 ml/100g to about 106 ml/100g, from about 98 ml/100g to about 104 ml/100g, or about 101 ml/100g; a HI_{ASD} of from about 2.9 to about 3.9, from about 3.1 to about 3.7, or about 3.4; a HI_{PSD} of from about 1.45 to about 1.55, from about 1.47 to about 1.53, or about 1.50; a Divergence Ratio of from about 1.91 to about 2.91, from about 2.11 to about 2.71, or about 2.41; and a SSHI (Type 4) of from about 4.00 to about 5.00, from about 4.20 to about 4.80, or about 4.50. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 4.00 to about 5.00, together with any one or more other properties recited in this paragraph.

[00107] In one aspect, the Inventive Carbon Black can have an NSA of from about 75 m^2/g to about 85 m^2/g, from about 77 m^2/g to about 83 m^2/g, or about 80 m^2/g; an STSA of from about 75 m^2/g to about 85 m^2/g, from about 77 m^2/g to about 83 m^2/g, or about 80 m^2/g; an OAN of from about 92 ml/100g to about 102 ml/100g, from about 94 ml/100g to about 100 ml/100g, or about 97 ml/100g; a COAN of from about 82 ml/100g to about 92 ml/100g, from about 84 ml/100g to about 90 ml/100g, or about 87 ml/100g; a HI_{ASD} of from about 3.2 to about 4.2, from about 3.4 to about 4.0, or about 3.7; a HI_{PSD} of from about 1.35 to about 1.45, from about 1.37 to about 1.43, or about 1.40; a Divergence Ratio of from about 2.13 to about

3.13, from about 2.33 to about 3.03, or about 2.63; and a SSHI (Type 4) of from about 4.57 to about 5.57, from about 4.77 to about 5.37, or about 5.07. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 4.57 to about 5.57, together with any one or more other properties recited in this paragraph.

[00108] In one aspect, the Inventive Carbon Black can have an NSA of from about 78 m^2/g to about 88 m^2/g, from about 80 m^2/g to about 86 m^2/g, or about 83 m^2/g; an STSA of from about 78 m^2/g to about 88 m^2/g, from about 80 m^2/g to about 86 m^2/g, or about 83 m^2/g; an OAN of from about 106 ml/100g to about 116 ml/100g, from about 108 ml/100g to about 114 ml/100g, or about 111 ml/100g; a COAN of from about 87 ml/100g to about 97 ml/100g, from about 89 ml/100g to about 95 ml/100g, or about 92 ml/100g; a HI_{ASD} of from about 2.9 to about 3.9, from about 3.1 to about 3.7, or about 3.4; a HI_{PSD} of from about 1.47 to about 1.57, from about 1.49 to about 1.55, or about 1.52; a Divergence Ratio of from about 1.74 to about 2.74, from about 1.94 to about 2.54, or about 2.24; and a SSHI (Type 4) of from about 3.50 to about 4.50, from about 3.70 to about 4.30, or about 4.00. In another aspect, the Inventive Carbon Black can have an SSHI (Type 4) of from about 3.50 to about 4.50, together with any one or more other properties recited in this paragraph.

[00109] In one aspect, the Inventive Carbon Black has a multi-modal aggregate size distribution. In another aspect, the Inventive Carbon Black has a bi-modal aggregate size distribution.

[00110] In one aspect, the Inventive Carbon Black has a Divergence Ratio greater than 1.5, a particle size heterogeneity index less than about 1.7, an oil absorption number less than about 170 ml/100g, and an STSA greater than about 120 m^2/g. In another aspect, the Inventive Carbon Black has a Divergence Ratio greater than 1.5, a particle size heterogeneity index less than about 1.7, an oil absorption number less than about 125 ml/100g, and an STSA greater than about 120 m^2/g. In another aspect, the Inventive Carbon Black has a Divergence Ratio greater than 1.5, a particle size heterogeneity index less than about 1.7, an oil absorption number less than about 200 ml/100g, and an STSA greater than about 120 m^2/g. In another aspect, the Inventive Carbon Black has a Divergence Ratio greater than 1.5, a particle size heterogeneity index less than about 1.7, an oil absorption number less than about 170 ml/100g, and an STSA from about 70 m^2/g to about 90 m^2/g. In another aspect, the Inventive Carbon Black has a Divergence Ratio greater than about 2.0. In still another aspect, the Inventive Carbon Black has a Divergence Ratio greater than about 1.7 and an aggregate

size heterogeneity index greater than about 2.8. In still another aspect, the Inventive Carbon Black has a shape specific heterogeneity index for Type 4 (branched) aggregates of at least 2.0 or at least 2.1. In yet another aspect, the Inventive Carbon Black has a significantly higher number percent of low structure spheroidal and ellipsoidal aggregates and a lower number of high structures, branched aggregates, than a corresponding ASTM grade carbon black having the same or similar colloidal properties.

[00111] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates of at least 2.1, more preferably at least of 2.5. In one aspect, the Inventive Carbon Black of the present invention has a shape specific heterogeneity index for branched shape aggregates of less than 6.0, preferably of less than 5.5. In one aspect, the Inventive Carbon Black of the present invention has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, preferably ranging from 2.8 to 5.1, even more preferably ranging from 3.4 to 4.6. The shape specific heterogeneity index for branched shape aggregates is mesuread as described above.

[00112] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates of at least 2.1 and a divergence ratio of at least 1.5. In one aspect the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates of at least 2.5 and a divergence ratio of at least 1.6. In one aspect the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates of less than 6.0 and a divergence ratio of less than 4.0. In one aspect the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates of less than 5.5 and a divergence ratio of less than 3.5. The divergence ratio is measured as described above.

[00113] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a divergence ratio raging from 1.7 to 3.0. In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.8 to 5.1 and a divergence ratio raging from 1.8 to 2.9. In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6 and a divergence ratio raging from 2.2 to 2.6.

[00114] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a COAN ranging from 60 to 130 ml/100g, more preferably ranging from 65-125 ml/100g. The COAN is measured according to ASTMD3493-2018.

[00115] In one aspect, the Inventive Carbon Black of the present has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a STSA ranging from 30 to 150 m^2/g, more preferably ranging from 60 to 145 m^2/g. The STSA is measured according to D6556-2017.

[00116] In one aspect, the Inventive Carbon Black of the present has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a NSA ranging from 30 to 160 m^2/g, more preferably ranging from 40 to 150 m^2/g.; the NSA being measured according to ASTM D6556-2017.

[00117] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 80 to 130 ml/100g and a STSA ranging from 90 to 145 m^2/g. More preferably, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 85 to 120 ml/100g and a STSA ranging from 100 to 130 m^2/g.

[00118] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 55 to 120 ml/100g and a STSA ranging from 60 to 100 m^2/g. More preferably Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 60 to 110 ml/100g and a STSA ranging from 60 to 95 m^2/g

[00119] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a divergence ratio ranging from 1.7 to 3.0, a COAN ranging from 55 to 120 ml/100g and a STSA ranging from 60 to 100 m^2/g. More preferably Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.8 to 5.1, a divergence ratio ranging from 1.80 to 2.9, a COAN ranging from 60 to 110 ml/100g and a STSA ranging from 60 to 95 m^2/g.

[00120] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a divergence ratio ranging from 1.70 to 3.0, a COAN ranging from 80 to 130 ml/100g and a STSA ranging from 90 to 145 m^2/g. More preferably, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 2.8 to 5.1, a divergence catio ranging from 1.8 to 2.9, a COAN ranging from 85 to 120 ml/100g and a STSA ranging from 100 to 130 m^2/g.

[00121] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 80 to 130 ml/100g and a STSA ranging from 90 to 145 m^2/g. More preferably, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 3.4 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 85 to 120 ml/100g and a STSA ranging from 100 to 130 m^2/g.

[00122] In one aspect, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 55 to 120 ml/100g and a STSA ranging from 60 to 110 m^2/g. More preferably, the Inventive Carbon Black has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 60 to 110 ml/100g and a STSA ranging from 60 to 90 m^2/g.

Rubber Compositions comprising Inventive Carbon Blacks

[00123] In various aspects, rubber samples containing the Inventive Carbon Blacks can exhibit a reduction in tan delta values of at least about 5%, 7%, 9%, 11%, 13%, 15%, 17%, 19%, 21%, 23%, 25%, or more, than rubber samples containing a comparable ASTM grade carbon black. In another aspect, rubber samples containing the Inventive Carbon Blacks can exhibit a reduction in tan delta values of from about 5% to about 15%, from about 10% to about 25%, from about 10% to about 20%, from about 15% to about 30%, or from about 15% to about 25%, compared to samples containing a comparable ASTM grade carbon black. In another aspect, reductions in tan delta can vary with the loading of carbon black in a given rubber sample. In various aspects, the reduction in tan delta can be greatest at carbon black loadings of from about 40 phr to about 70 phr, from about 45 phr to about 65 phr, or from about 50 phr to about 60 phr. In other aspects, the reduction in tan delta can be greatest at carbon black loadings less than or greater than any particular value recited herein.

[00124] In another aspect, use of the Inventive Carbon Blacks in rubber can improve the balance of hysteresis and tear, essentially maintaining or improving the tear properties of the rubber compound but at significantly lower hysteresis. Tear strength, such as Vieth Tear Strength, indicates the median load value divided by the sample thickness. Knotty tear index is the difference between the median tearing load and the median load where tear propagation along a prescribed path ceases. In one aspect, a rubber compound comprising the Inventive Carbon Blacks can exhibit an improvement in the ratio of Rebound to Vieth tear strength of at least about 5%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, or more, as compared to a rubber compound comprising a ASTM grade carbon black of similar OAN and surface area. In another aspect a rubber compound comprising the Inventive Carbon Blacks can exhibit an improvement in the ratio of Rebound to Vieth tear strength of from about 5% to about 25%, from about 5% to about 35%, from about 10% to about 35%, from about 10% to about 25%, from about 10% to about 15%, from about 15% to about 25%, from about 15% to about 20%, or from about 20% to about 35%, as compared to a rubber compound comprising a ASTM grade carbon black. Similarly, a rubber compound comprising the Inventive Carbon Blacks can exhibit an improvement in Knotty tear index of at least about 5%, at least about 10%, at least about 15%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, at least about 85%, at least about 90%, or more, compared to a rubber compound comprising a ASTM grade carbon black. In another aspect, a rubber compound comprising the Inventive Carbon Blacks can exhibit an improvement in Knotty tear index of from about 5% to about 40%, from about 10% to about 90%, from about 20%, to about 90%, from about 30% to about 90%, from about 40% to about 90%, from about 50% to about 90%, from about 60% to about 90%, from about 70% to about 90%, from about 25% to about 100%, from about 30% to about 100%, or from about 40% to about 100%, compared to a rubber compound comprising a ASTM grade carbon black.

[00125] Mechanical Rubber Goods or MRG products (all rubber goods that are non-tire components) are often composed of carbon black reinforced polymer systems that are based on natural rubber (NR) or blends of NR and synthetic polymers (e.g., butadiene rubber (BR), ethylene propylene diene monomer (EPDM), nitrile rubber and variants thereof, and fluorinated elastomers). Among the polymers, e.g., rubbers, suitable for use with the current invention are any natural rubbers, synthetic rubbers, and blends of natural and synthetic.

These include, for example, NR, BR, styrene butadiene rubber (SBR), emulsion styrene butadiene rubber (ESBR), solution polymerization styrene butadiene rubber (SSBR), ethylene propylene diene monomer rubber (EPDM), butyl rubber, halobutyl rubber, or a mixture thereof. The choice of and amount of polymer can be determined by one of skill in the art based on those suitable for a desired application.

[00126] In other aspects, the present disclosure provides elastomeric compounds, for example, comprising one or more natural and/or synthetic rubber compounds that can be useful, for example, in tire compounds, wherein the compound comprises one or more Inventive Carbon Black as described above . In another aspect, the present disclosure provides a polymer comprising a shape modified carbon black, as described herein. In yet another aspect, the present disclosure comprises a tire tread compound comprising a shape modified carbon balck, as described herein. In yet another aspect, the present disclosure comprises a passenger tire tread compound comprising a shape modified carbon black, as described herein. In yet another aspect, the present disclosure comprises a truck tire tread compound comprising a shape modified carbon black, as described herein. In yet another aspect, the present disclosure provides a tire carcass compound comprising a shape modified carbon black, as described herein. In still another aspect, the present disclosure provides a tire, such as, for example, a passenger, truck, or bus tire, comprising one or more shape modified carbon blacks, as described herein. In yet other aspects, a rubber compound can comprise a composition equivalent or similar to that described in ASTM D3191, or similar to tire compounds known in the art. One of skill in the art would readily be able to prepare a tire compound using a shape modified carbon black, as described herein.

[00127] Another object of the present invention relates to a rubber composition based on at least one diene elastomer, at least one reinforcing filler and at least one crosslinking system, wherein the reinforcing filler comprises at least one carbon black having a shape specific heterogeneity index for branched shape aggregates of at least 2.1, more preferably at least of 2.5. More preferably the carbon black of said rubber composition has a shape specific heterogeneity index for branched shape aggregates of less than 6.0, preferably of less than 5.5. More preferably, the rubber composition based on at least one diene elastomer, at least one reinforcing filler and at least one crosslinking system, wherein the reinforcing filler comprises at least one carbon black haing a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, preferably ranging from 2.8 to 5.1, even more

preferably ranging from 3.4 to 4.6. The shape specific heterogeneity index for branched shape aggregates is mesuread as described above.

[00128] The invention includes a composition comprising a polymer (e.g., elastomer, plastic, resins) and an Inventive Carbon Black of the present invention, as described above. The expression "composition based on" should be understood as meaning a composition comprising the mixture and/or the reaction product of the various constituents used, some of these base constituents being capable of reacting or intended to react with one another, at least in part, during the various phases of production of the composition, in particular during the crosslinking or vulcanization thereof.

[00129] In the context of the invention, the carbon-comprising compounds mentioned in the description can be of fossil origin or biosourced. In the latter case, they can partially or completely result from biomass or be obtained from renewable starting materials resulting from biomass. Polymers, plasticizers, fillers and the like are concerned in particular.

[00130] The rubber compositions in accordance with the invention comprise at least one elastomer, that is to say one elastomer or a mixture of several elastomers. Elastomers are polymers well known to those skilled in the art.

[00131] Preferentially, the elastomer is a diene elastomer.

[00132] It is recalled here that elastomer (or "rubber", the two terms being regarded as synonymous) of the "diene" type should be understood, in a known way, as meaning an (one or more is understood) elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomer(s) (i.e. monomer(s) bearing two conjugated or non-conjugated carbon-carbon double bonds).

[00133] Diene elastomers can be classified into two categories: "essentially unsaturated" or "essentially saturated". "Essentially unsaturated" is generally intended to mean a diene elastomer resulting at least in part from conjugated diene monomers having a molar content of units of diene origin (conjugated dienes) which is greater than 15% (mol%); thus, diene elastomers such as butyl rubbers or copolymers of dienes and of α-olefins of EPDM type do not fall under the preceding definition and may especially be termed "essentially saturated" diene elastomers (low or very low molar content, always less than 15% (mol%), of units of diene origin). In the category of "essentially unsaturated" diene

elastomers, "highly unsaturated" diene elastomer is intended to mean in particular a diene elastomer having a molar content of units of diene origin (conjugated dienes) which is greater than 50% (mol%).

[00134] Given these definitions, "diene elastomer capable of being used in the rubber compositions in accordance with the invention" is intended more particularly to mean:

(a) any homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms;

(b) any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic compounds having from 8 to 20 carbon atoms;

(c) a ternary copolymer obtained by copolymerization of ethylene and of an α-olefin having from 3 to 6 carbon atoms with a non-conjugated diene monomer having from 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene and propylene with a non-conjugated diene monomer of the abovementioned type, such as, especially, 1,4-hexadiene, ethylidene norbornene or dicyclopentadiene;

(d) a copolymer of isobutene and of isoprene (butyl rubber) and also the halogenated versions, in particular chlorinated or brominated versions, of this type of copolymer.

[00135] Although it applies to any type of elastomer, especially diene elastomer, those skilled in the art will understand that the present invention is preferably employed with essentially unsaturated diene elastomers, in particular of the above type (a) or (b).

[00136] In the case of copolymers (b), the latter may contain from 20% to 99% by weight of diene units and from 1% to 80% by weight of vinylaromatic units.

[00137] As conjugated dienes, the following are especially suitable: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C_1-C_5 alkyl)-1,3-butadienes such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene, or 2,4-hexadiene.

[00138] The following, for example, are suitable as vinylaromatic compounds: styrene, ortho-, meta- or para-methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-

butyl)styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene or vinylnaphthalene.

[00139] Preferentially, the diene elastomer(s) of the composition according to the invention may be selected preferentially from the group of diene elastomers consisting of polybutadienes (abbreviated to BRs), synthetic polyisoprenes (abbreviated to IRs), natural rubber (abbreviated to NR), butadiene copolymers, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more preferentially selected from the group consisting of butadiene/styrene copolymers (abbreviated to SBRs), whether the latter are prepared by emulsion polymerization (ESBR) or solution polymerization (SSBR), isoprene/butadiene copolymers (abbreviated to BIRs), isoprene/styrene copolymers (abbreviated to SIRs) and isoprene/butadiene/styrene copolymers (abbreviated to SBIRs). Preferably, the diene elastomer is selected from the group consisting of polybutadienes (BRs), butadiene/styrene copolymers (SBRs), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs), isoprene/butadiene/styrene copolymers (SBIRs) ethylene/butadiene copolymers (EBR) and the mixtures of these copolymers.

[00140] Among the diene elastomers, the following are suitable: polybutadienes and in particular those having a content (mol%) of 1,2- units of between 4% and 80% or those having a content (mol%) of cis-1,4- units of greater than 80%, polyisoprenes, butadiene/styrene copolymers and in particular those having a Tg (glass transition temperature Tg, measured according to ASTM D3418, 1999) of between 0°C and -70°C and more particularly between -10°C and -60°C, a styrene content of between 5% and 60% by weight and more particularly between 20% and 50% by weight, a content (mol%) of 1,2-bonds of the butadiene part of between 4% and 75% and a content (mol%) of trans-1,4-bonds of between 10% and 80%, butadiene/isoprene copolymers and especially those having an isoprene content of between 5% and 90% by weight and a Tg ranging from -40°C to -80°C, or isoprene/styrene copolymers and especially those having a styrene content of between 5% and 50% by weight and a Tg of between -5°C and -50°C. In the case of butadiene/styrene/isoprene copolymers, those having a styrene content of between 5% and 50% by weight and more particularly of between 10% and 40%, an isoprene content of between 15% and 60% by weight and more particularly of between 20% and 50%, a butadiene content of between 5% and 50% by weight and more particularly of between 20% and 40%, a content (mol%) of 1,2- units of the butadiene part of between 4% and 85%, a

content (mol%) of trans-1,4- units of the butadiene part of between 6% and 80%, a content (mol%) of 1,2- plus 3,4- units of the isoprene part of between 5% and 70% and a content (mol%) of trans-1,4- units of the isoprene part of between 10% and 50%, and more generally any butadiene/styrene/isoprene copolymer having a Tg of between -5°C and -70°C, are especially suitable.

[00141] According to a specific embodiment, the diene elastomer is predominantly (i.e., for more than 50 phr) an SBR, whether this is an SBR prepared in emulsion ("ESBR") or an SBR prepared in solution ("SSBR"), or an SBR/BR, SBR/NR (or SBR/IR), BR/NR (or BR/IR) or else SBR/BR/NR (or SBR/BR/IR) blend (mixture). In the case of an SBR (ESBR or SSBR) elastomer, use is especially made of an SBR having a moderate styrene content, for example of between 20% and 35% by weight, or a high styrene content, for example from 35% to 45% by weight, a content (mol%) of vinyl bonds of the butadiene part of between 15% and 70%, a content (mol%) of trans-1,4- bonds of between 15% and 75% and a Tg of between -10°C and -55°C; such an SBR can advantageously be used as a mixture with a BR preferably having more than 90% (mol%) of cis-1,4- bonds.

[00142] According to another specific embodiment of the invention, the diene elastomer of the composition according to the invention comprises a blend (mixture) of a BR (as low Tg elastomer) having a content (mol%) of cis-1,4- linkages of greater than 90% with one or more S-SBRs or E-SBRs (as high Tg elastomer(s)).

[00143] The elastomers may have any microstructure, which depends on the polymerization conditions used, especially on the presence or absence of a modifying and/or randomizing agent and on the amounts of modifying and/or randomizing agent employed. These elastomers may, for example, be block, random, sequential or microsequential elastomers and be prepared in dispersion or in solution; they may be coupled and/or star-branched or else functionalized with a coupling and/or star-branching or functionalization agent.

[00144] The Inventive Carbon black used in the rubber composition of the invention may have the following features. In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates of at least 2.1 and a divergence ratio of at least 1.5. In one aspect the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape

aggregates of at least 2.5 and a divergence ratio of at least 1.6. In one aspect the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates of less than 6.0 and a divergence ratio of less than 4.0. In one aspect the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates of less than 5.5 and a divergence ratio of less than 3.5. The divergence ratio is measured as described above.

[00145] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a divergence ratio raging from 1.7 to 3.0. In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.8 to 5.1 and a divergence ratio raging from 1.8 to 2.9. In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6 and a divergence ratio raging from 2.2 to 2.6.

[00146] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a COAN ranging from 60 to 130 ml/100g, more preferably ranging from 65-125 ml/100g. The COAN is measured according to ASTMD3493-2018.

[00147] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and a STSA ranging from 30 to 150 m^2/g, more preferably ranging from 60 to 145 m^2/g. The STSA is measured according to D6556-2017.

[00148] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3 and an NSA ranging from 30 to 160 m^2/g, more preferably ranging from 40 to 150 m^2/g.; the NSA being measured according to ASTM D6556-2017.

[00149] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 80 to 130 ml/100g and a STSA ranging from 90 to 145 m^2/g. More preferably, the Inventive Carbon Black used in the rubber composition has a shape specific

heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 85 to 120 ml/100g and a STSA ranging from 100 to 130 m^2/g.

[00150] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 55 to 120 ml/100g and a STSA ranging from 60 to 100 m^2/g. More preferably Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a COAN ranging from 60 to 110 ml/100g and a STSA ranging from 60 to 95 m^2/g

[00151] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a divergence ratio ranging from 1.7 to 3.0, a COAN ranging from 55 to 120 ml/100g and a STSA ranging from 60 to 100 m^2/g. More preferably Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.8 to 5.1, a divergence ratio ranging from 1.80 to 2.9, a COAN ranging from 60 to 110 ml/100g and a STSA ranging from 60 to 95 m^2/g.

[00152] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.6 to 5.3, a divergence ratio ranging from 1.70 to 3.0, a COAN ranging from 80 to 130 ml/100g and a STSA ranging from 90 to 145 m^2/g. More preferably, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 2.8 to 5.1, a divergence catio ranging from 1.8 to 2.9, a COAN ranging from 85 to 120 ml/100g and a STSA ranging from 100 to 130 m^2/g.

[00153] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 80 to 130 ml/100g and a STSA ranging from 90 to 145 m^2/g. More preferably, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 3.4 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 85 to 120 ml/100g and a STSA ranging from 100 to 130 m^2/g.

[00154] In one aspect, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6, a

divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 55 to 120 ml/100g and a STSA ranging from 60 to 110 m^2/g. More preferably, the Inventive Carbon Black used in the rubber composition has a shape specific heterogeneity index for branched shape aggregates ranging from 3.5 to 4.6, a divergence ratio ranging from 2.2 to 2.6, a COAN ranging from 60 to 110 ml/100g and a STSA ranging from 60 to 90 m^2/g.

[00155] The amount of the Inventive Carbon Black in the rubber composition of the invention can be determined by one of ordinary skill, for example, from 10 to 110 parts per hundred rubber (phr), preferably from 20 to 100 phr, more preferably 40 to 80 phr. One of ordinary skill in the art can determine a suitable amount of the carbon black to use in a particular application as well as a suitable ratio relative to the other components.

~~[00156]~~ In addition to the Inventive Carbon Black used in the rubber composition, the reinforcing filler may also comprise at least one reinforcing inorganic filler. As "reinforcing inorganic filler" should be understood here to mean, in a known way, any inorganic or mineral filler, irrespective of its colour and its origin (natural or synthetic), also known as "white filler", "clear filler" or else "non-black filler", in contrast to carbon black, this inorganic filler being capable of reinforcing, by itself, without means other than an intermediate coupling agent, a rubber composition especially intended for the manufacture of semi-finished products for tyres or of tyres, in other words capable of replacing, in its reinforcing role, a tyre-grade carbon black for rubber compositions, especially intended for the manufacture of semi-finished products for tyres or of tyres. Such a filler is generally characterized by the presence of functional groups, especially hydroxyl (–OH) functional groups, at its surface, requiring in that regard the use of a coupling agent or system intended to provide a stable chemical bond between the elastomer and said filler.

[00157] Mention may be made, as reinforcing inorganic filler, of fillers of the siliceous type, such as silica, or of the aluminous, silica-alumina or titanium oxide type.

[00158] The silica used may be any reinforcing silica known to those skilled in the art, especially any precipitated or fumed silica having a BET surface area and also a CTAB specific surface area both of less than 450 m^2/g, preferably from 30 to 400 m^2/g, especially between 60 and 300 m^2/g. As highly dispersible precipitated silicas ("HDSs"), mention will be made, for example, of the Ultrasil 7000 and Ultrasil 7005 silicas from Degussa, the Zeosil 1165MP, Zeosil 1135MP, Zeosil 1115MP and Zeosil Premium 200 MP silicas from Rhodia,

the Hi-Sil EZ150G silica from PPG, the Zeopol 8715, 8745 and 8755 silicas from Huber and the silicas having a high specific surface area as described in application WO 03/016387.It is specified that the CTAB specific surface area is determined according to French standard NF T 45-007 of November 1987 (method B).

[00159] In order to couple the reinforcing inorganic filler, especially silica, to the diene elastomer, use is made, in a known way, of an at least bifunctional coupling agent (or bonding agent) intended to provide a sufficient connection, of chemical and/or physical nature, between the inorganic filler (surface of its particles) and the diene elastomer, in particular bifunctional organosilanes or polyorganosiloxanes. Use is made in particular of silane polysulfides, referred to as "symmetrical" or "asymmetrical" depending on their specific structure, such as described, for example, in applications WO 03/002648 (or US 2005/016651) and WO 03/002649 (or US 2005/016650).

[00160] The reinforcing filler may also comprise another carbon black being different of the Inventive Carbon black used in the rubber composition of the invention. Said other carbon black can be selected from the group consisting in the HAF, ISAF or SAF carbon black type. In another aspect, said carbon black can be selected from the group comprising HAF, ISAF, or SAF carbon black types. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series (ASTM grades).

[00161] In one aspect, the Inventive Carbon Black used in the rubber composition of the invention constitutes at least 30% by weight, preferably at least 60%, indeed even at least 80% by weight, of the total amount of the weight of reinforcing filler.

[00162] Optionally, the polymeric composition can comprise additional components. For example, the composition can comprise curatives, oils, antioxidants, fillers, or a mixture thereof. The choice of additional components and amount of each can be determined by one of skill in the art based on those suitable for a desired application.

[00163] The rubber compositions in accordance with the invention may also comprise all or a portion of the usual additives generally used in the elastomer compositions intended for the manufacture of tyres, in particular of treads, such as, for example, plasticizing agents or extending oils, whether the latter are aromatic or non-aromatic in nature, pigments, protection agents, such as antiozone waxes, chemical antiozonants or antioxidants, antifatigue agents, reinforcing resins, methylene acceptors (for example phenolic novolak resin) or

methylene donors (for example HMT or H3M), as described, for example, in Application WO 02/10269 (or US2003-0212185), a crosslinking system based either on sulfur or on sulfur-donating agents and/or on peroxide and/or on bismaleimides, vulcanization accelerators or vulcanization activators, with zinc-based activators of course being excluded.

[00164] Preferably, these compositions comprise, as preferred non-aromatic or very weakly aromatic plasticizing agent, at least one compound selected from the group consisting of naphthenic oils, paraffinic oils, MES oils, TDAE oils, glycerol esters (in particular trioleates), plasticizing hydrocarbon resins having a high Tg preferably of greater than 30°C, and the mixtures of such compounds.

[00165] Mention will especially be made, among the above plasticizing hydrocarbon resins (it will be remembered that the name "resin" is reserved by definition for a solid compound), of resins formed of homo- or copolymers of alpha-pinene, beta-pinene, dipentene or polylimonene, C_5 fraction, for example formed of C_5 fraction/styrene copolymer, which can be used alone or in combination with plasticizing oils, such as MES or TDAE oils.

[00166] The rubber compositions in accordance with the invention comprise a chemical crosslinking system. Any type of crosslinking system known to those skilled in the art for rubber compositions may be used.

[00167] The crosslinking system is preferably a vulcanization system, that is to say a system based on sulfur (or on a sulfur-donating agent) and on a primary vulcanization accelerator. Various known secondary vulcanization accelerators or vulcanization activators, such as zinc oxide, stearic acid or equivalent compounds, or guanidine derivatives (in particular diphenylguanidine), may be added to this base vulcanization system, being incorporated during the first non-productive phase and/or during the productive phase, as described subsequently.

[00168] When sulfur is used, it is used at a preferential content of between 0.5 and 12 phr, in particular between 1 and 10 phr. The primary vulcanization accelerator is used at a preferential content of between 0.5 and 10 phr, more preferentially of between 0.5 and 5.0 phr.

[00169] The vulcanization system of the composition in accordance with the invention may also comprise one or more additional accelerators, for example compounds of the family

of the thiurams, zinc dithiocarbamate derivatives, sulfenamides, guanidines or thiophosphates. Use may in particular be made of any compound capable of acting as accelerator of the vulcanization of diene elastomers in the presence of sulfur, especially accelerators of thiazoles type and also their derivatives, accelerators of the thiurams type, and zinc dithiocarbamates.

[00170] Methods of making the polymeric composition of the invention comprising the Inventive Carbon Black can utilize techniques generally known in the polymer, e.g., rubber, compounding arts. Variations on these methods can be determined by those skilled in the art. The carbon black can be added to the polymer and the combination can be mixed until the carbon black is dispersed to the desired degree. Additional steps and components can be added as determined by one of skill in the art.

[00171] The rubber compositions that are embodiments of the present invention may be produced in suitable mixers, such as in internal mixer, in a manner known to those having ordinary skill in the art. There are typically two successive preparation phases, a first phase of thermo-mechanical working at high temperature, followed by a second phase of mechanical working at lower temperature wherein the crosslinking agent is added.

[00172] The first phase of thermo-mechanical working (sometimes referred to as "non-productive" phase) is intended to mix thoroughly, by kneading, the various ingredients of the composition, with the exception of the vulcanization system. It is carried out in a suitable kneading device, such as an internal mixer or an extruder, until, under the action of the mechanical working and the high shearing imposed on the mixture, a maximum temperature generally from 130° C to 200° C, more narrowly between 145° C and 185° C, is reached.

[00173] In one embodiment, the Inventive Carbon Black may, for example, be already incorporated in an diene elastomer, in particular in natural rubber, in the form of a masterbatch (see, for example, patent application WO 97/36724, WO 99/16600, WO 2017103518 and WO 2019/129999 incorporated by reference). More specifically, the masterbatch comprising the Inventive Carbon Black is obtained by a continuous process comprising the following steps:

- preparing a fluid consisting of an aqueous dispersion of the Inventive Carbon Black particles, this aqueous dispersion being prepared by dispersing the Inventive Carbon Black particles in water using one or more mills, and the aqueous dispersion of filler

also passing through a homogenizer in order to obtain a particle size distribution for said Inventive Carbon Black that is as narrow as possible,

- incorporating a continuous stream of a first fluid consisting of an elastomeric latex, in particular natural rubber, into the mixing zone of a coagulation reactor, incorporating a second continuous stream of a second fluid consisting of the aqueous dispersion of the Inventive Carbon Black obtained above under pressure into the mixing zone to form a mixture with the elastomeric latex; the compounding of these two fluids being sufficiently energetic to make it possible to almost completely coagulate the elastomeric latex with the Inventive Carbon Black before the outlet orifice of the coagulation reactor,
- drying the coagulum by passing through a dryer (dewatering extruder) and then passing through a drying extruder (FCM) to obtain a dried masterbatch. During these drying steps, the mixture may be in the form of strips. The dried masterbatch has a moisture content of less than 2% by weight.

[00174] The masterbatch is then added into the internal mixer with the other ingredient of the rubber composition such as for example the pasticizer, with the exception of the vulcanization system.

[00175] After cooling of the mixture, a second phase of mechanical working is implemented at a lower temperature. Sometimes referred to as "productive" phase, this finishing phase consists of incorporating by mixing the vulcanization (or cross-linking) system (sulfur, accelerators, activators), in a suitable device, for example an open mill although some or all of the accelerators and activators may be mixed in the non-productive phase. It is performed for an appropriate time (typically between 1 and 30 minutes, for example between 2 and 10 minutes) and at a sufficiently low temperature that is lower than the vulcanization temperature of the mixture, so as to protect against premature vulcanization.

[00176] The rubber composition can be formed into useful articles, including treads for use on vehicle tires. The treads may be formed as tread bands and then later made a part of a tire or they be formed directly onto a tire carcass by, for example, extrusion and then cured in a mold. As such, tread bands may be cured before being disposed on a tire carcass or they may be cured after being disposed on the tire carcass. Typically, a tire tread is cured in a known manner in a mold that molds the tread elements into the tread, including, *e.g.*, the sipes molded into the tread blocks or ribs.

[00177] Particular embodiments of the present invention include tire treads, tire under-tread layer, belt wedges, carcass plies and bead filler rubber and tires having such components, and other useful articles manufactured at least in part with the rubber compositions disclosed herein. It has been found that when tires are made from such rubber compositions, an improved rolling resistance and improved electrical conductivity of the tire can be achived while maintaining tire durability. The use of the Inventive Carbon Black as described above with or without additional reinforcing fillers, surprisingly provide enhanced physical characteristics of the finished rubber product.

[00178] As is known generally, a tire tread is the road-contacting portion of a vehicle tire that extends circumferentially around the tire. It is designed to provide the handling characteristics required by the vehicle; *e.g.*, traction, dry braking, wet braking, cornering and so forth - all being preferably provided with a minimum amount of noise being generated and at a low rolling resistance.

[00179] The bead filler, alternatively called the "bead apex", is layer of rubber above the bead of the tire. Generally, the bead filler has a triangular cross section and is positioned to the outside of the carcass ply, or between the carcass ply and a portion of the carcass ply that wraps around the bead. The bead filler provides additional stiffness and support to the lower sidewall.

EXAMPLES

[00180] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices, and/or methods described and claimed herein are made and evaluated and are intended to be purely exemplary and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in degrees °C, or is at ambient temperature (23°C, 1 atm.), and pressure is at or near atmospheric. References to spray locations, unless specified otherwise, are intended to refer to the distance upstream from the choke outlet. Unless specified otherwise, the compositions of fuel oil and carbon black feedstock oil are the same for a given grade. Only reasonable and routine experimentation will be required to optimize such process conditions.

Example 1 – Production of Comparative Carbon Black A

[00181] A comparative N134 type reference carbon black was made in a standard carbon black tread reactor. The reactor was an 8 inches (20.3 cm) choke diameter tread reactor similar to the Columbian Axial Tread (CAT) reactor (as taught generally in U.S. Pat. No. 4,927,607 (for example, at column 4, line 59 to column 6, line60) and U.S. Pat. No. 5,256,388 (for example, at column 4, line 61 to column 6, line 62)). The reactor was operated at a total air load of 9,780 Nm^3/hr with a fuel oil rate of 466 kg/hr and an inlet air temperature of 850 °C. A conventional Fluidized Catalyst Cracker residuals or FCC carbon black feedstock fuel oil was preheated to a temperature of about 238° C and was injected radially via four Monarch model F-94, M30, 80 degree sprays (available from Monarch Mfg Works, 7249-B Browning Road Pennsauken, NJ 08109 USA), positioned -8 inches (20.3 cm) upstream from the choke outlet and operating at a pressure of 15 kg/cm^2. Material structure was controlled by adding a 0.2 wt.% aqueous solution of potassium formate at about 29 kg/hr and mixed with the feedstock before injection into the reactor. The carbon black formation reaction was quenched via water injected at a position 70 inches (177.8 cm) downstream from the choke outlet.

[00182] The resultant material, Comparative Carbon Black A ("Comp. CB A"), an ASTM N134 type carbon black, was dried and collected.

Example 2 – Production of Shape-Modified Inventive Carbon Blacks, Sample 1

[00183] Inventive Carbon Black 1 of the present invention was made in a standard carbon black tread reactor. The reactor was an 8 inch (20.3 cm) choke diameter tread grade reactor similar to Columbian Axial Tread (CAT) reactor (as taught generally in U.S. Pat. Nos. 4,927,607 and 5,256,388, as referenced in Example 1). The reactor was operated at an air load of 9,840 Nm^3/hr with a fuel at a rate of 469 Nm^3/hr and an inlet air temperature of 850 °C. A conventional FCC carbon black feedstock oil was preheated to a temperature of about 221 °C and was injected radially via Monarch model F-94, M30, 80 degree sprays (also available from Monarch Mfg Works), in equal amounts in conversion oil spray planes located at -5 inches (-12.7 cm) and -28 inches (-71.1 cm) upstream from the choke outlet, and operated at a pressure of about 25 kg/cm^2. Material structure was controlled using a 24 wt.% aqueous solution of potassium formate at a flow rate of about 14 kg/hr and mixed with the feedstock before injection into the reactor. For Inventive Carbon Black 1, the aqueous

solution of potassium formate was injected only at the -5 inch (-12.7 cm) spray to induce shape-modification of the carbon black aggregates. The carbon black formation reaction was quenched via water injected at a position 60 inches (152,4 cm) downstream from the choke outlet.

[00184] The resultant material, Inventive Carbon Black 1 ("Inv. CB 1"), was dried and collected.

Example 3 – Production of Shape-Modified Inventive Carbon Blacks, Samples 2 through 5

[00185] The Inventive Carbon Blacks of this Example 3 were made in a standard carbon black tread reactor. The reactor was an 8 inch (20.3 cm) choke diameter tread grade reactor similar to Columbian Axial Tread (CAT) reactor (as taught generally in U.S. Pat. Nos. 4,927,607 and 5,256,388, as referenced in Example 1). The reactor was operated at an air load of about 10,900 Nm^3/hr with a fuel at a rate of about 519 Nm^3/hr and an inlet air temperature of 850 °C. A conventional FCC carbon black feedstock oil was preheated in the range of 194 to 212 °C and was injected radially via Monarch model F-94, 80 degree, M30 sprays (also available from Monarch Mfg Works), positioned as noted in Table 1 below, in different ratios in conversion oil spray planes located at -5 inches (-12.7 cm) and -28 inches upstream from the choke outlet, operating at a pressure of about 21 kg/cm^2 (e.g., 19 to 23.7 kg/cm^2). Material structure was controlled using a 40 wt.% aqueous solution of potassium formate at a flow rate in the range of about 2.5 to 37 kg/hr, as also detailed in Table 1, below, and mixed with the feedstock before injection into the reactor only at the -5 inch (-12.7 cm) conversion oil spray plane. The carbon black formation reaction was quenched via water injected at a position 60 inches (152.4 cm) downstream from the choke outlet.

[00186] The resulting materials, Inventive Carbon Blacks 2-5 ("Inv. CB 2, Inv CB3, Inv CB 4 and Inv CB 5"), were dried and collected.

[00187] Table 1. Process parameters for the manufacture of Inventive Carbon Blacks 2-5

Process Parameter	Inv. CB 1	Inv. CB 2	Inv. CB 3	Inv. CB 4	Inv. CB 5
Air Rate, Nm^3/h	9,840	10,900	10,900	10,850	10,950
Fuel Rate, kg/h	469	519	519	517	521
Conversion Oil Rate, kg/h	2,779	2,890	2,830	2,890	2,570
Conversion Oil Spray Plane #1					
•Position	•-5" (127mm)	•-5" (127mm)	•-5" (127mm)	•-5" (127mm)	•-5" (127mm)
•Oil Flow, kg/hr	•1,389	•1,651	•1,651	•2,037	•758
•Potassium Solution, %	•24%	•40%	•40%	•40%	•40%
•Potassium Solution, Flow Rate, kg/hr	•14	•17	•2.5	•37	•37
Conversion Oil Spray Plane #2					
•Position	•-28" (771.2mm)	•-28" (711.2mm)	•-28" (711.2mm)	•-28" (711.2mm)	•-28" (711.2mm)
•Oil Flow, kg/hr	•1,389	•1,238	•1,238	•1,549	•1,811
•Potassium Solution, %	•0%	•0%	•0%	•0%	•0%
•Potassium Solution, Flow Rate, kg/hr	•0	•0	•0	•0	•0

Example 4 – Production of Comparative Carbon Black B

[00188] A comparative N347 type reference carbon black was made in a standard carbon black tread reactor. The reactor was a 9 inch (22.9 cm) choke diameter tread reactor similar to the Columbian Axial Tread (CAT) reactor (as taught generally in U.S. Pat. Nos. 4,927,607 and 5,256,388, as referenced in Example 1). The reactor was operated at a total air load of 6,500 Nm^3/hr with an inlet air temperature of 900 °C. A conventional FCC carbon black feedstock oil was preheated in the range of 300 °C and was injected radially via Monarch model F-94, 60 degree, M60 sprays (also available from Monarch Mfg Works), positioned -8 inches (20.3 cm) upstream from the choke outlet and operating at a pressure of 15 kg/cm^2. The carbon black formation reaction was quenched via water injected at a position 120 inches (304.8 cm) downstream from the choke outlet. Material structure was controlled using a 3 wt.% aqueous solution of potassium formate at about 2.4 kg/hr injected with the feedstock.

[00189] The resulting material, Comparative Carbon Black B ("Comp. CB B"), an N347 type carbon black, was dried and collected.

Example 5 – Other Comparative Carbon Blacks

[00190] Comparative Carbon Black C ("Comp. CB C), named Propel E7™ was bought from Cabot Corporation.

[00191] Comparative Carbon Black D ("Comp. CB D"), a N330 ASTM type carbon black, was bought from Birla Carbon.

Example 6 – Production of Shape-Modified Inventive Carbon Blacks, Samples 6 through 10

[00192] The Inventive Carbon Blacks of this Example 6 were made in a standard carbon black tread reactor. The reactor was a 12 inch (30.5 cm) choke diameter tread grade reactor similar to Columbian Axial Tread (CAT) reactor (as taught generally in U.S. Pat. Nos. 4,927,607 and 5,256,388, as referenced in Example 1). The reactor was operated at a total air load of about 11,500 Nm^3/hr with a natural gas fuel rate of about 650 Nm^3/hr (e.g., 616 Nm^3/hr to 661 Nm^3/hr) and an inlet air temperature of about 850 °C (e.g., 813 °C to 846 °C). A conventional FCC carbon black feedstock oil was preheated and injected radially via Monarch sprays (also available from Monarch Mfg Works), as detailed in Table 2 below, operating at a pressure of from about 9.3 bar to about 11.6 bar. The carbon black formation reaction was quenched via water injected at a position (300 cm, 118.1 inch) downstream from the choke outlet. Material structure was controlled using a 46 wt.% aqueous solution of potassium formate at about 5.6 to 30.1 kg/hr injected with the feedstock. For Inventive Carbon Blacks 6 - 10, the aqueous solution of the potassium formate-based compound was injected only at the -8 inch (-20.3 cm) conversion oil spray plane and the oil split between the –8 inch (-20.3 cm) and the -40 inch (-101.6 cm) spray planes was varied as listed in Table 2 to achieve the desired COAN.

[00193] The resulting material, Inventive Carbon Blacks 6-10 were dried and collected, as detailed in Table 2, below.

[00194] Table 2. Process Parameters for the manufacture of Inventive Carbon Blacks 6-10

Process Parameter	Inv. CB 6	Inv. CB 7	Inv. CB 8	Inv. CB 9	Inv. CB 10
Air Rate, Nm^3/h	11,550	11,900	11,100	11,400	11,550
Fuel Oil Rate, kg/h	--	--	--	--	--
Natural Gas Rate, Nm^3/h	642	661	616	633	642
Conversion Oil Rate, kg/h	5,160	4,700	5,180	5,190	5,160
Conversion Oil Spray Plane #1					
•Position	•-8" (203.2mm)	•-8" (203.2mm)	•-8" (203.2mm)	•-8" (203.2mm)	•-8" (203.2mm)
•Oil Flow, kg/hr	•2,884	•2,189	•2,176	•3,114	•2,833
•Potassium Solution, %	•46%	•46%	•46%	•46%	•46%
•Potassium Solution, Flow Rate, kg/hr	•9.8	•5.6	•18.3	•30.1	•25.8
Conversion Oil Spray Plane #2					
•Position	•-40" (1,016mm)	•-40" (1,016mm)	•-40" (1,016mm)	•-40" (1,016mm)	•-40" (1,016mm)
•Oil Flow, kg/hr	•2,276	•2,511	•3,004	•2,076	•2,322
•Potassium Solution, %	•0%	•0%	•0%	•0%	•0%
•Potassium Solution, Flow Rate, kg/hr	•0	•0	•0	•0	•0

Colloidal Properties of Comparative and Inventive Carbon Blacks

[00195] The Comparative and Inventive Carbon Blacks produced in Examples 1 through 6 were subjected to routine colloidal tests, the results of which are detailed in Tables 3 through 5, below.

[00196] As can be seen, the Comparative and Inventive Carbon Blacks in Examples 1 through 6 in Table 3 are N100 series materials, which ASTM D1765 defines as carbon blacks with NSA values in the range of 121 to 150 m^2/g. Thus, these Inventive Carbon Blacks 1 through 5, are compared to Comparative Carbon Black A, which is an N134 type carbon black.

[00197] Essentially, the STSA of the Shape-Modifed Inventive Carbon Blacks 1 through 5 was kept constant at approximately 130 m^2/g, but the overall average structure level as measured by COAN, was varied from approximately 80 ml/100g to 125 ml/100 g. This was done to demonstrate the utility of the shape modification process and materials therefrom over a wide range of structure or COAN that provides for wider applicability of these materials over a range of compounds and applications as might be recognized by those skilled in the art of compounding polymeric compositions.

[00198] Additionally, Table 4 show examples of Shape-Modified Inventive Carbon Blacks in the N300 series surface area range with NSA values in the range of 76 to 83 m^2/g. ASTM D1765 defines N300 series carbon blacks with NSA values in the range of 70 to 99 m^2/g. Comparative CB B is an N347 type Carbon Black and Comparative CBs C and D listed in Table 5 are Propel™ E7 from Cabot Corporation and N330, respectively.

[00199] Note also that as for the Shape-Modified N100 series Inventive Carbon Blacks 1 through 5, the N300 series Shape-Modified Inventive Carbon Blacks 6 through 10 were also produced over a wide range of COAN from about 87 ml/100g to 110 ml/100g, again demonstrating the utility of the Shape Modification process and its materials. These examples serve to highlight that the Shape-Modification process can be expanded over a wide range of surface area and structure.

[00200] Table 3. Colloidal Properties of Carbon Blacks

Test	ASTM Method	Comparative CB A	Inv. CB 1	Inv. CB 2	Inv. CB 3	Inv. CB 4	Inv. CB 5
NSA, m^2/g	D6556-2017	140	137	139	140	135	135
STSA, m^2/g	D6556-2017	134	133	133	130	134	128
Iodine, mg/g	D1510	135	142	142	146	133	142
Tint, %ITRB	D3265	134	118	118	119	118	112
OAN, ml/100g	D2414-2018	124	121	142	153	98.6	184
COAN, ml/100g	D3493-2018	102	99	105	117	81.0	124

[00201] Table 4. Colloidal Properties of Carbon Blacks

Test	ASTM Method	Comparative CB B	Inv. CB 6	Inv. CB 7	Inv CB 8	Inv. CB 9	Inv. CB 10
NSA, m^2/g	D6556-2017	82	76	81	78	80	83
STSA, m^2/g	D6556-2017	81	76	80	78	80	83
Iodine, mg/g	D1510	90	81	83	80	82	83
Tint, %ITRB	D3265	104	96	97	97	101	89
OAN, ml/100g	D2414-2018	126	122	133	131	97	111
COAN, ml/100g	D3493-2018	104	102	110	101	87	92

[00202] Table 5. Colloidal Properties of Carbon Blacks of Comparative Black Carbon C and D

Test	ASTM Method	Comparative CB C	Comparative CB D
NSA, m^2/g	D6556-2017	121	73
STSA, m^2/g	D6556-2017	112	73
Iodine, mg/g	D1510	127	81
Tint, %ITRB	D3265	112	100
OAN, ml/100g	D2414-2018	133	100
COAN, ml/100g	D3493-2018	109	87

Analysis of Carbon Black Aggregate Size and Distribution by Disc Centrifuge Photosedimentometry (DCP)

[00203] The morphological properties of the carbon black materials produced in Examples 1 through 6 were studied using Disc Centrifuge Photosedimentometry (DCP) using a Brookhaven DCP, according to ISO 15825:2017 (ISO 15825:2004/Cor.1:2006(E)).

[00204] For the DCP analysis, a one liter, water/ethanol (80%/20% v/v) dispersion fluid was prepared, containing 0.05% of a non-ionic type surfactant such as Triton X-100. The pH of the dispersion fluid was adjusted to a level of about 9-10 with sodium hydroxide (NaOH). A one liter solution of the spin fluid was prepared and is composed of demineralized water containing 0.05% of a non-ionic type surfactant such as Triton X-100.The pH of the spin fluid was adjusted to a level of about 9-10 with sodium hydroxide (NaOH). The carbon black was dispersed in the dispersion fluid at a weight of 25 to 50 mg in 50 ml of dispersion fluid, and then sonicated for 10 minutes at 70% amplitude with a power setting of 750 watts using a probe type sonicator, such as MicrosonXL-2000 (up to 100W) with a 1/4 to 1/8 inch (0.635 to 0.3175 cm) probe.

[00205] An SRB B5 or IRB No.7 reference standard was used to ensure that the instrument was calibrated and working properly. An average aggregate diameter of 113 nm +/- 5 nm should be obtained for the standard. The disc and instrument is first warmed up by injecting 15 ml of water and running for 30 minutes at the chosen speed for analysis to ensure the temperature panel reads a value of 25 +/-3°C. Remove the disc and clean and dry and reinstall. Inject 0.2 ml of ethanol and start centrifuge by pressing the MOTOR button on the instrument. Inject 15 ml of spin fluid to underlay the ethanol and then inject 0.1 ml of Dodecane on top of the gradient layer to reduce evaporative cooling and wait 3 minutes. Click on the "Start" menu in the computer window to prepare the instrument. Inject 0.25 ml of the prepared sample into the spinning disc and immediately press Start for data acquisition. Carcass or soft grades of carbon black with a surface area ranging from 10 to 50 m^2/g were analyzed with a disc speed of 5,000 rpm for 30 minutes; tread or hard grades or carbon black with surface areas ranging from 50 to 125 m^2/g (N400 to N200 series grades) were analyzed at disc speeds of 9,000 rpm for 60 minutes; and carbon blacks with surface areas >125 m^2/g

(N100 series grades and others with surface areas >125m^2/g) were analyzed at 11,000 rpm for 60 minutes.

[00206] Tables 6 through 9 below detail the aggregate size distribution properties (ASD properties) as determined by DCP. The basic terms used to describe these ASDs are the Mean, Mode, and Span. The Mean is defined as (see ISO 15825:2017 (en)) the average diameter calculated from the differential mass distribution curve of the ASD; the Mode is defined as the most frequent diameter of the ASD that represents the peak in the ASD and there can be more than one mode; the Span is an indicator of the breadth of the ASD. This parmeter is calculated as follows: Span = (D_{90}-D_{10})/D_{50}, where the Dx values represent the diameter under which x wt% of the aggregate population resides. For exemple D_{10} is the diameter below which 10 % of the mass of the aggregate population resides. The D_{10}, D_{50} and D_{90} can be derived from the cumulative aggregate size distribution curves.

[00207] These various morphological parameters from the DCP ASD plots are shown graphically in FIG. 4, highlighting the terms D_{10}, D_{50}, D_{90}, Delta D_{50}, Mean, Left Mode, Right Mode and Anti-Mode of the DCP ASD plots.

[00208] The Span of these Shape-Modified Inventive Carbon Blacks (1 through 10) is larger and broader than their Comparative ASTM references and reflects the nature of the broad ASD of these Inventive Carbon Blacks due to the impact of the Shape Modification process.

[00209] FIGS. 5A through 5E illustrate the DCP aggregate size distributions (ASDs) as the differential volume distribution of carbon black aggregates vs. diameter.

[00210] These differences in ASD between Comparative Carbon Black A and Inventive Carbon Black 1 are realized through Shape Modification of the Carbon Black aggregates. For example, in the Inventive Carbon Black 1, the volume fractions of the smaller-sized, lower structure, less complex shaped aggregates, and the larger-sized, higher structure, more complex shaped aggregates in its DCP ASD plot are extended to smaller and larger diameters, respectively versus the Comparative Carbon Black A. FIGS. 6A and 6B show TEM micrographs of the Comparative Carbon Black A, N134 type, and the Shape-Modified Inventive Carbon Black 1. It is evident the the Shape-Modified Inventive Carbon Black 1 has a different aggregate size distribution with the ASD broadened by extending the range of smaller-sized, lower structure, less-complex-shaped aggregates and larger-sized,

higher structure, more-complex-shaped aggregtaes versus the Comparative Carbon Black A. Note that both carbon blacks, Comparative Carbon Black A and Inventive Carbon Black 1, both have similar STSA, COAN, mean particle size and particle size distribution.

[00211] Thus overall as seen in the ASD plots of the Shape-Modified Inventive Carbon Blacks versus the Comparative Carbon Black controls (ASTM type materials), the ASDs are broader, bimodal in character, with a higher proportion of smaller aggregates and larger aggregates, which is a direct result of the shape-modification process in that the smaller aggregates are lower structured, spheroidal and ellipsoidal aggregates, while the largrer aggregates are the higher structured, linear and branched aggregates.

[00212] Table 6. DCP ASD Properties

Parameter	Comparative CB A	Inv. CB 1	Inv. CB 2	Inv. CB 3	Inv. CB 4	Inv. CB 5
Mean, nm	70	103	103	97	106	99
Mode, nm	61	39	111	107	38	100
Span (D_{90}-D_{10})/D_{50}	0.890	1.273	1.217	1.201	1.367	0.977

[00213] Table 7. DCP ASD Properties

Parameter	Comparative CB B	Inv. CB 6	Inv. CB 7	Inv. CB 8	Inv. CB 9	Inv. CB 10
Mean, nm	105	123	122	123	118	123
Mode, nm	102	134	131	123	57	58
Span (D_{90-10})/D_{50}	0.84	1.13	1.05	1.18	1.31	1.21

[00214] Table 8. DCP ASD Properties

Parameter	Comparative CB C	Comparative CB D
Mean, nm	86	97
Mode, nm	55	95
Span (D_{90-10})/D_{50}	1.151	0.770

[00215] The ability to alter the ASD of the shape-modified carbon blacks is revealed from the ASD plots of the Inventive Carbon Blacks versus the ASTM counterparts.

Typically, the shape modified carbon blacks of the present invention can display a bi-modal distribution as a result of the shape modification and the relative peak heights of the Left peak and the Right peak, as shown in FIG. 4, can be controlled via the shape-modification process to optimize the carbon black for a given process or compound. In these Inventive examples, if we take the ratio of the Left peak to the Right peak as an indicator of the range of ASD and shape control of the carbon black aggregates, we can see in Table 9 below that the ratio can range from an ASD with approximately equal Left and Right peak heights, to an ASD with the Left peak significantly lower in peak height, such as for Inv. CB 7 with a 0.67 : 1.00 ratio, to an ASD with the Left peak height significantly higher than the Right peak height, such as for Inv. CB 4 with a ratio of 1.00 : 0.62. Hence shape modification allows significant control and manipulation of the ASD of the carbon black materials, in the ratio of the peaks in a bimodal distribution, and in their degree of separation and resolution, all at a constant mean particle size or surface area or over a very wide range of mean particle sizes and surface areas and OAN as denoted by the ASTM N – series designations, from tread to carcass.

[00216] Table 9: DCP ASD Properties

Material	Left Mode Peak Height	Right Mode Peak Height	Ratio Left Mode : Right Mode
Comparative CB A	100.00	0.00	1.00 : 0.00
Comparative CB B	100.000	0.00	1.00 : 0.00
Comparative CB C	100.00	0.00	1.00 : 0.00
Comparative CB D	100.00	0.00	1.00 : 0.00
Inv CB 1	100.00	93.00	1.00 : 0.93
Inv CB 2	88.29	100.00	0.88 : 1.00
Inv CB 3	96.33	100.00	0.96 : 1.00
Inv CB 4	100.00	61.66	1.00 : 0.62
Inv CB 5	36.00	100.00	0.36 : 1.00
Inv CB 6	86.06	100.00	0.86 : 1.00
Inv CB 7	67.51	100.00	0.67 : 1.00
Inv CB 8	76.21	100.00	0.76 : 1.00

Inv CB 9	100.00	70.32	1.00 : 0.70
Inv CB 10	100.00	97.57	1.00 : 0.98

Analysis of Comparative and Inventive Carbon Blacks by TEM/AIA

[00217] The particle size distributional properties (PSD), the aggregate size distributional properties (ASD), and shape distributional properties of the carbon blacks produced in Examples 1 through 6 were also determined using TEM/AIA, according to ASTM D3849-14A (method A) and as explained above. Particle size distributional properties were determined from cellulose acetate butyrate (CAB) chips to break down the primary structure in accordance with the mean-chord model used for PSD characterization. The PSD and ASD properties were determined from various image analysis properties, as measured on two-dimensional projections of the aggregates, such as area, perimeter, ferret diameters, and various skeletonization parameters (e.g., ends and branches).

[00218] Tables 10 through 12 below detail the particle size distributional properties (PSD), as determined by TEM/AIA. The particle size distributional data for the Comparative Carbon Black A and the Shape-Modified Inventive Carbon Blacks 1 through 6 (N100 series grades) are shown in Table 10. The Mean particle size ranges from 16 to 21 nm, and the Weight Mean particle size ranges from 25 nm to 31 nm. The electron microscope surface areas (EMSAs) of these materials range from 119 m^2/g to 140 m^2/g.

[00219] The particle size distributional data for the Comparative Carbon Black B and the Shape-Modified Inventive Carbon Blacks 6 through 10 (N300 series grades), are shown in Table 11, where the Mean particle size ranges from 31 to 36 nm, and the Weight Mean particle size ranges from 45 to 53 nm. The EMSA values range from 70 m^2/g to 80 m^2/g.

[00220] Additionally, a TEM/AIA term called the Heterogeneity Index (Weight Mean / Mean) or HI, which is used as an indicator of the polydispersity or breadth of the PSD or ASD, shows that the ASTM Comparative Carbon Black A, B, C and D are similar, with PSD HI or HI_{PSD} values of 1.40 to 1.48 and can be described as narrow to normal for typical ASTM materials. On the other hand, the Shape-Modified Inventive Carbon Black materials 1 through 10, whether they are N100 or N300 series materials, also have a relatively normal

HI_{PSD}, being only slightly broader with HI_{PSD} values ranging from 1.40 to1.61, with only one material, Inventive Carbon Black 4, having a broad PSD HI of 1.74.

[00221] These PSD results indicate that the Shape-Modified Inventive Carbon Blacks have a narrow to normal PSD, but a very broad ASD (as evidenced by DCP), which is a distinctive characteristic, essentially decoupling the PSD and ASD, where the PSD can be maintained in a narrow to normal distributional width, while the ASD can be manipulated through aggregate shape modification to be made broad and very broad in aggregate size distributional width.

[00222] FIGS. 7A and 7B show higher magnification TEM micrographs of the purposely Shape-Modified Inventive Carbon Black 1, where the overall aggregate size and structure are shown at lower magnification (as in FIG. 6A), while one of the higher structured, larger aggregates is imaged at relatively high magnification (as in FIG. 7B). It is evident that this aggregate in FIG. 7B is composed of numerous small particles, similar in size to the smaller, lower structure aggregates. Hence the combination of DCP aggregate size data and the TEM/AIA PSD data shows that the ASD and PSD have been decoupled, since the ASDs of the Inventive Carbon Blacks are very broad while the PSDs are normal to narrow.

[00223] Table 10. PSD Properties

Parameter	Comparative CB A	Inv. CB 1	Inv. CB 2	Inv. CB 3	Inv. CB 4	Inv. CB 5
Mean, nm	17.6	16.7	20.5	18.7	19.1	19.6
Weight Mean, nm	25.8	26.5	31.1	32.6	30.7	31.3
Heterogeneity Index (HI_{PSD}, WM/M)	1.48	1.58	1.52	1.74	1.61	1.60
Electron Microscopy Surface Area (EMSA), m^2/g	139	140	119	119	123	120

[00224] Table 11. PSD Properties

Parameter	Comparative CB B	Inv. CB 6	Inv. CB 7	Inv. CB 8	Inv. CB 9	Inv. CB 10
Mean, nm	32.3	36.1	31.0	28.6	32.5	33.3
Weight Mean, nm	45.7	52.7	49.9	43.3	45.4	50.7

Heterogeneity Index (HI_{PSD}, WM/M)	1.42	1.46	1.61	1.50	1.40	1.52
Electron Microscopy Surface Area (EMSA), m^2/g	79.2	69.6	75.4	85.0	79.4	73.0

[00225] Table 12. PSD Properties

Parameter	Comparative CB C	Comparative CB D
Mean, nm	21.6	30.9
Weight Mean, nm	36.9	41.7
Heterogeneity Index (HI_{PSD}, WM/M)	1.7	1.4
Electron Microscopy Surface Area (EMSA), m^2/g	102	85

[00226] Aggregate size distribution properties were also determined using TEM/AIA morphological analysis, according to ASTM D3849-14A (method A), on the Comparative Carbon Blacks and on the Inventive Carbon Blacks. The ASD results are shown in Tables 13 through 15 below.

[00227] Table 13. ASD Properties

Parameter	Comparative CB A	Inv. CB 1	Inv. CB 2	Inv. CB 3	Inv. CB 4	Inv. CB 5
Mean, nm	75	59	59.3	60.3	58.2	71.6
Weight Mean, nm	154	216	257	242	267	271
Heterogeneity Index (HI_{ASD}, WM/M)	2.1	3.7	4.3	4.0	4.6	3.8
Void Volume, V'/V	2.5	2.8	3.31	3.16	2.79	4.04
Divergence Ratio (HI_{ASD}/HI_{PSD})	1.42	2.34	2.86	2.30	2.85	2.37

[00228] Table 14. ASD Properties

Parameter	Comparative CB B	Inv. CB 6	Inv. CB 7	Inv. CB 8	Inv. CB 9	Inv. CB 10
Mean, nm	141	93.6	109	98.8	91.2	91.0

Weight Mean, nm	281	327	332	338	336	312
Heterogeneity Index (HI_{ASD}, WM/M)	2.0	3.5	3.0	3.4	3.7	3.4
Void Volume, V'/V	2.63	2.64	2.80	2.79	2.43	2.5
Divergence Ratio (HI_{ASD}/HI_{PSD})	1.40	2.39	1.89	2.41	2.63	2.24

[00229] Table 15. ASD Properties

Parameter	Comparative CB C	Comparative CB D
Mean, nm	81.5	120
Weight Mean, nm	231	228
Heterogeneity Index (HI_{ASD})	2.8	1.9
Void Volume, V'/V	2.85	2.1
Divergence Ratio (HI_{ASD}/HI_{PSD})	1.67	1.35

[00230] As feedstock hydrocarbon injection nozzles are moved farther apart and the Shape Modification process is instituted, the mean aggregate sizes can drop significantly, while the weight mean aggregate sizes increase. This indicates the production of smaller and larger aggregates, while the particle size distributions are kept relatively narrow to slightly broad. The Shape-Modified Inventive Carbon Black 4 has the smallest Mean and largest Weight Mean, indicating the production of a higher number of smaller, lower structure (i.e., spheroidal and ellipsoidal) aggregates, together with a fewer number, but larger, more complex (i.e., liner and branched) aggregates in agreement with the DCP ASD plots. This shift in the Mean and Weight Mean aggregate sizes from the TEM/AIA data is observed for all Shape-Modified Inventive Carbon Blacks versus the Comparative Carbon Blacks shown in Tables 13 through 15 for both the N100 and N300 series materials.

[00231] As a result of this shift in the ASD (smaller Mean and larger Weight Mean due to the Shape Modification process), the aggregate size becomes broader in distribution as evident by the aggregate size HI_{ASD} values. It can be seen in Tables 13 through 15 that all

Shape-Modified Inventive samples (1 through 10), have higher HI_{ASD} values that range from 3.0 to 4.6 versus the ASTM Comparative Carbon Blacks A, B, C and D all with aggregate HI_{ADS} values of approximately 2.0.

[00232] As described previously, a term called the Divergence Ratio, that is an indicator of the breakpoint from classical coupling of the ASD and PSD for broad distribution carbon blacks, can be used to demonstrate the distinctive ASD and PSD balance of these Shape-Modified Inventive Carbon Blacks. The Divergence Ratio is calculated as the ratio of the ASD HI / PSD HI.

[00233] The Shape-Modified Inventive Carbon Blacks 1 through 10 have Divergence Ratios that are significantly higher than that of other analyzed carbon blacks, with Inventive Carbon Black Divergence ratios ranging from 1.89 to 2.85 and Comparative ASTM Carbon Black Divergence Ratios all approximately 1.4. The higher values for the Divergence ratios for the Inventive Carbon Blacks 1 through 10 indicates they possess a very broad ASD and narrow to normal PSD suggesting that the Inventive Carbon Blacks can provide a very distinctive balance of properties such as low hysteresis with similar durability as compared to ASTM Comparative Carbon Blacks. Additionally, the Divergence Ratio values demonstrate that the broad ASD of the Inventive Carbon Blacks does not necessarily derive from a broad particle size distribution, yet primarily occurs due to shape modification of the individual carbon black aggregates and hence the carbon black aggregate shape distribution.

Shape Distributional Analysis

[00234] As described above, shape classification of carbon black aggregates via TEM/AIA can be performed utilizing discrimination analysis techniques based on a set of shape descriptors including aggregate shapes from numerous grades of carbon blacks. These techniques were utilized to determine the shape distributional properties of the Comparative Carbon Blacks and the Shape-Modified Inventive Carbon Blacks, the results of which are illustrated below in Tables 16 through 18. Shape distributional properties are provided in both a number (or frequency) percent and on a weight percent basis. Breaking down the shape distributional data into number and weight percent bases can allow one to distinguish between the relative volume or weight contribution of each shape category, which can be useful when considering its impact on the ASD and the distinctiveness of the shape distribution and the subsequent properties of polymeric composites.

[00235] Table 16. Aggregate Shape Distributional Properties

Shape Type		Comp CB A	Inv. CB 1	Inv CB 2	Inv CB 3	Inv CB 4	Inv CB 5
Number %	1 (Spheroidal)	5.9	20.8	16.3	15	18.2	14.3
	2 (Ellipsoidal)	15.0	31.1	24.4	25.7	29.9	21.4
	3 (Linear)	43.1	33.4	39.1	38.6	34.7	38.9
	4 (Branched)	36.0	14.7	20.2	20.7	17.3	25.5
Weight %	1 (Spheroidal)	0.6	5.2	1.6	1.5	2.1	0.6
	2 (Ellipsoidal)	7.6	18.1	8.2	9.9	15	4.9
	3 (Linear)	29.4	23.7	19.3	18.2	16.9	20.7
	4 (Branched)	62.4	53.0	70.9	70.5	66.1	73.7
	Shape Specific HI (SSHI) Type 4	1.73	3.60	3.51	3.41	3.82	2.89

[00236] As detailed in Tables 16 through 18, the number percent of Type 1 (spheroidal) and Type 2 (ellipsoidal) aggregates increases in the Shape-Modified Inventive Carbon Blacks, as compared to their Comparative Carbon Black references; whereas the number percent of Type 3 (linear) and Type 4 (branched) aggregates decreases compared to their Comparative Carbon Blacks.

[00237] As an example, in Table 16, Comparative Carbon Black A and the Shape-Modifed Inventive Carbon Black 1 are compared, and it can be seen that the number percent of Type 1 and Type 2 aggregates increases from 20.9% to 51.9% in going from Comparative CB A to Shape-Modified Carbon Black 1, while the number percent of Type 3 and Type 4 aggregates decreases from 79.1% to 48.1% in going from Comparative CB A to the Shape-Modified Carbon Black 1. When the shape classification categories are compared on a weight percent basis, the Type 1 and Type 2 aggregates increase from 8.2% to 23.3% in going from Comparative CB A to Shape-Modifed Carbon Black 1, while the weight percent of Type 3 and 4 aggregates decreases from 91.8% to 76.7% in going from the Comparative CB 1 to Shape-Modified Carbon Black 1. On a weight percent basis, this trend of decreasing amount for the shape modified carbon black Type 3 and 4 aggregates, is not always observed as for the Type 3 and 4 aggregate amounts on a number percent basis, and in many cases, the Type 3 and 4 weight percent values for these shape categories may be similar to higher than as compared to the Comparative Carbon Blacks. This surprising finding reveals one of the most distinctive and unique changes in the shape distribution when examining the weight versus number percent for the Type 4 appgregates. In this instance, the weight percent of Type 4

aggregates remains similar to or larger than the Comparative examples, while the Number percent of Type 4 aggregates for the Shape-Modified Carbon Blacks is much smaller than the Comparative examples, meaning that as a result of their shape modification, these Type 4 aggregates for the Inventive Carbon Blacks are significantly larger than the Comparative Carbon Blacks' Type 4 aggregates. Hence the ratio of Type 4 weight percent to number percent has been identified as a key indicator of shape modification and is described as the Shape-Modification Heterogeneity Index or SSHI. The SSHI may vary in magnitude between the various shape modied carbon blacks or Inventive Carbon Blacks depending upon the necessary level of shape modification required to meet overall structure levels or OAN and COAN for a given rubber compound as may be used in tires or rubber goods.

[00238] Tables 17 through 18 below show additional Shape Classification data for the Comparative Carbon Blacks A, B, C and D and the remainder of the Inventive Carbon Blacks 2 through 10. The same trends as described above for Comparative Carbon Black A and the Inventive Carbon Black 1 are seen for the Comparative Carbon Blacks B, C and D and the other Shape-Modified Inventive Carbon Blacks 2 to 10. It is apparent that the resulting SSHI of type 4 aggregagtes is >3 for all Inventive Carbon Blacks with Shape Modification. This data indicates this trend is distinctive and a key differentitator that predicts the achievement of a shape-modified aggregate size and shape distribution.

[00239] Table 17: Aggregate Shape Distributional Properties

Shape Type		**Comparative CB B**	**Inv CB 6**	**Inv CB 7**	**Inv. CB 8**	**Inv CB 9**	**Inv CB10**
Number %	**1 Spheroidal**	5.8	26.7	17.6	26.0	23.5	21.7
	2 Ellipsoidal	19.2	28.9	27.1	31.3	34.2	29.7
	3 Linear	40.1	30.6	34.6	29.2	31.4	35.2
	4 Branched	34.9	13.9	20.6	13.5	10.9	14.1
Weight %	**1 Spheroidal**	0.5	2.9	1.6	2.9	3.8	2.6
	2 Ellipsoidal	8	14	10.8	13.5	19.3	16.2
	3 Linear	33.2	24.9	23.9	22.8	21.6	24.7
	4 Branched	58.3	58.2	63.7	60.8	55.3	56.4
	Shape Specific HI (SSHI) Type 4	1.67	4.19	3.09	4.50	5.07	4.0

[00240] Table 18: Aggregate Shape Distributional Properties

Shape Type		Comparative CB C	Comparative CB D
Number %	**1 Spheroidal**	5.9	9.7
	2 Ellipsoidal	16.3	24.5
	3 Linear	41.0	40.7
	4 Branched	36.8	25.1
Weight %	**1 Spheroidal**	0.5	1.4
	2 Ellipsoidal	7.1	14.9
	3 Linear	21.2	32.6
	4 Branched	71.3	51.1
	Shape Specific HI (SSHI) Type 4	1.94	2.03

Example 7: Testing comparative Carbon Blacks and Inventive Carbon Blacks in various rubber compositions

[00241] This example aims to demonstrate the improvement in the compromise of properties conductivity, rigidity and rolling resistance (hyteresis) obtained for various rubber compositions according to the invention used at different positions in the tire, such as tread tire rubber composition, carcass ply rubber composition and bead filler rubber composition compared to rubber compositions comprising carbon blacks of the prior art as described below. The rubber compositions of the present invention comprise the Inventive Carbon Blacks as described above.

Dynamic properties

[00242] The dynamic properties G* and $\tan(\delta)_{max}$ are measured on a viscosity analyser (Metravib V A4000) according to Standard ASTM D 5992-96. The response of a sample of vulcanized composition (cylindrical test specimen with a thickness of 4 mm and a cross section of 400 mm^2), subjected to a simple alternating sinusoidal shear stress, at a frequency of 10 Hz, under determined temperature conditions according to Standard ASTM D 1349-14(2019), is recorded. A peak-to-peak strain amplitude sweep is carried out from 0.1% to 100% (outward cycle) and then from 100% to 0.1% (return cycle). For the return cycle, the maximum value of tan(δ) observed (tan(δ)max) is indicated. The tan(δ)max values given below are measured at 60°C. The rigidity G* is measured at the same temperature at 50% strain on the return cycle.

Surface x Rigidity Index :

[00243] Compounds with higher total interfacial area (ie the total amount of surface area exposed by the carbon black to the polymer, which can be approximated by the product of carbon black surface area in m^2/g and filler loading in phr) and rigidity are beneficial to tire tread abrasion performance. When trying to improve the balance between tire wear performance and rolling resistance, it is thus desirable to maintain a high surface x rigidity product while reducing the coumpound hysteresis. The surface x rigidity index is calculated as the product of STSA measured according to ASTM D6556-2017 (carbon black surface area in m^2/g), filler loading in the compound (in phr), and compound rigidity: surface x rigidity index = STSA x CB loading x G*. G* is measured as described above.

Electrical conductivity

[00244] The electrical volume resistivity ρ (ohm.cm), expressed as $\log_{10}$ ρ, is measured at 23°C and 50% relative humidity as described in the ASTM D4496-2021 standard. For each rubber composition, 6 samples are prepared and measured after 30s equilibration time, and an average value of log10 ρ_{av} is calculated. Electrical conductivity values are defined as the inverse of $\log_{10}$ ρ_{av} values. Thus, a sample with an electrical conductivity value of 110 means it is 10% more conductive on a $\log_{10}$ basis than the reference composition.

Preparation of the rubber compositions

[00245] The following rubber compositions are carried out in the following way: the diene elastomer, the reinforcing filler, and then, after kneading for one to two minutes, the various other ingredients, with the exception of the vulcanization system, are introduced into an internal mixer which is 70% filled and which has an initial vessel temperature of approximately 90°C. Thermomechanical working is then carried out (non-productive phase) in one step (total duration of the kneading equal to approximately 5 min), until a maximum "dropping" temperature of approximately 165°C is reached. The mixture thus obtained is recovered and cooled and then the vulcanization system (sulfur and sulfenamide accelerator) is added on an external mixer (homofinisher) at 70°C, everything being mixed (productive phase) for approximately 5 to 6 min.

[00246] The compositions thus obtained are subsequently calendered in the form of slabs (thickness of 2 to 3 mm) of rubber for the measurement of their physical or mechanical properties.

Example 8a: Tire Tread Rubber Composition

[00247] This test aims to demonstrate the improvement in the compromise of properties obtained for tire tread rubber compositions in accordance with the invention, compared to tire tread rubber compositions comprising carbon blacks of the prior art.

[00248] For this purpose, four compositions are prepared in accordance with the above-described process, which differ from one another essentially by the following technical characteristics:

- T1 is a comparative rubber composition based on natural rubber (100 phr) and comprising a carbon black having an STSA specific surface area of approximately 130 m^2/g,
- T2 is a comparative rubber, identical to the composition T1 apart from the nature of the carbon black: the carbon black of T2 has the same COAN as the carbon black of T1 but has a different STSA specific surface area (STSA of approximately 80 m^2/g,
- T3 is a comparative rubber, identical to the composition T1 apart from the nature of the carbon black: the carbon black of T3 has a different COAN and STSA than the carbon black of T1,
- C1 is a composition in accordance with the invention, identical to the composition T1 except for the nature of the carbon black, which is the Inventive Carbon Black 1 described above.

[00249] The following Tables 19 and 20 give respectively the formulation of the different compositions (Table 19, contents of the different constituents, expressed in phr or

parts by weight per hundred parts of elastomer) and the dynamic properties measured after curing at 130°C for 60 minutes for compositions T1 to T3 and C1 (Table 20).

[00250] Table 19: Formulation of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T1	T2	T3	C1
Dienic elastomer (1)	100	100	100	100
Comparative carbon black A (2)	58	-	-	-
Comparative Carbon black B (3)	-	58	-	-
Comparative Carbon black C (4)	-	-	58	-
Inventive Carbon black 1	-	-	-	58
Antioxidant (6)	2	2	2	2
Paraffin	1	1	1	1
ZnO	3	3	3	3
Stearic acid	2	2	2	2
Sulfur	1	1	1	1
vulcanization accelerator (7)	1	1	1	1

(1) Dienic elastomer: natural rubber,

(2) Comparative carbon A of example 1,

(3) Comparative carbon B of example 4,

(4) Comparative carbon C of exemple 5,

(5) Inventive Carbon Black: Shape modified carbon black 1 (Inv CB 1) according to the invention obtained by the process described in paragraph of example 2,

(6) Antioxidant: N-(1,3-dimethylbutyl)-N-phenyl-para-phenylenediamine sold by Flexsys under the reference Santoflex 6-PPD,

(7) Accelerator: N-cyclohexyl-2-benzothiazolesulfenamide sold by Flexsys under the reference Santocure CBS,

[00251] Table 20: Properties of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T1	T2	T3	C1
$tan(\delta)_{max}$	100	89	90	81
Surface x Rigidity index	100	72	100	108
Electrical conductivity	100	92	108	108

[00252] Considering Table 20, it is observed that, in regard with the comparative rubber composition T1 which is taken as a reference, comparative compositions T2 has improved hysteresis properties but a lower surface*rigidity index and lower electrical conductivity. The control compoisition T3 compared to the control composition T1 has improved hysteresis properties and electrical conductivity but no improved surface * rigidity index.

[00253] On the contrary, for the composition of the invention C1, an improvement in the hysteresis properties is observed. Additionally, the composition of the invention C1 provides unexpected results related to Surface x Rigidity index and electrical conductivity. Indeed, it is the only composition which presents both an improvement in electrical conductivity and a better surface * rigidity index compared to T2 and T3.

Example 8b: Tire Tread Rubber Composition

[00254] This test aims to demonstrate the improvement in the compromise of properties obtained for tire tread rubber compositions in accordance with the invention, compared to tire tread rubber compositions comprising carbon blacks of the prior art.

[00255] For this purpose, four compositions are prepared in accordance with the above-described process, which differ from one another essentially by the following technical characteristics:

- T4 is a comparative rubber composition based on natural rubber (100 phr) and comprising a carbon black having an STSA specific surface area of approximately 130 m^2/g,
- T5 is a comparative rubber, identical to the composition T1 apart from the nature of the carbon black: the carbon black of T2 has the same COAN as the carbon black of T1, but has a different STSA specific surface area (STSA of approximately 80 m^2/g),
- T6 is a comparative rubber, identical to the composition T1 apart from the nature of the carbon black: the carbon black of T3 and T6 is the same and has a different COAN and STSA than the carbon black of T1,
- C2 is a composition in accordance with the invention, identical to the composition T1 except for the nature of the carbon black, which is the Inventive Carbon Black 1 described above.

[00256] The following Tables 21 and 22give respectively, the formulation of the different compositions (Table 21, contents of the different constituents, expressed in phr or parts by weight per hundred parts of elastomer) and the dynamic properties measured after curing at 130°C for 60 minutes for compositions T4 to T6 and C2 (Table 22).

[00257] Table 21: Formulation of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T4	T5	T6	C2
Dienic elastomer (1)	60	60	60	60
Dienic elastomer (8)	20	20	20	20
Dienic elastomer (9)	20	20	20	20
Comparative Carbon black A (2)	58	-	-	-
Comparative Carbon black B (3)	-	58	-	-
Comparative Carbon black C (4)	-	-	58	-
Inventive Carbon black CB 1	-	-	-	58
Antioxidant (6)	2	2	2	2
Paraffin	1	1	1	1
ZnO	3	3	3	3
Stearic acid	2	2	2	2
Sulfur	1	1	1	1
vulcanization accelerator (7)	1	1	1	1

Compounds (1) to (7) are the same as the one for Table 19.

(8) Dienic elastomer: Buna® Nd 24 EZ, polybutadiene rubber having a cis 1-4 content of more than 96% and a Tg =-105°C measured according to the standard ASTM D3418 (2008).

(9) Dienic elastomer: styrene butadiene copolymer having 15,5% by weight of styrene monomer relative to the toal weight of the copolymer, for the butadiene part; 24 % by weight of 1,2 unit and 30% by weight of 1,4-cis unit, Tg=-65°C measured according to the standard ASTM D3418 (2008)

[00258] Table 22: Properties of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T4	T5	T6	C2
$tan(\delta)_{max}$	100	89	90	85
Surface x Rigidity index	100	87	103	104
Electrical conductivity	100	64	94	100

[00259] Again, considering Table 20, it is observed that, in regard with the comparative rubber composition T4, which is taken as a reference, comparative compositions T5 and T6 have improved hysteresis properties lower electrical conductivity.

[00260] On the contrary, for the composition of the invention C2, an improvement in the hysteresis properties is observed. Additionally, the composition of the invention C2 provides unexpected results related to Surface x Rigidity index and electrical conductivity. Indeed, it is the only composition, compared to T5 and T6, which presents the best Surface x Rigidity index without decreasing electrical conductivity properties.

Example 8c: Tire Carcass-Ply Rubber Compositions

[00261] This test aims to demonstrate the improvement in the compromise of properties obtained for carcass-ply rubber compositions in accordance with the invention, compared to carcass-ply rubber compositions comprising carbon blacks of the prior art It is critical that the rubber composition for a carcass ply has a good compromise of properties such as stiffness (rigidity), hysteresis and electrical conductivity. The wear property is not a main property which is sought for a carcass-ply rubber composition since it is not in contact with the ground when the tire is running, unlike a composition for a tread.

[00262] The following Tables 23 and 24, give respectively, the formulation of the different compositions (Table 23, contents of the different constituents, expressed in phr or parts by weight per hundred parts of elastomer) and the dynamic properties measured after curing at 130°C for 60 minutes for compositions T7 and C3 and C4 (Table 24).

[00263] Table 23: Formulation of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T7	C3	C4
Dienic elastomer (1)	100	100	100
Comparative Carbon black A (2)	45	-	-
Inventive Carbon Black 8 (12)	-	45	-
Inventive Carbon Black 6 (13)	-	-	45
Antioxidant (6)	2	2	2
ZnO	9	9	9
Stearic acid	1	1	1
Cobalt salt (10)	1	1	1
Sulfur	6	6	6

vulcanization accelerator (11)	1	1	1

Compounds (1), (2) and (10) are the same as the one disclosed for Table 19.

(10) cobalt salt : cobalt naphtenate No product 60830 from Sigma-Aldrich

(11) DCBS N,N'-dicyclohexyl-2-benzothiazol-sulfenamide sold under « Santocure DCBS » by Flexsys

(12) Inventive Carbon black: shape modified carbon black 8 (Inv CB8) according to the invention obtained by the process described in paragraph of exemple 8.

(13) Inventive Carbon black: shape modified carbon black 6 (Inv CB6) according to the invention obtained by the process described in paragraph of exemple 6

[00264] Table 24: Properties of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T7	C3	C4
$tan(\delta)_{max}$	100	81	85
G*	100	93	99
Electrical conductivity	100	117	132

[00265] Considering Table 24, it is observed surprisingly that, in regard with the control rubber composition T7, the compositions of the present invention C3 and C4 have a decreased hysteresis with a little or no decrease in rigidity. An improvement in the hysteresis-rigidity performance compromise is observed for the composition of the invention C3 and C4, which is not observed for the control composition T7.

[00266] Additionally, the compositions of the present invention also have the best electrical conductivity properties compared to T7.

Example 8d: Tire Carcass-Ply Rubber Compositions

[00267] This test aims to demonstrate the improvement in the compromise of properties obtained for rubber compositions for carcass-ply tyre in accordance with the

invention, compared to carcass-ply rubber compositions comprising carbon blacks of the prior art.

[00268] The following Tables 25 and 26 give respectively the formulation of the different compositions (Table 25, contents of the different constituents, expressed in phr or parts by weight per hundred parts of elastomer) and the dynamic properties measured after curing at 130°C for 60 minutes for compositions T8 and C5 (Table 26).

[00269] Table 25 : Formulation of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T8	C5
Dienic elastomer (1)	100	100
Comparative black carbon D	45	-
Inventive Carbon Black 10 (14)	-	45
Antioxidant (6)	2	2
ZnO	9	9
Stearic acid	1	1
Cobalt salts (10)	1	1
Sulfur	6	6
DCBS (11)	1	1

Compounds (1) and (6) are the same as the one disclosed in Table 19. Compounds (10) and (11) are the same as the one disclosed in Table 23.

(14) Inventive Carbon black: shape modified carbon black 10 (Inv CB10) according to the invention obtained by the process described in paragraph of exemple 6

[00270] Table 26: Properties of polymeric compositions comprising Comparative and Inventive Carbon Blacks

	T8	C5
$\tan(\delta)_{max}$	100	89
G*	100	101
Electrical conductivity	100	112

[00271] Considering Table 26, it is observed surprisingly that, in regard with the control rubber composition T8, the compositions of the present invention C5 have a decreased hysteresis with a little or no decrease in rigidity. An improvement in the hysteresis-rigidity performance compromise is observed for the composition of the invention C5, which is not observed for the control composition T8.

[00272] Additionally, the compositions of the present invention have also the best electrical conductivity properties compared to T8.

Example 8e: Tire Bead-Rubber Composition

[00273] This test aims to demonstrate the improvement in the compromise of properties obtained for bead-rubber compositions in accordance with the invention, compared to bead-rubber compositions comprising carbon blacks of the prior art.

[00274] The following Tables 27 and 28 give respectively the formulation of the different compositions (Table 27, contents of the different constituents, expressed in phr or parts by weight per hundred parts of elastomer) and the dynamic properties measured after curing at 130°C for 60 minutes for compositions T9 and C7 (Table 27).

[00275] Table 27

	T9	C7
Dienic elastomer (1)	100	100
Comparative Carbon black B (2)	50	-
Inventive Carbon Black 8 (12)	-	50
Antioxidant (6)	1	1
ZnO	4	4
Stearic acid	1	1
Sulfur	3	3
vulcanization accelerator (7)	1	1

[00276] Compounds (1), (6), (7) are the same as the one disclosed for Table 19. Compound (12) is the same as the one disclosed in table 23.

[00277] Table 28

	T9	C7
$tan(\delta)_{max}$	100	82
G*	100	97
Electrical conductivity	100	99

[00278] Considering Table 28, it is observed surprisingly that, in regard with the control rubber composition T9, the compositions of the present invention C7 have a decreased hysteresis without modification of rigidity properties. An improvement in the hysteresis-rigidity performance compromise is observed for the bead composition of the invention C7 without deteriorating its electrical conductivity properties.

[00279] The present invention includes the following aspects/embodiements/features in any order and//or in any combinaison:

1. A carbon black having a shape specific heterogeneity index for branched shape aggregates of at least 2.1, preferably of at least 2.5.

2. The carbon black of any preceeding aspect/embodiment/feature, wherein the shape specific heterogeneity index for the branched shape aggregates is of less than 6.0; preferably of less than 5.5.

3. The carbon black of any preceeding aspects/embodiments/features, wherein the shape specific heterogeneity index for the branched shape aggregates ranging from 2.6 to 5.3; preferably from 2.8 to 5.1; even more preferably from 3.4 to 4.6.

4. The carbon black of any preceeding aspects/embodiments/features, wherein the carbon black has a Divergence Ratio of at least 1.5; preferably of at least 1.6.

5. The carbon black of any preceeding aspects/embodiments/features, wherein the Divergence Ratio is less than 4.0, preferably less than 3.5.

6. The carbon black of any preceeding aspects/embodiments/features, wherein the Divergence Ratio is ranging from 1.7 to 3.0, preferably from 1.8 to 2.9, or more preferably 2.2 to 2.6.

7. The carbon black of any preceeding aspects/embodiments/features, wherein the aggregate size heterogeneity index HI_{ASD} of the carbon black is greater or equal to 2.2.

8. The carbon black of any preceeding aspects/embodiments/features, wherein the aggregate size heterogeneity index HI_{ASD} ranges from 2.2 to 5.5, preferably from 2.4 to 4.8.

9. The carbon black of any preceeding aspects/embodiments/features, wherein the aggregate size heterogeneity index HI_{ASD} ranges from 2.9 to 5.5 or from 2.9 to 4.8.

10. The carbon black of any preceeding aspects/embodiments/features, wherein the particle size heterogeneity index HI_{PSD} of the carbon black is greater or equal to 1.2.

11. The carbon black of any preceeding aspects/embodiments/features, wherein the particle size heterogeneity index HI_{PSD} ranges from 1.3 to 2.0; preferably from 1.3 to 1.9.

12. The carbon black of any preceeding aspects/embodiments/features, wherein the particle size heterogeneity index HI_{PSD} ranges from 1.3 to 1.7.

13. The carbon black of any preceeding aspects/embodiments/features, wherein the carbon black has a statistical thickness surface area, STSA, measured according to ASTM D6556-2017 ranging from 30 m^2/g to 200 m^2/g; preferably from 30 m^2/g to 150 m^2/g; more preferably from 60 m^2/g to 145 m^2/g.

14. The carbon black of any preceeding aspects/embodiments/features, wherein the carbon black has a statistical thickness surface area, STSA, measured according to ASTM D6556-2017 ranging from 90 m^2/g to 145 m^2/g; preferably ranging from 100 m^2/g to 130 m^2/g.

15. The carbon black of any preceeding aspects/embodiments/features 1 to 13, wherein the carbon black has a statistical thickness surface area, STSA, measured according to

ASTM D6556-2017 ranging from 60 m^2/g to 110 m^2/g; preferably ranging from 65 m^2/g to 95 m^2/g.

16. The carbon black of any preceeding aspects/embodiments/features, wherein, the carbon black has a compressed oil absorption number, COAN, measured according to ASTM D3493-2018, ranging from 60 to 150 ml/100g, preferably from 60 to 140 ml/100g, more preferably from 60 to 130 ml/100g, or even more preferably from 65 to 125 ml/100g.

17. The carbon black of any preceeding aspects/embodiments/features, wherein the carbon black has a compressed oil absorption number, COAN, measured according to ASTM D3493-2018, ranging 80 to 130 ml/100g, preferably ranging from 85 to 120 ml/100g.

18. The carbon black of any preceeding aspects/embodiments/features 1 to 16, wherein the carbon black has a compressed oil absorption number, COAN, measured according to ASTM D3493-2018, ranging 55 to 120 ml/100g, preferably ranging from 60 to 120 ml/100g.

19. The carbon black of any preceeding aspects/embodiments/features, wherein the carbon black has a nitrogen surface area, NSA, measured according to ASTM D6556-2017, ranging from 40 to 160 m^2/g, preferably from 50 to 150 m^2/g.

20. The carbon black of any preceeding aspects/embodiments/features, wherein the carbon black may have a nitrogen surface area, NSA, measured according to ASTM D6556-17, ranging from 100 to 150 m^2/g, preferably from 115 to 140 m^2/g.

21. The carbon black of any preceeding aspects/embodiments/features 1-19, wherein the carbon black may have a nitrogen surface area, NSA, measured according to ASTM D6556-17, ranging from 60 to 100 m^2/g, preferably from 70 to 95 m^2/g.

22. A rubber composition comprising at least one diene elastomer, a reinforcing filler and a crosslinking system, characterized in that the reinforcing filler comprises a carbon black according to any one of the preceeding aspects/embodiments/features 1 to 21.

23. The rubber composition of any preceeding aspect/embodiment/feature 22, wherein the carbon black of the rubber composition represents more than 60% by weight of the total weight of reinforcing filler into the rubber composition.

24. The rubber composition of any preceeding aspects/embodiments/features 22-23, wherein the carbon black of the rubber composition represents more than 90% by weight of the total weight of reinforcing filler.

25. The rubber composition of any preceeding aspects/embodiments/features 22-24, wherein the carbon black of the rubber composition represents the only reinforcing filler of the composition.

26. The rubber composition of any preceeding aspects/embodiments/features 22-25, wherein the rubber composition further comprises an inorganic reinforcing filler.

27. The rubber composition of any preceeding aspects/embodiments/features 22-26, wherein the inorganic reinforcing filler is a silica.

28. The rubber composition of any preceeding aspects/embodiments/features 22-27, wherein the diene elastomer is selected from the group consisting of polybutadienes, synthetic polyisoprenes, natural rubber, butadiene copolymers, isoprene copolymers and the mixtures of these elastomers.

29. The rubber composition of any preceeding aspects/embodiments/features 22-28, wherein the total content of reinforcing filler ranges from 10 to 110 phr, preferably from 20 to 100 phr.

30. The rubber composition of any preceeding aspects/embodiments/features 22-29, wherein the rubber composition is a tire rubber composition.

31. A tire tread comprising a rubber composition of any preceeding aspect/embodiments/features 22-29.

32. A ply carcass comprising a rubber composition of any preceeding aspects/embodiments/features 22-29.

33. A bead filler comprising a rubber composition of any preceeding aspects/embodiments/features 22-29.

34. Tyre comprising a carbon black according to any preceeding aspects/embodiements/features 1 to 21 or at least one rubber composition according to any preceeding aspects/embodiments/features 22-29.

35. A method for manufacturing a carbon black, the method comprising providing a carbon black reactor and injecting a material into the carbon black reactor in a non-uniform manner, wherein the material comprises at least one of a hydrocarbon oil or a structure control additive.

36. The method of any preceeding aspects/embodiments/features 35, wherein the material comprises a hydrocarbon oil.

37. The method of any preceeding aspects/embodiments/features 36, wherein the material comprises a structure control additive.

38. The method of any preceeding aspects/embodiments/features 37, wherein the material comprises a potassium containing compound.

39. The method of any any preceeding aspects/embodiments/features 35-38, wherein injecting the material in a non-uniform manner comprises injecting a first portion of the material into a first axial plane of the carbon black reactor and injecting a second portion of the material into a second axial plane of the carbon black reactor, wherein a rate of injection into the first axial plane and a rate of injection into the second axial plane are not equal.

40. The method of any preceeding aspects/embodiments/features 35-38, wherein injecting the material in a non-uniform manner comprises injecting a first portion of the material into a first axial plane of the carbon black reactor and injecting a second portion of the material into a second axial plane of the carbon black reactor, wherein a concentration of the first portion and a concentration of the second portion are not equal.

41. The method of any preceeding aspects/embodiments/features 39 or 40, wherein the first axial plane and the second axial plane are located in a choke section of the carbon black reactor, a combustion section of the carbon black reactor, or a combination

thereof.

42. The method of any preceeding aspects/embodiments/features 39, wherein a third portion of the material is injected into a third axial plane of the carbon black reactor.

43. The method of any preceeding aspects/embodiments/features 42, wherein a fourth portion of the material is injected into a fourth axial plane of the carbon black reactor.

44. The method of any preceeding aspects/embodiments/features 40, wherein a third portion of the material is injected into a third axial plane of the carbon black reactor.

45. The method of any preceeding aspects/embodiments/features 44, wherein a fourth portion of the material is injected into a fourth axial plane of the carbon black reactor.

46. The method of any preceeding aspects/embodiments/features 35, wherein a first portion of the hydrocarbon oil material is injected into a first axial plane of the carbon black reactor, a second portion of the hydrocarbon oil material is injected into a second axial plane of the carbon black reactor, a first portion of the structure control additive is injected into a third axial plane of the carbon black reactor, and a second portion of the structure control additive is injected into a fourth axial plane of the carbon black reactor, wherein each of the hydrocarbon oil and the structure control additive is injected in a non-uniform manner.

47. The method of any preceeding aspects/embodiments/features 35, wherein the carbon black reactor has a single combustion section.

48. The method of any preceeding aspects/embodiments/features 35, wherein the carbon black reactor comprises two or more combustion sections.

49. A carbon black reactor comprising a plurality of hydrocarbon injection ports disposed in two or more axial planes of a choke section of the carbon black reactor, a combustion section of the carbon black reactor, or a combination thereof.

50. A carbon black reactor comprising a plurality of structure control additive injection ports disposed in two or more axial planes of a choke section of the carbon black reactor, a combustion section of a carbon black reactor, or a combination thereof.

CLAIMS

What is claimed is:

1. A carbon black having a shape specific heterogeneity index for Type 4 aggregates of at least 2.1.

2. A carbon black having a shape specific heterogeneity index for Type 4 (branched) aggregates of from about 2.1 to about 6.0.

3. The carbon black of claim 1 or claim 2, having a Divergence Ratio greater than 1.6.

4. The carbon black of claim 1 or claim 2, having a Divergence Ratio greater than about 1.8.

5. The carbon black of claim 1 or claim 2, having a Divergence Ratio greater than about 1.9.

6. The carbon black of claim 1 or claim 2, having a Divergence Ratio greater than about 2.

7. The carbon black of claim 1 or claim 2, having a particle size heterogeneity index HI_{PDS} less than about 1.7.

8. The carbon black of claim 1 or claim 2, having a particle size heterogeneity index HI_{PDS} less than about 1.6.

9. The carbon black of claim 1 or claim 2, having a particle size heterogeneity index HI_{PDS} less than about 1.5.

10. The carbon black of claim 1 or claim 2, having an aggregate size heterogeneity index HI_{ADS} greater than about 2.5.

11. The carbon black of claim 1 or claim 2, having an aggregate size heterogeneity index HI_{ADS} greater than about 2.8.

12. The carbon black of claim 1 or claim 2, having an aggregate size heterogeneity index HI_{ADS} greater than about 2.9.

13. The carbon black of claim 1 or claim 2, having an aggregate size heterogeneity index HI_{ADS} greater than about 3.

14. The carbon black of claim 1 or claim 2, having an aggregate size heterogeneity index HI_{ADS} greater than about 3.5.

15. The carbon black of claim 1 or claim 2, wherein the carbon black has one or more colloidal properties of an ASTM N100 series carbon black.

16. The carbon black of claim 1 or claim 2, wherein the carbon black has one or more colloidal properties of an ASTM N300 series carbon black.

17. The carbonblack of claim 1 or claim 2, having an oil absorption number less than about 200.

18. The carbon black of claim 1 or claim 2, having an oil absorption number less than about 170.

19. The carbon black of claim 1 or claim 2, having an oil absorption number less than about 140.

20. The carbon black of claim 1 or claim 2, wherein the carbon black is a furnace carbon black.

21. The carbon black of claim 1 or claim 2, wherein the carbon black is a tread grade carbon black.

22. The carbon black of claim 1 or claim 2, wherein the carbon black is a carcass grade carbon black.

23. The carbon black of claim 1 or claim 2, having an oil absorption number of less than about 110.

24. The carbon black of claim 1 or claim 2, having an oil absorption number of less than about 90.

25. The carbon black of claim 1 or claim 2, having an oil absorption number of at least about 80.

26. The carbon black of claim 1 or claim 2, having an oil absorption number of from about 80 to about 200.

27. A carbon black having a Divergence Ratio greater than 1.6, and one or more of the following: a particle size heterogeneity index less than about 1.7, an aggregate size heterogeneity index greater than about 2.0, an oil absorption number less than about 200; and an STSA greater than about 120.

28. The carbon black of claim 27, having an oil absorption number less than about 125.

29. The carbon black of claim 27, having a Divergence Ratio greater than about 1.7 and an aggregate size heterogeneity index greater than about 2.8.

30. A polymeric composition comprising the carbon black of any preceding claim.

31. The polymeric composition of claim 30, comprising one or more of NR, BR, SBR, EPDM, and butyl rubber.

32. The rubber composition of claim 30, wherein the rubber composition comprises from about 35 phr to about 65 phr of the carbon black.

33. A tire comprising a polymeric composition comprising the carbon black of any preceding claim.

34. A method for manufacturing a carbon black, the method comprising providing a carbon black reactor and injecting a material into the carbon black reactor in a non-uniform manner, wherein the material comprises at least one of a hydrocarbon oil or a structure control additive.

35. The method of claim 34, wherein the material comprises a hydrocarbon oil.

36. The method of claim 34, wherein the material comprises a structure control additive.

37. The method of claim 34, wherein the material comprises a potassium containing compound.

38. The method of any one of claims 34-37, wherein injecting the material in a non-uniform manner comprises injecting a first portion of the material into a first axial plane of the carbon black reactor and injecting a second portion of the material into a second axial plane of the carbon black reactor, wherein a rate of injection into the first axial plane and a rate of injection into the second axial plane are not equal.

39. The method of any one of claims 34-37, wherein injecting the material in a non-uniform manner comprises injecting a first portion of the material into a first axial plane of the carbon black reactor and injecting a second portion of the material into a second axial plane of the carbon black reactor, wherein a concentration of the first portion and a concentration of the second portion are not equal.

40. The method of claim 38, wherein the first axial plane and the second axial plane are located in a choke section of the carbon black reactor, a combustion section of the carbon black reactor, or a combination thereof.

41. The method of claim 39, wherein the first axial plane and the second axial plane are located in a choke section of the carbon black reactor, a combustion section of the carbon black reactor, or a combination thereof.

42. The method of claim 38, wherein a third portion of the material is injected into a third axial plane of the carbon black reactor.

43. The method of claim 42, wherein a fourth portion of the material is injected into a fourth axial plane of the carbon black reactor.

44. The method of claim 39, wherein a third portion of the material is injected into a third axial plane of the carbon black reactor.

45. The method of claim 44, wherein a fourth portion of the material is injected into a fourth axial plane of the carbon black reactor.

46. The method of claim 34, wherein a first portion of the hydrocarbon oil material is injected into a first axial plane of the carbon black reactor, a second portion of the hydrocarbon oil material is injected into a second axial plane of the carbon black reactor, a first portion of the structure control additive is injected into a third axial plane of the carbon black reactor, and a second portion of the structure control additive is injected into a fourth axial plane of the carbon black reactor, wherein

each of the hydrocarbon oil and the structure control additive is injected in a non-uniform manner.

47. The method of claim 34, wherein the carbon black reactor has a single combustion section.

48. The method of claim 34, wherein the carbon black reactor comprises two or more combustion sections.

49. A carbon black reactor comprising a plurality of hydrocarbon injection ports disposed in two or more axial planes of a choke section of the carbon black reactor, a combustion section of the carbon black reactor, or a combination thereof.

50. A carbon black reactor comprising a plurality of structure control additive injection ports disposed in two or more axial planes of a choke section of the carbon black reactor, a combustion section of a carbon black reactor, or a combination thereof.

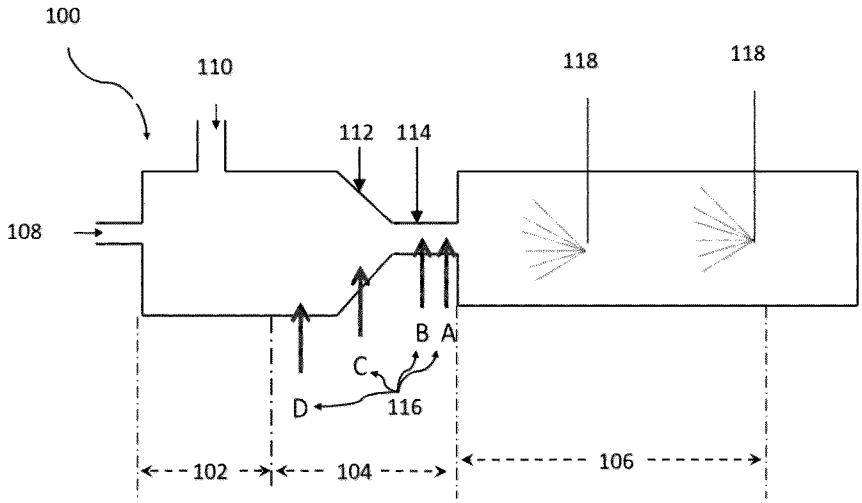


FIG. 1

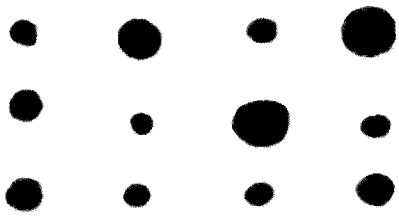


FIG. 2A

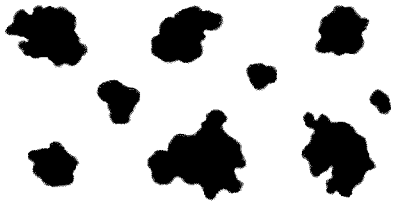


FIG. 2B

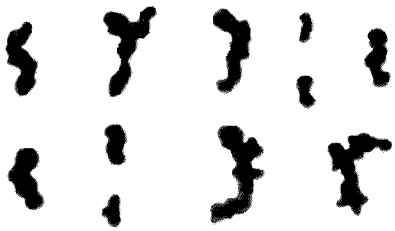


FIG. 2C

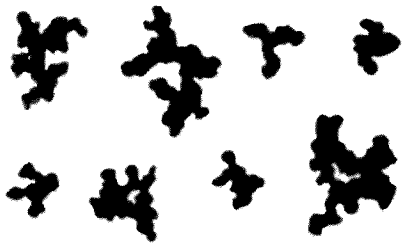


FIG. 2D

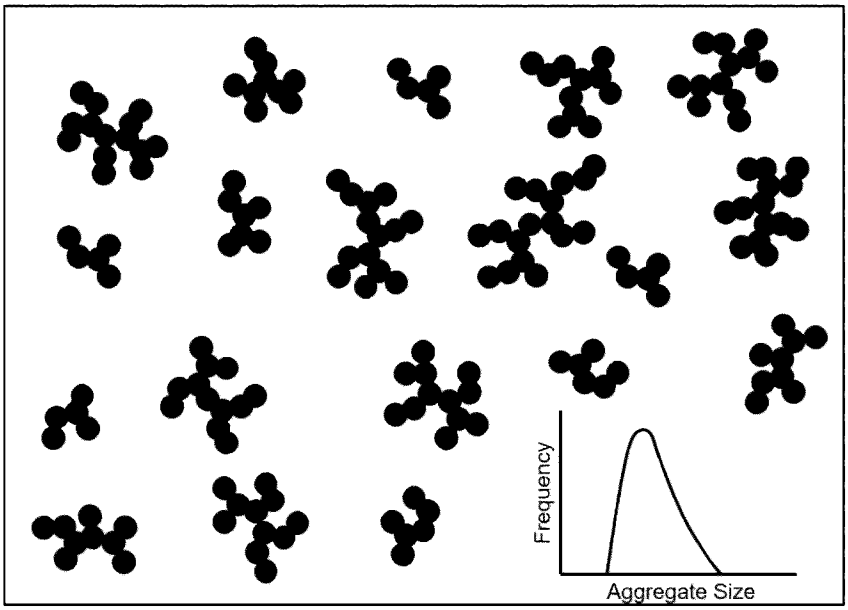


FIG. 3A

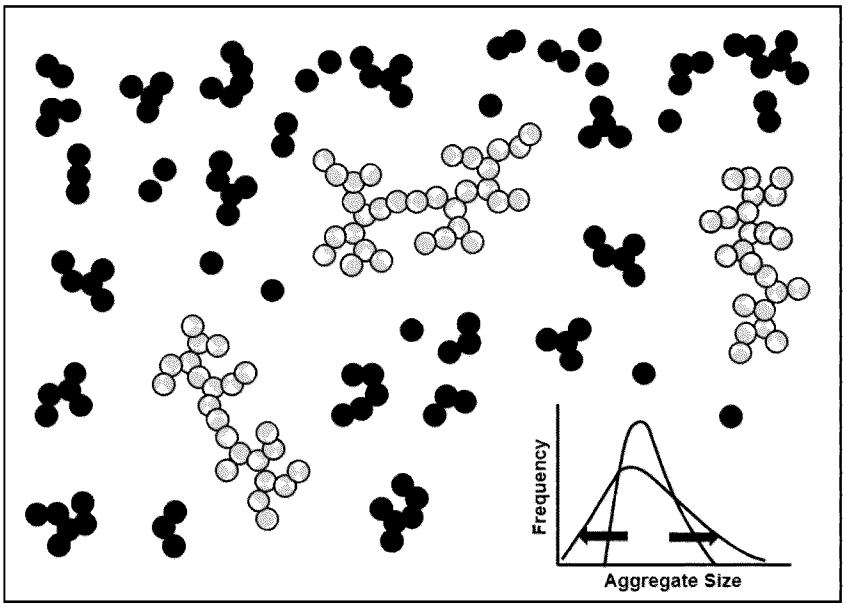
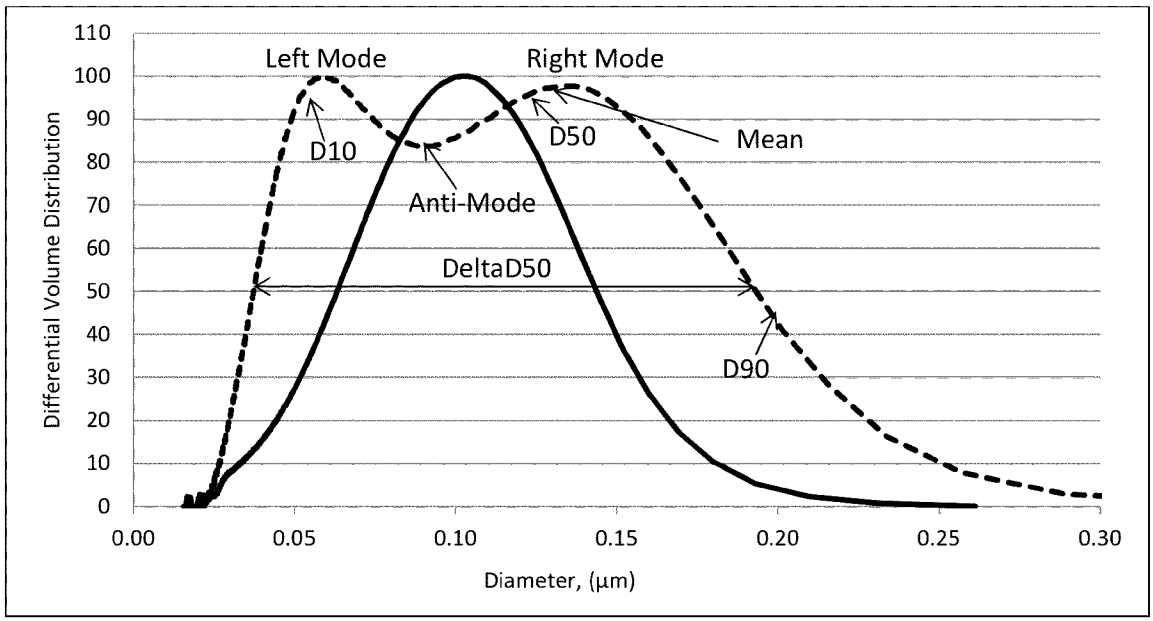


FIG. 3B


Left Mode
Right Mode
D10
D50
Mean
Anti-Mode
DeltaD50
D90
Differential Volume Distribution
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90
80
70
60
50
40
30
20
10
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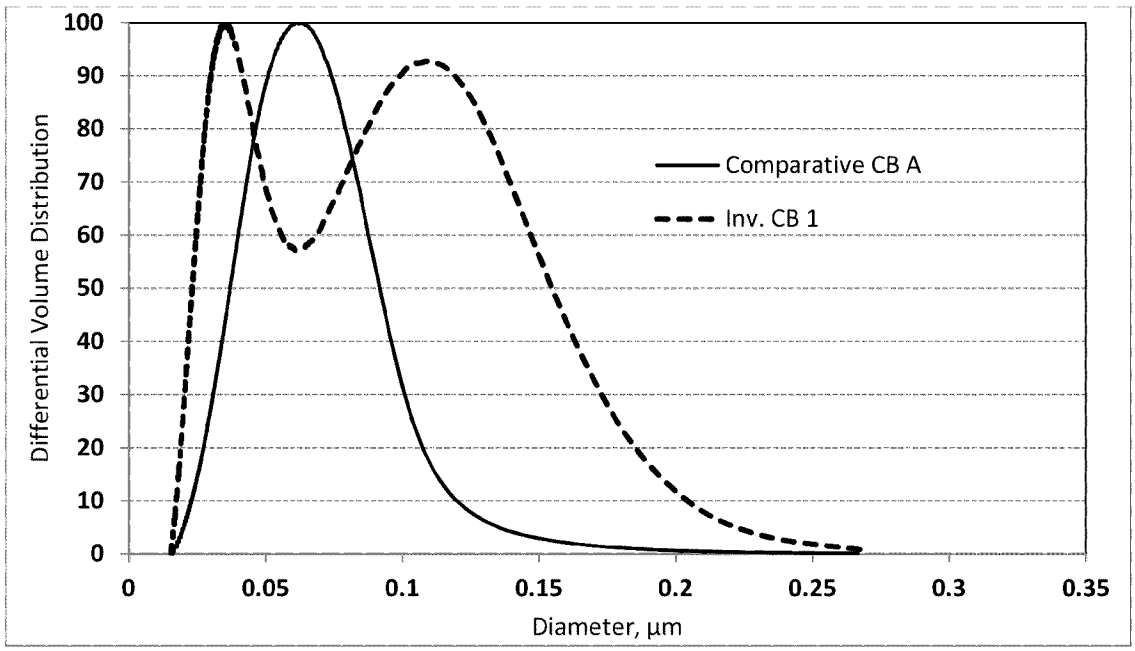
0.00
0.05
0.10
0.15
0.20
0.25
0.30

FIG. 4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Inv. CB 1
Differential Volume Distribution
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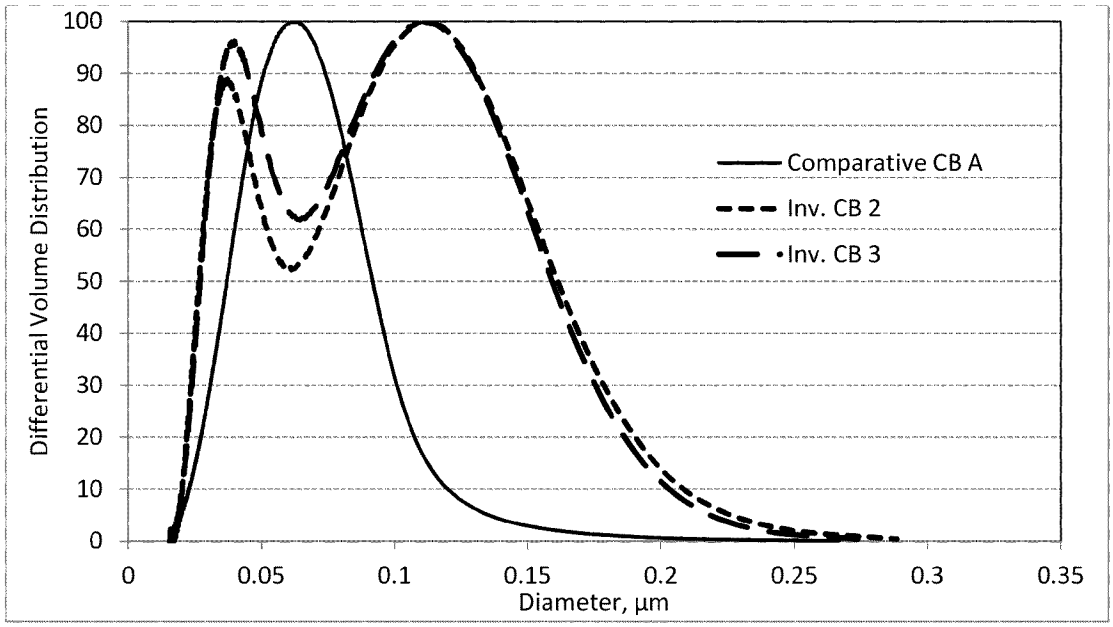
0.05
0.1
0.15
0.2
0.25
0.3
0.35

FIG. 5A


Differential Volume Distribution
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80
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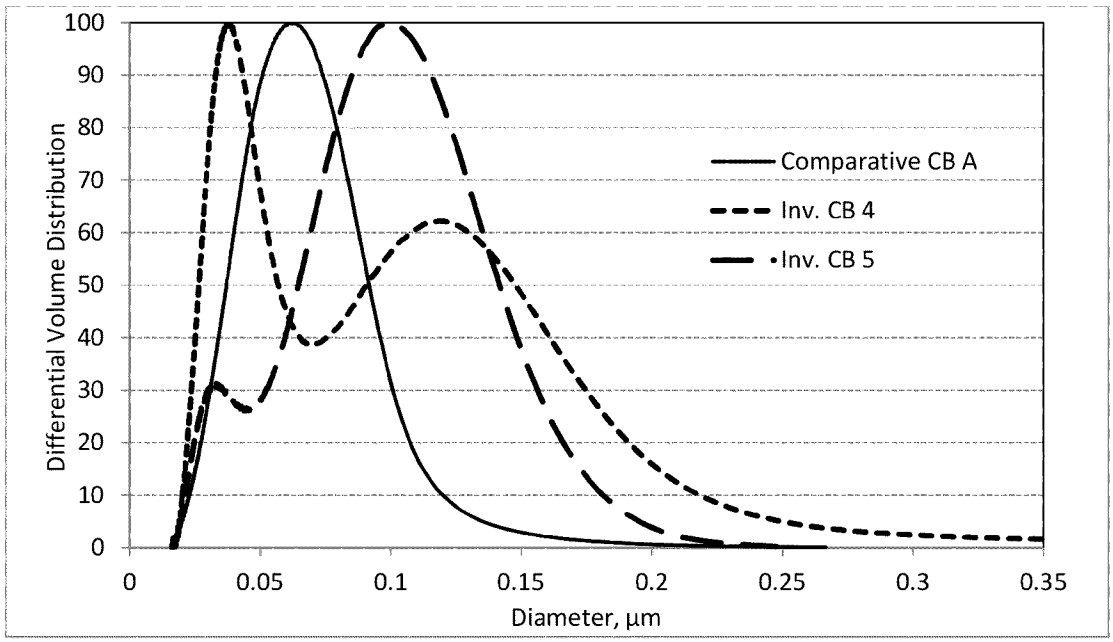
60
50
40
30
20
10
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Diameter, µm
Comparative CB A
Inv. CB 2
Inv. CB 3

FIG. 5B


Differential Volume Distribution
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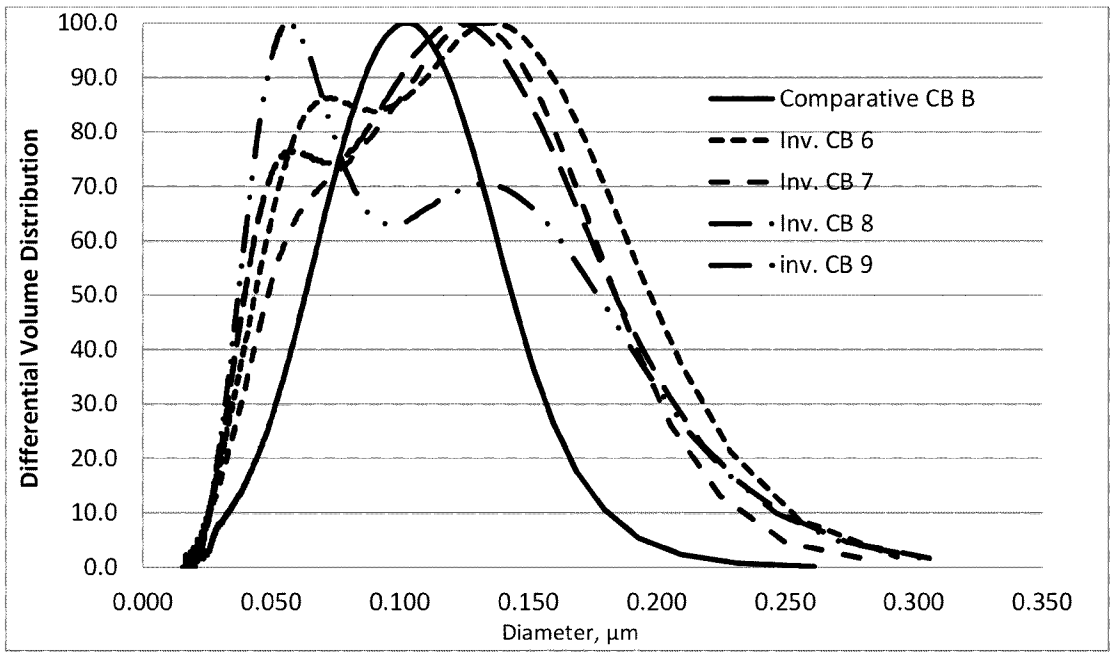
70
60
50
40
30
20
10
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Diameter, µm
Comparative CB A
Inv. CB 4
Inv. CB 5

FIG. 5C


Differential Volume Distribution
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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.000
0.050
0.100
0.150
0.200
0.250
0.300
0.350
Diameter, µm
Comparative CB B
Inv. CB 6
Inv. CB 7
Inv. CB 8
inv. CB 9

FIG. 5D

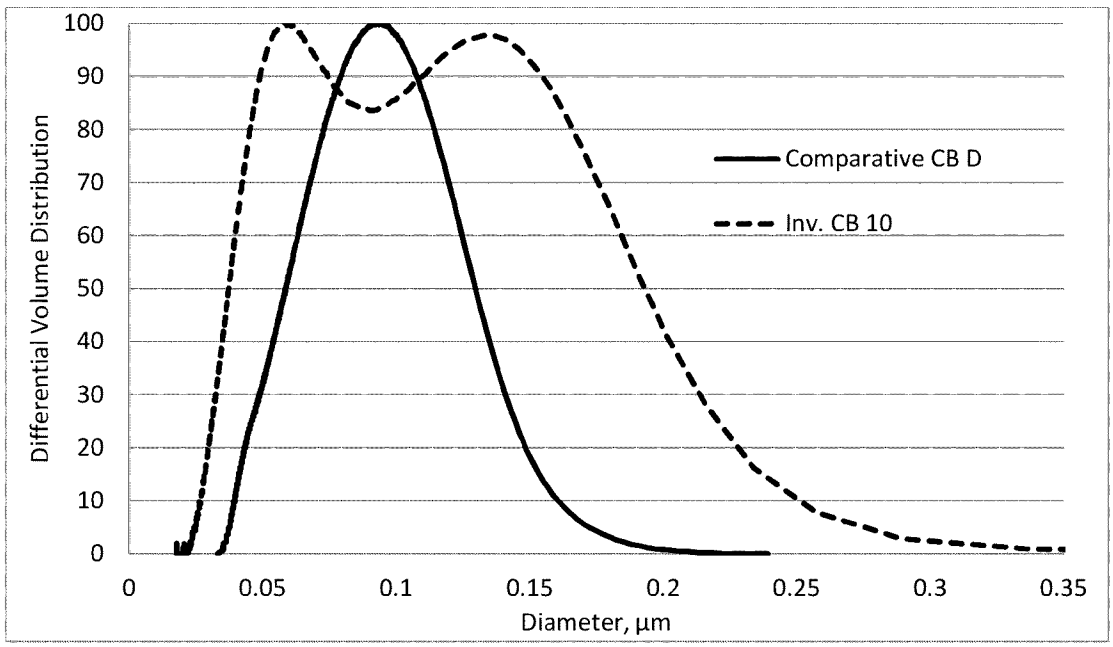
Differential Volume Distribution
100
90
80
70
60
50
40
30
20
10
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Diameter, µm
Comparative CB D
Inv. CB 10

FIG. 5E

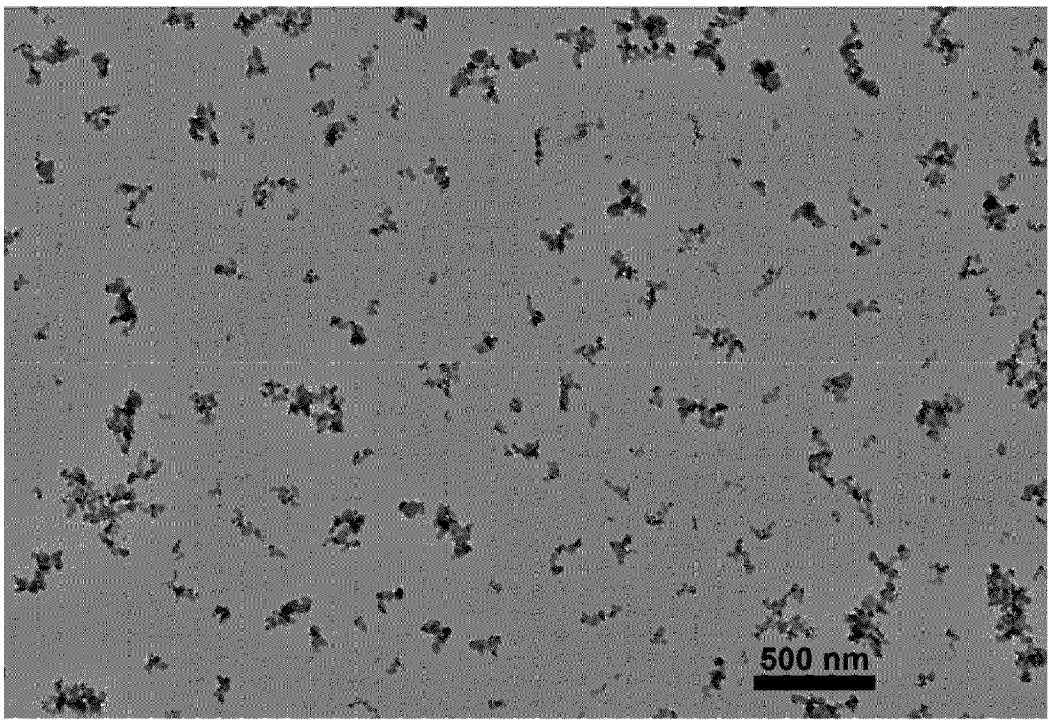

FIG. 6A

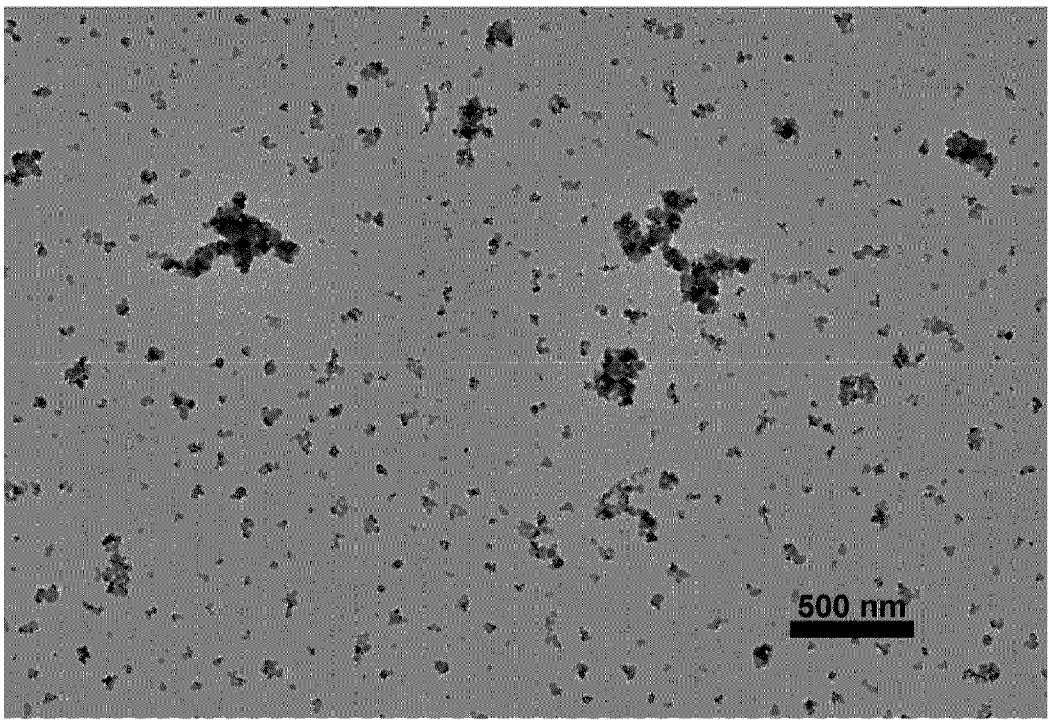

FIG. 6B

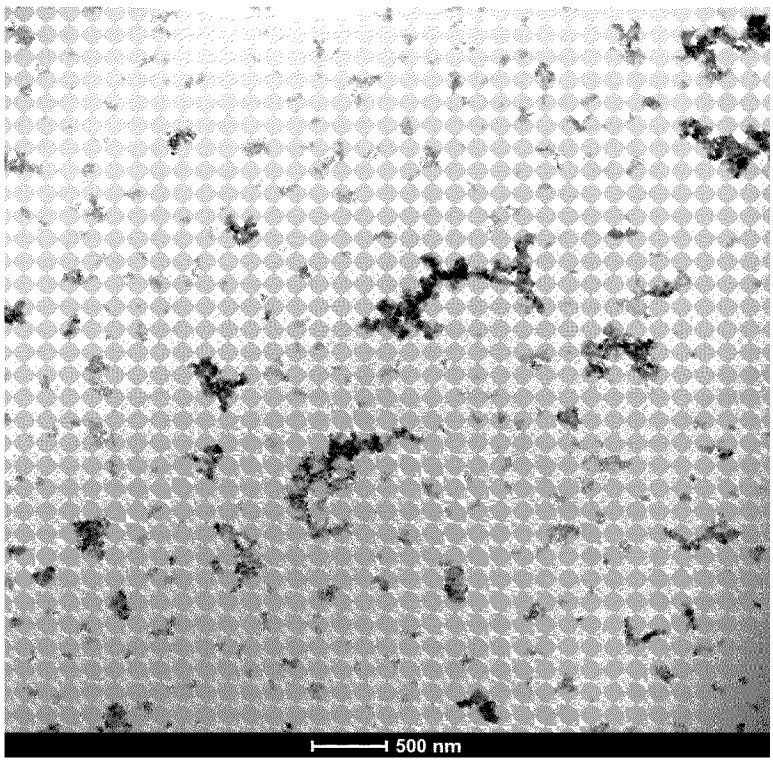

FIG. 7A

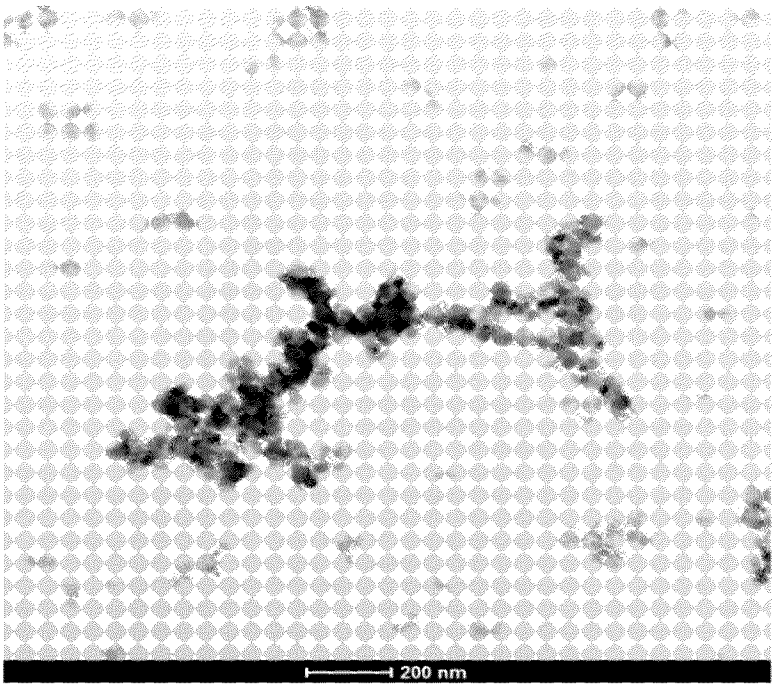

FIG. 7B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/085448

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09C1/50
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/113688 A2 (COLUMBIAN CHEM [US]; WANG WEIDONG [US] ET AL.) 1 December 2005 (2005-12-01) claims 1,22; example all	1,2,30, 31,34, 35,48
X	US 2023/323073 A1 (SAKAKIBARA AKIHIRO [JP] ET AL) 12 October 2023 (2023-10-12) paragraphs [0108] - [0112]; figure 5; examples 1-12	1,2,27, 34,35
X	EP 0 411 160 A1 (NIPPON STEEL CHEMICAL CO [JP]) 6 February 1991 (1991-02-06) figures 6-7; examples 1-6	1-50
X	US 6 391 274 B1 (VOGLER CONNY [DE] ET AL) 21 May 2002 (2002-05-21) claims 1,8; figure 1; example all	1-50

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 July 2024	09/09/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Mattheis, Chris

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2023/085448

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005113688 A2	01-12-2005	AR 048842 A1	31-05-2006
		AR 087658 A2	09-04-2014
		AT E553161 T1	15-04-2012
		BR PI0509785 A	23-10-2007
		CA 2566650 A1	01-12-2005
		CN 101426862 A	06-05-2009
		CN 102161842 A	24-08-2011
		EP 1753828 A2	21-02-2007
		EP 2088174 A2	12-08-2009
		ES 2385990 T3	06-08-2012
		MY 144288 A	29-08-2011
		TW I378126 B	01-12-2012
		US 2005256249 A1	17-11-2005
		US 2009247686 A1	01-10-2009
		WO 2005113688 A2	01-12-2005
US 2023323073 A1	12-10-2023	CN 115443315 A	06-12-2022
		JP 7087219 B1	20-06-2022
		JP WO2022208924 A1	06-10-2022
		US 2023323073 A1	12-10-2023
EP 0411160 A1	06-02-1991	CN 1045593 A	26-09-1990
		EP 0411160 A1	06-02-1991
		JP 2559517 B2	04-12-1996
		JP H03223367 A	02-10-1991
		KR 920700267 A	19-02-1992
		US 5254325 A	19-10-1993
		WO 9010038 A1	07-09-1990
US 6391274 B1	21-05-2002	NONE	