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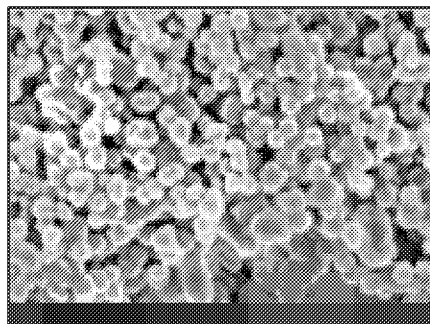


FIG. 1

(57) Abstract: Filtration articles having a honeycomb filter body with a honeycomb structure of a plurality of axial porous walls defining a plurality of cells comprising a plurality of axial channels in an axial direction, and filtration material deposits disposed within the honeycomb filter body comprised of agglomerates of primary particles, wherein the primary particles having an average particle size of 300 nm or less, and wherein the primary particles have a BET surface area of 17 m²/g or less. 41. The filtration article may have a layer structure disposed on the porous walls comprised of dangling agglomerates or dangling agglomerate chains which are attached to both the walls and other individual agglomerates and/or agglomerate chains. Also, methods for treating a plugged honeycomb filter body comprising filtration depositing of agglomerates comprised of primary particles which are nanoparticles having a BET surface area of 17 m²/g or less, such as primary particles having an average particle size of 300 nm or less, which may be spheroidal.

FILTRATION ARTICLES HAVING NANOPARTICLE BASED FILTRATION MATERIAL**Cross Reference to Related Application****BACKGROUND**

[0001] This application claims the benefit of priority under 35 U.S.C. §119 of U.S. Provisional Application Serial No. 63/601,800, filed on November 22, 2023, the content of which is relied upon and incorporated herein by reference in its entirety.

Field

[0002] The present specification relates to filtration articles, such as comprised of porous bodies, such as porous ceramic honeycomb bodies, which comprise filtration material deposits, which are comprised of agglomerates of primary particles, and methods of making such filtration articles.

Technical Background

[0003] Wall-flow filters are employed to remove particulates from fluid exhaust streams, such as from combustion engine exhaust. Examples include diesel particulate filters used to remove particulates from diesel engine exhaust gases and gasoline particulate filters (GPF) used to remove particulates from gasoline engine exhaust gases. Exhaust gas to be filtered enters inlet cells and passes through the cell walls to exit the filter via outlet channels, with the particulates being trapped on or within inlet cell walls as the gas traverses and then exits the filter.

[0004] As vehicle exhaust regulation is getting stricter worldwide, there is a continuing need to improve GPF filtration performance with respect to filtration efficiency and pressure drop penalty. There is also a continuing need to utilize raw materials efficiently.

SUMMARY

[0005] Aspects of the disclosure pertain to filtration articles and methods for their manufacture and use.

[0006] Aspects disclosed herein include filtration articles comprising: a honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of cells comprising a plurality of axial channels in an axial direction; and filtration material deposits disposed within the honeycomb filter body comprised of agglomerates of primary

particles, wherein the primary particles having an average particle size of 300 nm or less, as measured by SEM with at least 200 sample particles, and wherein the primary particles have a BET surface area of $17 \text{ m}^2/\text{g}$ or less.

[0007] Aspects disclosed herein also include methods for treating a plugged honeycomb filter body comprising filtration depositing of agglomerates comprised of primary particles which are nanoparticles having a BET surface area of $17 \text{ m}^2/\text{g}$ or less, such as primary particles having an average particle size of 300 nm or less, which may be spheroidal.

[0008] Aspects disclosed herein also include methods for treating a plugged honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of axial channels in an axial direction, the methods comprising: atomizing primary particles of a filtration material into particulate droplets comprised of a liquid vehicle, a binder material, and the first particles; evaporating substantially all of the liquid vehicle from the droplets to form agglomerates comprised of the primary particles and the binder material; depositing the agglomerates within the honeycomb filter body; wherein the agglomerates are disposed on, or in, or both on and in, the axial porous walls to yield filtration material deposits disposed within the honeycomb filter body; wherein the primary particles are nanoparticles having a BET surface area of $17 \text{ m}^2/\text{g}$ or less.

[0009] In an aspect, a filtration article comprises: a honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of axial channels in an axial direction; and filtration material deposits disposed within the honeycomb filter body comprised of agglomerates that comprise a multimodal size distribution.

[0010] In an aspect, a method for applying a surface treatment to a plugged honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of axial channels in an axial direction comprises: atomizing first particles of a filtration material into a first set of liquid-binder-particulate droplets comprised of a first liquid vehicle, a first binder material, and the first particles; evaporating substantially all of the first liquid vehicle from the first set of droplets to form first agglomerates comprised of the first particles and the first binder material; depositing the first agglomerates within the honeycomb filter body; atomizing second particles of a filtration material into a second set of liquid-binder-particulate droplets comprised of a second liquid vehicle, a second binder material, and the second particles; evaporating substantially all of the second liquid vehicle from the second set of droplets to form second agglomerates comprised of the second particles and the second binder material; and depositing the second agglomerates within the

honeycomb filter body; wherein the first and second agglomerates are disposed on, or in, or both on and in, the axial porous walls to yield filtration material deposits disposed within the honeycomb filter body, the agglomerates comprising a multimodal size distribution.

[0011] Additional features and advantages will be set forth in the detailed description, which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, comprising the detailed description, which follows, the claims, as well as the appended drawings.

[0012] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIGS. 1-6 show SEM images of various different primary particle types that were used to create agglomerates according to the present disclosure.

[0014] FIG. 1 is an SEM image showing generally spherical (or nearly spherical) primary particles having an aspect ratio of about 1 to 2. FIG. 2 is an SEM image showing a closeup of a portion of FIG. 1.

[0015] FIG. 3 is an SEM image showing generally irregular shaped and/or rod-like shaped primary particles having an aspect ratio of about 2 to 10. FIG. 4 is an SEM image showing a closeup of a portion of FIG. 3.

[0016] FIG. 5 is an SEM image showing generally string-like and/or fibrous shaped primary particles having an aspect ratio of about 30 to 50. FIG. 6 is an SEM image showing a closeup of a portion of FIG. 5.

[0017] FIG. 7 shows SEM images of primary particles of various shapes and sizes used to create agglomerates (or “secondary particles”) with a spray dry process. FIG. 7 shows primary particle reference name / average particle size: 30 nm / 45nm; 80 nm / 62 nm; S200nm / 125 nm; AKP700 / 162 nm; Alunol 30 / 335 nm; AA03 244 nm; AA04 / 326 nm; AKP20 / 630 nm; AKP 15 / 874 nm; and AA1.5 / 1107 nm.

[0018] FIG. 8 schematically illustrates a process flow chart in which the primary particles undergo a series of treatments to create a homogenous suspension which can then serve as a spray feed and a spray dry apparatus.

[0019] FIG. 9 shows SEM images of the resulting agglomerates size using some of the primary particles (AA03 244 nm; AA04 / 326 nm; AA1.5 / 1107 nm; AKP700 / 162 nm; Alunol 30 / 335 nm; and AKP 15 / 874 nm) of FIG. 7 under similar spray process conditions with a spray dry apparatus.

[0020] FIG. 10 shows SEM images of the resulting agglomerates size using others of the primary particles (S200nm (125 nm); AKP20 / 630 nm) of FIG. 7 under similar spray process conditions with a spray dry apparatus.

[0021] FIGS. 11-12 show SEM images of packing behavior of dried particle resulting from different primary particle morphology.

[0022] FIG. 11 shows agglomerate formed by primary size with relatively large aspect ratio (AKP20, average size 630nm), showing non-spherical appearance with rugged surface as well as visible voids and loose structure.

[0023] FIG. 12 shows agglomerate formed by primary particle size with relatively small aspect ratio (S200, average size 125nm), showing near-spherical agglomerate structure and smooth surface.

[0024] FIGS. 13-15 illustrate the formation of agglomerates and the packing structure between secondary agglomerates formed by different aspect ratio.

[0025] FIG. 13 schematically illustrates a droplet formed after being sprayed from a nozzle, where the white areas represent the primary particles each droplet contains and the area represent the particle concentration inside the droplet.

[0026] FIG. 14 schematically illustrates agglomerate structure being formed after solvent has been evaporated during the drying process.

[0027] FIG. 15 shows an SEM cross-sectional view of an internal agglomerate structure after being treated with Focused Ion Beam (FIB). Under similar suspension concentration, high aspect ratio material tends to form more porous and loosely packed structure, and consumes more space (or volume) after the final agglomerate has been formed.

[0028] FIG. 16 graphically illustrates a comparison of filtration performance of porous honeycomb filter bodies containing deposited agglomerates formed from various exemplary primary particles at low (left side of the graph) and high concentration (right side of the graph), along with representative SEM images of a honeycomb wall having the deposited agglomerates.

[0029] FIG. 17 graphically illustrates filtration deposits (agglomerates, any un-agglomerated primary particles) loadings of various corresponding primary particle types that were delivered in suspension to the nozzle with 1% and 11% solids concentration with mixture formulation as disclosed herein, which was loaded onto a porous ceramic honeycomb filter substrate to achieve 99.5% filtration efficiency.

[0030] FIG. 18 graphically illustrates median (“D50”) agglomerate size (in micrometers) versus alumina primary particle size (in nm) with (“linear”) correlations between primary particle size and the resulting agglomerate size after spray dry process at 1% and 11% solids concentration.

[0031] FIG. 19 graphically illustrates the water durability of various filter bodies containing deposited agglomerates formed from various primary particle types and solids concentrations, at various filtration deposit loadings.

[0032] FIG. 20 graphically illustrates that, for various different raw materials such as size and type of primary particles, and binder level, FE loss due to nebulizer water exposure test can be reduced by increasing the filtration deposit loading amount, or binder level (binder concentration in terms of binder amount per primary particle surface area, or both), and/or decreasing the primary particle surface area.

[0033] FIG. 21 lists a table of various combinations of types/sizes of alumina primary particles (Alunol 30, AKP 700, S200nm) and binder concentrations (25%, 40%, 50%) (alkoxysiloxane) along with measured clean FE loss after 650° calcination.

[0034] FIGS. 22 and 23 are SEM images of surfaces of a honeycomb wall comprising filtration deposits comprised of agglomerates of Alunol 30 alumina primary particles (FIG. 22) and agglomerates of S200 alumina primary particles (FIG. 23).

[0035] FIG. 24 lists for the primary particle types corresponding to FIGS. 22 and 23 the primary particle size in micrometers (μm), primary particle surface area by BET in m^2/g , average agglomerate size in μm , agglomerate loading on a porous ceramic honeycomb filter body required to achieve a clean filtration efficiency of 99.5% in g/liter of honeycomb body volume, and clean filtration performance of the filter body.

DETAILED DESCRIPTION

[0036] Reference will now be made in detail to embodiments of filtration articles and methods for forming honeycomb bodies comprising a porous honeycomb body comprising filtration material deposits on, or in, or both on and in, the porous ceramic walls of the honeycomb body matrix, embodiments of which are illustrated in the accompanying drawings.

Deposits comprise material that was deposited into the honeycomb body, as well as compounds that may be formed, for example, by heating, from one or materials that were originally deposited. For example, a binder may be transformed by heating into an organic component which is eventually burned off or volatilized, while an inorganic component (such as silica) remains contained within the honeycomb filter body. Whenever possible, the same reference numerals will be used throughout the drawings to refer to the same or like parts.

Definitions

[0037] As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” encompass embodiments having plural referents, unless the content clearly dictates otherwise. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[0038] As used herein, “have”, “having”, “include”, “including”, “comprise”, “comprising” or the like are used in their open ended sense, and generally mean “including, but not limited to”.

[0039] A “honeycomb body,” as referred to herein, comprises a ceramic honeycomb structure of a matrix of intersecting walls that form cells wherein the surfaces of the intersecting walls or cell walls define channels such as axial channels which extend from one end of the structure to an opposite end. The ceramic honeycomb structure can be formed, extruded, or molded from a plasticized ceramic or ceramic-forming batch mixture or paste. A honeycomb body may comprise an outer peripheral wall, or skin, which was either extruded along with the matrix of walls or applied after the extrusion of the matrix. For example, a honeycomb body can be a plugged ceramic honeycomb structure which forms a filter body comprised of cordierite or other suitable ceramic material. A plugged honeycomb body has one or more channels plugged at one, or both ends of the body.

[0040] Unless otherwise specifically noted herein, “particle size” refers to an average particle size or mean particle size, and “pore size” refers to an average pore size or mean pore size.

Filtration Articles

[0041] A honeycomb filter body disclosed herein comprises a ceramic honeycomb structure comprising at least one wall carrying one or more filtration material deposits which is configured to filter particulate matter from a gas stream. The filtration material deposits can be in discrete regions or in some portions or some aspects can form one or more layers of filtration material at a given location on the wall of the honeycomb body. The filtration material deposits

according to some aspects comprise inorganic material, in some aspects organic material, and in some aspects both inorganic material and organic material. For example, a honeycomb body may, in one or more aspects, be formed from cordierite or other porous ceramic material and further comprise filtration material deposits, including inorganic material deposits, disposed on or below wall surfaces (within the walls) of the cordierite honeycomb structure.

[0042] The filtration material deposits comprise inorganic deposits comprising one or more of ceramic or refractory materials, for example alumina or silica or cordierite or silicon carbide or other ceramic or refractory materials or combinations thereof. In some aspects, the filtration material deposits comprise an inorganic material to yield inorganic deposits. In some aspects, the filtration material deposits, including inorganic deposits comprise alumina particles, including alumina nanoparticles, which may agglomerate and/or aggregate.

[0043] Filtration articles herein include advantageous surface layer microstructures effective to improve filtration efficiency (FE) with minimal impact on pressure drop. Features of the microstructures include one or more of the following: filtration material deposits of agglomerates of smaller particles (for example micron-sized agglomerates of nano-sized particles or nanoparticles). Preferably at least a portion of the honeycomb walls comprises a thin layer of filtration material deposits, wherein agglomerates are distributed along a channel (axial) direction of the filtration articles.

[0044] Methods have been disclosed for creating agglomerates from nano-sized particles via a spray dry process and forming a layered structure that improves the filtration efficiency of a filtration article comprising a honeycomb structure without filtration deposits.

[0045] In aspects disclosed herein a layer structure on the base wall of the honeycomb structure is a porous wall comprised of dangling agglomerates or dangling agglomerate chains which can attach strongly with both the honeycomb wall and other individual agglomerates and/or agglomerate chains, which can form an inter-connected layer or discrete patches of filtration material deposits. Attachment can be achieved by an inorganic binder component, such as a silicon-containing inorganic binder material. We have unexpectedly found that nanoparticles from which the agglomerates are made influence the appearance and/or shape of the formed agglomerates as well as the resulting pore structure of the layer of agglomerates or agglomerate layer on and/or in the base wall portion of the honeycomb structure.

[0046] FIGS. 1-6 show SEM images of various different primary particle types that were used to create agglomerates according to the present disclosure.

FIG. 1 is an SEM image showing generally spherical (or nearly spherical) primary particles having an aspect ratio of about 1 to 2. FIG. 2 is an SEM image showing a closeup of a portion of FIG. 1.

[0047] FIG. 3 is an SEM image showing generally irregular shaped and/or rod-like shaped primary particles having an aspect ratio of about 2 to 10. FIG. 4 is an SEM image showing a closeup of a portion of FIG. 3.

[0048] FIG. 5 is an SEM image showing generally string-like and/or fibrous shaped primary particles having an aspect ratio of about 30 to 50. FIG. 6 is an SEM image showing a closeup of a portion of FIG. 5.

[0049] FIG. 7 shows SEM images of primary particles of various shapes and sizes used to create agglomerates (or “secondary particles”) with a spray dry process. FIG. 7 shows primary particle reference name / average particle size: 30 nm / 45nm; 80 nm / 62 nm; S200nm / 125 nm; AKP700 / 162 nm; Alunol 30 / 335 nm; AA03 244 nm; AA04 / 326 nm; AKP20 / 630 nm; AKP 15 / 874 nm; and AA1.5 / 1107 nm.

[0050] FIG. 8 schematically illustrates a process flow chart in which the primary particles undergo a series of treatments to create a homogenous suspension which can then serve as a spray feed and a spray dry apparatus. The process comprises introducing a dispersant to help break up soft aggregates and/or to prevent re-agglomeration, including mechanical force to facilitate further break up, and adding sufficient amount of binder and promoter into the slurry to reliably apply a thin layer of agglomerates generated during the spray dry process. As depicted in FIG. 8, in some aspects the process comprises the following steps: alumina primary particles are dried in an oven at 150° C for 1 hour; ethanol is measured and added in a container; dispersant is measured and added into the same container; the contents of the container are magnetically stirred for 5 minutes; the dried alumina is measured and added into the container; the mixture (suspension) is horn sonicated for 40 minutes, while keeping the temperature under 25°; additional dispersant is added to the suspension; the suspension is magnetically stirred for 1 hour; binder is added to the suspension; the suspension is again magnetically stirred for 1 hour; and then the formulation is ready to be used in a spray dry process to create agglomerates from the respective primary particles.

[0051] FIG. 9 shows SEM images of the resulting agglomerates size using some of the primary particles (AA03 244 nm; AA04 / 326 nm; AA1.5 / 1107 nm; AKP700 / 162 nm; Alunol 30 / 335 nm; and AKP 15 / 874 nm) of FIG. 7 under similar spray process conditions with a spray dry apparatus and system comprising a co-flow spray deposition system with standard two-fluid external nozzle. The carrier flow used in these runs was 30 Nm³/hr. The atomizing

gas was set at 10 Nm³/hr per nozzle, corresponding to 170 psi of pressure. Liquid flow was kept at 15 ml/min with a syringe pump to maintain steady, continuous flow during the spray process. The overall temperature inside the chamber was 140° C. After exiting the nozzle, the droplet created by the shear force from two fluid nozzles was quickly evaporated into dried (secondary) particles (i.e. agglomerates) that contained the binding composition, which agglomerates may further undergo collisions or interactions during the deposition phase to form secondary agglomerates (“aggregates”). Once these secondary agglomerates or aggregates reach already laid down agglomerates and/or aggregates or the bare wall surface portion, the agglomerates and Nora contents can interconnect with each other and develop into and/or construct a 3-D web-like structure having its own pore size and porosity depending on the agglomerate size and morphology.

[0052] FIG. 10 shows SEM images of the resulting agglomerates size using others of the primary particles (S200nm (125 nm); AKP20 / 630 nm) of FIG. 7 under similar spray process conditions with the spray dry apparatus described above.

[0053] FIGS. 11-12 show SEM images of packing behavior of dried particle resulting from different primary particle morphology. FIG. 11 shows agglomerate formed by primary size with relatively large aspect ratio (AKP20, average size 630nm), showing non-spherical appearance with rugged surface as well as visible voids and loose structure. FIG. 12 shows agglomerate formed by primary particle size with relatively small aspect ratio (S200, average size 125nm), showing near-spherical agglomerate structure and smooth surface.

[0054] FIGS. 13-15 illustrate the formation of agglomerates and the packing structure between secondary agglomerates formed by different aspect ratio. FIG. 13 schematically illustrates a droplet formed after being sprayed from a nozzle, where the white areas represent the primary particles each droplet contains and the area represent the particle concentration inside the droplet. FIG. 14 schematically illustrates agglomerate structure being formed after solvent has been evaporated during the drying process. FIG. 15 shows an SEM cross-sectional view of an internal agglomerate structure after being treated with Focused Ion Beam (FIB). Under similar suspension concentration, high aspect ratio material tends to form more porous and loosely packed structure, and consumes more space (or volume) after the final agglomerate has been formed.

[0055] FIG. 16 graphically illustrates a comparison of filtration performance of porous honeycomb filter bodies containing deposited agglomerates formed from various exemplary primary particles at low (left side of the graph) and high concentration (right side of the graph), along with representative SEM images of a honeycomb wall having the deposited

agglomerates. Overall, diluted suspensions result in more fractal, chain-like structures (see representative SEM images on left side of FIG. 16), while more concentrated suspensions form more spherical agglomerates (see representative SEM images on right side of FIG. 16). Observed fragments of particle/agglomerate were observed on the honeycomb structure substrate portion of the filter body, suggesting gradual chain formation inside the pore. Compared to densely packed spherical agglomerates (right side of FIG.16), such chain structure appears to be more fractal and loose (left side of FIG.16). The performance data indicates that the slender chain structure formation reduced cross honeycomb filter body pressure drop by ~6% for a measured clean filtration efficiency, which is obtained from lower concentration primary particle mixtures as disclosed herein.

[0056] FIG. 17 graphically illustrates filtration deposits (agglomerates, any un-agglomerated primary particles) loadings of various corresponding primary particle types that were delivered in suspension to the nozzle with 1% and 11% solids concentration with mixture formulation as disclosed herein, which was loaded onto a porous ceramic honeycomb filter substrate to achieve 99.5% filtration efficiency (“target FE”) on smoke FE bench to assess essentially clean filtration performance. As can be seen from graph, the loading required to reach target FE increased along with larger (increased) primary particle size. Also as seen from the graph in FIG. 17, high solids concentration results in higher loading required to reach a same filtration efficiency. By using a select primary particle size and amount in the formulation, a desired layer structural property (for example layer thickness, layer porosity, etc.) can be obtained.

[0057] FIG. 18 graphically illustrates median (“D50”) agglomerate size (in micrometers) versus alumina primary particle size (in nm) with (“linear”) correlations between primary particle size and the resulting agglomerate size after spray dry process at 1% and 11% solids concentration. FIGS. 17 and 18 together illustrate that the contribution of primary particle to the formation of the agglomeration size that serves as the building block of the resulting layer structure on the filter honeycomb substrate.

[0058] FIG. 19 graphically illustrates the water durability of various filter bodies containing deposited agglomerates formed from various primary particle types and solids concentrations, at various filtration deposit loadings. The set of bars on the right in FIG. 19 shows the loading corresponding to 99.5% clean filtration efficiency (right handside bar), and the set of bars on the left in FIG. 19 shows a loss in filtration efficiency (FE) that occurred after exposing the filter body to a standard water (nebulizer) test. As indicated by FIG. 19, smaller primary particles require lower filtration deposit loading to reach target FE compared to large primary particles. However, lower loading also results in higher water FE loss (that is, after water

exposure). In various aspects disclose herein, the materials and process can provide a fine balance between the agglomerate loading (filtration material) and water reliability of the final product. For example, smaller agglomerates and/or more porous structure are generally more susceptible to water attack with regard to filtration efficiency.

[0059] FIG. 20 graphically illustrates that, for various different raw materials such as size and type of primary particles, and binder level, FE loss due to nebulizer water exposure test can be reduced by increasing the filtration deposit loading amount, or binder level (binder concentration in terms of binder amount per primary particle surface area, or both), and/or decreasing the primary particle surface area, as we have found these factors to affect the clean FE loss after being exposed to water via nebulizer. The binder per surface area is a source for the layer structure reliability.

[0060] After evaluating surfaces by EDS measurement of agglomerates formed by alkoxy siloxane binder and small or large surface area alumina primary particles, we have found that by varying the raw materials surface morphology, a significant change in Si concentration can be obtained, indicating that the binder distribution on alumina surfaces is closely related to the primary particle surface property, in accord with FIG. 20, therefore a low (or minimal) Si concentration (i.e. corresponding to silicon-containing binder amount) on alumina surface, such as in the range of 1:10 to 1:2, or preferably 1:7 to 1:3, or 1:6 to 1:4, such as 1:5, are preferred.

[0061] Unless otherwise noted, filter bodies with filtration deposits were cured in a heating environment less than 650° C, and if being subjected to a water or nebulizer durability test then calcined or heat treated at 650° C.

[0062] FIG. 21 lists a table of various combinations of types/sizes of alumina primary particles (Alunol 30, AKP 700, S200nm) and binder concentrations (25%, 40%, 50%) (alkoxysiloxane) along with measured clean FE loss after 650° calcination, i.e. the FE loss at each binder level after the honeycomb filter body with agglomerates as filtration deposits undergoes heat treatment. High FE loss after calcination (650C) was observed when higher binder amounts were added into the suspension that supplied the nozzle for spray dry in the spray dry chamber. Without needing to be bound by theory, FE loss may occur potentially due to resin contraction during phase change causing dislocation of layer structure, resulting in potential change of pore size and porosity, which would surprisingly and counterintuitively result in higher FE loss (after calcination) even though a higher binder level is present among the agglomerates and/or particles. Thus, we believe this phenomenon imposes a limit on higher and higher binder usage in the solution in order to achieve an overall FE loss target (for example

<1% loss after calcination). Thus, to achieve a layer structure with smaller pore size and higher porosity, the primary particles that agglomerate and form aggregates and/or secondary chains of agglomerates need to be smaller, as indicated for example in FIG. 20. We have found that in order to accommodate potential water reliability compromise (FE loss) caused by filtration deposits loading decreases and surface area increases, an increase in binder amount is in order but not without limitation, as higher binder loadings would also suffer from FE loss after calcination due to structural instability, and therefore a balance between loading and binder level may provide best overall filter performance. Thus, in exemplary embodiments disclosed herein, particle size of 300nm or less with surface area less than 17 m²/g can be used with binder ratio above 30% to provide sufficient reliability but less than 50% to maintain the FE loss after heat treatment in an acceptable range.

[0063] FIGS. 22 and 23 are SEM images of surfaces of a honeycomb wall comprising filtration deposits comprised of agglomerates of Alunol 30 alumina primary particles (FIG. 22) and agglomerates of S200 alumina primary particles (FIG. 23). FIG. 22 shows larger, spherical agglomerates as filtration deposits, while FIG. 23 shows more fractal and branch-like filtration deposits. Also, the pore structure in FIG. 22 appears hollow and fluffy, while FIG. 23 appears much fuller and denser.

[0064] FIG. 24 lists for the primary particle types corresponding to FIGS. 22 and 23 the primary particle size in micrometers (μm), primary particle surface area by BET in m²/g, average agglomerate size in μm, agglomerate loading on a porous ceramic honeycomb filter body required to achieve a clean filtration efficiency of 99.5% in g/liter of honeycomb body volume, and clean filtration performance of the filter body (pressure drop through the filter body) in Pa with air passing through at 1.7 m/s, reduction/loss of filtration efficiency in % of calcined filter body after nebulizer water test at a filtration deposit (agglomerate) loading of 4 g/liter of honeycomb body volume).

[0065] As seen from FIG. 7 and FIGS. 22-24, as compared to irregular shaped particles (for example Alunol 30), a spherical morphology (for example S200) a size reduction can be achieved without a large difference in BET surface area, which relates to a reduction in the loading amount of filtration deposit material (e.g. agglomerates) needed to achieve target filtration performance while also providing water durability, or reliability, as indicated by lower FE losses upon exposure to water. A reduced loading of filtration deposit material (e.g. agglomerates) also can relate to a thinner application of filtration deposits, such as a thinner layer structure, which leads to reductions in pressure drop through the honeycomb walls and overall through the filter body. According to aspects disclosed herein, primary particle size and

morphology therefore contributes to an accumulated layer structure which can balance filtration performance and water resistance.

[0066] Alunol 30 is alumina particles with a d50 of 0.4 to 0.5 μm , and a BET surface area of 9.0 to 10.0 m^2/g (about 30% alumina in ethanol).

Methods

[0067] Aspects of the disclosure pertain to methods of forming porous bodies, such as porous ceramic honeycomb bodies, comprising a material such as a filtration material such as an inorganic material such as a ceramic or refractory material or even a porous ceramic or refractory material. The filtration material is preferably an aerosol-deposited filtration material. The filtration material comprises a plurality of inorganic particle agglomerates, wherein the agglomerates are comprised of inorganic, such as ceramic or refractory, material. The agglomerates may be porous, which may allow gas to flow through the agglomerates.

[0068] Aerosol deposition enables deposition of filtration material onto the porous ceramic walls, which can be discrete regions as small as a single agglomerate or larger such as a plurality of agglomerates, and in some aspects is in the form of a porous layer of filtration material, on or in, or both on and in, at least some surfaces of the walls of the ceramic honeycomb body.

[0069] In various aspects, an aerosol deposition process can be utilized which comprises: mixture preparation (e.g., particles of inorganic material, liquid vehicle, and a binder), atomizing the mixture with an atomizing gas with a nozzle to form agglomerates and/or aggregates, comprised of the inorganic material, the liquid vehicle, and the binder, drying the agglomerates and/or aggregates in the presence of a carrier gas or a gaseous carrier stream, depositing the aggregates and/or agglomerates onto the honeycomb bodies, and curing the material.

[0070] The process may comprise operations of: mixture preparation, atomizing to form droplets, intermixing droplets and a gaseous carrier stream; evaporating liquid vehicle to form agglomerates, depositing of material, e.g., agglomerates, on the walls of a wall-flow filter, and post-treatment to, for example, bind the material on, or in, or both on and in, the porous walls of the honeycomb body.

[0071] The aerosol deposition forms filtration material deposits, including inorganic material deposits, which are preferably porous material deposits. The material deposits can be in the form of discrete regions of filtration material, and at least some portions of the material deposits may be in the form of a porous inorganic layer.

[0072] **Mixture preparation.**

[0073] Commercially available inorganic particles can be used as a raw material in a mixture in the formation of an inorganic material for depositing. The particles may be selected from Al_2O_3 , SiO_2 , TiO_2 , CeO_2 , ZrO_2 , SiC , MgO and combinations thereof. In one or more aspects, the mixture is a suspension. The particles may be supplied as a raw material suspended in a liquid vehicle.

[0074] In one or more embodiments, the particles have an average primary particle size in a range of from about 10 nm to about 4 microns, about 20 nm to about 3 microns or from about 50 nm to about 2 microns, or from about 50 nm to about 900 nm or from about 50 nm to about 600 nm. The average primary particle size can be determined as a calculated value from the Brunauer, Emmett and Teller (BET) surface area of the aerosol particles, which in some embodiments is greater than or equal to $7.0 \text{ m}^2/\text{g}$ to less than or equal to $10 \text{ m}^2/\text{g}$, including all values and ranges therebetween, including $9 \text{ m}^2/\text{g}$.

[0075] In one or more embodiments, the primary particles comprise a ceramic particle, such as an oxide particle, for example Al_2O_3 , SiO_2 , MgO , CeO_2 , ZrO_2 , CaO , TiO_2 , cordierite, mullite, SiC , aluminum titanate, and mixtures thereof.

[0076] Binder is added to reinforce the agglomerates and to provide a stickiness or tackiness, and can comprise inorganic binder, to provide mechanical integrity to deposited material. The binder may provide binding strength between particles at elevated temperature ($>500^\circ\text{C}$). The starting material can be organic. After exposure to high temperature in excess of about 150°C , the organic starting material will decompose or react with moisture and oxygen in the air, and the final deposited material composition could comprise Al_2O_3 , SiO_2 , MgO , CeO_2 , ZrO_2 , CaO , TiO_2 , cordierite, mullite, SiC , aluminum titanate, or mixtures thereof.

[0077] Preferably, the binder is a silicon-containing compound. The silicon-containing compound is further preferably comprised of a siloxane or polysiloxane, silicone, a silicate, or a combination thereof. In embodiments, the silicon-containing compound is comprised of a silicone compound, polysiloxane, silicone resin, siloxane, alkoxysiloxane, or combinations thereof. In embodiments, the silicon-containing compound is comprised of a silicate, an alkaline silicate, a sodium silicate, or combinations thereof. Unless otherwise noted herein, alkoxy siloxane was the binder used in examples to generate data herein.

[0078] Catalyst can be added to accelerate the cure reaction of binder. An exemplary catalyst used to accelerate the cure reaction of the alkali-free binder is titanium butoxide. An exemplary catalyst content is 1% by weight of the binder.

[0079] **Atomizing to form droplets.** The mixture is atomized into fine droplets by high pressure gas through a nozzle.

[0080] In one or more embodiments, the liquid-particulate-binder droplets are directed into the chamber by one or a plurality of nozzles.

[0081] The pressure of the atomizing gas may be in the range of 20 psi to 230 psi. The pressure of the liquid may be in the range of 1 to 100 psi. The average droplet size according to one or more embodiments may be in the range of from 1 micron to 40 microns. The droplet size can be adjusted by adjusting the surface tension of the mixture, viscosity of the mixture, density of the mixture, gas flow rate, gas pressure, liquid flow rate, liquid pressure, and nozzle design.

[0082] The suspension flow rate is in the range of 10 to 80 g/minute, and the atomizing gas flow rate can be in the range of 2 to 20 Nm³/hr.

[0083] The suspension can comprise an inorganic material, a liquid vehicle, and a binder, which is supplied to the nozzle as a liquid-particulate-binder stream. The liquid-particulate-binder stream is atomized with the atomizing gas into liquid-particulate-binder droplets by the nozzle.

[0084] **Intermixing droplets and gaseous carrier stream.** The droplets are conveyed toward the honeycomb body by a gaseous carrier stream. Preferably, substantially all of the liquid vehicle is evaporated from the droplets to form agglomerates comprised of the particles and the binder.

[0085] The gaseous carrier stream can be heated prior to being mixed with the droplets.

[0086] The carrier gas is supplied to the apparatus to facilitate drying and carrying the liquid-particulate-binder droplets and resulting agglomerates through the apparatus and into the honeycomb body.

[0087] **Deposition in honeycomb body 425.** The agglomerates and/or aggregates thereof are deposited onto the porous walls of the plugged honeycomb body. The deposited agglomerates may be disposed on, or in, or both on and in, the porous walls. In one or more embodiments, the plugged honeycomb body comprises inlet channels which are plugged at a distal end of the honeycomb body, and outlet channels which are plugged at a proximal end of the honeycomb body. In one or more embodiments, the agglomerates and/or aggregates thereof are deposited on, or in, or both on and in, the walls defining the inlet channels, or the outlet channels, or both. The flow can be driven by a fan, a blower or a vacuum pump. An exemplary flow rate is in the range of 5 to 200 m³/hr. One exemplary honeycomb body is suitable for use as a gasoline particulate filter (GPF).

[0088] In one or more aspects, the average diameter of the secondary particles or agglomerates is in a range of from 300 nm to 10 microns, 300 nm to 8 microns, 300 nm

micron to 7 microns, 300 nm micron to 6 microns, 300 nm micron to 5 microns, 300 nm micron to 4 microns, or 300 nm micron to 3 microns. In specific embodiments, the average diameter of the secondary particles or agglomerates is in the range of 1.5 microns to 3 microns, including about 2 microns. The average diameter of the secondary particles or agglomerates can be measured by a scanning electron microscope.

[0089] In one or more embodiments, the average diameter of the secondary particles or agglomerates is in a range of from 300 nm to 10 microns, 300 nm to 8 microns, 300 nm to 7 microns, 300 nm to 6 microns, 300 nm to 5 microns, 300 nm to 4 microns, or 300 nm to 3 microns, including the range of 1.5 microns to 3 microns, and including about 2 microns.

[0090] In one or more embodiments, the depositing of the agglomerates onto the porous walls further comprises passing the gaseous carrier stream through the porous walls of the honeycomb body, wherein the walls of the honeycomb body filter out at least some of the agglomerates by trapping the filtered agglomerates on or in the walls of the honeycomb body. In one or more embodiments, the depositing of the agglomerates onto the porous walls comprises filtering the agglomerates from the gaseous carrier stream with the porous walls of the plugged honeycomb body.

[0091] Post-Treatment. A post-treatment may be used to adhere the agglomerates to the honeycomb body, and/or to each other. That is, in one or more embodiments, at least some of the agglomerates adhere to the porous walls. In one or more embodiments, the post-treatment comprises heating and/or curing the binder according to one or more embodiments. In one or more embodiments, the binder causes the agglomerates to adhere or stick to the walls of the honeycomb body. In one or more embodiments, the binder tackifies the agglomerates.

[0092] A calcination treatment is optional, which can be performed at a temperature $\leq 650^{\circ}\text{C}$. Exemplary curing conditions are: a temperature range of from 40°C to 200°C for 10 minutes to 48 hours.

[0093] In one or more embodiments, the agglomerates and/or aggregates thereof are heated after being deposited on the honeycomb body. In one or more embodiments, the heating of the agglomerates causes an organic component of the binder to be removed from the deposited agglomerates. In one or more embodiments, the heating of the agglomerates causes an inorganic component of the binder to physically bond the agglomerates to the walls of the honeycomb body. In one or more embodiments, the heating of the agglomerates causes an inorganic component of the binder to form a porous inorganic structure on the porous walls of the honeycomb body. In one or more embodiments, the heating of the deposited agglomerates burns off or volatilizes an organic component of the binder from the deposited agglomerates.

Apparatus

[0094] Generally, apparatuses suitable for methods herein include a duct that defines a chamber. The duct may have several sections defining differing spaces and chambers. In one or more embodiments, the droplets and the gaseous carrier stream are conveyed through a duct having an outlet end proximate a plugged honeycomb body. The duct may comprise a converging section for engaging a proximal end of the honeycomb body.

[0095] Agglomerates and the gaseous carrier stream pass into the honeycomb body such that the gaseous carrier stream passes through the porous walls of the honeycomb body, and the walls of the honeycomb body trap the agglomerates, wherein the agglomerates and/or aggregates thereof are deposited on or in the walls of the honeycomb body. The inorganic material binds to the ceramic honeycomb body upon post-treatment cure to the ceramic honeycomb body.

[0096] General Overview of Honeycomb Bodies

[0097] The ceramic articles herein comprise honeycomb bodies comprised of a porous ceramic honeycomb structure of porous walls having wall surfaces defining a plurality of inner channels.

[0098] In some embodiments, a honeycomb body comprises a porous ceramic honeycomb body comprising a first end, a second end, and a plurality of walls having wall surfaces defining a plurality of inner channels. A deposited material such as a filtration material, which may be in some portions or some embodiments a porous inorganic layer, is disposed on one or more of the wall surfaces of the honeycomb body. The deposited material such as a filtration material, which may be a porous inorganic layer has a porosity as measured by mercury intrusion porosimetry, SEM, or X-ray tomography in a range of from about 20% to about 95%, or from about 25% to about 95%, or from about 30% to about 95%, or from about 40% to about 95%, or from about 45% to about 95%, or from about 50% to about 95%, or from about 55% to about 95%, or from about 60% to about 95%, or from about 65% to about 95%, or from about 70% to about 95%, or from about 75% to about 95%, or from about 80% to about 95%, or from about 85% to about 95%, from about 30% to about 95%, or from about 40% to about 95%, or from about 45% to about 95%, or from about 50% to about 95%, or from about 55% to about 95%, or from about 60% to about 95%, or from about 65% to about 95%, or from about 70% to about 95%, or from about 75% to about 95%, or from about 80% to about 95%, or from about 85% to about 95%, or from about 20% to about 90%, or from about 25% to about

90%, or from about 30% to about 90%, or from about 40% to about 90%, or from about 45% to about 90%, or from about 50% to about 90%, or from about 55% to about 90%, or from about 60% to about 90%, or from about 65% to about 90%, or from about 70% to about 90%, or from about 75% to about 90%, or from about 80% to about 90%, or from about 85% to about 90%, or from about 20% to about 85%, or from about 25% to about 85%, or from about 30% to about 85%, or from about 40% to about 85%, or from about 45% to about 85%, or from about 50% to about 85%, or from about 55% to about 85%, or from about 60% to about 85%, or from about 65% to about 85%, or from about 70% to about 85%, or from about 75% to about 85%, or from about 80% to about 85%, or from about 20% to about 80%, or from about 25% to about 80%, or from about 30% to about 80%, or from about 40% to about 80%, or from about 45% to about 80%, or from about 50% to about 80%, or from about 55% to about 80%, or from about 60% to about 80%, or from about 65% to about 80%, or from about 70% to about 80%, or from about 75% to about 80%, and the deposited material such as a filtration material, which may be a porous inorganic layer that has an average thickness of greater than or equal to 0.5 μm and less than or equal to 50 μm , or greater than or equal to 0.5 μm and less than or equal to 45 μm , greater than or equal to 0.5 μm and less than or equal to 40 μm , or greater than or equal to 0.5 μm and less than or equal to 35 μm , or greater than or equal to 0.5 μm and less than or equal to 30 μm , greater than or equal to 0.5 μm and less than or equal to 25 μm , or greater than or equal to 0.5 μm and less than or equal to 20 μm , or greater than or equal to 0.5 μm and less than or equal to 15 μm , greater than or equal to 0.5 μm and less than or equal to 10 μm . Various embodiments of honeycomb bodies and methods for forming such honeycomb bodies will be described herein with specific reference to the appended drawings.

[0099] In one or more embodiments, the primary particles are non-spherical. In one or more embodiments, "substantially spherical" refers to agglomerate having circularity in cross section in a range of from about 0.8 to about 1 or from about 0.9 to about 1, with 1 representing a perfect circle. In one or more embodiments, 75% of the primary particles deposited on the honeycomb body have a circularity of less than 0.8. In one or more embodiments, the secondary particles or agglomerates deposited on the honeycomb body have an average circularity greater than 0.9, greater than 0.95, greater than 0.96, greater than 0.97, greater than 0.98, or greater than 0.99.

[00100] Circularity can be measured using a scanning electron microscope (SEM). The term "circularity of the cross-section (or simply circularity)" is a value expressed using the equation shown below. A circle having a circularity of 1 is a perfect circle.

$$\text{Circularity} = (4\pi \times \text{cross-sectional area}) / (\text{length of circumference of the cross-section})^2.$$

[00101] With reference now to FIG. 11, a honeycomb body 100 according to one or more embodiments shown and described herein is depicted. The honeycomb body 100 may, in embodiments, comprise a plurality of walls 115 defining a plurality of inner channels 110. The plurality of inner channels 110 and intersecting channel walls 115 extend between first end 105, which may be an inlet end, and second end 135, which may be an outlet end, of the honeycomb body. The honeycomb body may have one or more of the channels plugged on one, or both of the first end 105 and the second end 135. The pattern of plugged channels of the honeycomb body is not limited. In some embodiments, a pattern of plugged and unplugged channels at one end of the honeycomb body may be, for example, a checkerboard pattern where alternating channels of one end of the honeycomb body are plugged. In some embodiments, plugged channels at one end of the honeycomb body have corresponding unplugged channels at the other end, and unplugged channels at one end of the honeycomb body have corresponding plugged channels at the other end.

[00102] In one or more embodiments, the honeycomb body may be formed from cordierite, aluminum titanate, enstatite, mullite, forsterite, corundum (SiC), spinel, sapphirine, and periclase. In general, cordierite has a composition according to the formula $Mg_2Al_4Si_5O_{18}$.

[00103] In some embodiments, walls of the honeycomb body may have an average thickness from greater than or equal to 25 μm to less than or equal to 250 μm , such as from greater than or equal to 45 μm to less than or equal to 230 μm , greater than or equal to 65 μm to less than or equal to 210 μm , greater than or equal to 65 μm to less than or equal to 190 μm , or greater than or equal to 85 μm to less than or equal to 170 μm . The walls of the honeycomb body can be described to have a base portion comprised of a bulk portion (also referred to herein as the bulk), and surface portions (also referred to herein as the surface). The surface portion of the walls extends from a surface of a wall of the honeycomb body into the wall toward the bulk portion of the honeycomb body. The surface portion may extend from 0 (zero) to a depth of about 10 μm into the base portion of the wall of the honeycomb body. In some embodiments, the surface portion may extend about 5 μm , about 7 μm , or about 9 μm (i.e., a depth of 0 (zero)) into the base portion of the wall. The bulk portion of the honeycomb body constitutes the thickness of wall minus the surface portions. Thus, the bulk portion of the honeycomb body may be determined by the following equation:

$$t_{total} - 2t_{surface}$$

where t_{total} is the total thickness of the wall and $t_{surface}$ is the thickness of the wall surface.

[00104] In one or more embodiments, the bulk of the honeycomb body (prior to applying any filtration material) has a bulk median pore size from greater than or equal to 7 μm to less than or equal to 25 μm , such as from greater than or equal to 12 μm to less than or equal to 22 μm , or from greater than or equal to 12 μm to less than or equal to 18 μm . For example, in some embodiments, the bulk of the honeycomb body may have bulk median pore sizes of about 10 μm , about 11 μm , about 12 μm , about 13 μm , about 14 μm , about 15 μm , about 16 μm , about 17 μm , about 18 μm , about 19 μm , or about 20 μm . Generally, pore sizes of any given material exist in a statistical distribution. Thus, the term "median pore size" or "d50" (prior to applying any filtration material) refers to a length measurement, above which the pore sizes of 50% of the pores lie and below which the pore sizes of the remaining 50% of the pores lie, based on the statistical distribution of all the pores.

[00105] In specific embodiments, the median pore size (d50) of the bulk of the honeycomb body (prior to applying any filtration material) is in a range of from 10 μm to about 16 μm , for example 13-14 μm , and the d10 refers to a length measurement, above which the pore sizes of 90% of the pores lie and below which the pore sizes of the remaining 10% of the pores lie, based on the statistical distribution of all the pores is about 7 μm . In specific embodiments, the d90 refers to a length measurement, above which the pore sizes of 10% of the pores of the bulk of the honeycomb body (prior to applying any filtration material) lie and below which the pore sizes of the remaining 90% of the pores lie, based on the statistical distribution of all the pores is about 30 μm . In specific embodiments, the mean or average diameter (D50) of the secondary particles or agglomerates is greater than 0.5 microns and less than 5 microns, d90 greater than 1 microns and less than 5 microns and d10 greater than 0.3 microns and less than 2 microns.

[00106] In some embodiments, the bulk of the honeycomb body may have bulk porosities, not counting a coating, of from greater than or equal to 50% to less than or equal to 75% as measured by mercury intrusion porosimetry. Other methods for measuring porosity include scanning electron microscopy (SEM) and X-ray tomography, these two methods in particular are valuable for measuring surface porosity and bulk porosity independent from one another. In one or more embodiments, the bulk porosity of the honeycomb body may be in a range of from about 50% to about 75%, in a range of from about 50% to about 70%, in a range of from about 50% to about 65%, in a range of from about 50% to about 60%, in a range of from about 50% to about 58%, in a range of from about 50% to about 56%, or in a range of from about 50% to about 54%, for example.

[00107] In one or more embodiments, the surface portion of the honeycomb body has a surface median pore size from greater than or equal to 7 μm to less than or equal to 20 μm , such as from greater than or equal to 8 μm to less than or equal to 15 μm , or from greater than or equal to 10 μm to less than or equal to 14 μm . For example, in some embodiments, the surface of the honeycomb body may have surface median pore sizes of about 8 μm , about 9 μm , about 10 μm , about 11 μm , about 12 μm , about 13 μm , about 14 μm , or about 15 μm .

[00108] In some embodiments, the surface of the honeycomb body may have surface porosities, prior to application of a filtration material deposit, of from greater than or equal to 35% to less than or equal to 75% as measured by mercury intrusion porosimetry, SEM, or X-ray tomography. In one or more embodiments, the surface porosity of the honeycomb body may be less than 65%, such as less than 60%, less than 55%, less than 50%, less than 48%, less than 46%, less than 44%, less than 42%, less than 40%, less than 38%, or less than 36% for example.

[00109] Referring now to FIGS. 12 and 13, a honeycomb body in the form of a particulate filter 200 is schematically depicted. The particulate filter 200 may be used as a wall-flow filter to filter particulate matter from an exhaust gas stream 250, such as an exhaust gas stream emitted from a gasoline engine, in which case the particulate filter 200 is a gasoline particulate filter. The particulate filter 200 generally comprises a honeycomb body having a plurality of channels 201 or cells which extend between an inlet end 202 and an outlet end 204, defining an overall length L_a (shown in FIG. 13). The channels 201 of the particulate filter 200 are formed by, and at least partially defined by a plurality of intersecting channel walls 206 that extend from the inlet end 202 to the outlet end 204. The particulate filter 200 may also include a skin layer 205 surrounding the plurality of channels 201. This skin layer 205 may be extruded during the formation of the channel walls 206 or formed in later processing as an after-applied skin layer, such as by applying a skinning cement to the outer peripheral portion of the channels.

[00110] In various aspects, it is desirable to maintain the median pore size of the channel wall in a range of from about 8 microns to about 30 microns, for example, in a range of from 10 microns to about 20 microns.

[00111] As mentioned above, the material, which in some portions or some embodiments may be an inorganic layer, on walls of the honeycomb body is very thin compared to thickness of the base portion of the walls of the honeycomb body. As will be discussed in further detail below, the material, which may be an inorganic layer, on the honeycomb body can be formed by methods that permit the deposited material to be applied to surfaces of walls of the

honeycomb body in very thin applications or in some portions, layers. In embodiments, the average thickness of the material, which may be deposit regions or an inorganic layer, on the base portion of the walls of the honeycomb body is greater than or equal to 0.5 μm and less than or equal to 50 μm , or greater than or equal to 0.5 μm and less than or equal to 45 μm , greater than or equal to 0.5 μm and less than or equal to 40 μm , or greater than or equal to 0.5 μm and less than or equal to 35 μm , or greater than or equal to 0.5 μm and less than or equal to 30 μm , greater than or equal to 0.5 μm and less than or equal to 25 μm , or greater than or equal to 0.5 μm and less than or equal to 20 μm , or greater than or equal to 0.5 μm and less than or equal to 15 μm , greater than or equal to 0.5 μm and less than or equal to 10 μm .

[00112] In embodiments, the material, which may in some portions or some embodiments be an inorganic layer, on the walls of the honeycomb body extends from the first end of the honeycomb body to the second end of the honeycomb body. In some embodiments, the material, which may be an inorganic layer, on the walls of the honeycomb body extends the entire distance from the first surface of the honeycomb body to the second surface of the honeycomb body (*i.e.*, extends along 100% of a distance from the first surface of the honeycomb body to the second surface of the honeycomb body).

[00113] The selection of a honeycomb body having a low pressure drop in combination with the low thickness and porosity of the filtration material on the honeycomb body according to embodiments allows a honeycomb body of embodiments to have a low initial pressure drop when compared to other honeycomb bodies. In embodiments, the loading of the layer is in a range of from 0.3 to 30 g/L on the honeycomb body, such as in a range of from 1 to 30 g/L on the honeycomb body, or in a range of from 3 to 30 g/L on the honeycomb body. In other embodiments, the loading of the layer is in a range of from 1 to 20 g/L on the honeycomb body, such as in a range of from 1 to 10 g/L on the honeycomb body. In specific embodiments, the loading of the layer is in a range of from 1 to 9 g/L, 1 to 8 g/L, 1 to 7 g/L, 1 to 6 g/L, 1 to 5 g/L, 1 to 4 g/L, 1 to 3 g/L, 2 to 10 g/L, 2 to 9 g/L, 2 to 8 g/L, 2 to 7 g/L, 2 to 6 g/L, 2 to 5 g/L, 2 to 4 g/L, 3 to 10 g/L, 3 to 9 g/L, 3 to 8 g/L, 3 to 7 g/L, 3 to 6 g/L, 3 to 5 g/L, 4 to 10 g/L, 4 to 9 g/L, 4 to 8 g/L, 4 to 7 g/L, or 4 to 6 g/L on the honeycomb body.

[00114] The material, which is in some embodiments an inorganic filtration material, on the walls of the honeycomb body according to embodiments is thin and has a porosity, and in some embodiments also has good chemical durability and physical stability. The chemical durability and physical stability of the filtration material deposits on the honeycomb body can be determined, in embodiments, by subjecting the honeycomb body to test cycles comprising burn out cycles and an aging test and measuring the initial filtration efficiency before and after the

test cycles. A small change in filtration efficiency (ΔFE) from before the test cycles to after the test cycles indicates better chemical durability and physical stability of the filtration material deposits on the honeycomb body. In some embodiments, the ΔFE is less than or equal to 5%, such as less than or equal to 4%, or less than or equal to 3%. In other embodiments, the ΔFE is less than or equal to 2%, or less than or equal to 1%.

[00115] In some embodiments, the composition of the filtration material deposits on the walls of the honeycomb body is the same as the composition of the honeycomb body. However, in other embodiments, the composition of the filtration material is different from the composition of the walls of the matrix of the honeycomb body.

[00116] Plugged Honeycomb Bodies Comprising Inorganic Material

[00117] Embodiments of the disclosure pertain to plugged honeycomb bodies comprising porous walls and inorganic material deposited on or in or both on and in the porous walls, which provide a filtration article configured to filter particulate from an exhaust gas stream. In specific embodiments, the filtration article comprises a gasoline particulate filters (GPF) used to remove particulates from gasoline engine exhaust gases. Exhaust gas to be filtered enters inlet cells and passes through the cell walls to exit the filter via outlet channels, with the particulates being trapped on or within the inlet cell walls as the gas traverses and then exits the filter. According to one or more embodiments, porous walls of the filtration article having inorganic material deposited on or in or both on and in the porous walls provide improved filtration efficiency and excellent durability, including durability when exposed to water.

[00118] In one or more embodiments, the inorganic material in or on or in and one the porous walls of the filtration article in the form of a plugged honeycomb body is present "clusters" or "chains" of agglomerates and/or aggregates.

[00119] In embodiments, the loading of the inorganic material present on the honeycomb body in a range of from 0.3 to 30 g/L on the honeycomb body, such as in a range of from 1 to 30 g/L on the honeycomb body, or in a range of from 3 to 30 g/L on the honeycomb body. In other embodiments, the loading of the inorganic material is in a range of from 1 to 20 g/L on the honeycomb body, such as in a range of from 1 to 10 g/L on the honeycomb body. In specific embodiments, the loading of the inorganic material is in a range of from 1 to 9 g/L, 1 to 8 g/L, 1 to 7 g/L, 1 to 8 g/L, 1 to 5 g/L, 1 to 4 g/L, 1 to 3 g/L, 2 to 10 g/L, 2 to 9 g/L, 2 to 8 g/L, 2 to 7 g/L, 2 to 6 g/L, 2 to 5 g/L, 2 to 4 g/L, 3 to 10 g/L, 3 to 9 g/L, 3 to 8 g/L, 3 to 7 g/L, 3 to 6 g/L, 3 to 5 g/L, 4 to 10 g/L, 4 to 9 g/L, 4 to 8 g/L, 4 to 7 g/L, or 4 to 6 g/L on the honeycomb body. Loading of the inorganic material is weight of added material in grams divided by the geometric

part volume in liters. The geometric part volume is based on outer dimensions of the honeycomb filter body (or plugged honeycomb body).

[00120] In one or more embodiments, the particles of the inorganic material have a surface area in a range of from 5 m²/g to 15 m²/g, 5 m²/g to 14 m²/g, 5 m²/g to 13 m²/g, 5 m²/g to 12 m²/g, 5 m²/g to 12 m²/g, or 5 m²/g to 10 m²/g.

[00121] In one or more embodiments, prior to heat treatment of the honeycomb body comprising inorganic material on or in or on and in the porous wall, the honeycomb body further comprises a water soluble binder, for example a water soluble silicon-containing binder, a water soluble silicate binder, a water soluble aluminate binder. In one or more embodiments, the binder is present in a range of from 5 wt% to 40 wt%, 5 wt% to 35 wt%, 5 wt% to 30 wt%, 5 wt% to 25 wt%, 5 wt% to 20 wt%, 5 wt% to 15 wt% or 5 wt% to 10 wt% based on the weight of the organic material on the honeycomb body. In one or more embodiments, the binder is silicon-containing. In one or more embodiments, the silicon-containing binder is a silicone resin, or a siloxane, or an alkoxysiloxane, or a silicate. In one or more embodiments, the silicon-containing binder is comprised of an inorganic component and an organic component. In one or more embodiments, the silicon-containing binder transitions to silica upon application of heat. In one or more embodiments, the silicon-containing binder is comprised of an inorganic component and an organic component, and wherein upon application of heat the organic component is driven off and the inorganic component transitions to silica.

EXAMPLES

[00122] Embodiments will be further understood by the following non-limiting examples.

[00123] **Wall-flow filters.** The diameter and length of the wall-flow filter substrates used in the examples were: 5.2 inches (13.2 cm) and 4.724 inches (12 cm), respectively. The CPSI and wall thickness were 200 and 8 mils, respectively. The bulk median pore size was 13.5 microns.

[00124] **Raw Materials.** Unless specified otherwise in the examples, the following raw materials were used. Inorganic material being deposited was alumina, atomizing gas was nitrogen, and particle dispersants and a binder were present. The carrier gas was air.

[00125] Alumina was used as precursor nanoparticles of deposited agglomerates. The alumina was supplied as 30% solids loading in a suspension with ethanol. The alumina particles had: mean size of primary alumina particle of about 0.45 μm, and BET surface area of about 9m²/g.

[00126] Adhesion Promoter: Pluronic L-121, which is an ethylene oxide (EO)/propylene oxide (PO) block copolymer, 10% EO (triblock).

[00127] Particle Dispersant: Triethanolamine (TEA).

[00128] Binder: Dowsil™ US-CF-2405 available from The Dow Chemical Company.

[00129] Ratio of Alumina: TEA: Pluronic: TEA: Dowsil 2405 was fixed at 11:1:1:1.65 (weight ratio).

[00130] A suspension was prepared as follows. The 30% alumina in ethanol suspension was mixed with the TEA dispersant by overhead mechanical stirring. The triblock adhesion promoter was added to this with further mixing by overhead mechanical stirring. The Dowsil 2405 resin was added to this with further mixing by overhead mechanical stirring. A suspension of 11% alumina resulted.

[00131] The liquid vehicle used during processing was absolute ethanol.

[00132] All the examples were prepared by a co-flow aerosol deposition system in accordance with FIG. 9. This system contained one nozzle in chamber center. A temperature of the chamber internals was maintained at 140°C when atomizing the suspension. Conditions included: alumina solids loading, atomizing gas flow rate, liquid flow rate, and carrier gas flow rate.

[00133] SMOKE FILTRATION EFFICIENCY (FE)

[00134] The smoke filtration efficiency performance of the deposited inorganic material disposed within the honeycomb filter bodies can be evaluated using a smoke filtration test.

[00135] The filtration efficiency (in percent %) is calculated as: $FE = \left(1 - \frac{C_{outlet}}{C_{inlet}}\right) * 100$, where C is the smoke concentration on the outlet and inlet side of the part, respectively.

[00136] Two particle counter units (Lighthouse 2016, USA) are used simultaneously at upstream and downstream positions with respect to the article at the underfloor position of a dilution chamber. A cigarette is lit in a smoke generator to provide desired quantity of soot particles into the dilution chamber and the concentration is maintained at a certain level (500,000 particles/cm³) before the smoke travels into the inlet side of the tunnel. The flow is driven by a blower which carries the soot particles through the tunnel and eventually into the wall flow filter parts. When the concentration at upstream of GPF reaches a stable state, the two particle counters reset to begin counting for 20 seconds and filtration efficiency (FE) was calculated based on the differential of total particle count of 0.3 µm and above. The pressure drop (dP) measured by pressure gauges located upstream and downstream from the article is also recorded at a fixed flow of 84 Nm³/hr.

[00137] CLEAN FILTRATION EFFICIENCY

[00138] As used herein, the "clean filtration efficiency" of a honeycomb body or filtration article refers to a new or regenerated honeycomb body that does not comprise any measurable soot loading. In embodiments, the clean filtration efficiency of the honeycomb body or filtration article is greater than or equal to 70%, such as greater than or equal to 80%, or greater than or equal to 85%. In yet other embodiments, the initial filtration efficiency of the honeycomb body or filtration article is greater than 90%, such as greater than or equal to 93%, or greater than or equal to 95%, or greater than or equal to 98%.

[00139] As used herein, "Clean Filtration Efficiency Test" refers to testing an article as follows.

[00140] After pre-test canning for 6 hours, an air stream is supplied by a blower upstream of the article at a ramped rate, and clean pressure drop is measured across the filter using a differential pressure sensor/gauge at room temperature (about 25° C). The flow rate of the air stream was ramped from 25.5 m³/h to 356.8 m³/h over 10 step increases, where the flow rate was maintained for one minute at each new step increase. Each step increase was in a range of about 8 to 68 m³/h. Next, an air stream containing soot particles at a concentration of 8 mg/m³ and a flow rate of 22.5 m³/h is introduced upstream of the filter for 45 minutes. The soot is generated at ~110 nm particle size from a commercially-available propane burner. Clean filtration efficiency at 30° C is determined by measuring the difference between a number of particulates that are introduced into the article and a number of particulates that exit the article before and after exposure to the flow conditions. After the clean filtration efficiency is measured, post-test cleanout is conducted for 6 hours.

[00141] WATER EXPOSURE TEST: WATER NEBULIZER TEST

[00142] As used herein, "Water Nebulizer Test" refers to testing an article as follows. The article is placed in a can which contains a bladder. The bladder is inflated with air to hold the filter in place. Next, clean pressure drop is measured across the filter using a differential pressure sensor/gauge at room temperature (about 25° C). The flow rate of the exhaust gas upstream from the assembly is ramped from 25.5 Nm³/h to 356.8 Nm³/h over 10 step increases, where the flow rate was maintained for one minute at each new step increase. Each step increase is in a range of about 8 - 68 Nm³/h. Next, filtration efficiency is measured at 30° C, with the exhaust flow rate at 21 Nm³/h and 120 nm median particle diameter soot particles at a concentration of 8.5 mg/m³ introduced upstream of the filter using a propane burner for 45 minutes. Particle mass and particle number is measured upstream and downstream of the filter using a AVL microsoot sensor and TSI Engine Exhaust Particle Sizer (EEPS), respectively.

After the filtration efficiency is measured, the article is removed from the can and placed in an oven at 650° C and held at 650° C for 9 hours so that the soot that was loaded into the article was burned out of the honeycomb.

[00143] The article is weighed at room temperature. The article is exposed to a fine mist or spray of water using a nebulizer or atomizer as described in United States Patent No. 7,520,918 until the part is exposed to 15 g/L of water. Next the article is dried in an oven using 250° C for 3 hours. Then, the article and can assembly are tested for filtration efficiency at 21 Nm³/hr at 30° C and 8.5 mg/m³ and the filtration efficiency at 0 g/L soot is compared to that measured before the 650° C heat treatment and nebulizer water exposure. Then, a cleanout procedure is performed on the article in an oven at 650° C for 12 hours. The filter is then removed from the can and exposed to a fine mist or spray of water using a nebulizer or atomizer as described in United States Patent No. 7,520,918 until the part was exposed to 15 g/L of water. Next the article is dried in an oven using 650° C for 9 hours. Then, the article and can assembly are tested for filtration efficiency at 21 Nm³/hr at 30° C and 8.5 mg/m³. Filtration efficiency at 0 g/L soot measured after the second nebulizer water exposure is compared to the baseline filtration efficiency at 0 g/L soot prior to the first 650° C heat treatment and nebulizer water exposure.

[00144] SOOT LOADED PRESSURE DROP TEST

[00145] After pre-test canning for 6 hours, soot is loaded into the article with a flow rate of an exhaust gas upstream from the assembly ramped from 25.5 m³/h to 356.8 m³/h over 10 step increases at about 25° C, where the flow rate was maintained for one minute at each new step increase. Each step increase was in a range of about 8 - 68 m³/h. Soot loading was increased from 0 g/L to 3 g/L. A soot loaded pressure drop is measured across the filter using a differential pressure sensor/gauge at room temperature (about 25° C) after the filter is loaded with soot. After the soot loaded pressure drop was measured, post-test cleanout is conducted for 6 hours.

[00146] Water durability is a robustness attribute. A 70g nebulizer water test was used to evaluate the water resistance performance.

[00147] Thus, aspects disclosed herein include filtration articles comprising: a honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of cells comprising a plurality of axial channels in an axial direction; and filtration material deposits disposed within the honeycomb filter body comprised of agglomerates of primary particles, wherein the primary particles having an average particle size of 300 nm or

less, as measured by SEM with at least 200 sample particles, and wherein the primary particles have a BET surface area of $17 \text{ m}^2/\text{g}$ or less.

[00148] In various of these aspects, the agglomerates comprise nanoparticles.

[00149] In various of these aspects, the filtration material deposits comprise an inorganic material to yield inorganic deposits.

[00150] In various of these aspects, the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size and a second peak corresponding to a second peak agglomerate size, the first peak agglomerate size being greater than the second peak agglomerate size.

[00151] In various of these aspects, a majority of the agglomerates corresponding to the second peak agglomerate size are disposed nearer to surfaces of the axial porous walls of the honeycomb filter body than a majority of the agglomerates corresponding to the first peak agglomerate size.

[00152] In various of these aspects, a local minimum in the multimodal size distribution between the first peak and the second peak occurs at an intermediate agglomerate size which is greater than the second peak agglomerate size and less than the first peak agglomerate size, and wherein the agglomerates corresponding to the first peak agglomerate size are disposed in closer proximity to centers of the axial porous walls in a transverse direction to the axial direction than the agglomerates having the second peak agglomerate size.

[00153] In various of these aspects, the agglomerates corresponding to the second peak agglomerate size are intermingled with the agglomerates corresponding to the first peak agglomerate size.

[00154] In various of these aspects, the honeycomb filter body comprises a bulk median pore size in a range of greater than or equal to $7 \text{ }\mu\text{m}$ to less than or equal to $25 \text{ }\mu\text{m}$.

[00155] In various of these aspects, the honeycomb filter body comprises a bulk median bulk pore size, and a ratio of the first peak agglomerate size to the bulk median pore size is in a range of greater than or equal to 0.02 to less than or equal to 0.225.

[00156] In various of these aspects, the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size in a range of 0.30 to $3.0 \text{ }\mu\text{m}$, and a second peak corresponding to a second peak agglomerate size in a range of 0.30 to $1.7 \text{ }\mu\text{m}$, wherein the first peak has a different value from the second peak.

[00157] In various of these aspects, the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size

near 1.95 μm , and a second peak corresponding to a second peak agglomerate size near 0.44 μm .

[00158] In various of these aspects, the multimodal size distribution comprises two or more number frequency peaks, wherein a ratio of a second peak corresponding to a second peak agglomerate size to a first peak corresponding to a first peak agglomerate size 0.225 to less than 1.

[00159] In various of these aspects, the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size that is greater than or equal to 2.2% to less than or equal to 22.5% of a bulk median pore size of the honeycomb filter body, and a second peak corresponding to a second peak agglomerate size that is 22.5% to less than 100% of the first peak agglomerate size.

[00160] In various of these aspects, the agglomerates comprise particles of differing compositions.

[00161] In various of these aspects, the agglomerates comprise particles of differing BET surface areas.

[00162] In various of these aspects, the agglomerates are comprised of a first set of agglomerates having a first d50 median size and a second set of agglomerates having a second d50 median size.

[00163] In various of these aspects, the first set of agglomerates and the second set of agglomerates are of the same composition.

[00164] In various of these aspects, the first set of agglomerates and the second set of agglomerates are of differing compositions.

[00165] In various of these aspects, the first set of agglomerates and the second set of agglomerates independently have a BET surface area of greater than or equal to 7.0 m^2/g to less than or equal to 10 m^2/g .

[00166] In various of these aspects, the filtration material deposits are bound to the honeycomb filter body.

[00167] In various of these aspects, the filtration material deposits are fused to the honeycomb filter body.

[00168] In various of these aspects, the filtration material deposits are sintered to the honeycomb filter body.

[00169] In various of these aspects, the filtration material deposits are bound to each other, to the honeycomb filter body, or to both, by a silicon-containing binder.

[00170] In various of these aspects, the filtration material deposits are disposed on, or in, or both on and in, at least some of the axial porous walls.

[00171] In various of these aspects, the filtration article comprises a clean filtration efficiency before being exposed to a water nebulizer test of greater than or equal to 88% as measured by a clean filtration efficiency test and the clean filtration efficiency of the filtration article after being exposed to the water nebulizer test is greater than or equal to 83% of the clean filtration efficiency of the filtration article before the water nebulizer test. In various aspects, the clean filtration efficiency of the filtration article after being exposed to the water nebulizer test is greater than or equal 85%, or is greater than or equal to 87%, or is greater than or equal to 90%, or is greater than or equal to 95%.

[00172] In various of these aspects, the filtration material deposits disposed within the honeycomb filter body are at a loading of less than or equal to 15 grams of the filtration material deposits per liter of the honeycomb filter body, or less than or equal to 10 grams of the filtration material deposits per liter of the honeycomb filter body, less than or equal to 7 grams of the filtration material deposits per liter of the honeycomb filter body, or less than or equal to 5 grams of the filtration material deposits per liter of the honeycomb filter body.

[00173] In various of these aspects, the filtration material deposits disposed within the honeycomb filter body are at a loading of greater than or equal to 1 grams of the filtration material deposits per liter of the honeycomb filter body.

[00174] In various of these aspects, the filtration material deposits are free of precious metals.

[00175] In various of these aspects, the porous walls comprise a porosity of greater than or equal to 40% to less than or equal to 70%, or the porosity of the porous ceramic walls is greater than or equal to 45% to less than or equal to 65%, or the porosity of the porous ceramic walls is greater than or equal to 50% to less than or equal to 60%, or the porosity of the porous ceramic walls is greater than or equal to 45% to less than or equal to 50%.

[00176] In various of these aspects, the agglomerates comprise alumina nanoparticles.

[00177] In various of these aspects, the agglomerates comprise refractory metal oxide nanoparticles.

[00178] In various of these aspects, at least a portion of the refractory metal oxide nanoparticles are bonded by silicon or a silicon-containing compound.

[00179] In various of these aspects, at least 50% of the primary particles are substantially spherical, spherical, or globular.

[00180] In various of these aspects, at least 75% of the primary particles are substantially spherical, spherical, or globular.

[00181] In various of these aspects, at least 90% of the primary particles are substantially spherical, spherical, or globular.

[00182] In various of these aspects, the agglomerates are present on at least some of the axial porous walls with a branchlike surface morphology comprised of filaments of agglomerates.

[00183] In various of these aspects, the filtration material deposits are disposed on, or in, or both on and in, at least some of the axial porous walls.

[00184] In various of these aspects, the axial walls extend from an inlet end to an outlet end of the honeycomb structure.

[00185] In various of these aspects, the filtration article further comprises a plurality of plugs disposed in at least some of the cells which seal respective channels of the cells comprising plugs.

[00186] Aspects disclosed herein also include methods for treating a plugged honeycomb filter body comprising filtration depositing of agglomerates comprised of primary particles which are nanoparticles having a BET surface area of $17 \text{ m}^2/\text{g}$ or less, such as primary particles having an average particle size of 300 nm or less, which may be spheroidal.

[00187] Aspects disclosed herein also include methods for treating a plugged honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of axial channels in an axial direction, the methods comprising: atomizing primary particles of a filtration material into particulate droplets comprised of a liquid vehicle, a binder material, and the first particles; evaporating substantially all of the liquid vehicle from the droplets to form agglomerates comprised of the primary particles and the binder material; depositing the agglomerates within the honeycomb filter body; wherein the agglomerates are disposed on, or in, or both on and in, the axial porous walls to yield filtration material deposits disposed within the honeycomb filter body; wherein the primary particles are nanoparticles having a BET surface area of $17 \text{ m}^2/\text{g}$ or less.

[00188] In various of these aspects, the primary particles having an average particle size of 300 nm or less.

[00189] In various of these aspects, at least 50% of the primary particles are substantially spherical, spherical, or globular.

[00190] In various of these aspects, at least 75% of the primary particles are substantially spherical, spherical, or globular.

[00191] In various of these aspects, a first portion of the primary particles are substantially spherical, spherical, or globular, and a second portion of the primary particles are rod-like, elongated, oblong, non-spherical, or irregularly shaped.

[00192] In various of these aspects, the first portion constitutes a majority of the primary particles.

[00193] In various of these aspects, at least 90% of the primary particles are spherical, substantially spherical, nearly spherical, or globular.

[00194] In various of these aspects, the method further comprises curing the binder material to affix the agglomerates to the honeycomb structure, to each other, or both.

[00195] In various of these aspects, the agglomerates are present on at least some of the axial porous walls with a branchlike surface morphology comprised of filaments of agglomerates.

[00196] In various of these aspects, the plugged honeycomb filter body further comprises a plurality of plugs disposed in at least some of the cells which seal respective channels of the cells comprising plugs.

[00197] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus, it is intended that the specification cover the modifications and variations of the various embodiments described herein provided such modification and variations come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A filtration article comprising:
a honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of cells comprising a plurality of axial channels in an axial direction; and
filtration material deposits disposed within the honeycomb filter body comprised of agglomerates of primary particles, wherein the primary particles having an average particle size of 300 nm or less, as measured by SEM with at least 200 sample particles, and wherein the primary particles have a BET surface area of 17 m²/g or less.
2. The filtration article of claim 1, wherein the agglomerates comprise nanoparticles.
3. The filtration article of claim 1 or 2, wherein the filtration material deposits comprise an inorganic material to yield inorganic deposits.
4. The filtration article of any one of claims 1 to 3, wherein the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size and a second peak corresponding to a second peak agglomerate size, the first peak agglomerate size being greater than the second peak agglomerate size.
5. The filtration article of claim 4, wherein a majority of the agglomerates corresponding to the second peak agglomerate size are disposed nearer to surfaces of the axial porous walls of the honeycomb filter body than a majority of the agglomerates corresponding to the first peak agglomerate size.
6. The filtration article of claim 4, wherein a local minimum in the multimodal size distribution between the first peak and the second peak occurs at an intermediate agglomerate size which is greater than the second peak agglomerate size and less than the first peak agglomerate size, and wherein the agglomerates corresponding to the first peak agglomerate size are disposed in closer proximity to centers of the axial porous walls in a transverse direction to the axial direction than the agglomerates having the second peak agglomerate size.

7. The filtration article of claim 4, wherein the agglomerates corresponding to the second peak agglomerate size are intermingled with the agglomerates corresponding to the first peak agglomerate size.
8. The filtration article of any one of claims 1 to 7, wherein the honeycomb filter body comprises a bulk median pore size in a range of greater than or equal to 7 μm to less than or equal to 25 μm .
9. The filtration article of claim 4, wherein the honeycomb filter body comprises a bulk median bulk pore size, and a ratio of the first peak agglomerate size to the bulk median pore size is in a range of greater than or equal to 0.02 to less than or equal to 0.225.
10. The filtration article of any one of claims 1 to 9, wherein the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size in a range of 0.30 to 3.0 μm , and a second peak corresponding to a second peak agglomerate size in a range of 0.30 to 1.7 μm , wherein the first peak has a different value from the second peak.
11. The filtration article of any one of claims 1 to 9, wherein the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size near 1.95 μm , and a second peak corresponding to a second peak agglomerate size near 0.44 μm .
12. The filtration article of any one of claims 1 to 9, wherein the multimodal size distribution comprises two or more number frequency peaks, wherein a ratio of a second peak corresponding to a second peak agglomerate size to a first peak corresponding to a first peak agglomerate size 0.225 to less than 1.
13. The filtration article of any one of claims 1 to 9, wherein the multimodal size distribution comprises two or more number frequency peaks, including a first peak corresponding to a first peak agglomerate size that is greater than or equal to 2.2% to less than or equal to 22.5% of a bulk median pore size of the honeycomb filter body, and a second peak corresponding to a second peak agglomerate size that is 22.5% to less than 100% of the first peak agglomerate size.

14. The filtration article of any one of claims 1 to 13, wherein the agglomerates comprise particles of differing compositions.
15. The filtration article of any one of claims 1 to 14, wherein the agglomerates comprise particles of differing BET surface areas.
16. The filtration article of any one of claims 1 to 15, wherein the agglomerates are comprised of a first set of agglomerates having a first d50 median size and a second set of agglomerates having a second d50 median size.
17. The filtration article of claim 16, wherein the first set of agglomerates and the second set of agglomerates are of the same composition.
18. The filtration article of claim 16, wherein the first set of agglomerates and the second set of agglomerates are of differing compositions.
19. The filtration article of claim 16, wherein the first set of agglomerates and the second set of agglomerates independently have a BET surface area of greater than or equal to $7.0 \text{ m}^2/\text{g}$ to less than or equal to $10 \text{ m}^2/\text{g}$.
20. The filtration article of any one of claims 1 to 19, wherein the filtration material deposits are bound to the honeycomb filter body.
21. The filtration article of any one of claims 1 to 19, wherein the filtration material deposits are fused to the honeycomb filter body.
22. The filtration article of any one of claims 1 to 19, wherein the filtration material deposits are sintered to the honeycomb filter body.
23. The filtration article of any one of claims 1 to 22, wherein the filtration material deposits are bound to each other, to the honeycomb filter body, or to both, by a silicon-containing binder.
24. The filtration article of any one of claims 1 to 23, wherein the filtration material deposits are disposed on, or in, or both on and in, at least some of the axial porous walls.

25. The filtration article of any one of claims 1 to 24 comprising a clean filtration efficiency before being exposed to a water nebulizer test of greater than or equal to 88% as measured by a clean filtration efficiency test and the clean filtration efficiency of the filtration article after being exposed to the water nebulizer test is greater than or equal to 83% of the clean filtration efficiency of the filtration article before the water nebulizer test.

26. The filtration article of claim 25, wherein the clean filtration efficiency of the filtration article after being exposed to the water nebulizer test is greater than or equal to 85%, or is greater than or equal to 87%, or is greater than or equal to 90%, or is greater than or equal to 95%.

27. The filtration article of any one of claims 1 to 26, wherein the filtration material deposits disposed within the honeycomb filter body are at a loading of less than or equal to 15 grams of the filtration material deposits per liter of the honeycomb filter body, or less than or equal to 10 grams of the filtration material deposits per liter of the honeycomb filter body, less than or equal to 7 grams of the filtration material deposits per liter of the honeycomb filter body, or less than or equal to 5 grams of the filtration material deposits per liter of the honeycomb filter body.

28. The filtration article of any one of claims 1 to 27, wherein the filtration material deposits disposed within the honeycomb filter body are at a loading of greater than or equal to 1 grams of the filtration material deposits per liter of the honeycomb filter body.

29. The filtration article of any one of claims 1 to 28, wherein the filtration material deposits are free of precious metals.

30. The filtration article of any one of claims 1 to 29, wherein the porous walls comprise a porosity of greater than or equal to 40% to less than or equal to 70%, or the porosity of the porous ceramic walls is greater than or equal to 45% to less than or equal to 65%, or the porosity of the porous ceramic walls is greater than or equal to 50% to less than or equal to 60%, or the porosity of the porous ceramic walls is greater than or equal to 45% to less than or equal to 50%.

31. The filtration article of any one of claims 1 to 30, wherein the agglomerates comprise alumina nanoparticles.

32. The filtration article of any one of claims 1 to 30, wherein the agglomerates comprise refractory metal oxide nanoparticles.
33. The filtration article of claim 32 wherein at least a portion of the refractory metal oxide nanoparticles are bonded by silicon or a silicon-containing compound.
34. The filtration article of any one of claims 1 to 33 wherein at least 50% of the primary particles are substantially spherical, spherical, or globular.
35. The filtration article of any one of claims 1 to 33 wherein at least 75% of the primary particles are substantially spherical, spherical, or globular.
36. The filtration article of any one of claims 1 to 33 wherein at least 90% of the primary particles are substantially spherical, spherical, or globular.
37. The filtration article of any one of claims 1 to 36 wherein the agglomerates are present on at least some of the axial porous walls with a branchlike surface morphology comprised of filaments of agglomerates.
38. The filtration article of any one of claims 1 to 37 wherein the filtration material deposits are disposed on, or in, or both on and in, at least some of the axial porous walls.
39. The filtration article of any one of claims 1 to 38 the axial walls extend from an inlet end to an outlet end of the honeycomb structure.
40. The filtration article of any one of claims 1 to 39 further comprising a plurality of plugs disposed in at least some of the cells which seal respective channels of the cells comprising plugs.
41. The filtration article of any one of claims 1 to 40 wherein a layer structure is disposed on the porous walls of the honeycomb structure and is comprised of dangling agglomerates or dangling agglomerate chains which are attached to both the porous walls and other individual agglomerates and/or agglomerate chains.

42. A method for treating a plugged honeycomb filter body comprising a honeycomb structure of a plurality of axial porous walls defining a plurality of axial channels in an axial direction, the method comprising:

atomizing primary particles of a filtration material into particulate droplets comprised of a liquid vehicle, a binder material, and the first particles;

evaporating substantially all of the liquid vehicle from the droplets to form

agglomerates comprised of the primary particles and the binder material;

depositing the agglomerates within the honeycomb filter body;

wherein the agglomerates are disposed on, or in, or both on and in, the axial porous walls to yield filtration material deposits disposed within the honeycomb filter body;

wherein the primary particles are nanoparticles having a BET surface area of $17 \text{ m}^2/\text{g}$ or less.

43. The method of claim 42 wherein the primary particles having an average particle size of 300 nm or less.

44. The method of any of claims 42 to 43 wherein at least 50% of the primary particles are substantially spherical, spherical, or globular.

45. The method of any of claims 42 to 44 wherein at least 75% of the primary particles are substantially spherical, spherical, or globular.

46. The method of any of claims 42 to 45 wherein a first portion of the primary particles are substantially spherical, spherical, or globular, and a second portion of the primary particles are rod-like, elongated, oblong, non-spherical, or irregularly shaped.

47. The method of claim 46 wherein the first portion constitutes a majority of the primary particles.

48. The method of any of claims 42 to 47 wherein at least 90% of the primary particles are spherical, substantially spherical, nearly spherical, or globular.

49. The method of any of claims 42 to 48 further comprising curing the binder material to affix the agglomerates to the honeycomb structure, to each other, or both.

50. The method of any of claims 42 to 49 wherein the agglomerates are present on at least some of the axial porous walls with a branchlike surface morphology comprised of filaments of agglomerates.

51. The method of any of claims 42 to 50 wherein the plugged honeycomb filter body further comprises a plurality of plugs disposed in at least some of the cells which seal respective channels of the cells comprising plugs.

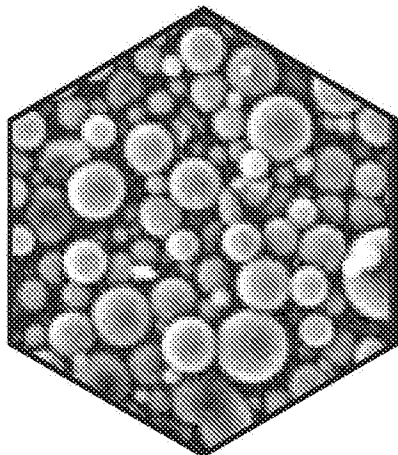


FIG. 2

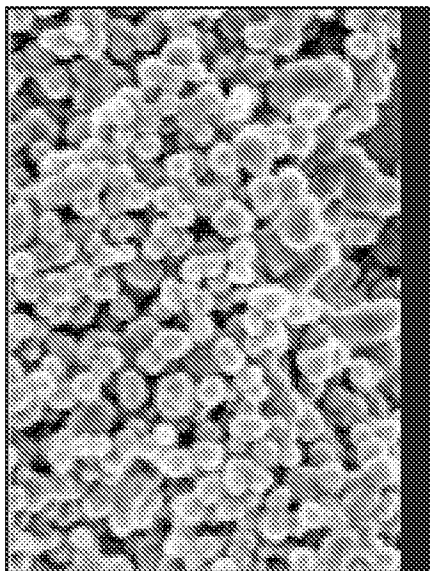


FIG. 1

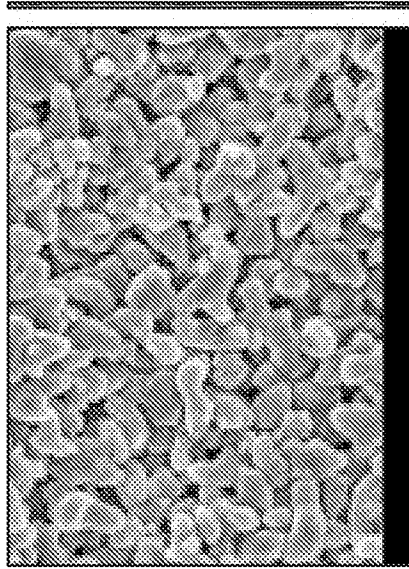


FIG. 4

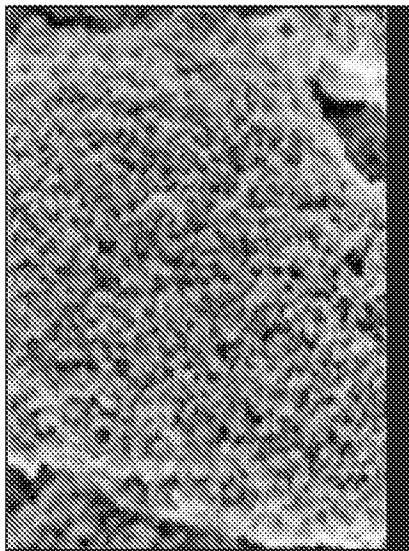


FIG. 3

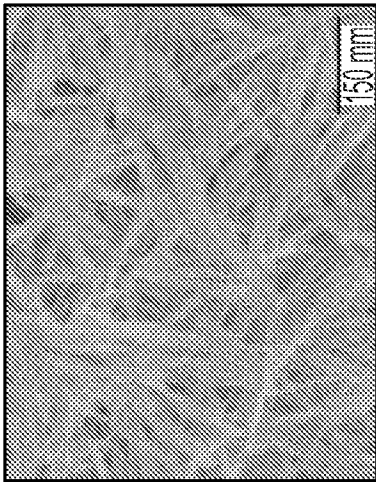


FIG. 6

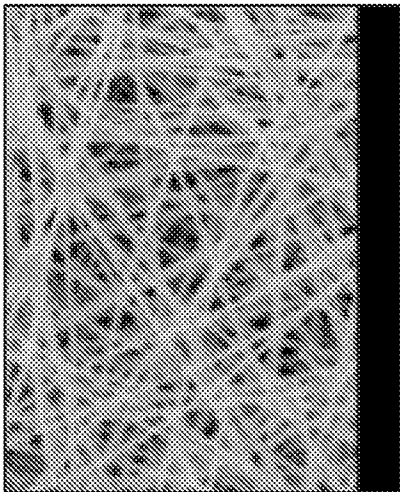


FIG. 5

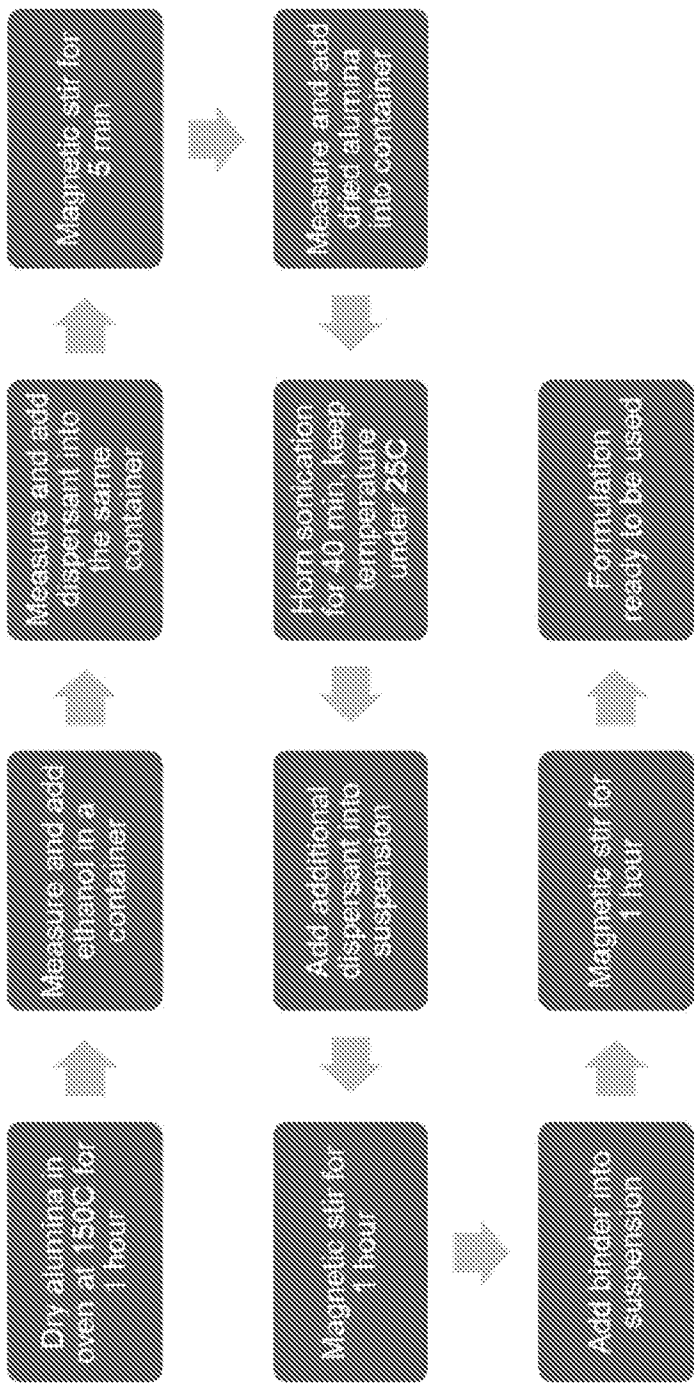


FIG. 8

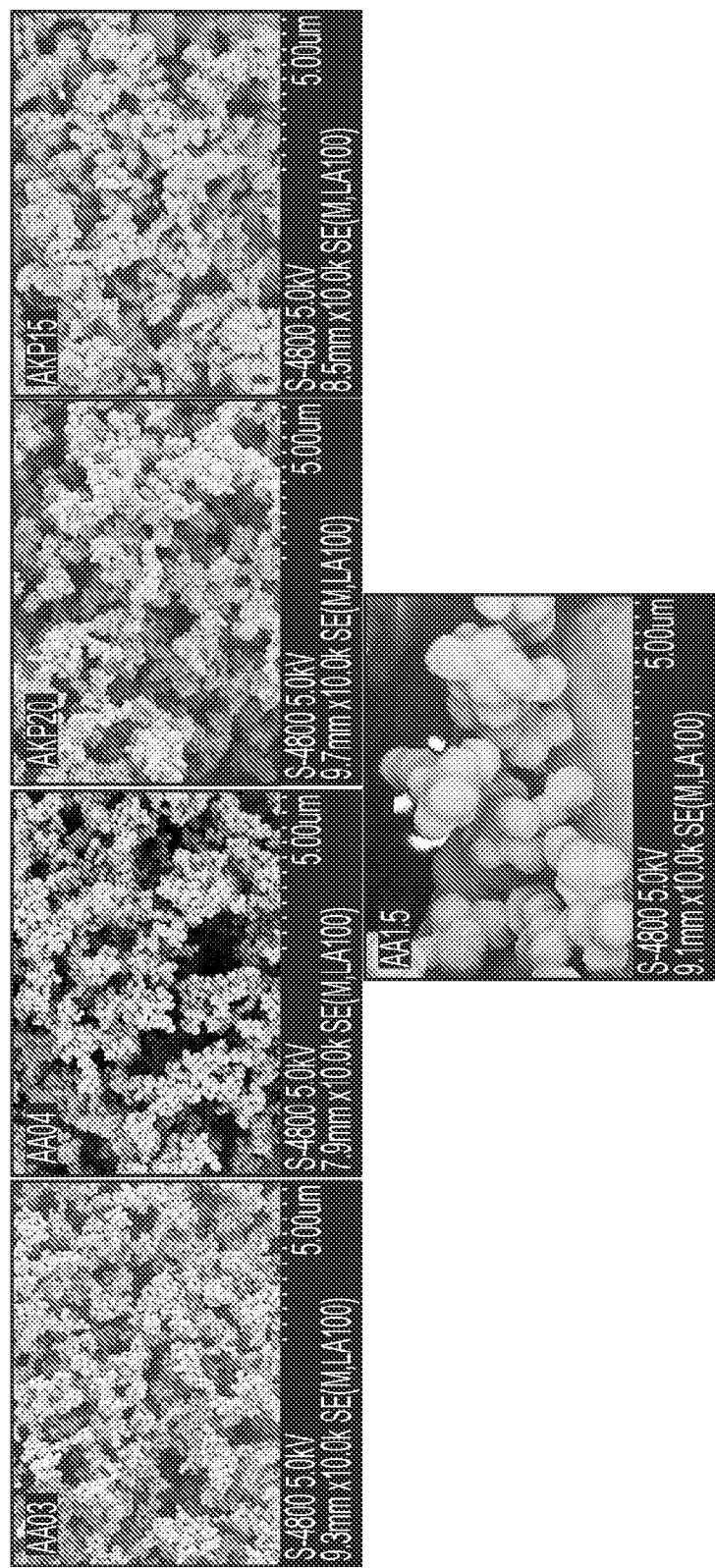


FIG. 9

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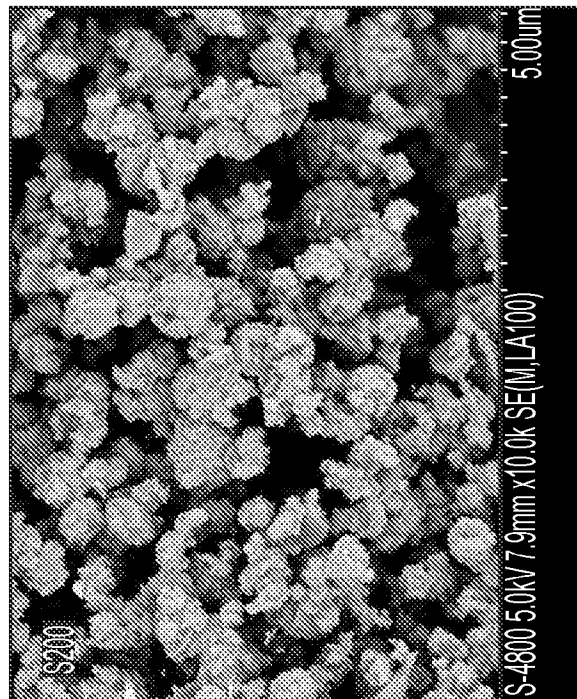
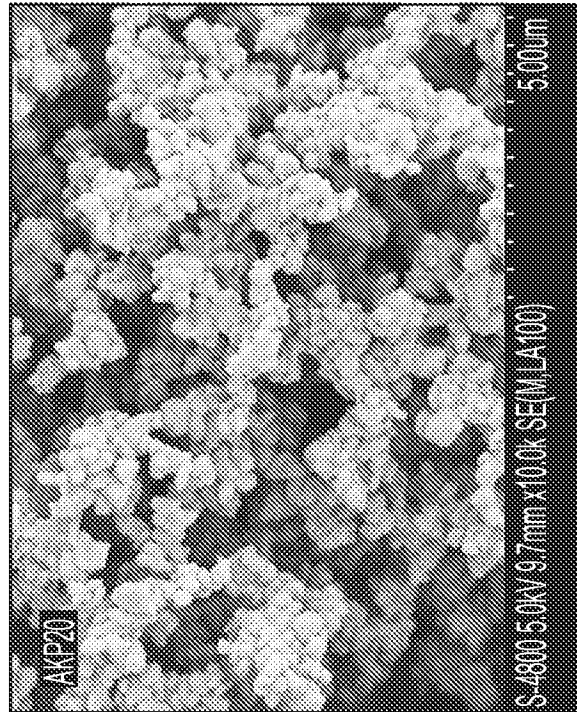


FIG. 10

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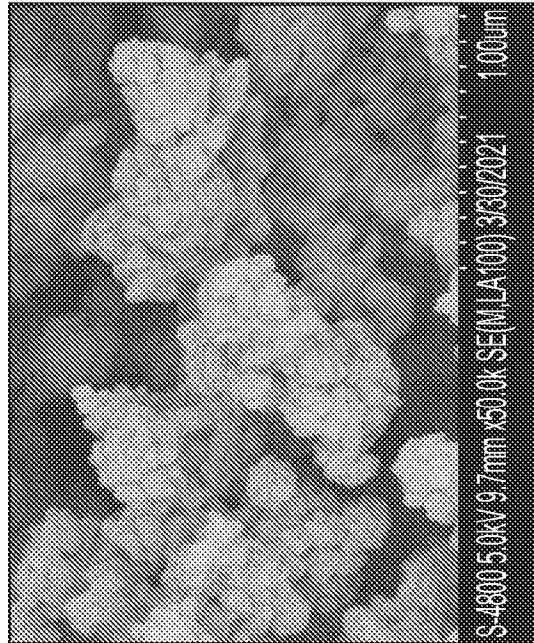


FIG. 12

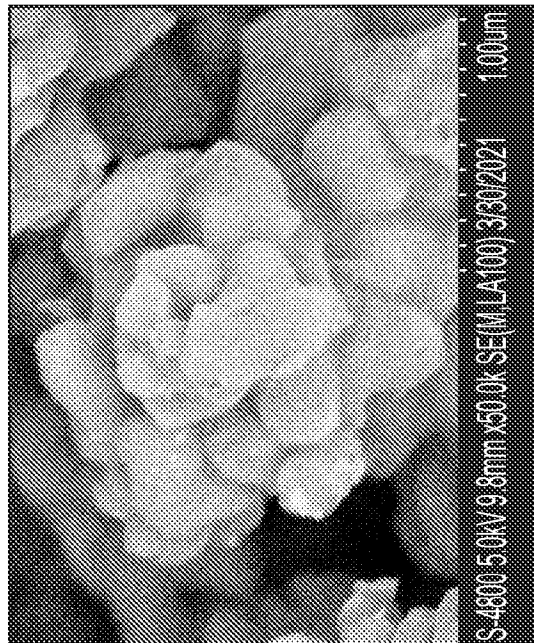


FIG. 11

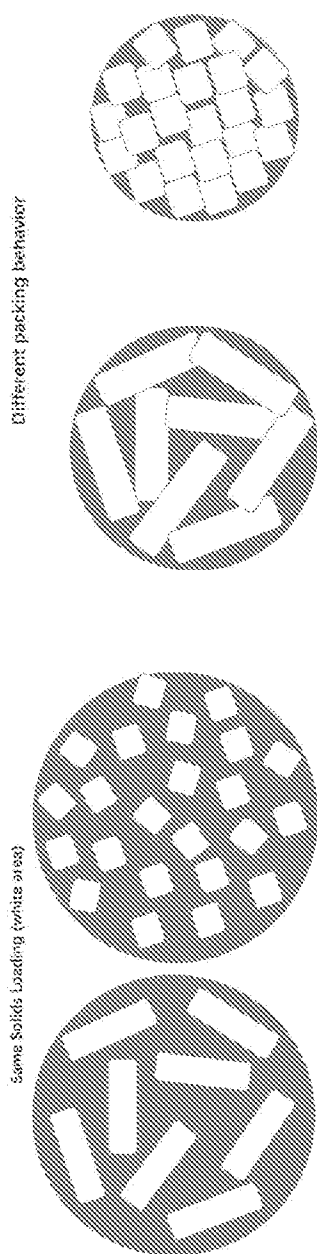
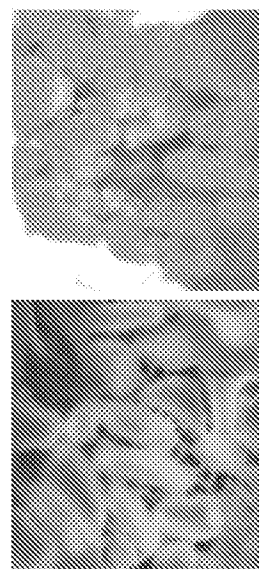


FIG. 14



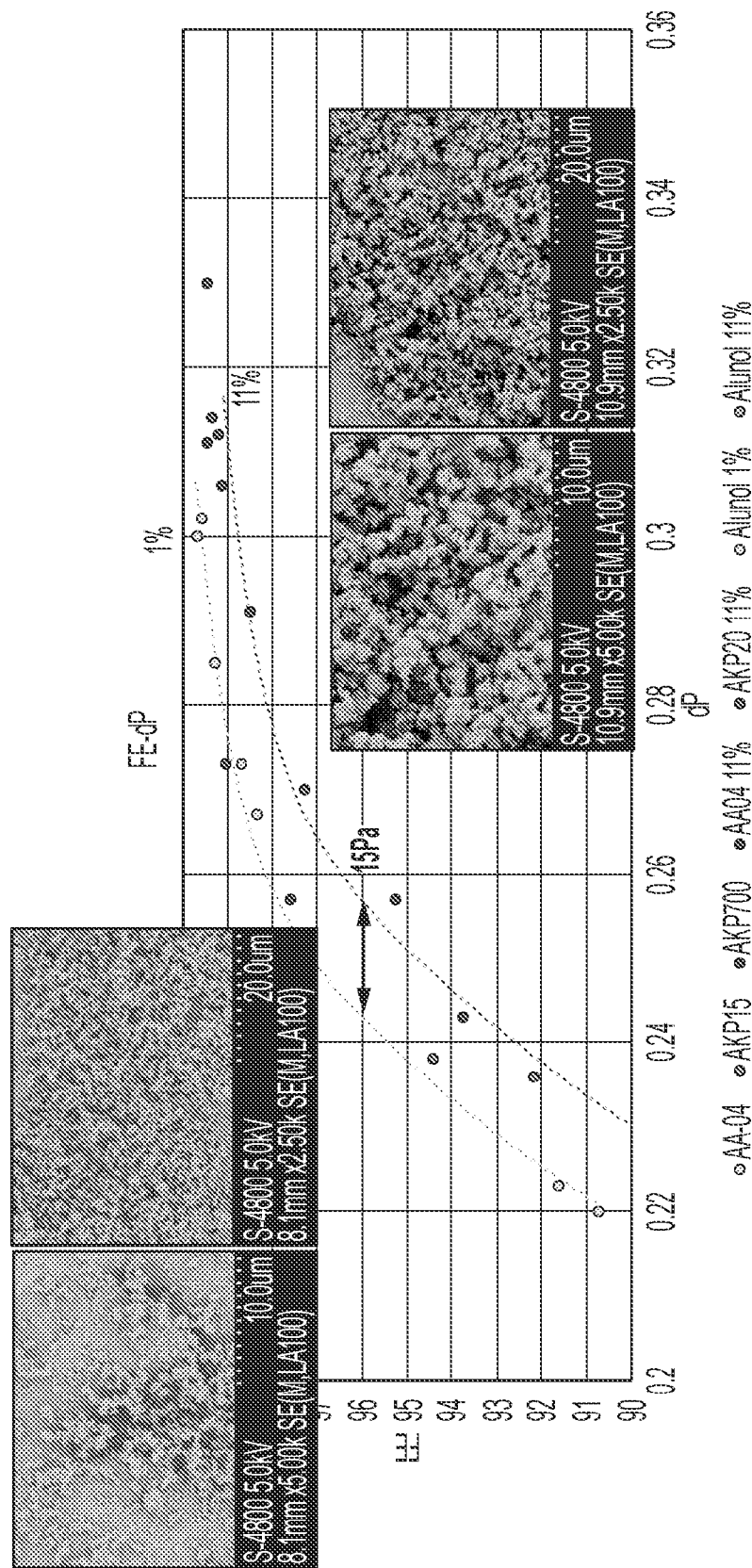


FIG. 16

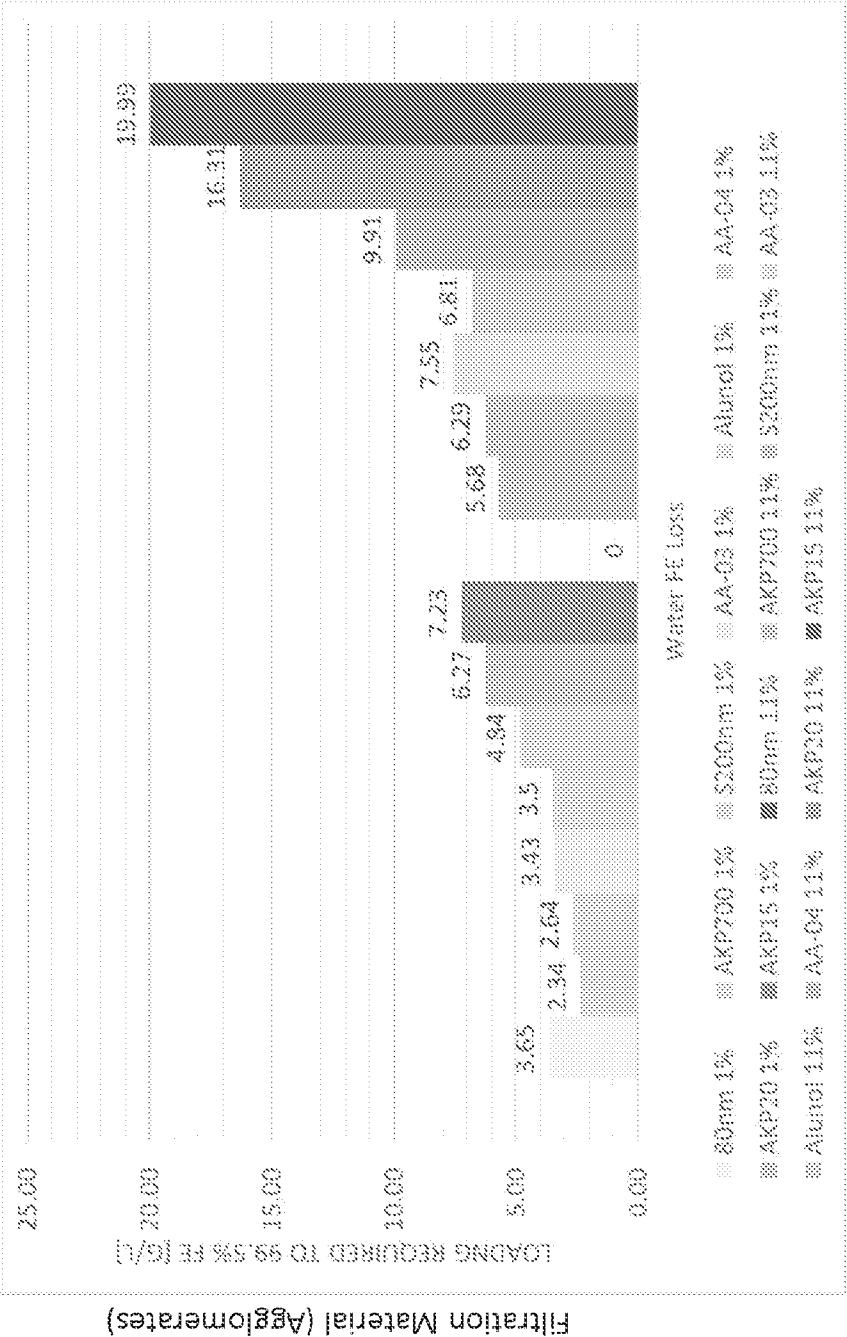


FIG. 17

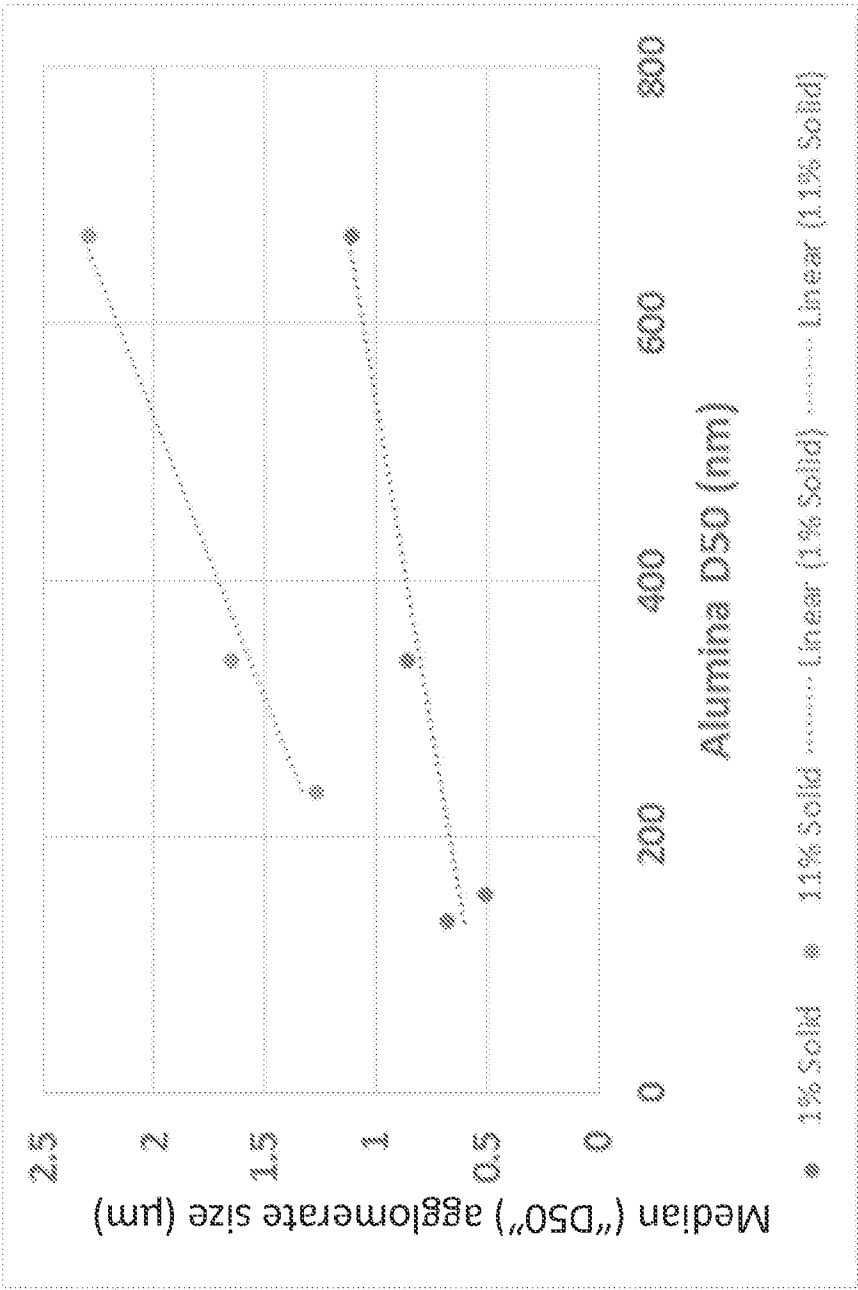


FIG. 18

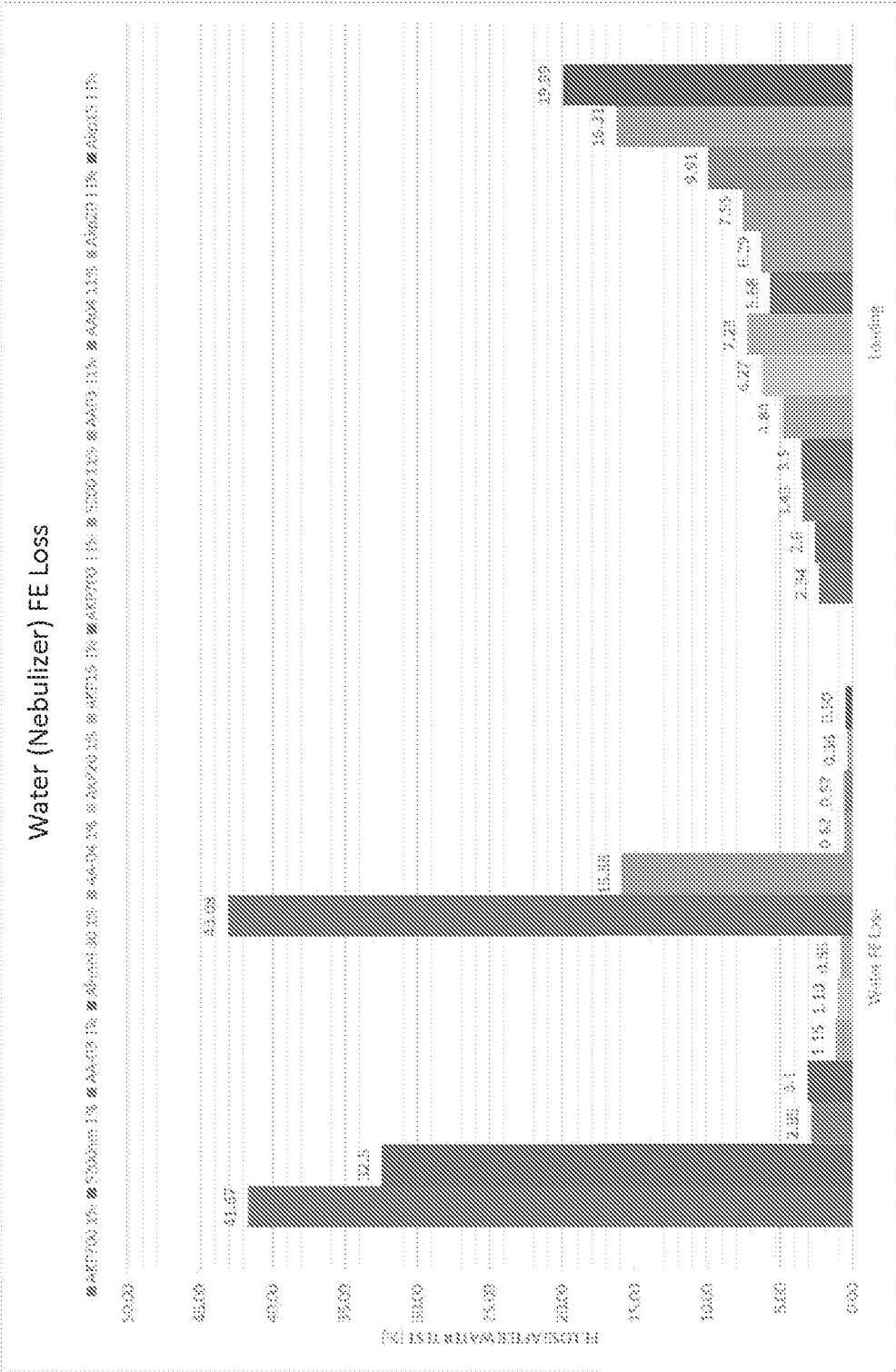


FIG. 19

Primary Particle	Binder Concentration	FE Loss after 850°C Calcination
Alund 30	25%	0.33
Alund 30	40%	0.44
Alund 30	50%	0.63
AKP 700	25%	*
AKP 700	40%	0.31
AKP 700	50%	0.59
S200nm	25%	0.22
S200nm	40%	0.44
S200nm	50%	0.67

FIG. 21

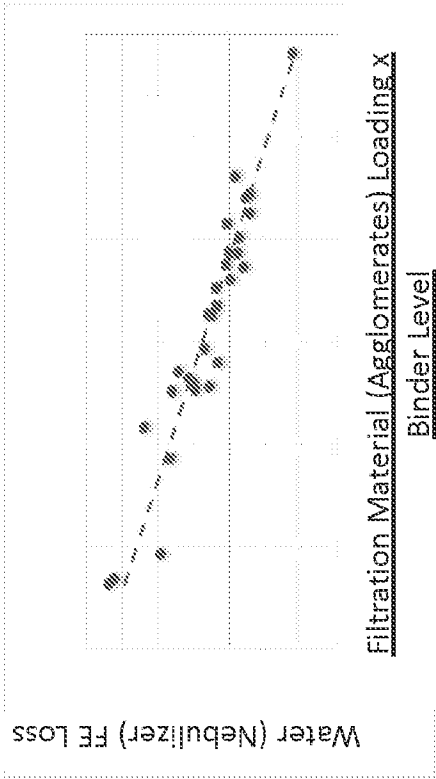


FIG. 20

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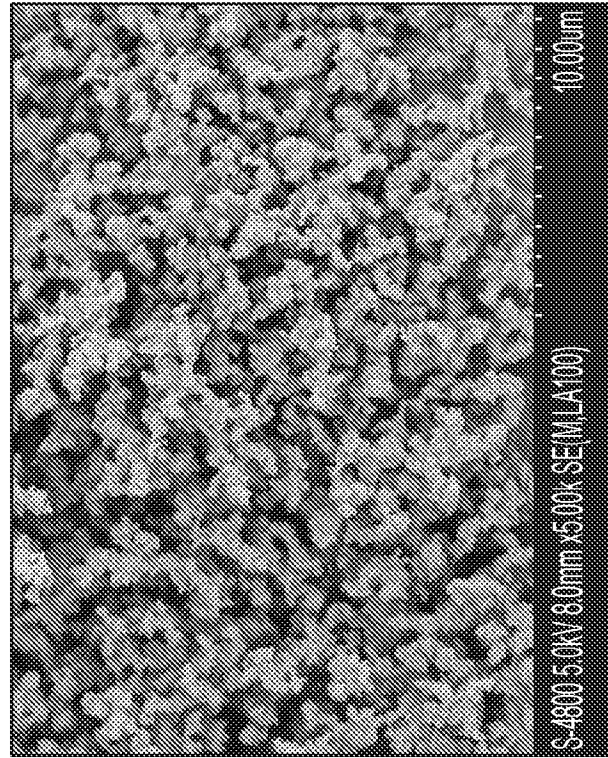


FIG. 23

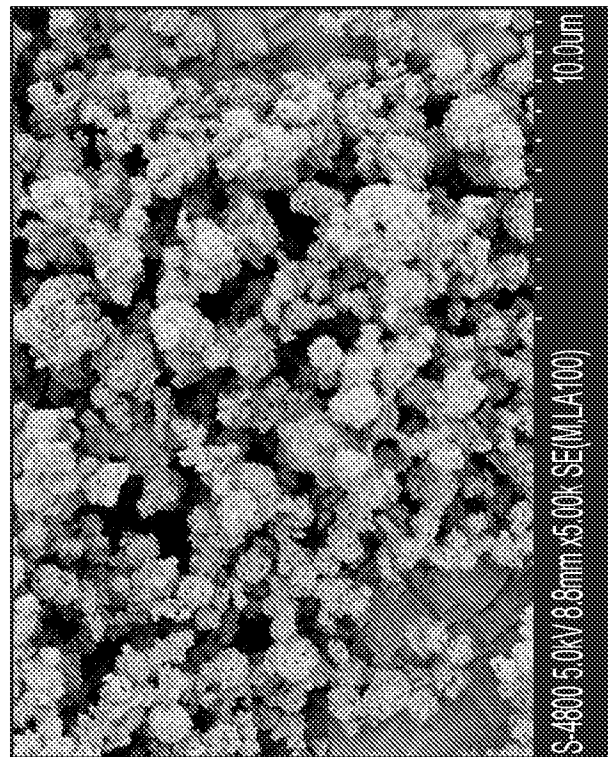


FIG. 22

Primary particle type	Alunol 30	S200
Primary particle size [µm]	0.34	0.13
Primary particle surface area [m2/g]	9	13
Avg. agglomerate size [µm]	1.1	0.6
Loading [g/L] to 99.5% FE	9.3	3.6
dP@1.7m/s [Pa]	325	309
FE Loss after water test @ 4g/L loading [%]	2.7	0.7

FIG. 24

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/055418

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C04B41/45	C04B41/00	C04B41/87	B01D46/24	C04B38/00
	F01N3/022	F01N3/28			
ADD.	C04B111/00				
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)					
C04B B01D F01N					
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					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	WO 2020/047479 A1 (CORNING INC [US])				1-3,8,
	5 March 2020 (2020-03-05)				20-51
Y	paragraphs [0005], [0037], [0043],				4-7,9-19
	[0045], [0053], [0056], [0060],				
	[0073], [0075] - [0077], [0079] -				
	[0081], [0147], [0166], [0180],				
	[0185]; claims; figures; examples; tables				

Y	US 2011/252773 A1 (ARNOLD MIRKO [DE] ET				4-7,9-19
	AL) 20 October 2011 (2011-10-20)				
	examples 10-20; tables 7-9				

X,P	WO 2024/113256 A1 (CORNING INC [US]; WU				1-51
	HUIQING [CN]) 6 June 2024 (2024-06-06)				
	claims; figures; examples; tables				

☐ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
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"A" document defining the general state of the art which is not considered to be of particular relevance			"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		
"E" earlier application or patent but published on or after the international filing date			"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		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"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		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
18 February 2025			28/02/2025		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Bonneau, Sébastien		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/055418

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WO 2024113256	A1	06-06-2024				NONE		
