

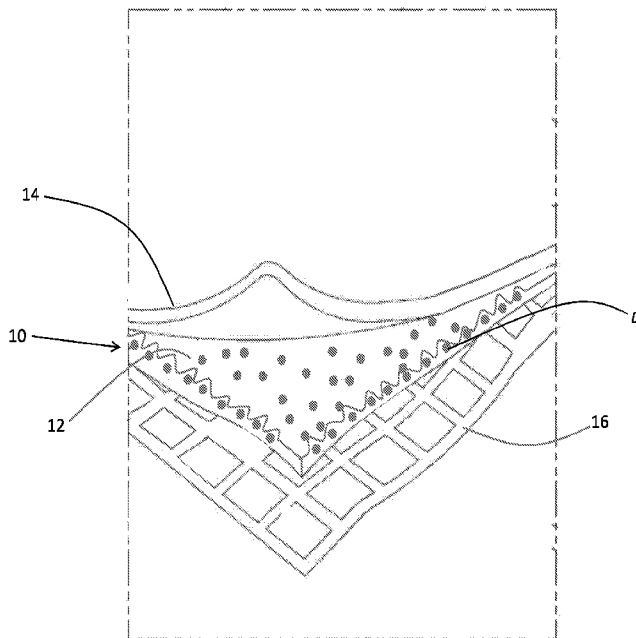


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[Continued on next page]

(54) **Title:** FIBERS AND OTHER CONSTRUCTS TREATED WITH DIATOMITE PARTICLES



(3L Garment Construction)

FIG. 5

(57) **Abstract:** Constructs consisting of diatomized fibers, filaments, yarns, woven and non-woven textiles, fiber-based films, mats, and membranes, other constructs and finished products made from the foregoing. The inventive subject matter is particularly directed to apparel products and molded footwear outsoles, and other molded or textile-based products, wherein a plurality of diatomite particles embedded in the surface of a construct impart desired functionalities, such as moisture management, odor control, or traction or grip enhancement, water and dirt repellency, and wear resistance.

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## **FIBERS AND OTHER CONSTRUCTS TREATED WITH DIATOMITE PARTICLES**

### **BACKGROUND**

In certain aspects, the inventive subject matter is generally directed to moisture management for fiber, yarns and textile-based products. It is particularly directed to moisture absorbing and transporting particles that are applied to fibers, yarns or textiles to enhance dissipation of moisture or transfer of moisture away from surfaces of the substrate material in which the particles are embedded. The inventive subject matter is particularly directed to fibers, yarns and textile-based products, such as fabrics, garments, tents, upholstery, etc., that incorporate particles of diatomaceous earth, which is also known as “diatomite”. In other aspects, the inventive subject matter is directed to other articles with diatomite embedded at surfaces, e.g., outsoles for footwear that incorporate particles of diatomite and gloves.

In the fiber and textiles industries there is a need for improved, engineered products and components that provide desired performance attributes. Moisture and thermal management are among such attributes. For example, in the sports and outdoor apparel industry, various known base layer and mid layer systems exist that help transport moisture user’s skin and evaporate the moisture. Some known solutions are based on incorporating carbonaceous particles derived from biomaterials, such as coconut and spent coffee grounds, at surfaces of fibers and textiles. Fibers treated with bio-based particles have been used in everything from waterproof, breathable laminates to knits in jackets, base layers, hats and gloves, for example. The porous bio-based particles used in the textile fibers work with a user’s body to regulate temperature by accelerating moisture removal and improving dry time.

Despite the advantages of bio-based particle-based technologies, an ever present need remains for the next generation of better performing technologies, and technologies that are easier to use in manufacturing, lower cost, easily sourced from a variety of geographical locations, and more environmentally friendly, and which address other needs of the applicable industries and end user.

Among the disadvantages of carbonaceous, bio-based materials is that they come from sources that are limited or geographically dispersed. For example, coconut derived

materials must come from dispersed coconut-growing regions, which also results in decreased availability or added transportation costs. Carbonaceous materials derived from biomaterials are relatively soft and susceptible to wear under aggressive conditions. For example, they are unsuitable for use under high-abrasion conditions, such as in footwear outsole applications or work or sport gloves applications. The prior art materials, being carbonaceous, biomaterials may not be sufficiently inert to be easily handled or worked in intended applications. For the foregoing and other reasons that will be apparent to persons skilled in the art from the teachings herein and otherwise, a strong need remains for improved, performance enhancing particle technologies in fibers, textiles and apparel, and footwear industries, as well as other industries contemplated herein.

### SUMMARY

The inventive subject matter addresses the foregoing and other needs and is generally directed to constructs consisting of diatomized fibers, filaments, yarns, woven and non-woven textiles, fiber-based films, mats, membranes, and other constructs and finished products made from the foregoing, as contemplated in more detail herein. The inventive subject matter is particularly directed to apparel products and molded natural or synthetic rubber footwear outsoles, and other molded or textile-based products, wherein a plurality of diatomite particles embedded in the surface of a construct impart desired functionalities, such as moisture management, odor control, or traction or grip enhancement, water and dirt repellency, and wear resistance.

The diatomite particles are advantageously lightweight and non-bulky. They may be fused with a base thermoplastic material to form durable, wear and wash resistant constructs.

When used in apparel items, the absorbent and wicking power of the surface-embedded diatomite particles enable the user to stay drier and more comfortable in a wide range of weather conditions and environments. The inventive subject matter may be used in a wide range of apparel products, including, without limitation, base layers and midlayers for running, snow sports, climbing, and hiking applications. They may also be used in underwear, running shorts, biking jerseys, golf shirts, etc., wherever moisture management is desired.

Other advantages include that the particles are natural products that are available from a variety of sources, including ocean, lake, and land sources. They are affordable, stable, and inert. They are easily handled in manufacturing. And they can be chemically modified to provide special functions.

The foregoing is not intended to be an exhaustive list of embodiments and features of the inventive subject matter. Persons skilled in the art are capable of appreciating other embodiments and features from the following detailed description in conjunction with the drawings. These and other embodiments are described in more detail in the following detailed descriptions and the figures. The following is a description of various inventive lines under the inventive subject matter. The appended claims, as originally filed in this document, or as subsequently amended, are hereby incorporated into this Summary section as if written directly in.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

The appended figures show embodiments according to the inventive subject matter, unless noted as showing prior art.

### **DETAILED DESCRIPTION**

#### Overview

Referring again to FIGs. 1-2, diatoms are a type of fresh water or marine algae. The cell walls of diatoms, which are known as “frustules”, are made of opaline silica (SiO<sub>2</sub>) and have a porous structure. Minor amounts of potassium, iron, calcium, magnesium, phosphate, sodium, titanium and other elements may also be included in diatomite.

Large quantities of frustules may be found in some ocean and lake sediments and may be mined therefrom. Diatomite has long been used commercially as filters, mineral fillers, mechanical insecticide, insulation material, anti-caking agents, fine abrasive, and other uses. Diatomaceous earth is generally considered non-toxic and inert.

Representative embodiments according to the inventive subject matter are shown in Figs. 3-22, wherein the same or generally similar features share common reference numerals.

The inventive subject matter is generally directed to constructs consisting of diatomized fibers, filaments, yarns, woven and non-woven textiles, fiber-based films, mats, and membranes, and finished products made from the foregoing, particularly apparel and footwear products, wherein a plurality of diatomite particles embedded in or otherwise applied to the surface of a construct impart desired functionalities, such as moisture management (absorption and transport), thermal management (evaporative cooling), odor control, traction or grip enhancement, wear resistance, or water repellency (in the case of particles made hydrophobic). (As used herein, a “diatomized” construct is one that is treated with diatomite particles embedded in a construct’s surface or coated or otherwise deposited on a construct’s surface.

The surfaces may be some or all the exterior and/or interior surfaces of the substrate material. The surfaces could be the generally exterior cylindrical surfaces of a fiber. In some embodiments, the fibers may be hollow, in which case the surface may include the interior surfaces of the fiber. In other cases, the construct may be a textile, in which case the surfaces could be one or both sides of the textile. In other cases, the construct may be a mat, film or web, in which cases the surfaces may be any one or more exterior side surfaces of the construct or surfaces within the construct consisting of voids, pores of fiber surfaces.

#### Diatomized Fibers

In certain aspects, the inventive subject matter is directed to fibers having a multitude of embedded particles of diatomite. The particles are exposed generally uniformly over one or more surfaces of the fibers or at desired spacings. The fibers are collected in bulk or they may be collected on spools and may be spun into yarns, used as monofilaments, or collected into mats, films or membranes to form non-woven articles.

In other aspects, the inventive subject matter is directed to textiles and other fiber-based constructs that use diatomized yarns, monofilaments and/or multifilaments to form knit or woven textiles or other fiber-based constructs. The textiles may be combined with other textiles to form composite textiles, for example, laminates of single layer units. The textiles may then be formed into various end products, such as apparel products or footwear products.

In another aspect, the inventive subject matter is directed to processes for making fibers incorporating diatomite particles. For instance, the particles are added to a

feedstock for a polymer melt and are dispersed into the melt. The melt composition is then formed into fibers using any of various known fiber-forming techniques, including spin melting, extrusion, blow melting, electrospinning, forcespinning and other techniques based on expelling a polymer melt stream under force from a tiny orifice. Another possibility is printing of the particles onto substrate materials using, for example, an ink-jet type printing system wherein the particles are dispersed in a binder. An advantage of this approach is the ability to create selected patterns on the substrate.

In yet other applications, the diatomite particles can be sprayed to substrates, similar to how anti-slip surfaces, e.g., boat decks, are coated with sand or sand-like particles. In still other applications, diatomite particles can be coated on a substrate in a thin layer as a PU film, thermoplastic film, or rubber (natural or synthetic) film. As discussed below, plasma processing can be used to fix the particles on the fiber. The particles can be added in the plasma feed monomer solution and set onto the fabric via plasma. Or the particles may be applied pre-plasma, and the fabric or rubber material can then be placed into the plasma where the plasma polymerizes the carrier monomers and fixes the diatomite particles into the polymers and on the substrate surface. FIG. 1 shows representative diatomite powder. FIG. 2 shows representative diatomite particles *D*, i.e., diatom frustules. Frustules come in a multiplicity of configurations, each with a multiplicity of holes or pores. The holes or pores usually are of three distinct sizes, ranging from a few microns in diameter down to submicron diameters. The number and sizes of holes vary with the diatom species. Varying properties of diatomite are based on the combination of the natural silica composition, the overall structure of the frustule particle, and the network of holes in the structure. Some properties of diatomite are as follows:

*High Porosity:* 85% of the diatomite particle consists of interconnected pores. Diatomite particles are almost more air than diatom.

*High Absorption:* A diatomite particle can absorb approximately 100% of weight in liquid and still maintain some properties of dry diatom powder.

*High Surface to Particle Ratio:* Diatom particles exist in irregular shapes. Diatoms usually range in particle sizes of less than 1 micron to several hundred microns but typically are in the range of 2-200 microns. The interconnected channels increase the surface area several times as compared to particles of the

same diameters. This increases the reactive surface area without adding weight. Crushing of the diatom frustules can produce fractioned frustule particle sizes in the nanoscale, with the fractionated frustules retaining a porous network that provides the same functionality as intact frustules.

*Absorption and deodorization:* these are natural features of diatomaceous earth.

Diatomite generally comes in two grades: food grade (generally fresh water derived) and industrial grade (generally salt water derived and used in swimming pools). Food grade has low crystal silica (<2%) content as opposed industrial grade which is heated and treated to have approximately 60+ % of crystal silica content. Crystal silica may be bad for respiration and ingestion. Food grade diatoms have countless uses in today's products and processes, from toothpaste to cigars, plastics to paprika. For pools the diatomite is heated to crystalline the structure, so pool diatomite is industrial grade not food grade. In general, to help ensure human compatibility, the inventive subject matter contemplates the use of FDA-approved food grade diatomite, as opposed to Industrial Grade (filter grade) diatomite.

In certain aspects, the inventive subject is directed to fibers having surfaces with embedded diatomite particles. The fibers can be incorporated into textile products to achieve improved moisture management, e.g., absorption, transport or other functional effects, such as absorption of odorous molecules, enhanced traction or other frictional effect. For example, the products may be apparel products that enable the user to stay drier, more comfortable in a wide range of weather conditions and environments. The diatomite particles are lightweight and do not add appreciable weight or bulk. When incorporated at the surface of a substrate by methods disclosed herein, they are durable, and wear and wash resistant. Diatomite particles are high on the hardness scale and will not easily wear down during the normal use of products.

The novel diatomite fiber constructs, which may be referred to herein as "diatomized fibers" (and like expressions), may be formed by admixing diatomite with the feedstock for a fiber and then forming the fiber. The resulting fibers will have embedded diatomite particles, including ones exposed at the surface of the fiber. Accordingly, known fiber forming methods and systems may be used to form fibers with diatomite particles partially embedded in the fiber base material and partially exposed at a



surface of the material. This results in an increase in fiber surface area, which, in conjunction with the porous nature of the particles, promotes evaporative drying and cooling.

As used herein, the terms “fiber” and “filaments” may be used interchangeably. The term “filament” may generally refer to fiber of high aspect ratio, e.g., a fiber of relatively long or continuous lengths that can be spooled around a desired object. Further, synthetic fibers are generally produced as long, continuous filaments. In contrast, “staple fibers” usually refers to natural fibers, which tend to be relatively short because that is how they are typically grown. Long synthetic filaments can be chopped into short staple fibers. In summation, a filament is a fiber, but a fiber can be in different lengths (staple or long or continuous). Filament also generally means a thin strand of material and encompasses yarns, threads, fibers, wires, cables and like thin, strand structures that maybe used to create a knitted, woven and nonwoven textiles. A filament 1, as seen in FIG. 3, may be in a single filament or a multiple filament construct 2, e.g., a yarn, arranged to function as a single strand of material, as seen in FIG. 4.

As used herein in connection to fiber or filament dimensions, “diameter” means the diameter of a circular cross-section, in the strict sense of the word “diameter”, and for filaments that have non-circular cross-sections, e.g., ovals and polygons, diameter means the non-circular filament has a cross-sectional area that corresponds to a circular cross-section that gives the same cross-sectional area. In case of filaments that do not have uniform diameters or cross-sectional areas along the length, an average for the length of a filament may be used. (Averages may also be used for other non-uniform structural or material parameters pertaining to this specification.)

The polymeric fibers formed using the methods and devices of the inventive subject matter may be of a range of lengths based on aspect ratios of at least 100, 500, 1000, 5000 or higher relative to the foregoing fiber diameters. In one embodiment, the length of the polymeric fibers is dependent at least in part, on the length of time the device is rotated or oscillated and/or the amount of polymer fed into the system. For example, it is believed that the polymeric fibers may be formed having lengths of at least 0.5 micrometer, including lengths in the range of about 0.5 micrometers to 10 meters, or more. Additionally, the polymeric fibers may be cut to a desired length using any suitable instrument. Sizes and ranges intermediate to the recited lengths are also part of the inventive subject matter.

The inventive subject matter is not limited to any particular size of fibers, filaments or yarns. For applications in the textile, footwear and outdoor equipment fields, such materials will typically have filaments or yarns with deniers of 50-300D or thereabout. Some suitable yarn or other multifilament configurations for such applications may include, without limitation: 100 Denier with 144 filaments; 75 Denier yarn with 72 filaments; 50 Denier with 48 filaments; and 50 Denier with 36 filaments. Monofilaments with the indicated overall deniers may also be suitable for various applications. A ratio of denier/filament number of 0.25 to 2, or 0.5 to 1.5, 0.75 to about 1.25, or 1.0, or thereabout any of the foregoing ranges, is believed to promote moisture and thermal management by optimizing surface area against other yarn parameters, such as strength, durability and workability of the yarn. It is generally believed that the closer the denier/filament ratio is to 1, the better will be the wicking performance and moisture management, particularly for yarns formed of microfibers.

In one exemplary embodiment, a suitable fiber size for yarns is about 1 Denier (microfiber) or thereabout. A fiber of this size is expected to have good wicking capability. A 1-Denier polyester fiber filament has a linear mass of 0.11mg/meter of fiber, a density of approximately 1.38, and a diameter of approximately 10 microns. Diatomite particle size ranges can range from the nanoscale up to 5 microns in diameter (for use in fiber). Diatomite particles have non-uniform geometries, but will be processed or milled to pass through sieves of specified size ranges. For a 1 Denier polyester fiber, the lower limit of diatomite particles added would be 1% or thereabout by fiber weight, and the upper limit would be 5% or thereabout. Therefore, in 1 meter of a 1 Denier polyester fiber, 0.011mg/m, the amount of diatoms (1% by fiber weight) would be 0.0011mg of diatoms/meter fiber. The amount of diatoms on the surface would ideally be 100% and uniformly distributed. The small surface area of fiber filaments, combined with the diatomite particles, and the increased surface area attributable to the particles, results in the diatomized fiber interacting well with water molecules, wetting the fiber and promoting wicking (movement of moisture) and drying of the fibers and fabric

As the yarn size changes, e.g., 50D/36 filaments, 50D/48 filaments, 70D/72 filaments, etc., the filaments change in diameter and the linear weight of each filament will change. As the filaments increase in diameter, the weight will increase resulting in an increase in diatoms per weight of fiber. However, diatom additions will still fall in the

1-5% diatoms per fiber weight. Naturally, filaments with a Denier>1 will have more diatoms than specified above.

In addition, the above description assumes round cross-section fibers. As fiber cross-sections and geometries change, this could influence the surface area of the fiber available for diatoms to be located. Hollow core, round, and core/sheath fibers are examples where diameter could be similar but linear weight different. However, the range of diatoms added will still be 1-5% by fiber weight.

Depending on the application, diatomite particles may cover from above 0% to 100% of the surface of a construct made of a base material incorporating the particles. In general, for moisture management particles, a high coverage of the surface of fibers with particles is desirable so that the particles can hand-off water molecules in an active transport process. However, too high a weight percentage of the particles in the fiber's base material can cause the fibers to become brittle and unstable. A weight-percent of diatomite particles to thermoplastic base material of equal to or less than 5% or thereabout is believed not to affect substantially the stability of the underlying base material.

#### Processing and Diatomized Fibers and Textile Constructs

Most synthetic and cellulosic manufactured fibers are created by forcing a thick, viscous liquid through the tiny holes of a device called a spinneret to form continuous filaments of semi-solid polymer. In their initial state, the fiber-forming polymers are typically solids and therefore must be first converted into a fluid state for extrusion. This is usually achieved by melting, if the polymers are thermoplastic synthetics or by dissolving them in a suitable solvent if they are non-thermoplastic cellulose. If they cannot be dissolved or melted directly, they must be chemically treated to form soluble or thermoplastic derivatives. Recent technologies have been developed for some specialty fibers made of polymers that do not melt, dissolve, or form appropriate derivatives. For these materials, the small fluid molecules are mixed and reacted to form the otherwise intractable polymers during the extrusion process.

Spinnerets used in the production of most manufactured fibers are well known. A spinneret may have from one to several hundred holes. As the filaments emerge from the holes in the spinneret, the liquid polymer congeals to a rubbery state and then solidifies. This process of extrusion and solidification of endless filaments is called spinning, not to

be confused with the textile operation of the same name, where short pieces of staple fiber are twisted into yarn. There are four methods of spinning filaments of manufactured fibers: wet, dry, melt, and gel spinning.

In all such methods, the polymer being spun first must be converted into a fluid state. If the polymer is a thermoplastic then can be simply melted, otherwise it is dissolved in a solvent or chemically treated to form soluble or thermoplastic derivatives. The molten polymer is then forced through the spinneret, and then it cools to a rubbery state, and then a solidified state. If a polymer solution is used, then the solvent is removed after being forced through the spinneret.

#### Wet spinning

Wet spinning is the oldest of the five processes. This process is used for polymers that need to be dissolved in a solvent to be spun. The spinneret is submerged in a chemical bath that causes the fiber to precipitate, and then solidify, as it emerges. The process gets its name from this "wet" bath. Acrylic, Rayon, Aramid, modacrylic, and Spandex are produced via this process.

A variant of wet spinning is dry jet-wet spinning, where the solution is extruded into air and drawn, and then submerged into a liquid bath. This method is used in Lyocell spinning of dissolved cellulose.

#### Dry spinning

Dry spinning is also used for polymers that must be dissolved in solvent. It differs in that the solidification is achieved through evaporation of the solvent. This is usually achieved by a stream of air or inert gas. Because there is no precipitating liquid involved, the fiber does not need to be dried, and the solvent is more easily recovered. Acetate, triacetate, acrylic, modacrylic, polybenzimidazole fiber, spandex, and vinyon are produced via this process.

#### Melt spinning

Melt spinning is used for polymers that can be melted. The polymer solidifies by cooling after being extruded from the spinneret. Nylon, olefin, polyester, saran, and sulfar are produced via this process.

### Extrusion spinning

Pellets or granules of the solid polymer are fed into an extruder. The pellets are compressed, heated and melted by an extrusion screw, then fed to a spinning pump and into the spinneret.

### Direct spinning

The direct spinning process avoids the stage of solid polymer pellets. The polymer melt is produced from the raw materials, and then from the polymer finisher directly pumped to the spinning mill. Direct spinning is mainly applied during production of polyester fibers and filaments and is dedicated to high production capacity (>100 ton/day).

### Gel spinning

Gel spinning, also known as dry-wet spinning, is used to obtain high strength or other special properties in the fibers. The polymer is in a "gel" state, only partially liquid, which keeps the polymer chains somewhat bound together. These bonds produce strong inter-chain forces in the fiber, which increase its tensile strength. The polymer chains within the fibers also have a large degree of orientation, which increases strength. The fibers are first air dried, then cooled further in a liquid bath. Some high strength polyethylene and aramid fibers are produced via this process

### Electrospinning

Electrospinning uses an electrical charge to draw very fine (typically on the micro or nano scale) fibers from a liquid--either a polymer solution or a polymer melt. Electrospinning shares characteristics of both electrospaying and conventional solution dry spinning of fibers. The process does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes the process particularly suited to the production of fibers using large and complex molecules. Melt electrospinning is also practiced; this method ensures that no solvent can be carried over into the final product.

### Forcespinning

Forcespinning is another spinneret-based technique that may be used. Forcespinning uses centrifugal force to force a stream of polymer material through a micro-orifice, with the polymer stream attenuating into fine fibers, which may be at the

nanoscale. The forcespinning teachings in PCT/US2014/045484, entitled Forcespinning of Fibers and Filaments, international filing date, 03 July 2014, are hereby incorporated by reference in their entirety.

#### Drawing

Following spinning, the fibers may be drawn to increase strength and orientation. This may be done while the polymer is still solidifying or after it has completely cooled.

#### Yarn Spinning

The collected diatomized fibers can be carded for spinning into yarn. The yarn may be used in, for example, apparel, footwear, and equipment end products, to take advantage of the unique properties that may be exhibited by the diatomized fibers.

In addition to the foregoing spinneret-based streams of polymer, any other system for ejecting a stream of polymer material may be used. Fibers may be formed using the known technique of meltblowing or other known techniques. For example, US 6392007, entitled “Multi-Pixel Liquid Streams, Especially Fiber-Forming Polymeric Streams, And Methods and Apparatus for Forming Same”, discloses systems and methods where at least two different liquid streams are sub-divided into a dense plurality of individually separated parallel pixels oriented in respective misregistered arrays. Therefore, an individual pixel of one of the liquid stream arrays will be surrounded by pixels of the other liquid stream array. These individual pixel arrays are then brought into contact with one another to form a multi-pixel liquid stream comprised of the misregistered pixel arrays of the two different liquid streams. The “pixelated” liquid stream—that is, the liquid stream containing in cross-section the misregistered pixel arrays of the two different liquid streams—may then be further processed. For example, the pixelated liquid stream may be subjected to further mixing by being directed along a tortuous flow path.

Suitable base or feedstock polymer materials include natural and synthetic polymers, polymer blends, and other fiber-forming materials. The materials include thermoplastic polyurethane, polyamide, polyester, polypropylene, polytetrafluoroethylene (PTFE) polypropylene (PP), polyurethanes (PU), Polylactic acid (PLA), nylon, bismuth, and beta-lactam fibers, and polyolefin. Polymers and other fiber-forming materials may consist of or include biomaterials (e.g., biodegradable and bioreabsorbable materials,

plant-based biopolymers, bio-based fermented polymers), metals, metallic alloys, ceramics, composites and carbon superfine fibers.

Fiber may include a blending of multiple materials, as indicated above. Fibers may also include holes (e.g., lumen or multi-lumen) or pores. Multi-lumen fibers may be achieved by designing, for example, one or more outlet ports with concentric openings. In certain embodiments, such openings may comprise split openings (i.e., an opening that possesses one or more dividers such that two or more smaller openings are made). Such features may be utilized to attain specific physical properties. For instance, the fibers may be produced for use as thermal insulation, such as in the insulation applications described below, or for use as elastic (resilience) or inelastic force attenuators.

In certain embodiments, textile constructs and films and fibrous webs of the present disclosure may include elastic fibers, such as elastane, polyurethane, and polyacrylate based polymers, to impart stretchability to the nonwoven textiles made according to the inventive subject matter.

In one exemplary embodiment, the inventive subject matter provides diatomized fibers consisting predominantly of polyethylene terephthalate as a fiber-forming polymer, characterized in that the fibers contain about 0.1 to 5 wt % or thereabouts of diatomite to polymer.

Depending on the application, the pores of the diatomite particles may or may not be blocked by the thermoplastic or other base material. The master batch usually creates a suspension that evenly distributes the particles and, during extrusion, ensures that the particles are on the surface of the fiber and the pores are open. Blockage can be determined by microscopy, e.g., scanning electron microscopy. In some cases, blockage will not occur because of, for example, the relative pores sizes in the particles versus (1) the molecular weight or size of the polymer used in the base material, (2) the viscosity of the base material during admixing, and/or (3) the surface tension of the base material during admixing. If the base material is capable of pore blockage, the particles may be pre-treated with a substance that removably blocks pores. Various processes are known, including those disclosed in US 7247374, which is hereby incorporated by reference in its entirety. In general, the removable materials may be thermoplastics or waxes that selectively react to environmental conditions differently from the associated base material. For example, the removable substance may dissolve in a particular solvent in

which the base material is relatively insoluble. Similarly, a specific heating or washing process can be used to remove anything that may have been used to infill or otherwise protect the pores, or that may have unintentionally entered into the pores. As another example, the removable substance could degrade under certain electromagnetic wavelengths whereas the base material is stable.

In some embodiments the exposed area of particles on the surface of the base material for a fiber or other construct is from 3%-50%, or thereabout, of the surface area of the base material. Diatom particle size is typically approximately 1-3 microns and does not exceed approximately 5% of the fiber by linear weight. Particles size in micron size fibers can range from nanometers to approximately 5 microns in diameter. In the case of nanofibers, the particles used may be on the size range of approximately 100-500 nm.

A fabric made with diatomized fibers according to the inventive subject matter can include between 0% to 100% diatomized fibers (in a generally uniform distribution of e.g., weft and/or warp directions in the case of a weavon). In some applications, such as moisture management, it is believed suitable performance attributes are attained if 10% to 100% of the yarns in textile are diatomized. It is believed that particularly suitable performance attributes are attained if the textile has 30% or thereabout diatomized yarns. It is believed that 30% or more diatomized yarns in the textile will provide especially suitable performance attributes.

A non-limiting example of one suitable polymer feedstock to which diatomite particles may be added is polyethylene terephthalate (PET), which may be used to form polyester materials. PET or "polyester" generally includes the polyesters that contain at least 80% polyethylene terephthalate units and a maximum 20% units that come from a diol other than ethylene glycol, such as diethylene glycol, tetramethylene glycol, or a dicarboxylic acid other than terephthalic acid, for example, isophthalic acid, hexahydroterephthalic acid, dibenzoic acid.

In an exemplary embodiment, the inventive subject matter provides a method for the production of melt-spun fibers comprising polyethylene terephthalate as a fiber-forming polymer, through polycondensation or melting of the fiber-forming polymer and subsequently melt spinning the melt into fibers. The method includes the steps of mixing 0.1-5.0 wt % diatomite into the polymer feedstock or the polymer melt material before the melt spinning. In general, the particles will be homogeneously dispersed in the



melted material. During the melt spinning, spinning speeds of 500 to 10,000 m/min should be suitable for many applications. During melt spinning, the fibers are extruded from one or more orifices of the spinneret of the melt spinning system.

The PET itself may also contain the customary additives such as delustering agents (titanium dioxide), stabilizers, catalysts, dyestuffs, etc. Polyethylene terephthalate can optionally be modified with small molar quantities of a branching agent with 3-4 functional alcohol or acid groups, such as trimethylpropane, trimethyloletane, pentaerythrite, glycerin, trimesic acid, trimellitic acid, or pyromellitic acid.

The starting polyester can, however, also contain known additives in order to modify the capability of the coloring, such as sodium-3,5-dicarboxybenzol sulfonate.

In the melt line, for example, there is the possibility of using other dynamic and/or static mixers. For this, dynamic and/or static mixers can also be placed directly in front of the spin pack.

In one embodiment of the invention, the ready-to-use, dispersed, melt mixture that can be produced by any one of the intermixing variants described is not first spun into fibers, but granulated. The granulate can later be processed on conventional spinning machines with a melting extruder, and spun into fibers. In the process, the secondary processor, for example, a customer of the granulate manufacturer, has all the advantages of the polyester modified according to the invention without having to equip its conventional spinning machine with expensive metering and mixing facilities and without having to buy a separate additive. Thus, the entire handling is as simple for the secondary processor as with normal PET granulate.

In addition to novel diatomized fiber constructs, the inventive subject matter is also directed generally to the formation of woven, nonwoven, and knitted textile constructs based on fusion of selected filaments, e.g., yarns or fibers, in a lattice formed of the yarns or fibers to create in the textile asymmetric surfaces or layers in a textile construct. (Herein, products and components therefor, or sections or portions of products or components, may generally be referred to as “constructs.”) As used herein, “lattice” means an arrangement of points or elements in a generally regular periodic pattern, particularly in a crisscrossing, interlacing, inter-looping or intertwined pattern, as in knitted or woven structures. Although not technically within this description due to their irregularity in crisscrossing or intertwining of fiber elements, textiles having a non-

woven, mat or felt form are intended to be included as lattice structures herein unless context dictates otherwise. The textile construct may be formed from a knit or woven structure based on various techniques known in the art. It may be formed from mat or felt structures based on various techniques known in the art.

FIG. 5 schematically shows a construct 10 comprising three layers: diatomized fabric layer 12, optional outer layer 14, and optional inner layer 16. The diatomized layer may be used to control moisture. In an apparel application, the outer layer could be a shell layer in an outdoor jacket. The inner layer could be a comfort liner that goes against a user's skin made of, for example, a mesh fabric. If optional layers 14, 16 are omitted, the diatomized layer 12 could be a base layer used for sports, outdoor applications, and other such uses where moisture management or other functions provided by a diatomized material may be desirable.

FIG. 6 schematically shows an example of an upper body apparel item 18, e.g., a jacket, and lower body apparel item 20, e.g., pants, that may be made in whole or part with construct 10.

More particularly, textiles may be defined as any manufacture from filaments having a generally two-dimensional structure (i.e., a length and a width that are substantially greater than a thickness). In general, textiles may be classified as non-woven textiles or mechanically-manipulated textiles. Non-woven textiles are webs or mats of filaments that are bonded, fused, interlocked, or otherwise joined. As an example, a non-woven textile may be formed by randomly depositing a plurality of polymer filaments upon a surface, such as a moving conveyor. Mechanically-manipulated textiles are often formed by weaving or inter-looping (e.g., knitting) a yarn or a plurality of yarns, usually through a mechanical process involving looms or knitting machines. Whereas woven textiles include yarns that cross each other at right angles (i.e., warp and weft yarns), knitted textiles include one or more yarns that form a plurality of intermeshed loops arranged in courses and wales.

As used herein, "film" means a thin, monolithic layer of material. A film may or may not have porosity but if porous, it has a substantially solid surface area, i.e., open pores do not account for a majority of the surface area. For example, a film may have at least a solid surface area of about 50% to about 100%, and includes, 50%, 65%, 70%,

75%, 80%, 85%, 90%, 95%, 96%, 97%, 98%, 99%, 99.9%, and 99.99% solid surface area.

As used herein, “membrane” means a film that separates two fluids (e.g., water or air external to a garment and air or vapor in the internal (user side) of a garment) and acts as a selective barrier, allowing some particles to pass through preferentially relative to others, e.g., allows water in vapor phase to pass through (e.g., a microporous and hydrophobic membrane) but not water in liquid phase, unless the membrane is a hydrophilic membrane.

The fibers, yarns, threads, and textiles disclosed herein may be used in various articles of apparel (e.g., outerwear, shirts and footwear) and a variety of other articles. For example, the textile constructs may be used in seamless and seamed products and components of products, such as apparel; footwear; gloves; headwear; tents; backpacks; containers or carriers in the nature of luggage and other carriers of items; upholstery for furniture; bed coverings; table coverings; linens; vehicle coverings; tarps; towels; medical textiles; geotextiles; and agrotextiles, wherein the construct comprises at least a portion of any of the constructs claimed herein to diatomized fibers, filaments, yarns, textiles, mats, films or membranes. Various configurations of the textile constructs may also be utilized for industrial purposes, as in automotive and aerospace applications, filter materials, medical textiles, geotextiles, agrotextiles, and industrial apparel. The diatomized fibers and textiles could also be used in gloves, providing a grip side with better grip. Accordingly, the textile constructs may be utilized in a variety of articles for both personal and industrial purposes.

In certain embodiments, the inventive subject matter is directed to a textile construct, and related methods of construction, wherein fusible filaments, such as thermoplastic yarns or fibers 3 in a lattice 90 (FIG. 7) are melted to form a textile construct 100 or 200 that has a partially fused film (FIG. 8) or fully fused film 4 (FIGS. 9-10) on one side or layer while another side or layer is maintained in a discrete knitted or woven structure. The diatomized filaments or yarns in the textile may be at one or both sides or layers of constructs 90, 100, and 200. US application No. 61/943,349, entitled Textile Constructs Formed with Fusible Elements, filed 22 Feb 2014, discloses various textile constructs having fusible filaments and is hereby incorporated by reference in its entirety. The fused film may provide a membrane side or layer that has desired attributes such as waterproofness or water resistance and breathability. The fused film may provide

various functional or performance attributes. For example, it may serve as a complete or partial barrier to air and water, depending on the materials used and/or the degree of fusion. It may serve as a stretchable layer for form fitting. It may serve as durable or protective layer against abrasion or impact force. Any combination of such functional properties may be engineered into a textile construct according to the inventive subject matter.

FIG. 7 shows an example of a plated yarn knit structure for forming a construct 90 with one of the plated yarns consisting of a diatomized yarn 2 and fusible fiber 3. (The fusible yarn has a lower softening or melting temperature relative to non-fusible materials.) The plating places each yarns 2 and 3 on opposite sides of the plated structure. On softening or melting of the fusible fibers, the fusible fibers form a partially or fully melted structure on one side of the construct and the discrete knitted structure will remain on the other side. FIG. 8 shows construct 100, which results from the partial melting of construct 90 from FIG. 7, from the side of the non-fusible yarns 2. FIG. 9 shows construct 100, which results from the complete melting of construct 90 from FIG. 7, from the side of the non-fusible yarns 2. FIG.9 shows construct 200, which results from the complete melting of construct 90 from FIG. 7, from the side of the fusible yarns 3, which now appears as a film 4.

Although a wide range of thermoplastic polymer materials may be used for fusible filaments, examples of suitable thermoplastic polymer materials include thermoplastic polyurethane, polyamide, polyester, polypropylene, and polyolefin. Although fusible filaments may be formed from any of the thermoplastic polymer materials mentioned above, utilizing thermoplastic polyurethane imparts various advantages. For example, various formulations of thermoplastic polyurethane are elastomeric and stretch over one-hundred percent, while exhibiting relatively high stability or tensile strength. In comparison with some other thermoplastic polymer materials, thermoplastic polyurethane readily forms thermal bonds with other elements, as discussed in greater detail below. Also, thermoplastic polyurethane may form foam materials and may be recycled to form a variety of products. In many configurations of a fusible yarn 2, each of the bundled component filaments 1 are entirely or substantially formed from one or more thermoplastic polymer materials. That is, at least 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, or 100% by weight of a filament 1 is a thermoplastic polymer material. Advantages of substantially forming filaments 1 from a thermoplastic polymer material

are uniform properties, the ability to form thermal bonds, efficient manufacture, elastomeric stretch, and relatively high stability or tensile strength. Although a single thermoplastic polymer material may be used, individual filaments 1 may be formed from multiple thermoplastic polymer materials. As an example, an individual filament 1 may have a sheath/core configuration, wherein an exterior sheath of the individual filament 1 is formed from a first thermoplastic polymer material, and an interior core of the individual filament 1 is formed from a second thermoplastic polymer material. As a similar example, an individual filament 1 may have a bi-component configuration, wherein one half of the individual filament 1 is formed from a first thermoplastic polymer material, and an opposite half of the individual filament 1 is formed from a second thermoplastic polymer material. Although each of filaments 1 may be formed from a common thermoplastic polymer material, different filaments 1 may also be formed from different materials. As an example, some of filaments 1 may be formed from a first type of thermoplastic polymer material, whereas other filaments 1 may be formed from a second type of thermoplastic polymer material.

In addition to thermal apparatuses that cause transformation of fusible filaments into films, other apparatuses or energy sources may be used to cause transformations into films, alone or in combination with thermal energy. For example, mechanical presses may be used to facilitate the formation of a film by using filaments that have wax or clay like properties under sufficient conditions and agglomerate and fuse under sufficient pressure. The filaments may also be polymerizable materials that can bond together in the presence of polymerization agent such as a chemical agent or energy source (e.g., electromagnetic radiation in UV or IR spectrum or ultrasonic energy). The filaments may also be of a nature that they soften and become fusible in the presence of a particular solvent or gas.

The polymer material of filaments 1 may be selected to have various stretch properties, and the material may be considered elastomeric. Depending upon the specific properties desired for yarn, filaments 1 may stretch between ten percent to more than eight-hundred percent prior to tensile failure. As a related matter, the thermoplastic polymer material utilized for filaments 1 may be selected to have various recovery properties. That is, yarn or filaments 1 may be formed to return to an original shape after being stretched. Many products that incorporate yarn, such as textiles and articles of apparel formed from the textiles, may benefit from properties that allow yarn to return or

otherwise recover to an original shape after being stretched by one-hundred percent or more. Although many thermoplastic polymer materials exhibit stretch and recovery properties, thermoplastic polyurethane exhibits suitable stretch and recovery properties for various textiles and articles of apparel.

The weight of yarn may vary significantly depending upon the thicknesses of individual filaments 1, the number of filaments 1, and the specific material selected for filaments 1, for example. In general, weight is measured by the unit “tex” or “denier”, which are weights in grams of a certain number meters of yarn, as understood by persons skilled in the art.

A variety of conventional processes may be used to manufacture yarn a composed of one or more thermoplastic and/or diatomized fibers or filaments 1. In general, a manufacturing process for yarn 1 includes (a) extruding or otherwise forming a plurality of filaments 1 from a diatomized and/or thermoplastic polymer material and (b) collecting or bundling filaments 1. Once bundled, filaments 1 may be twisted. Depending upon the specific characteristics desired, yarn may also be subjected to an air texturing operation or other post-processing operations. Fusing processes, as discussed below, may also be performed to form thermal bonds between adjacent filaments 1.

The inventive subject matter also contemplates textile constructs where the diatomization of the constituent filaments or yarns occurred after formation of the filament, yarn or textile. For example, such articles could be formed in whole or part of thermoplastic materials and diatomite could be embedded into the surface of the item while in melted or softened state. This could happen for example by mechanically pressing or kneading the particles into the thermoplastic substrate or air jets forcing the particles into the surface.

The particles could also be attached via chemical bonding into softened, melted or solid substrate surfaces of both thermoplastic materials and non-thermoplastic materials. For example, diatomite particles could be dispersed in epoxy solutions and applied to the substrate.

As already noted, textile constructs according to the inventive subject matter may be incorporated into a variety of products, including various articles of apparel (e.g., shirts pants, footwear). Taking a set of outer garments consisting of, for example, a jacket

or shell 18 and pants 20 (FIG. 6) as an example, a diatomized textile construct may form a majority of each garment, including a torso region and two arm regions for the jacket or shell and a waist and leg regions for the pants. One or more textile constructs may be selectively placed in areas where any of the aforementioned or performance attributes may be desired. For example, in a base layer, the diatomized constructs may be at the underarm areas, the chest and/or back areas, or any other area prone to sweating.

The inventive subject matter also contemplates use of diatomite particles that are modified to provide selective functions. For instance, US 8216674, entitled Superhydrophobic Diatomaceous Earth, discloses superhydrophobic diatomite. The diatomite is prepared by coating the diatomite particles with a hydrophobic coating on the particle surface such that the coating conforms to the topography of the diatomite particles. The hydrophobic coating can be a self-assembly monolayer of a perfluorinated silane coupling agent. The superhydrophobic powder can be applied as a suspension as an additive in polymer feedstock, as discussed above, or in a binder solution to a substrate, to produce a superhydrophobic surface on the substrate.

The hydrophobic diatomite may be used, for example, in yarn as a water repellent treatment on a construct. It may also enhance the durability of the construct via its hardness. For example, the hydrophobic diatomite may be used on yarns to enhance water repellency. It may be used on a textile to provide water repellency and abrasion resistance. In shoe outsoles (discussed below), the hydrophobic diatomite can help keep water out of diatomite particles.

The application, PCT/US2014/045484, which was incorporated by reference above, generally teaches nonwoven textiles consisting of webs of fibers, particularly "superfine" fibers, i.e., fibers with diameters in nanoscale or micron-scale ranges. In certain aspects, the inventive subject matter is directed to production of articles and components of the articles, using novel processes for forming jets of materials that solidify as diatomized fibers, which may be superfine diatomized fibers, and which form into two- or three-dimensional webs as they are collected. The inventive subject is also directed to systems and methods for collecting diatomized fibers of any scale in agglomerations of generally parallel strands for use in forming yarns, for example.

Referring to FIGS. 11-13 and 16-19, exemplary spinneret based systems are schematically shown. In one representative example, the system is a force-spinning system for producing diatomized fibers and collecting them into a desired form, e.g., oriented strands or a cohesive web, such as a film or mat. However, the principles disclosed herein will generally apply to other systems based on jetting of flowable polymer materials, such as those described earlier herein.

The system 210 includes a spinneret 212 that is fluidly coupled to a source of fluid or flowable material, which includes dispersed diatomite particles, that is formable into a diatomized fiber ('fiber-forming material'). The source of material may be a reservoir 214 for continuously feeding the spinneret. The spinneret could itself include a reservoir of polymer material with dispersed diatomite particles that is rotated with the spinneret. The flowable material could be molten material or a solution of material. The spinneret is mechanically coupled to a motor (not shown) that rotates the spinneret in a circular motion. In certain embodiments, the rotating element is rotated within a range of about 500 to about 100,000 RPM. In certain embodiments, the rotation during which material is ejected is at least 5,000 RPM. In other embodiments, it is at least 10,000 RPM. In other embodiments, it is at least 25,000 RPM. In other embodiments, it is at least 50,000 RPM. During rotation, a selected material, for example a polymer melt or polymer solution, is ejected as a jet of material 215 from one or more outlet ports 216 on the spinneret into the surrounding atmosphere. The outward radial centrifugal force stretches the polymer jet as it is projected away from the outlet port, and the jet travels in a curled trajectory due to rotation-dependent inertia. Stretching of the extruded polymer jet 215 is believed to be important in reducing jet diameter over the distance from the nozzle to a collector. The ejected material is expected to solidify into a diatomized fiber by the time it reaches a collector. The system includes a collector 218 for collecting the fiber in a desired manner. For example, the fibers could be ejected from the spinneret onto a surface disposed below the spinneret or on a wall across from outlet ports on the spinneret. The collecting surface could be static or movable. To form a sheet or mat 220 of fibrous material, the surface could be a flat surface. The flat surface could be static or movable.

A movable flat surface could be part of a continuous belt system that feeds the fibrous material into rolls or into other processing systems. Another processing system could be an in-line lamination or material deposition system for laminating or depositing



other materials onto sheet material produced using the force-spinning system or other system for producing sheeted material of superfine fibers. In other embodiments, the flat surface could support a layer of another material onto which the fibers are deposited. For example, the layer of materials onto which diatomized fibers are deposited could be an inner or outer layer for a composite assembly of layers for an end product, such as an item of apparel.

In certain embodiments, the collecting surface is a 3D object such as a mold or 3D component of an end product. FIGS. 11-12 schematically show examples of 3D objects 27, 28 for end products that are shoes or gloves. FIG. 5 schematically shows a 3D object in the form of a down plumule 222 with fiber extensions 1, which may be imitated, as discussed in more detail below. To direct fibers to a desired collecting surface (a “collector”), a fiber-directing system may be made a part of the force-spinning system. For example, the directional system may be configured to provide air from above and/or vacuum from below the desired collector to direct the fibers to the collector.

As the diatomized fibers are laid upon each other, contact points are made at intersections, and the membrane constituents bind together. If any web-bonding of the contact points is desired, it may be accomplished via application of heat (thermal bonding), heat and pressure, and/or chemical bonding. The force-spinning system may include heating elements, pressure applicators, and chemical bonding units for achieving such bonding.

Under the inventive subject matter, spinning of a fiber-forming polymer may be used to provide for multiple layers of diatomized or conventional fibers using combinations of spinneret orifice sizes, orifice geometries, and configurations.

Further diatomized fibers can be made having varying cross-sections in the form of circles, uncollapsed circle (i.e., basically a circular fiber, hollow in the center, that is compressed into an ellipse), or flat ribbons. Additionally, different spinnerets can be included in a force-spinning system, resulting in different fiber diameters or blends. For example, multiple spinnerets in a system can create fiber blends during the spinning. Spinnerets can also be configured with outlet ports that can create a core-sheath structure. Alternatively, a single spinneret with multiple outlet ports, each coupled to a reservoir of a different flowable, fiber-forming material can create blends of diatomized and conventional fibers.

Similarly, diatomized fiber properties can be controlled by providing on the rotary device different outlet ports of varying selected diameters. The inventive subject matter contemplates a range of outlet port diameters from between about 1 to about 1000 micrometers. Larger diameters are also contemplated if relatively high diameter fibers are desired. Channels or passages leading to outlet ports typically would have straight runs. They may be as long as 1-3 millimeters.

In a given system, the diameters and/or shapes or dimensions of the outlet ports may be uniform or they may be varied. In some embodiments, the outlet ports are formed as nozzles of a predetermined length that have decreasing taper toward the port. Outlet ports and associated passages or channels may be formed using known micromilling techniques, or to be discovered techniques. Known techniques include mechanical millings, chemical etching, and laser drilling and ablation. In addition to superfine fibers, forcespinning systems according to the inventive subject matter may be used to create fibers of standard textile size (e.g., 50-150 denier).

Superfine or other fibers may include functional additives such as, but not limited to, antimicrobials, metals, flame-retardants, and ceramics. These materials may be introduced into the spinneret along with the fiber-forming material. They may bond to the material covalently, by hydrogen bonds, ionic bonds or van der Waals forces, for example. A catalyst may be included in the material mixture to facilitate any such bonding.

In any case, for the above-mentioned end products, the fiber mats (ranging from different fiber sizes, materials, or blends) can be layered together to create whole garment composites, or in the case of 3D objects, whole end products, e.g., shoe composites and gloves.

The fiber-forming materials can be chosen by melt temperatures to provide different structural rigidity in the final end product when heat cured after forcespinning or other jetting technique. This may be especially important for 3D structures such as gloves and shoe uppers, which require relatively more durability than other end products, such as outerwear.

The inventive subject matter contemplates use of forcespinning to create diatomized, fiber layers or membranes for use in 2L, 2.5L, and 3L waterproof/breathable products. For example, a diatomized layer may be adjacent to a membrane layer to help

transport moisture through the membrane. Used as a liner fabric, diatoms can absorb moisture and transfer it directly to the membrane to then be transferred through the film. Diatoms adjacent to the film and adjacent to the skin layer can also provide a dry feel and keep the liquid moisture off the wearer.

After textile constructs or membranes are formed, they may, or may not, be coated with a protective film to protect the pores from contamination. Depending on membrane end use, the fibers may optionally be extruded with an oleophobic component to protect the membrane from contamination of dirt and oils, or a similar oleophobic coating can be applied after the membrane is spun. Coating with an oleophobic coating will not cover the pores in the membrane or adversely affect the breathability or air permeability, but will modify the nanofiber surface as to not attract dirt and oil and hence prevent contamination. Those skilled in the art will see the applications of a wet-cure process as well as a vapor/plasma deposition process as both examples of ways to apply an oleophobic, or other, coating to the diatoms without clogging the pores. Particles take on unique properties when at the nanoscale. It is believed that diatoms at the nanoscale, and treated with hydrophobic finishes at the nanoscale, can take on unique properties including super-hydrophobicity. These hydrophobic nanoscale particles when applied to the surface of a fabric can create super-hydrophobicity that is similar to the "lotus-leaf" effect, which provides water-repellency and self-cleaning, as described in more detail below.

Diatomized films or membranes may be directly spun onto the chosen face fabric of the final material, or the membranes may be spun onto contact paper and then laminated onto the chosen face fabric of the final material. The film or membrane, either deposited directly on the fabric, or material, or laminated on the material, may also be used in softshell constructions. The diameter of the diatomized fiber affects pore size of the film or membrane. The cross-sectional morphology of the fibers and fiber thickness affect the surface area of the fibers. Increasing the surface area of the fibers can reduce the pore size. Reducing the fiber diameter is a way to increase surface area/volume ratio. Therefore, fiber diameter is a way to control thickness, durability, and moisture vapor transfer. Thickness affects weight of the membrane. Collectively, these factors influence the breathability and durability of the diatomized fiber film or membrane. Diatomized fiber diameters according to the inventive subject matter can be at any fiber production size, including in the nanoscale range. A suitable range for some waterproof breathable

membrane applications described herein is believed to be about 100 nm to about 1000 nm. Pore size influences air permeability. Therefore, the air permeability for a membrane may be controlled for most applications using nanofibers in the foregoing size range. Fiber-forming materials of use for softshell and waterproof breathable applications, as well as other possible applications, include PFTE dispersions, polyurethanes, nylons, polyesters, bio-based materials, e.g., such cellulosic materials, silk proteins, and other fiber-forming materials that are to be discovered, including other polymers derived from natural and synthetic sources.

In certain embodiments, the flowable, fiber-forming material may be a mixture of two or more polymers and/or two or more copolymers. In other embodiments, the fiber-forming material polymers may be a mixture of one or more polymers and or more copolymers. In other embodiments, the fiber-forming material may be a mixture of one or more synthetic polymers and one or more naturally occurring polymers.

In some embodiments according to the inventive subject matter, the fiber-forming material is fed into a reservoir as a polymer solution, i.e., a polymer dissolved in an appropriate solution. In this embodiment, the methods may further comprise dissolving the polymer in a solvent prior to feeding the polymer into the reservoir. In other embodiments, the polymer is fed into the reservoir as a polymer melt. In such embodiment, the reservoir is heated at a temperature suitable for melting the polymer, e.g., is heated at a temperature of about 100° C to about 300° C.

In some embodiments according to the inventive subject matter, a plurality of micron, submicron or nanometer dimension polymeric diatomized fibers are formed. The plurality of micron, submicron or nanometer dimension polymeric fibers may be of the same diameter or of different diameters.

In some embodiments, in addition to conventional fiber sizes, the methods of the inventive subject matter result in the fabrication of diatomized fibers of micron, submicron or nanometer dimensions. For example, it is believed possible to fabricate polymeric fibers having diameters (or similar cross-sectional dimension for non-circular shapes) of about 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650,

660, 670, 680, 690, 700, 710, 720, 730, 740, 750, 760, 770, 780, 790, 800, 810, 820, 830, 840, 850, 860, 870, 880, 890, 900, 910, 920, 930, 940, 950, 960, 970, 980, 990, 1000 nanometers, or 2, 5, 10, 20, 30, 40, or about 50 micrometers. Sizes and ranges intermediate to the recited diameters are also part of the inventive subject matter. Forcespinning is believed one possible technique for creating the foregoing superfine, diatomized fibers

### Yarn Formation

After fibers are created, fibers are made into yarns. For synthetic fibers there are two types of yarns: filament yarns and spun yarns. Filament yarns are composed of many lengthy fibers agglomerated together and typically oriented with longitudinal axes in parallel with each other. A filament is a single continuous fiber that has been extruded. Filaments can be grouped or agglomerated together with the individual fibers in a generally parallel orientation. The bundle of grouped fibers is then twisted to create a thicker and stronger yarn. Fabrics use both multi-filament yarns and single monofilaments.

Synthetic spun yarns are produced using staple fibers. Staple fibers are short fibers of about 0.75 to 18 inches long. Excluding silk, natural fibers are staple fibers. To create synthetic staple fibers, the fiber is extruded, drawn and tensioned or crimped, and then cut to the staple fiber length. These staples are then baled for downstream processing into woven, knit, or nonwoven fabrics. Staple fibers are then combined together and spun to create yarn made up of thousands of short filaments. These spun yarns are produced in much the same way as cotton or wool yarn is produced.

Carding is the mechanical process that disentangles, cleans, and orients fibers into a continuous web that is used to spin yarn. The process breaks up clumps of unorganized fibers and aligns the fibers of similar lengths. Natural fibers, such as wool and cotton, are often in clumps of entangled fibers of different fiber lengths. These clumps are carded and combed into parallel, aligned staple fibers of similar length. These staple fibers are then spun into yarn that is used in woven and knitted fabrics.

In the case of cotton bundles, the basic carding process includes: opening the tufts into individual fibers, removing impurities, selecting fibers on the basis of length (removing the shortest ones), removing naps, orienting the fiber in a parallel fashion and stretching the fiber, transforming the lap into a sliver, resulting in a regular mass of

untwisted fiber. A sliver is the long bundle of created fiber that is used to spin yarn. All the foregoing discussion on yarns formation applies to yarns formed of diatomized filaments.

### Staple Fibers

As noted above, fibers can be cut and carded as staple fibers. It is possible to change the size of the spinnerets, increasing or decreasing the orifice diameters, to draw long, fibers of larger diameter size. For example, deniers ranging from 1 to 300 denier or thereabout are contemplated from forcespinning methods, for example. A given spinneret may have one or more orifices that are all of the same size. Or, it may have a plurality of orifices of different diameters or configurations for a plurality of fiber deniers or configurations.

Fiber mats consisting of fibers in the 1D-300D range can act similarly to that of bundles of natural fibers like cotton and wool. It is believed that using the novel systems disclosed and contemplated herein, loosely packed mats or battings, of long, continuous force spun fibers can be processed into staple fibers using the same processes used for natural fiber. Wool, cotton, jute, etc., may use different mechanisms for combing and carding machines. Therefore, there are many options available to separate the spun fibrous mats into desired lengths of staple fibers.

Creating staple fibers from forcespinning advantageously uses little energy. Long continuous filaments are agglomerated in generally parallel orientation, and they can easily be cut and carded to produce uniform staple fibers. Conventional processes are limited by fiber size. In addition, forcespinning provides the ability to create fibers from a variety of raw materials, as disclosed herein. In contrast, conventional processes have a limited ability to efficiently produce a variety of natural, synthetic, and bio-based fibers. For example, polyester can be extruded in long continuous filaments (like fishing line). These filaments can be used as is, or cut into staple fibers. For forcespinning, the fibers are relatively long, compared to electrospinning, and the mats can then be cut and carded like staple fibers. The fiber mats are representative of cotton bundles of unoriented staple fibers. However, it is contemplated that as the orifice sizes on the spinnerets increase to fiber deniers of 50 and above, the strength of the fiber increases. Because of this, the length of the extruded fibers can increase. It is contemplated that the parameters, such as rotating speed, orifice size, and solution melt can be adapted for a desired result without

undue experimentation. In any case, i.e., forcespinning of nanofibers to large denier fibers, the carding and cutting into staple fibers would follow similar approaches.

#### Forcespinning Continuous Filament Fibers

From the nanoscale to larger diameters, the inventive subject matter is directed to the production of longer more continuous diatomized filaments from forcespun fibers or other jetting techniques. Using Forcespinning as a representative example, relatively large fibers diameters of 1 denier to 300 denier or thereabout, as well as other deniers or diameters disclosed herein. Filament tensile strength is increased as fiber diameters increase.

Over traditional extrusion processes, the forcespinning approaches disclosed herein advantageously reduce the amount of heated drums and tension devices required to draw and orient the fiber because the forcespinning naturally orients the fibers. Traditional drawing and orienting of fibers, and extrusion, can require space of up to 3 stories of height. Forcespinning is a single apparatus of small dimension, quiet, and requires little energy. In the case of some fibers, the requirement may be to include heaters and tensioning devices. This is also envisioned, and can be included at points between the collector and spinneret or in post processing. However, post processing is envisioned at smaller scale than requirements of current manufacturing. Similar to nanofiber mats, larger fiber forcespun mats can be twisted into yarns directly from the mats. This twisting causes entanglements similar to that yarns from staple fibers. If a higher degree of fiber orientation is desired the mats can be carded as previously described.

FIGS. 11-21 show alternative embodiments of a force spinning or other jet extrusion system with a fiber collection system that collects diatomized or other filaments or fibers and spool them as continuous filaments or fibers. (System elements are not meant for conceptual illustration and are not meant to be at scale.) As a jet of fiber-forming material 215 exits the orifice of a spinneret and centrifugal force draws the filament or fiber, and it aligns the fiber and provides strength by orienting the polymer chains within the fiber. This is similar to other jet extrusion processes disclosed herein. For example, the jet may include a material selected from the group of polyesters, nylons, natural fibers (e.g., cellulose), bio-based (natural derived, synthesized), blends of biocomponent fibers and fibers of unique cross-sections (core-sheath), and any other

material disclosed or contemplated herein. The fiber-forming material may include dispersed particles to increase fiber performance or conductance, for example. Any of the fiber-forming materials may be collected as continuous filaments using a myriad of collection methods. A few representative methods are outlined below. However, these examples are not meant to be an exhaustive list. Those skilled in the art will realize from the teachings herein that many techniques and apparatuses can be employed to collect the diatomized fibers.

Use of a spinneret that ejects a jet or stream of material under centrifugal force offers similarities to the production of cotton candy. As used herein, “stream” or “jet” means a fibrous or filamentous flow of material in any state, e.g., liquid, softened, or solid. An example of a solid stream of material would be a moving yarn being pulled to or from a spool. As used herein, “structure” or “strand” in the context of fibers means a solid phase fibrous or filamentous material. In the processing steps contemplated herein, the structure or strand may be present in a dynamic state, as in a streaming state, or it may be present in a static state.

In cotton-candy makers, strands of cotton candy fiber are formed by spinning a liquid that exits from a spinneret centered in a collector. The collector in which the spinneret is centered is basically a round bowl. The strands collect on the surrounding, vertical walls of the collector. A spooler, which is an elongate object, e.g., a paper cone, is then moved in a circular path along the walls of the collector, with the longitudinal axis of the spooler oriented parallel to the collector’s walls. While the spooler circles the walls, it pulls off the fiber strands deposited on the walls. While the spooler is circling along the walls, it is also rotated around its longitudinal axis. This additional rotation winds the fibers around the spooler, to create a uniform deposition of fiber strands around the spooler. In the case of cotton candy, the fibers are weak, short, sticky, and wound without tension. Therefore, the process is not intended for use where compact spooling of fibers is needed, or where fibers are not sticky and easily attracted to a spooler from the walls on which they are deposited. Further, the cotton-candy maker approach offers no solution to the problem of how to wind the mat of collected fibers into a continuous filamentous form that is preferably, but not necessarily, under some tension to enable compact winding and spooling.

In the following examples, collection and spooling methods are disclosed for use with the forspinning or other spinning technique of continuous fibers intended for use



in textile applications. The inventive subject matter overcomes the deficiency of the simple cotton-candy maker approach, which is not concerned with reducing the cotton-candy mats to a lengthy filamentous form, which may be under some tension.

FIGS. 18-23 show examples of collection systems that include one or more collectors 18, 118, 218, 318, 418, 518 and 618, each having a surface for receiving streaming material from the spinneret. According to the inventive subject matter, a collector 318 may be associated with and rotated in coordination with the spinneret's spinning orifice 216. Alternatively, a stationary, non-orbital collector may be stationary and located beneath the geometric center of the spinneret 212 for a spinning system. The relative spin rates of the collector and spinneret are coordinated so that the filamentous fiber 215 is spooled onto the collector within a tension range that (1) achieves a desired state of compactness without straining the fiber to a breakage or deformation state; and (2) avoids a slackness in the streams of formed or forming filaments as they are spooled so as not to whip and break or deform the formed or forming filaments. In addition to the collector, the collection system may include other components, such as heaters and rollers between the spinneret and collector, or subsequently in post-processing of the fiber, to help manage tension and stream or filament orientation. The collection system would naturally include other components (not shown), such as electric motors for driving the collectors or other components, sensors or registers for determining rates of rotation of the spinning components, or flow rates from jet outlet ports or for measuring strain or loads of materials or components. The system may also include manual and/or computer controls, e.g., microprocessors and memory with stored programs, for managing the rates of relative rates of spinning and strain or load on the filaments being formed or formed.

FIGS. 18-19 are side and top schematic views of one possible collection system for streams of diatomized and/or other fiber materials extruded from a given spinneret. In this case, the collector 318, e.g., a drum or cylinder, orbitally rotates around the spinneret at some distance outwardly from the outlet port or ports for the spinneret, which may be disposed on or along the circumference of the spinneret. The collector is spaced sufficiently from the spinneret so as to allow proper extrusion and drawing of the filament or fiber via the centrifugal force of rotation. The distance of the collector from the outlet port, both radially and linearly, is determined by the outlet port size and the diameter of the fiber created. This is because the jet of fiber-forming material requires a certain distance of inertial draw to properly orient the polymer chains within the forming fiber.

Other parameters to consider are the properties of the material being extruded. For example, solution viscosity and polymer chain alignment within the fiber are factors that affect the extendable distance of the fiber using inertial force. Reducing the whipping effect of the fiber, as well as vortices caused by the rotating collector, are also factors to consider. Any of the foregoing factors may be considered and addressed empirically by persons skilled in the art without undue experimentation. Thereby, appropriate spacing of the collector from the spinneret may be determined empirically or otherwise, as well as relative rates of rotation for the collector and spinneret, as discussed below.

Referring to the system of FIGS. 18-19, the collector 318 is spaced away from the outside circumference of the spinneret 212 and orbits the spinneret. The collector simultaneously is spinning around its own longitudinal axis as it orbits the spinneret. The collector's axis of rotation is parallel to the spinneret's axis of rotation. The axial spinning of the collector causes the fiber 215 to wind closely to and agglomerate around the collector, with filaments or fibers oriented generally parallel to one another. In this example, the rotating spinneret and the collector can move relative to one another in the same plane or a plane parallel to the spinneret. In this example, the collector orbits a stationary spinneret (except for axial spinning). Alternatively, the spinneret can orbit the collector, which may be stationary. Either orbital arrangement allows for a uniform fiber take-up distance through an orbit. The rate (rpm) at which the collector spins may be calculated or determined according to specific filament or fiber materials and diameters. Spinning of the collector around its own axis creates tension in the winding of fiber material. The fiber strength will determine the amount of tension required on the winding to properly wind the filament or fiber about the collector. Breaking of the fiber can occur if the rpm of the collector is too fast, exceeding the tensile strength of the fiber or filament. If the rpm is too slow, the filament or fiber may whip. This can cause weak points in the filament or fiber or it can cause the filament or fiber to break. Collection conditions may vary from material to material but can be established empirically, as noted above. Those skilled in the art will understand that mechanisms required to guide the fiber onto the winding collector are numerous, and all such mechanisms are contemplated, even if not explicitly disclosed herein. A spinning collector with rpm's calibrated with a filament or fiber take-up speed equal to the slack in the inertial extension from the spinneret's outlet port may be achieved by other systems, not just the system of FIGS. 18-19.

While a spinneret can orient fibers in the same direction, directional air or other gas flow may be used to direct a stream of material extruded from a spinneret or even a stationary extrusion device. Mechanisms for directing airflow include both positive and negative pressure system, e.g., fans, vacuums, and pressurized gas sources. Airflow may be directed at any desired angle against a stream of material so as to redirect the streams into a desired path and orientation. For example, the stream of material may be directed onto a continuous belt. In this and any other embodiments, a movable flat surface could be part of a continuous belt system that feeds the fibrous material into rollers or spoolers or into other processing systems.

#### Diatomized Constructs for Footwear and Other Applications

The inventive subject matter is also directed to the use of diatomite particles in the outer, ground-contacting surface of a footwear sole unit. Diatoms have a hardness of approximately 7 on the Mohs scale as compared to diamonds (9), granite (7), and quartz (7). Because of this hardness, and because they are relatively non-brittle, the particles may be used to improve traction, particularly on slippery surfaces, such as icy ground or wet boat decks, skateboards, surfboards, etc.

As seen in FIG. 20, generic shoe 300, in general, has a sole unit 310 and a fully or partially enclosing shoe upper 312 secured to the sole unit. In the case of athletic sports and some outdoor shoes, a "sole unit" generally may include a midsole for energy absorption and/or return; an outsole material for surface contact and abrasion resistance and/or traction; or a single unit providing such midsole or outsole functions. The sole unit may also include an in-sole that fits between the user's foot and the midsole or other sole component. While a sole unit would generally extend along the length of the shoe, a sole unit could also comprise a unit that extends for a lesser area, such as, just the forefoot or rear-foot portion, or some other area of lesser length or width. The foot-facing side of the sole unit has a foot platform portion. The term "foot-platform portion," as used herein, generally refers to the part of the sole unit that supports the foot, formed by the upper surface of the sole unit.

In certain aspects, the inventive subject matter concerns a shoe having diatomite particles *D*, as described earlier herein, embedded in or bonded to its bottom surface. Depending upon the amount of surface area to be covered and the size of the particle used, typically at least 100, 1,000, 10,000, 100,000 or 1,000,000 or more such particles

may be used. Depending on the particle grain size and blend of fine, medium and course grain sizes, the coverage can be referred to any area, toe, forefoot, midfoot, heel that has a 10% coverage up to 100% coverage with a thickness of approximately 10 microns to 2 mm.

By exposing the particles at the surface of the base outsole material, they engage the ground during use and enhance traction. By creating a layer of particles through the normal wear depth of the outsole, the particles will continue to be exposed as the outsole wears during use.

A variety of different designs and materials may be utilized in the construction of an outdoor shoe. For example, the shoe's outsole may be made from any of a variety of different materials, including a rubbery material (e.g., cured natural rubber, thermoplastic rubber (TPR), or any other synthetic rubber), synthetic leather, ethylene vinyl acetate (EVA), a polyurethane elastomer, polyvinyl chloride (PVC), any other plastic materials, and/or any other suitable materials. An outdoor shoe may have an outsole that is at least  $\frac{1}{4}$  inch thick,  $\frac{3}{8}$  inch thick or  $\frac{1}{2}$  inch thick. The diatomite particles may be distributed fully or partially through the thickness of the outsole. For instance, they could be distributed through just the 1%, 2%, 3%, 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 90%, 95% or fully to 100% of the outsole's thickness in a given portion of the outsole. In some embodiments, the outsole has diatomized portions in just the forefoot and/or rearfoot portions of the outsole (FIG.21.). The thickness of a diatomized outsole or portions thereof need not be uniform and may vary. For example, the outsole could taper, becoming thicker going from low-wear portions of the outsole to high-wear portions. As an example, the midfoot portion could have little or no thickness of diatomite particles, while the forefoot and/or rearfoot could have relatively high thicknesses of particles.

The diatomite particles may be dispersed in the feedstock for the outsole material before the outsole is formed. The feedstock may be a granulate, liquid, or melt, as discussed above in connection with fibers. Such feedstock material may then be molded or cut into the shape of the outsole using various known techniques for molding of thermoplastic or rubbery materials. The techniques include, for example, injection molding or compression molding. The dispersion of diatomite may be created by admixing, kneading, pressing, or otherwise working of the diatomite into the feedstock material or a formed or partially formed outsole or substrate of an outsole in some stage

of formation. For instance, a sheet of rubbery outsole material could be melt softened and the particles worked into the softened material. The softened material would fuse around the particles on cooling.

The outsole portions that are diatomized generally but do not necessarily have a homogeneous distribution of particles. The portion may incorporate diatomite particles of 0.1 wt % to 5.0 wt % or more. It is believed that in terms of coverage per given square inch of outsole, the particles of any given grain size, or grain size combination, would cover at least 10% of the surface area per square inch up to 100% of the area per square inch. To provide for wear, the particles should provide coverage at depths of 10 microns to 2 mm or more.

Sand can be a combination of quartz, feldspar, mineral fragments, volcanic rock fragments, sedimentary rock fragments and metamorphic rock fragments, where the majority is quartz; a mineral of  $\text{SiO}_4$ . All the requirements and benefits of sand are naturally found in diatomite. Diatomite particles are naturally found in irregularly shapes. Grinding diatomite provides even more asymmetry to provide better traction control. Diatoms can be treated to be hydrophobic, which would increase the traction in wet conditions.

Advantageously, for traction control in footwear in wet, dry, icy, and rocky conditions, diatomite particles are a natural material that provides a harder and a more desirable alternative to current sand and ceramic options. Diatomite particles are 80-90% silica, with the remaining composition attributed to clay materials. In addition, it is a hard silica material that absorbs 2x its weight in water and still has characteristics of dry diatomite particles. Further diatomite particles are highly porous and come in irregular shapes naturally. In addition, they can withstand heat treatment, easily can be made hydrophobic, and can be milled to fine grain sizes, as well as coarse sizes.

The amount of traction depends on the coating method, the grade of particles applied, the density of particles, and, in the case of footwear, the intended surface of use, as well as the environmental conditions (e.g., temperature, snow, ice, water). The intended surfaces of use, maybe, for example, rock, ice, pavement, sandstone, boats, surfboards, stand up paddle boards, etc.

The coverage of the outsole envisions 10% surface coverage of diatomite particles for light traction and up to 100% in high traction, wet, and icy situations. Gradations of different percentages are envisioned for different applications, as well as for the use in

gloves, as discussed below, where a high particle density may not be desired because flexibility can be decreased. Particle grain size can be blends of diatoms and sand or sand-like materials. The blended particles may be selected from Fine grade (about 300 microns and lower), Medium grade (about 300-600 microns), and coarse) (about 600 microns and higher grade particles. For wet conditions or warmer ice conditions (>20 degrees Fahrenheit), fine grade diatoms would be used.

The inventive subject matter is also directed to novel constructs where agglomerations of diatomite particles are created to increase the effective size of diatomite particles beyond their natural size range. Discrete agglomerations of one or more particles may be attained by creating a dispersion of diatomite of greater than 5% by weight to a base material, such as the thermoplastic materials discussed above. The size of the agglomerated particles will increase with increasing weight % of diatomite. Known dispersants may be used to manage the level of particle agglomeration.

Similar to airport runways, outsoles used for cold ice, shoes used in alpine and glacial elevations, or anywhere the temperature is below 15 degrees Fahrenheit would use coarse grade particles. For traction on rock and ice, a coarser grade may be used, which may include particles of 2300 microns or higher.

Blends are ideal for multi-use traction rubber outsoles. In addition, the rubber outsoles can have a variation of coverage where diatoms are placed in the majority of one area; around the forefoot to the toe, or heel, or any combination of locations using varying blends of grain sizes, surface area coverage percent, and/or densities of the diatomized layer (10 microns-2 mm).

The application of diatomite can be as simply as coating the bottom of a compression mold for an outsole or other construct, with diatomite (pure or blended as discussed above). Here, the rubber or other moldable material is then injected, and the diatomite fuses to a surface, which may be the ground-facing surface of an outsole.

In another approach, diatomite can be incorporated within the master batch blend for rubber or other moldable material. In another approach, the diatomite can be applied to an outsole or other construct via a rolling, brushing, spraying, aerial broadcasting, or other coating process after the outsole or other construct is formed.

In addition to traction, diatomite may be used to provide abrasion resistance to a construct's surface. For example, the bottom of luggage, gear bags or other bags or carriers may be coated with diatomite to provide abrasion resistance. In apparel, high-

wear areas of garment may be coated with diatomite particles, e.g., shoulder, elbow, knee or buttocks areas. In such cases, a carrier, such as polyurethane, or print processes can be used to apply thin (e.g., 10 micron-2mm) coatings of diatomite, alone or blended, in any combination of fine, medium, or course grades. Print techniques may also be used to deposit diatomite particles on a construct to provide wear resistance or other properties. In the case of print applications for apparel and gear bags, luggage, etc., a surface coverage of 10%-100% would generally be suitable. Similar to the requirement of runway surfaces, the particles may serve to absorb and drain water for better traction. If necessary, for any application, the diatomite particles can be modified or treated to be hydrophobic to resist moisture uptake and keep high traction.

The diatomized portions may have a gradient distribution corresponding to high to low wear or traction areas, as an example of a non-homogeneous distribution.

The outsole may be independent components in an assembly of sole unit components or they may a portion of a monolithic sole unit. For example, a sole unit molded of EVA could provide both outsole and midsole functions. Such monolithic sole could have portions of multiple durometers. For example, a ground-facing diatomized portion could have a base material of higher, more wear-resistant durometer and foot-facing portion could have a cushionier, lower durometer.

In general, portion of sole unit (assembled or monolithic) that serves as outsole will have a durometer of between 70 to 85 or thereabout for rubber using an Asker Durometer. In contrast, the midsole portion, if any, may have the same or a relatively lower durometer of from 50 to 60 or thereabout for EVA using an Asker Durometer.

The portion of the diatomized portion of the sole unit need not be diatomized fully across its width and length. The diatomized regions could be just forefoot portion 314 and rearfoot portion 316, as seen in FIG. 21. For example, the portion may be defined by groups of diatomized particles *D* that are part of a pattern generally defining a portion of the outsole. For instance, as indicated in FIG. 20, the diatomized portion may consist of any one or more shapes, such as sets of bands, circles, triangles, curves, or any combination of shapes.

The diatomized sole units may be used on any kind of shoe where an enhanced traction or slip resistance may be desired. Non-limiting examples include footwear for

ice, climbing, track and field, fly fishing and wading, industrial footwear, e.g., footwear for roofers.

### Gloves

Similar to the friction-enhancing application for footwear, the inventive subject matter can provide enhanced grip in gloves by diatomizing the grip side of the gloves. This could be done by using diatomized textiles or rubbery materials in grip areas, e.g., one or more fingers, and/or palm regions. The textiles may be diatomized as disclosed earlier herein. Or the grip areas may be coated or made from a rubbery or plastic substance having the diatom particles. FIG. 22 shows an example glove 400 with grip area 410 having embedded diatomite particles *D*.

Analogous to apparel applications, in addition to or instead of diatomization of the grip area, the gloves may include a diatomized layer that provides moisture control in the glove, drawing moisture away from against a user's hand. The layer could be part of an overall waterproof/breathable glove assembly analogous to 2L, 2.5L, or 3L assemblies in apparel.

As in other applications, screen printing on fabric can be used. For example, a diatomized PU, preferably a water based polymer can be screen printed with diatom onto a fabric in designs or specific locations.

### Diatomized Surfaces for Water and Dirt Repellency

The Lotus Effect occurs when water encounters a micro-array of structures on a surface. It is well documented. See, e.g., [http://www.mecheng.osu.edu/nlbb/files/nlbb/Lotus\\_Effect.pdf](http://www.mecheng.osu.edu/nlbb/files/nlbb/Lotus_Effect.pdf).

In the FIG. 23, water beads up on a surface of hydrophobic diatomite particles embedded in or otherwise applied to a substrate surface.

Due to their high surface tension, water droplets tend to minimize their surface by trying to achieve a spherical shape. On contact with a surface, adhesion forces result in wetting of the surface. Either complete or incomplete wetting may occur depending on the structure of the surface and the fluid tension of the droplet. The cause of self-cleaning properties is the hydrophobic water-repellent double structure of the surface. This enables the contact area and the adhesion force between surface and droplet to be significantly reduced, resulting in a water-repelling and self-cleaning process. This hierarchical double



structure is formed out of a characteristic epidermis (its outermost layer called the cuticle) and the covering waxes. The epidermis of the lotus plant possesses papillae with 10 to 20  $\mu\text{m}$  in height and 10 to 15  $\mu\text{m}$  in width on which the so-called epicuticular waxes are imposed. These superimposed waxes are hydrophobic and form the second layer of the double structure.

The hydrophobicity of a surface can be measured by its contact angle. The higher the contact angle, the higher the hydrophobicity of a surface. Surfaces with a contact angle  $< 90^\circ$  are referred to as hydrophilic, and those with an angle  $> 90^\circ$  as hydrophobic. Some plants show contact angles up to  $160^\circ$  and are called super-hydrophobic. This means that only 2–3% of a drop's surface is in contact. Plants with a double structured surface like the lotus can reach a contact angle of  $170^\circ$ , resulting in a droplet's actual contact area being only 0.6%. All this leads to higher repellency and a self-cleaning effect. Dirt particles are picked up by water droplets on the substrate surface. If a water droplet rolls off, or is shaken off, such a contaminated surface the dirt particle is removed because of its higher adhesion to the water droplet than the substrate surface.

(Background information is sourced from [http://en.wikipedia.org/wiki/Lotus\\_effect](http://en.wikipedia.org/wiki/Lotus_effect).)

Diatomite particles may be arrayed on a substrate surface to mimic the structures and contact angles of the lotus leaf, as well as other super-hydrophobic surfaces known in the art. For example, parameters for Lotus-Effect surface patterns are disclosed in US 3354022, 6660363, and US 8486319, all of which are hereby incorporated by reference in their entireties for their teachings on Lotus-Leaf effect surface topologies. However, none of the foregoing patents discloses or suggests the use of diatomite particles used in the surface topology. The inventive subject matter is directed to innovative adaptations of the surface topologies known to provide the Lotus Effect.

US 3354022 describes water repellent surfaces having an intrinsic advancing water contact angle of more than  $90^\circ$  and an intrinsic receding water contact angle of at least  $75^\circ$  by creating a micro rough structure with elevations and depressions in a hydrophobic material. The high and low portions have an average distance of not more than 1,000 microns, an average height of high portions of at least 0.5 times the average distance between them. The air content is at least 60% and, in particular, fluorine-containing polymers are disclosed as the hydrophobic material. US 6660363 describes self-cleaning surfaces of objects made of hydrophobic polymers or permanently hydrophobized materials that have an artificial surface structure of elevations and

depressions. The distances between the elevations are in the range of from 5  $\mu\text{m}$  to 200  $\mu\text{m}$ , and the heights of the elevations are in the range of from 5  $\mu\text{m}$  to 100  $\mu\text{m}$ . At least the elevations consist of hydrophobic polymers or permanently hydrophobized materials. The elevations cannot be wetted by water or by water containing detergents by attaching PTFE particles (7 micron in diameter) to a polymer adhesive film containing surface and curing the structure or by using a fine mesh screen to emboss a polymer surface by hot pressing. As one possible option, diatomite particles could be embossed on substrate surface in a like way. To impart hydrophobicity to the diatoms without clogging the pores, typical bath applications can be used as well as vapor/plasma deposition. Vapor/plasma deposition can coat the surfaces with both fluorinated and non-fluorinated water repellent finishes. Diatom powder can be treated as is, or diatom agglomerates can be treated in powder form and then used for surface application for abrasion and traction control surfaces.

Lotus-Effect surface patterns based on elevations having primary and secondary structures are disclosed in US 8486319. The patent discloses creation of numerous pits and crevices or protrusions in at least portions of the outer surface of a substrate that are randomly and/or evenly distributed, which form the primary structure of the Lotus-Effect surface pattern. The patent discloses that the shape, size and population of sites such as recesses, pits, crevices, depressions, as defined by the topology of diatomite particles and the associated substrate surface, is believed to enable the entrapment of air thus providing for the Lotus Effect. The micro-sized surface structures, i.e., surface-exposed diatomite particles, may have a density of between 25 and 10,000 sites per  $\text{mm}^2$  area, or 100 and 5,000 sites per  $\text{mm}^2$  area, or a range of between 5 and 100 sites per  $\text{mm}$ , or thereabout. Surface sites may range from 5-100 micron in depth, or 10-50 micron in depth; or from 5-100 micron in diameter, or from 10-50 micron in diameter, or thereabout. Sites may be spaced between 5-100 micron apart, or 10 and 50 micron apart, or thereabout. Any of the constructs contemplated herein may be formed to provide a Lotus-Effect by diatomization of the construct's surface in a Lotus-Effect topology.

Definitions (as generally described in literature for the Outdoor and Textile Industries):

Waterproof/breathable (composite fabric): a textile (knit or woven) composite that withstands water penetration of a certain pressure as defined by different standards but it

also breathable, as measured by different standards allowing moisture to pass through the composite material. The composite can contain 1 textile layer and the waterproof breathable membrane (defined as a 2-layer waterproof-breathable composite), or the waterproof-breathable membrane can be sandwiched between 2 textile layers (defined as a 3-layer waterproof-breathable composite). In the case of a 2.5-layer waterproof breathable composite, the membrane typically has a print applied on the membrane surface opposite the outer textile side. This print can be a color, design, and/or include functional particles in any pattern. Textile layers can be woven or knitted structures of any fiber type (natural, synthetic, bio-based, biodegradable) or blends of any fiber types. All seams are sealed using seam tape to ensure waterproofness.

**Waterproof/Breathable Membrane:** A flexible material that is (1) waterproof, and (2) breathable to moisture, according selected standards. Membranes can be hydrophilic, hydrophobic, monolithic, or microporous. A bi-component membrane combines two layers, for example GORE-TEX ePTFE membranes and another layer of material.

**Air Permeability:** Ability of a textile, membrane, or composite to allow air to penetrate through the material; measured in CFM, cubic feet per minute.

**Moisture Vapor Breathability/Vapor Permeability:** Referred to the ability of a textile, waterproof/breathable membrane, or composite to allow moisture (liquid or water vapor) to pass through the material.

**Hardshell (2L, 2.5L, 3L):** A waterproof-breathable composite consisting of multiple layers 2, 2.5, or 3L that achieve a high degree of windproofness. The outerlayer is typically a more durable material, such as a Polyester or Nylon fabric. A typical fabric constriction is a ripstop.

**Softshell:** Textile composite with high water resistance, however, focusing on wind blocking. Wind block may be attained using a waterproof breathable membrane (sandwiched between two textile layers) or using an adhesive or glue to affix two textiles or substrates together. The glue is not air permeable and therefore meters air penetration in the composite. Textile fabrics are typically softer woven and knitted fabrics, hence the term softshell. By manipulating the design features for each textile composite, the air

permeability can range from between 0 to 100% wind block.

Nanofiber: Defined as fibers with diameters between 100-1000 nanometers.

Nanofibers provide high surface area and unique properties at the nanoscale level.

Nonwoven: fabric-like materials that are made from fibers bonded together by something other than a weaving process, such as chemical, heat, mechanical, or solvent processes. The fibers are entangled, creating a web structure. The entanglement creates pores between fibers, providing some degree of air permeability.

Persons skilled in the art will recognize that many modifications and variations are possible in the details, materials, and arrangements of the parts and actions which have been described and illustrated in order to explain the nature of the inventive subject matter, and that such modifications and variations do not depart from the spirit and scope of the teachings and claims contained therein.

All patent and non-patent literature cited herein is hereby incorporated by references in its entirety for all purposes.

As used herein, "and/or" means "and" or "or", as well as "and" and "or."

Moreover, any and all patent and non-patent literature cited herein is hereby incorporated by references in its entirety for all purposes.

The principles described above in connection with any particular example can be combined with the principles described in connection with any one or more of the other examples. Accordingly, this detailed description shall not be construed in a limiting sense, and following a review of this disclosure, those of ordinary skill in the art will appreciate the wide variety of systems that can be devised using the various concepts described herein. Moreover, those of ordinary skill in the art will appreciate that the exemplary embodiments disclosed herein can be adapted to various configurations without departing from the disclosed principles.

The previous description of the disclosed embodiments is provided to enable any person skilled in the art to make or use the disclosed innovations. Various modifications to those embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments without departing from the spirit or scope of this disclosure. Thus, the claimed inventions are not intended to be limited to the embodiments shown herein, but are to be accorded the full scope consistent with the language of the claims, wherein reference to an element in the singular, such as by use of the article "a" or "an" is not intended to mean "one and only one" unless

specifically so stated, but rather "one or more".

All structural and functional equivalents to the elements of the various embodiments described throughout the disclosure that are known or later come to be known to those of ordinary skill in the art are intended to be encompassed by the features described and claimed herein. Moreover, nothing disclosed herein is intended to be dedicated to the public regardless of whether such disclosure is explicitly recited in the claims. No claim element is to be construed as "a means plus function" claim under US patent law, unless the element is expressly recited using the phrase "means for" or "step for".

CURRENTLY CLAIMED INVENTIONS:

1. A diatomized construct, comprising a fiber, filament or yarn having a plurality of diatomite particles embedded in the surface of the construct generally uniformly over the entire surface area of the construct.
2. A diatomized construct, comprising a fiber, filament or yarn having a plurality of diatomite particles embedded in the construct surface of the construct so that the particles generally uniformly cover about 1-10% of the construct surface.
3. The construct of claim 1 wherein the particles generally uniformly cover 10-30% or thereabout of the construct surface.
4. The construct of claim 1 wherein the particles generally uniformly cover about 30% or more of the construct surface.
5. The construct of claim 1 wherein the construct comprises a thermoplastic material.
6. The construct of claim 5 wherein the construct comprises polyester material.
7. The construct of any of claims 1-5 wherein the diatomite particles are present at 0.1% to 5% by fiber weight or thereabout in a thermoplastic material forming the construct.
8. The construct of any of claims 1-5 wherein the particles have an average size of 1  $\mu\text{m}$  to 3 $\mu\text{m}$  or thereabout.
9. The construct of any of claims 1-5 wherein the particles have an average size of less than 5 $\mu\text{m}$  or thereabout.
10. The construct of claims 1-5 wherein the particles have an average size of more than 200 $\mu\text{m}$  or thereabout.
11. A construct comprising a diatomized woven or nonwoven textile comprising a plurality of diatomized fiber, filament, or yarn constructs arranged in a lattice structure, the constructs comprising a fiber, filament or yarn having a plurality of diatomite particles embedded in the surface of the construct generally uniformly over the entire surface area of the construct.
12. The textile of claim 11 wherein the lattice comprises a woven structure.

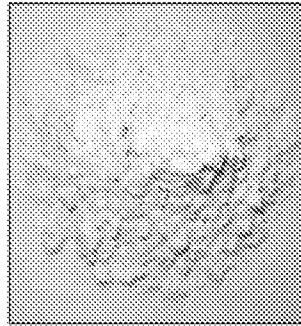
13. The textile of claim 11 wherein the lattice comprises a knit structure.
14. A construct comprising a diatomized mat, film or membrane comprising a plurality of diatomized fibers, filaments, or yarn constructs arranged in a lattice structure, the constructs comprising a fiber, filament or yarn having a plurality of diatomite particles embedded in the surface of the construct generally uniformly over the entire surface area of the construct.
15. A diatomized construct, comprising a first layer comprising a membrane, film, or mat and a second adjacent knit or woven layer in a discrete lattice comprising fibers, filaments, or yarns, one or both of the first layer and second layer having diatomized surfaces.
16. The diatomized construct of claim 15 wherein the first layer comprises a layer of fully or partially melted thermoplastic fibers, filaments or yarns that are fused to the second layer.
17. A construct comprising a substrate having a diatomized surface comprising diatomite particles wherein a plurality of the diatomite particles have been chemically modified or treated to provide functionality not inherent in the particles.
18. The construct of claim 17 wherein the substrate comprises a fiber, filament, yarn, or textile.
19. The construct of claim 18 wherein the diatomite particles have been chemically modified or treated to render them relatively more hydrophobic than in their inherent state.
20. A construct, comprising seamless and seamed products and components of products, such as apparel; footwear; gloves; headwear; tents; backpacks; containers or carriers in the nature of luggage and other carriers of items; upholstery for furniture; bed coverings; table coverings; linens; vehicle coverings; tarps; towels; medical textiles; geotextiles; filter media; and agrotextiles, wherein the construct comprises at least a portion of any of the constructs claimed in any of claims 1, 11, 14, 15, or 17.
21. A construct comprising a sole unit comprising a ground-engaging portion of an outsole wherein traction particles are embedded in or otherwise fixedly applied to

the surface of the portion, and the particles comprise diatomite particles (1) of about 300 or less microns; (2) a blend of diatomite particles of 1000-2360 microns, (3) blends of both less than about 300 microns and over about 1000 microns, (4) particles comprising discrete agglomerates of diatoms and blends of said agglomerates and other traction particles, or (5) diatomite particles or millings thereof of 200 nanometers to 1 micron, or thereabout, and wherein the particles are exposed over at least 1%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, or 90% of the portion's surface.

22. The sole unit of claim 21 wherein the particles comprise diatomite particles of about 300 or less microns.
23. The sole unit of claim 21 wherein the particles comprise a blend of diatomite particles of 1000-2360 microns or thereabout.
24. The sole unit of claim 21 wherein the particles comprise blends of particles of less than about 300 microns and over about 1000 microns.
25. The sole unit of claim 21 wherein the particles comprise blends of particles comprising discrete agglomerates of diatoms and blends of said agglomerates and other traction particles.
26. The sole unit of claim 21 wherein the particles comprise blends of particles comprising discrete agglomerates of diatoms and blends of said agglomerates and other traction particles.
27. The sole unit of claim 21 wherein the particles comprise diatomite particles or millings thereof of 200 nanometers to 1 micron, or thereabout
28. A construct comprising a diatomized glove comprising at least a diatomized portion of an inner or outer surface of the glove.
29. A method of forming a fiber, comprising dispersing diatomite particles into a solid or melted thermoplastic feedstock material and spinning the mixture into fibers.
30. The method of claim 29 further comprising using the fibers in making one of the constructs of claims 11, 14, 15, 17, 21, or 28.
31. The method of claim 29 further comprising collecting the fibers as continuous lengths of fiber.

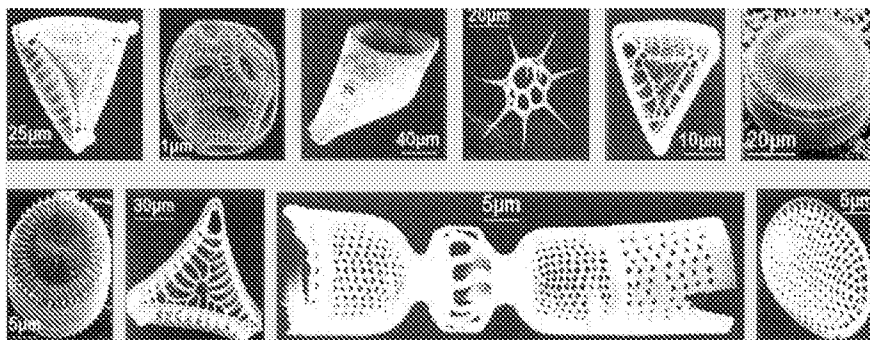


32. The method of claim 31 wherein the continuous length fibers are made into staple fibers
33. The method of claim 29 or 32 comprising forming the collected fibers into yarns or other multifilament structures.
34. The method of claim 29 further comprising collecting the fibers in mats, films or membranes.
35. The construct of any of claims 11, 14, 15, 17, 21, or 28, wherein the construct comprises a yarn or another assembly of multifilaments wherein the multifilament structure has a ratio of denier/filament number of 0.25 to 2.
36. The construct of claim 35 wherein the ratio is 1.0 or thereabout.
37. A construct comprising a substrate having a diatomized surface topology providing a Lotus Effect.
38. A construct comprising a diatomized surface comprising a base material and a plurality of discrete agglomerations of diatomite particles embedded in or applied to the base material and exposed at the surface of the base material.
39. A construct comprising a diatomized surface comprising a base material and a blend of (1) diatomite particles (and/or agglomerate particles) and (2) non-diatomite sand or sand-like embedded in or applied to the base material and exposed at the surface of the base material.



Powder of Diatomite

FIG. 1



Representative frustule forms of diatomite particles (*D*)

FIG. 2

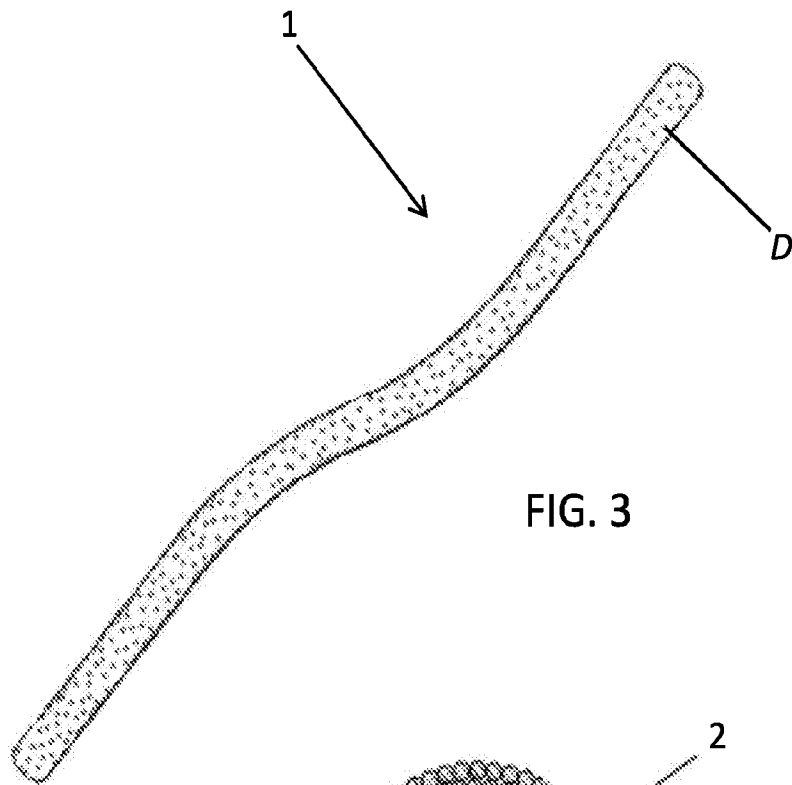


FIG. 3

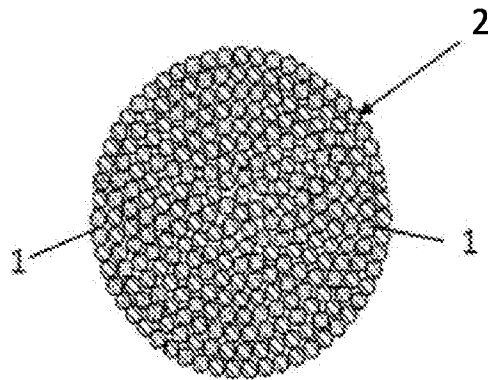
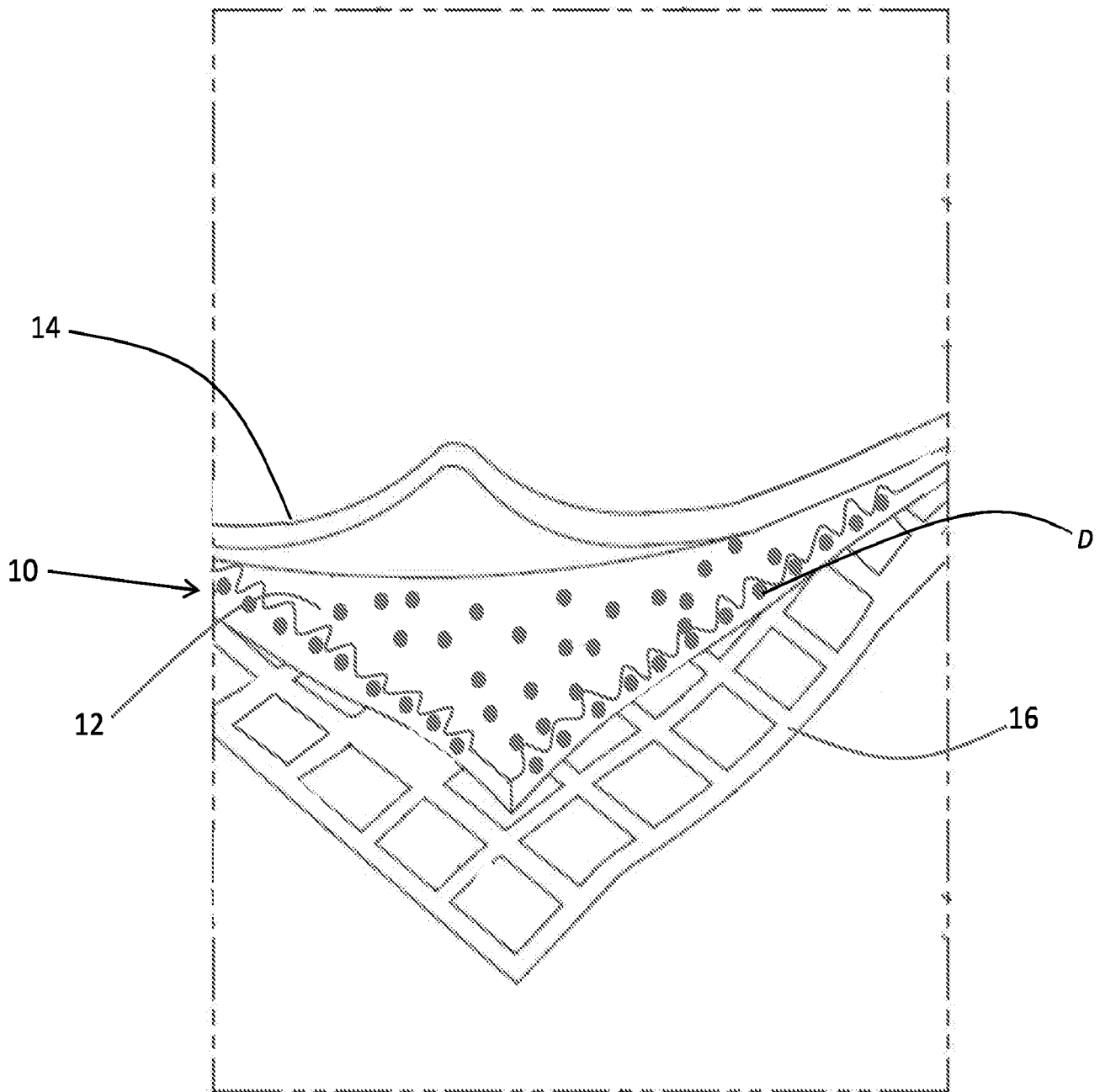


FIG. 4



(3L Garment Construction)

FIG. 5

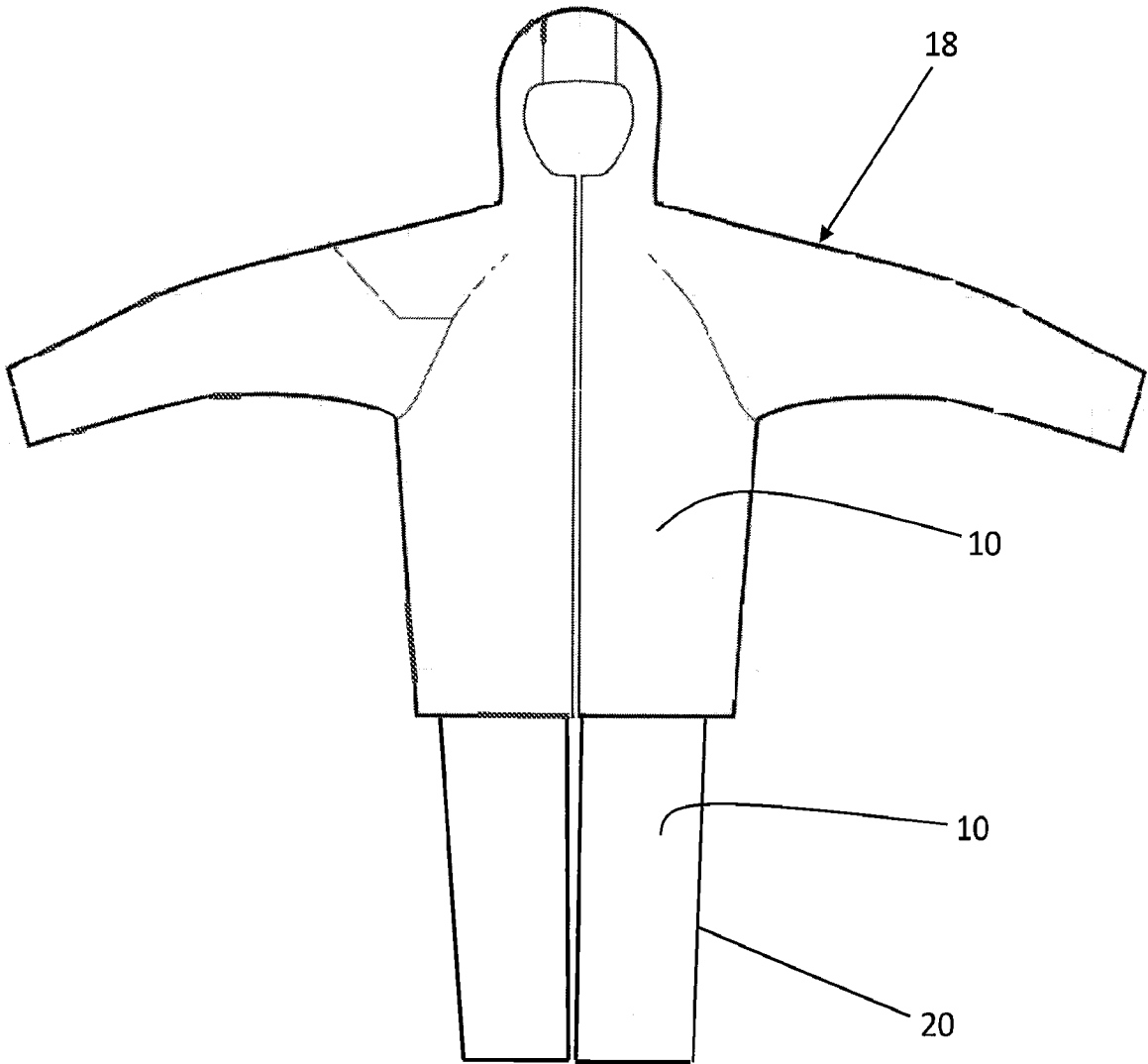


FIG. 6

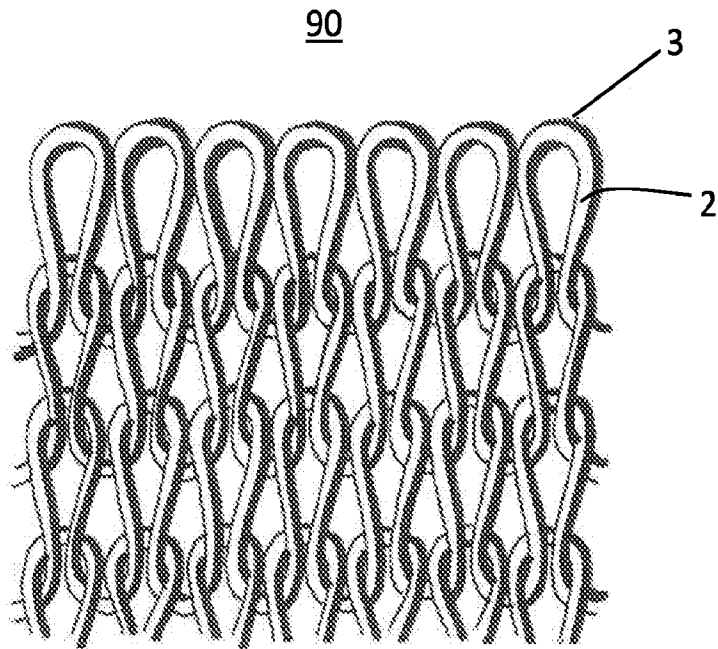


FIG. 7

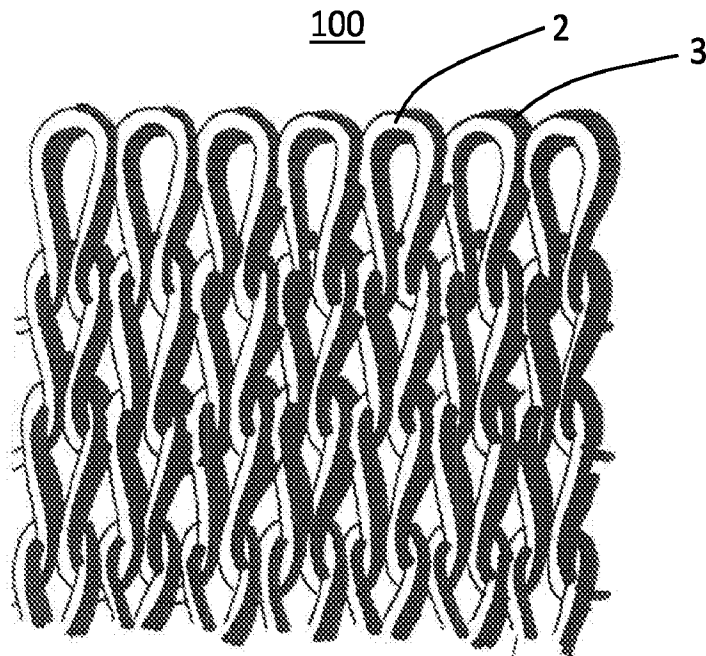


FIG. 8

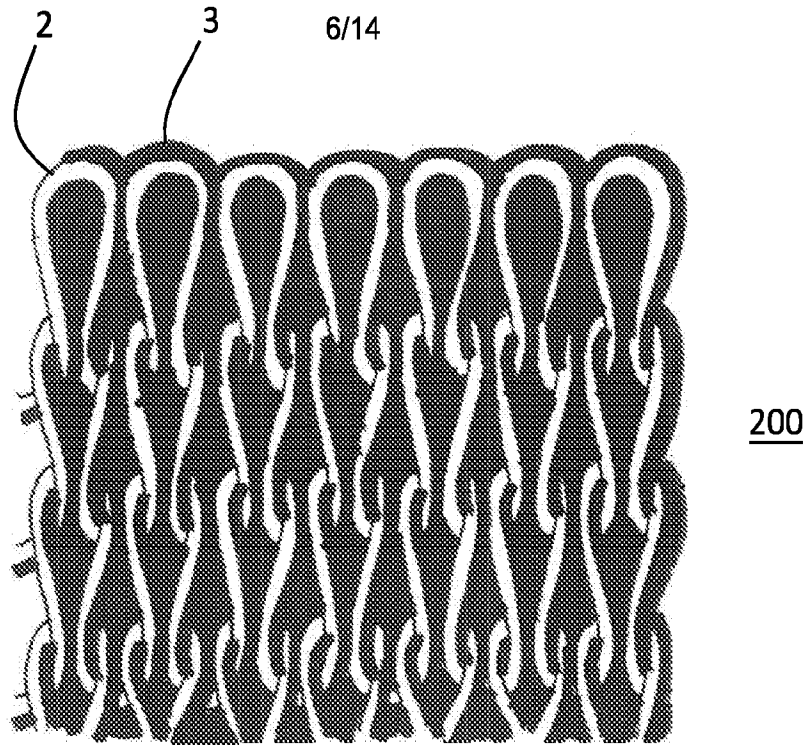


FIG. 9

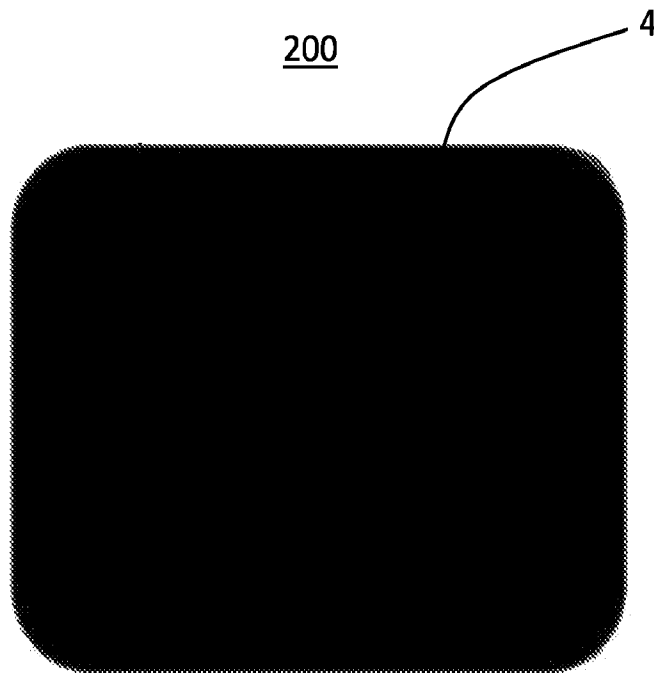


FIG. 10

210

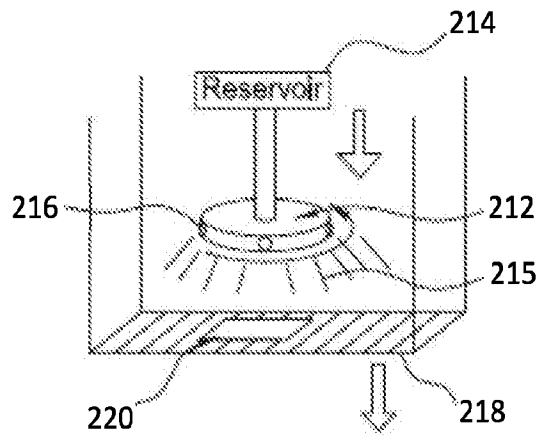


FIG. 11

210

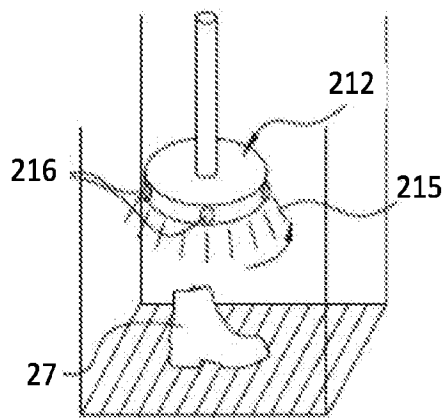


FIG. 12

210

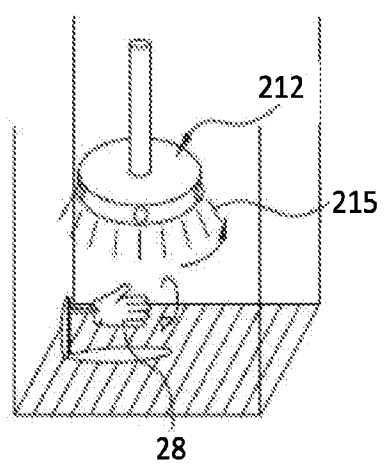
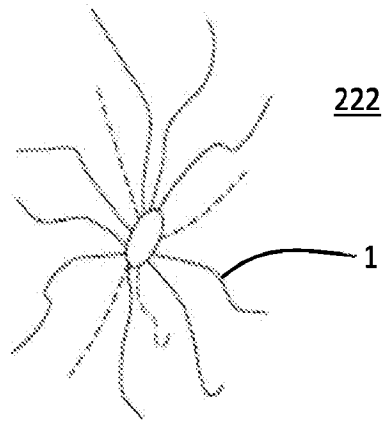


FIG. 13

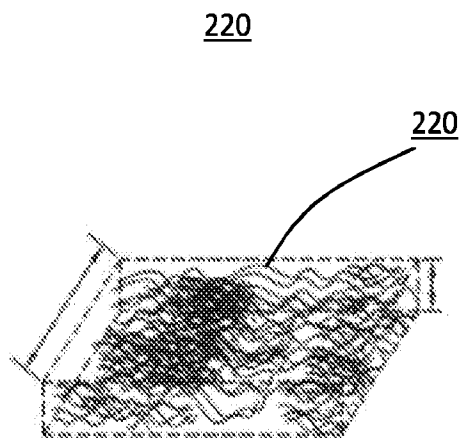




Goose/Duck

Down Plumule

FIG. 14



Synthetic Batting Insulation

FIG. 15

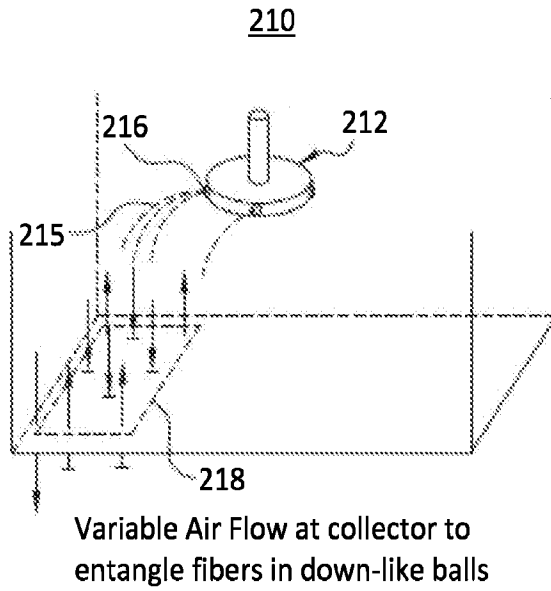


FIG. 16

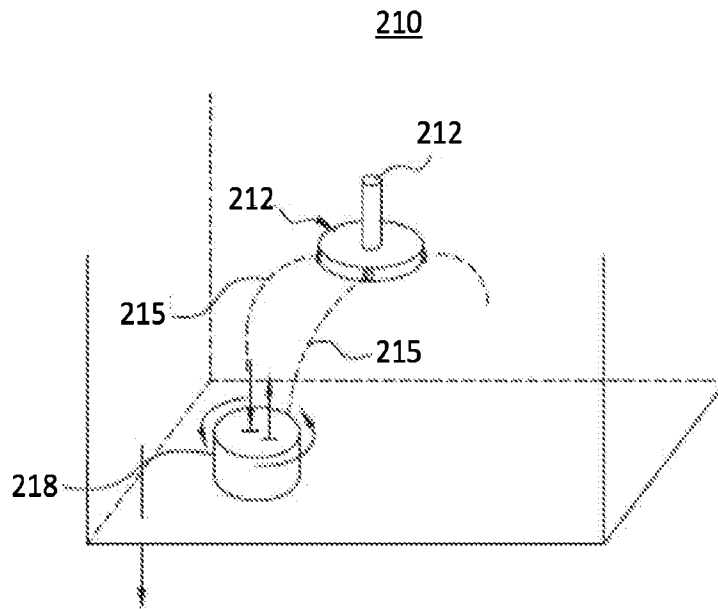


FIG. 17

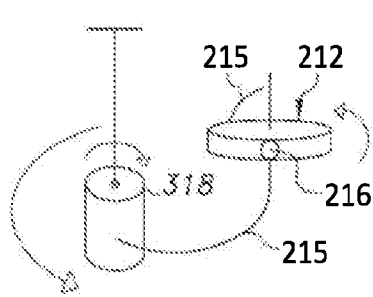


FIG. 18

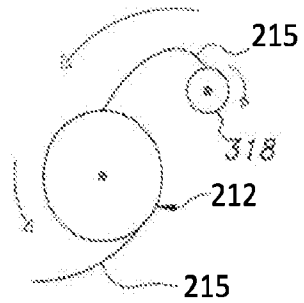


FIG. 19

300

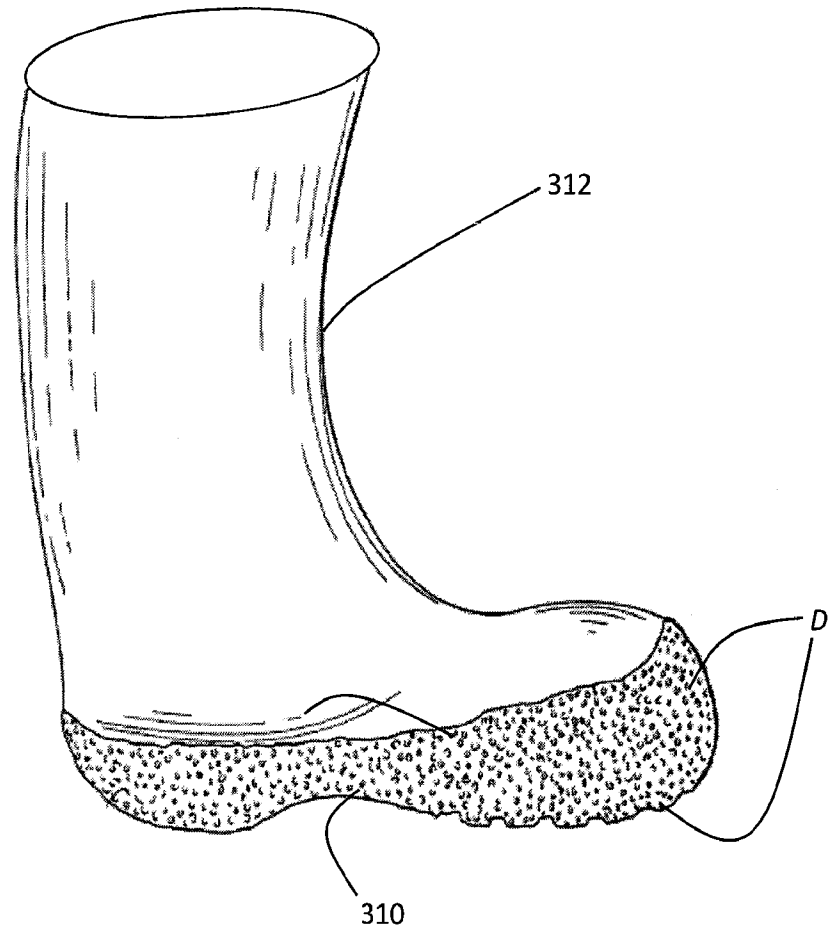


FIG. 20

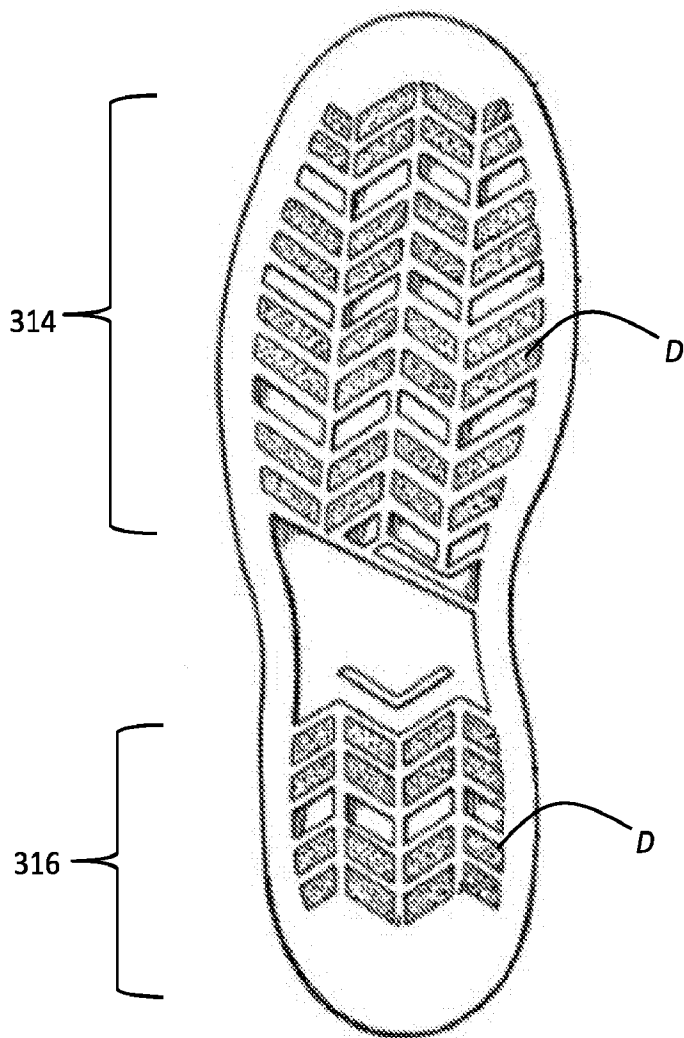


FIG. 21

400

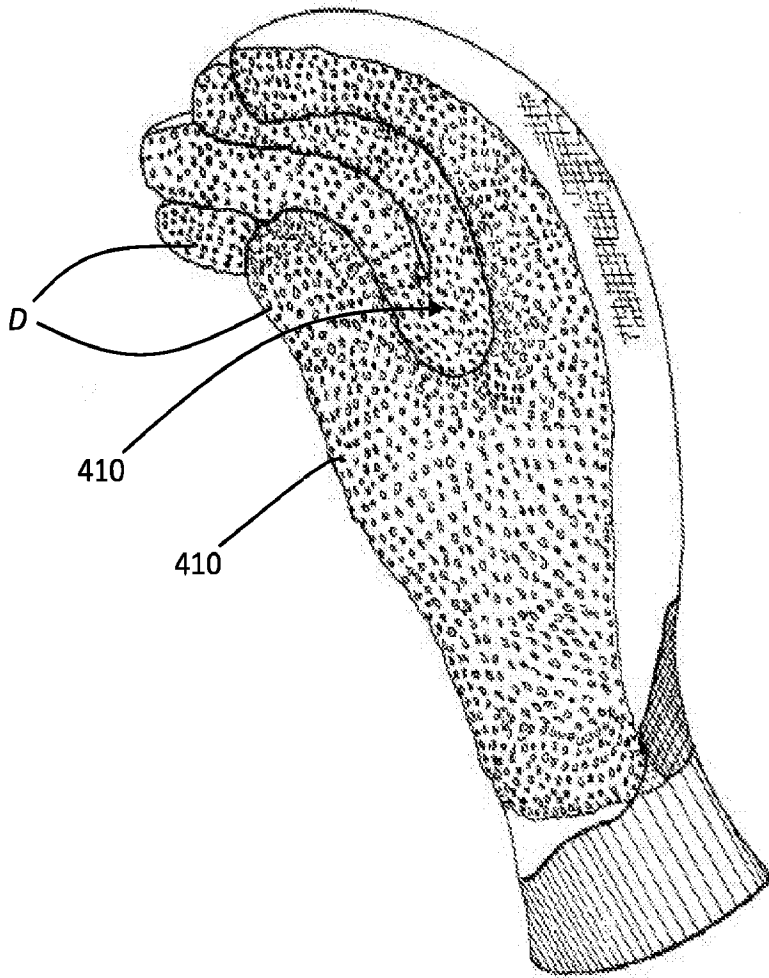


FIG. 22

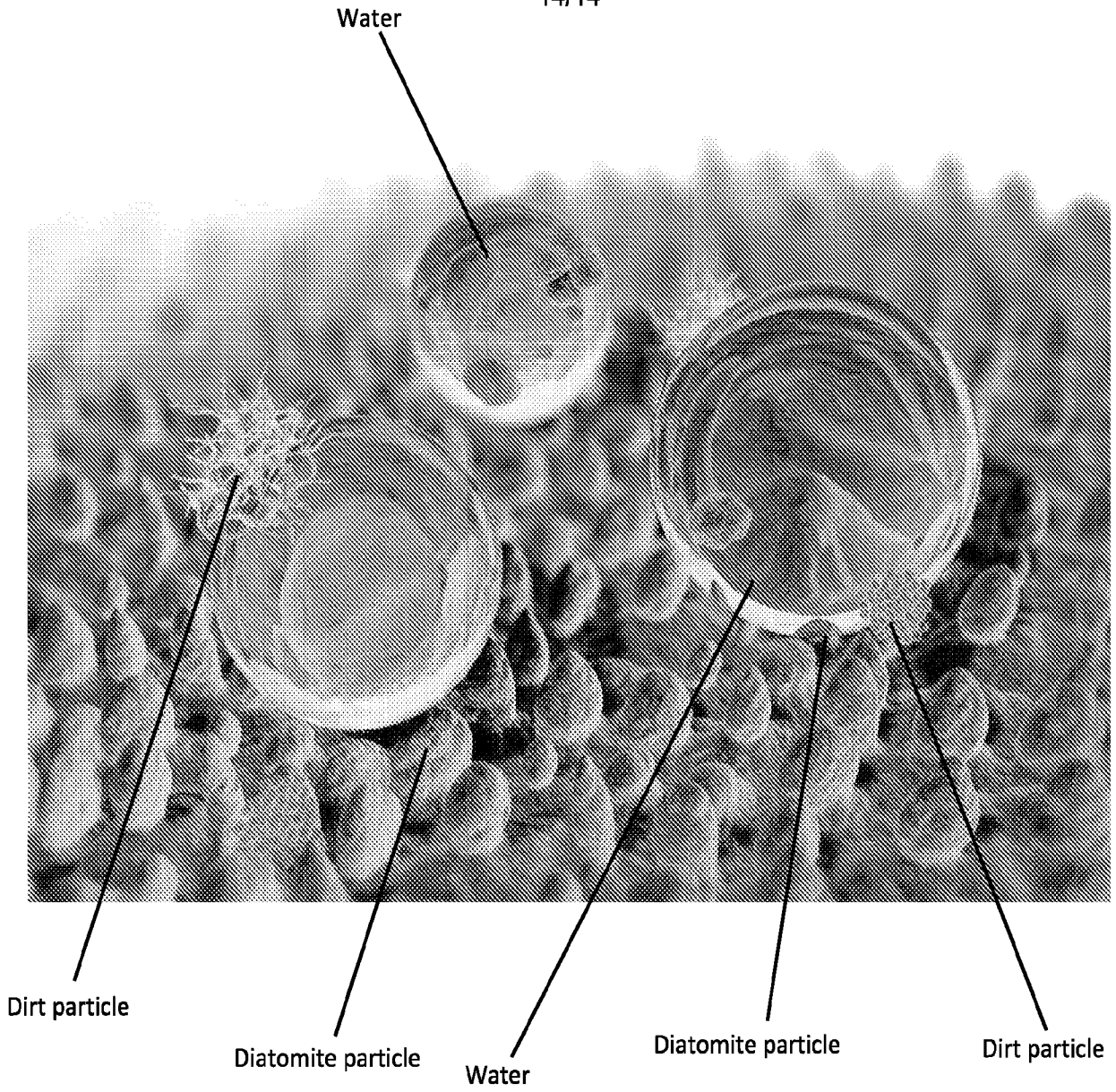


FIG. 23

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/22983

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(8) - C09B 67/00 (2016.01)  
 CPC - 09D 11/322; C09B 29/0037; C09B 33/12; B01J 20/14  
 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)  
 CPC: C09D11/322; C09B29/0037 ORC09B33/12; B01J20/14; Y10T442/2762; Y10T442/2861; Y10T442/2082; Y10T442/2131  
 IPC(8): C09B 67/00 (2016.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 USPC: 8/618; 8/674; 442/69; 427/2.3; 524/71; 525/523; 556/413; 525/342; 210/679; 210/502.1; 442/50; 442/381; 514/770; 423/335; 428/224; 106/607

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar; Search terms: diatomaceous diatomic particle fiber filament yarn embedded uniformly distributed surface apparel thermoplastic polyester size textile woven non-woven malt film membrane denier ratio kieselguhr kieselgur particulate conform attach

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 2007/0135006 A1 (MICHAELS et al.) 14 June 2007 (14.06.2007) para [0002], [0026], [0035], [0036], [0039], [0042], [0044]-[0046], [0048], [0051], [0055], [0062]; abstract; claim 1	1-14 and 35-36 ----- 20
Y	US 2014/0326656 A1 (GREENFIELD et al.) 06 November 2014 (06.11.2014) para [0003], [0018], [0032]; claim 9	20
A	US 2010/0286582 A1 (SIMPSON et al.) 11 November 2010 (11.11.2010); the entire document	1-14, 20 and 35-36
A	US 7,988,860 B2 (KALAYCI et al.) 02 August 2011 (02.08.2011); the entire document	1-14, 20 and 35-36
A	US 2013/0030340 A1 (VINCENT et al.) 31 January 2013 (31.01.2013); the entire document	1-14, 20 and 35-36
A	US 2014/0309343 A1 (VENEMA et al.) 16 October 2014 (16.10.2014); the entire document	1-14, 20 and 35-36

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 19 July 2016 (19.07.2016)	Date of mailing of the international search report <b>16 AUG 2016</b>
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Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young  PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/22983

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 30  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:  
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-14, 20 (in part), and 35-36 (in part), directed to a construct comprising a diatomized mat, film or membrane comprising a plurality of diatomized fibers, filaments, or yarn constructs arranged in a lattice structure.

Group II: Claims 15-16, 20 (in part), and 35-36 (in part), directed to a diatomized construct, comprising a first layer and a second layer.

Group III: Claims 17-19, 20 (in part), and 35-36 (in part), directed to a construct wherein the diatomite particles have been chemically modified.

\*\*please see the end of this form for continuation\*\*

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-14, 20 (in part), and 35-36 (in part)

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**\*\*continuation of Box III (Lack of Unity)\*\***

Group IV: Claims 21-27, and 35-36 (in part), directed to construct comprising a sole unit comprising a ground-engaging portion of an outsole wherein traction particles are embedded in or otherwise fixedly applied to the surface of the portion

Group V: Claims 28 and 35-36 (in part), directed a construct comprising a diatomized glove.

Group VI: Claims 29 and 31-34, directed to a method of forming a fiber.

Group VII: Claim 37, directed to a construct comprising a substrate having a diatomized surface topology providing a Lotus Effect.

Group VIII: Claims 38-39, directed a construct comprising a base material and a plurality of discrete agglomerations of diatomite particles embedded in or applied to the base material and nondiatomite sand or sand-like embedded in or applied to the base material.

The inventions listed as Group I-VIII do not relate to a single special technical feature under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

**Special Technical Feature:**

Group I requires the constructs diatomized construct, comprising a fiber, filament or yarn having a plurality of diatomite particles embedded in the surface of the construct generally uniformly over the entire surface area of the construct, not required by Groups II-VIII.

Group II requires a first layer comprising a membrane, film, or mat and a second adjacent knit or woven layer in a discrete lattice comprising fibers, filaments, or yarns, not required by groups I and III-VIII

Group III requires the plurality of the diatomite particles have been chemically modified or treated to provide functionality not inherent in the particles, not required by groups I-II and IV-VIII.

Group IV requires a sole unit comprising a ground-engaging portion of an outsole wherein traction particles are embedded in or otherwise fixedly applied to the surface of the portion, not required by groups I-III and V-VIII.

Group V requires a diatomized glove comprising at least a diatomized portion of an inner or outer surface of the glove, not required by groups I-IV and VI-VIII.

Group VI requires dispersing diatomite particles into a solid or melted thermoplastic feedstock material and spinning the mixture into fibers, not required by I-V and VII-VIII.

Group VII requires a substrate having a diatomized surface topology providing a Lotus Effect, not required by I-VI and VIII.

Group VIII requires a base material and a blend of diatomite particles (and/or agglomerate particles) and nondiatomite sand or sand-like embedded in or applied to the base material and exposed at the surface of the base material, not requires by groups I-VII

**Common Technical Features:**

Groups I -VIII share the feature of diatomized/diatomite. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by US 2010/0286582 A1 to Simpson et al. (hereinafter Simpson). Simpson teaches diatomized/diatomite (para [0005]; A breathable bandage, including a substrate and a plurality of superhydrophobic particles attached the substrate. The plurality of superhydrophobic particles can be porous diatomaceous earth).

Groups I-V and VII-VIII share the feature of diatomized construct or a construct with a diatomized surface. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches diatomized construct or a construct with a diatomized surface (para [0005]; A breathable bandage (construct), including a substrate and a plurality of superhydrophobic particles attached the substrate. The plurality of superhydrophobic particles can be porous diatomaceous earth).

Groups I, III, IV, VI and VIII share the feature of diatomized particles. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches diatomized particles (para [0005]; A breathable bandage, including a substrate and a plurality of superhydrophobic particles attached the substrate. The plurality of superhydrophobic particles can be porous diatomaceous earth).

Groups I, II and VI share the feature of fiber and diatomized particles. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches fiber and diatomized particles (para [0005], [0030]; A breathable bandage, including a substrate and a plurality of superhydrophobic particles attached the substrate. The bandage substrate can be an elastic material, such as a woven material containing elastomeric fibers).

**\*\*please see the next page for continuation\*\***

\*\*continuation of previous page (Box III (Lack of Unity))\*\*

Groups I, IV and VIII share the feature of a construct comprising diatomized particles are embedded in or otherwise fixedly applied to the surface. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches a construct comprising diatomized particles are fixedly applied to the surface (para [0005]; A breathable bandage (construct), including a substrate and a plurality of superhydrophobic particles attached the substrate). Groups I and II share the feature of a diatomized construct comprising a membrane, film, or mat; woven; and lattice comprising fibers, filaments, or yarns. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches a diatomized construct comprising a membrane, film, or mat (para [0005], [0030]; A breathable bandage (construct), including a substrate and a plurality of superhydrophobic particles attached the substrate. The plurality of superhydrophobic particles can be porous diatomaceous earth. Further, the bandage substrate can be selected from the group consisting of porous or perforated films); woven (para [0030]; The bandage substrate can be an elastic material, such as a woven material containing elastomeric fibers); and lattice comprising fibers (para [0005], [0030], [0049]; A breathable bandage, including a substrate and a plurality of superhydrophobic particles attached the substrate. The bandage substrate can be an elastic material, such as a woven material containing elastomeric fibers. Further, the surface of the substrate has self-assembled monolayers (SAMs), by the formation of at least one covalent bond, and a tail group is directed to the air interface to provide desired surface properties, such as hydrophobicity. Hence, the lattice structure includes covalent bonds).

Groups III and VII share the feature of a construct comprising a substrate having a diatomized surface. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches a construct comprising a substrate having a diatomized surface (para [0005]; A breathable bandage (construct), including a substrate and a plurality of superhydrophobic particles attached the substrate. The plurality of superhydrophobic particles can be porous diatomaceous earth).

Groups III and VII share the feature of a construct comprising a diatomized surface; the particles are embedded in or otherwise fixedly applied to the surface; and discrete agglomerations of diatomite particles. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by Simpson. Simpson teaches a construct comprising a diatomized surface; the particles are fixedly applied to the surface; and discrete agglomerations of diatomite particles (para [0005], [0057]; A breathable bandage (construct), including a substrate and a plurality of superhydrophobic particles attached the substrate. The plurality of superhydrophobic particles can be porous diatomaceous earth. Once the superhydrophobic diatomaceous earth particles are formed they can be used to generate a variety of articles, such as where they are used as discrete particles in a powder, as agglomerates or bound to each other or to an additional substrate).

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-VIII lack unity under PCT Rule 13.

Note:

Claim 30 is determined unsearchable because it is a dependent claim and is not drafted in accordance with the second and third sentences of Rule 6.4(a).