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# Remarks:

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#### **ACTIVE CONTAINING FIBROUS STRUCTURES WITH MULTIPLE REGIONS HAVING** (54)**DIFFERING DENSITIES**

(57)A fibrous structure including filaments wherein the filaments comprise one or more filament-forming materials and one or more active agents that are releasable from the filament when exposed to conditions of intended use, the fibrous structure further having at least two re-

gions with different properties, in particular wherein each region has different average densities. Methods of treating fabrics with a fibrous structure are also provided here-

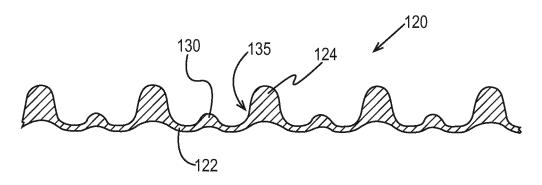


Fig. 6

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# Description

#### **TECHNICAL FIELD**

**[0001]** The present disclosure generally relates to fibrous structures comprising one or more active agents and also comprising differing regions and methods for making the same, and in particular, fibrous structures having regions with different densities.

# **BACKGROUND**

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**[0002]** Fibrous structures are known in the art. For example, a polyester nonwoven that is impregnated and/or coated with a detergent composition is known in the art as shown in prior art FIGS. 1 and 2. As shown in FIGS. 1 and 2, a known nonwoven substrate 10 is made of undissolvable fibers 12 wherein the nonwoven substrate 10 is coated and/or impregnated with an additive 14, such as an active agent. An example of such a web material is commercially available as Purex® Complete 3-in-1 Laundry Sheets from The Dial Corporation.

**[0003]** Further, a non-fibrous article of manufacture formed from a cast solution of a detergent composition is also known in the art and is commercially available as Dizolve® Laundry Sheets commercially available from Dizolve Group Corporation.

[0004] However, such known web materials and/or articles of manufacture exhibit negatives that make them problematic for consumers. For example, the known web materials and/or articles of manufacture are relatively stiff and/or inflexible, thereby prone to fracture upon simple handling. Further, the web materials and/or articles of manufacture typically deliver such a low level of detergent composition and/or detergent actives that the cleaning performance is less than desired by consumers. Another negative with is that the web materials and/or articles of manufacture may leave remnants of the web material and/or articles of manufacture after the washing operation, for example the polyester nonwoven substrate does not dissolve during the washing operation. Yet, another negative with such known web materials is there potential tendency for sticking to a washing machine surface or window during the washing cycle and therefore not be functional in delivering its intended use, namely cleaning clothing. Most importantly, in some cases the known web materials can block the draining mechanism of the washing machine. Additional negative includes removal of undissolved carrier substrates of the articles of manufacture, such as discarding of the polyester nonwoven substrate.

[0005] Accordingly, the present invention provides fibrous structures comprising one or more active agents and filaments such that the fibrous structures comprise two or more regions having distinct intensive properties for improved strength, while providing sufficient dissolution and disintegration during use.

# SUMMARY

[0006] In accordance with one embodiment, a fibrous structure comprises filaments having one or more filament-forming materials and one or more active agents that are releasable from the filament when exposed to conditions of intended use. The fibrous structure further comprises a continuous network region and a plurality of discrete zones. The continuous network region comprises a first average density and the plurality of discrete zones comprises a second average density. The discrete zones are dispersed throughout the network region and the first average density and the second average density are different.

[0007] In accordance with yet another embodiment, a fibrous structure comprises filaments having one or more filament-forming materials and one or more active agents that are releasable from the filament when exposed to conditions of intended use. The fibrous structure further comprises at least a first region and a second region. Each of the first and second regions having at least one common intensive property. The at least one common intensive property of the first region differs in value from the at least one common intensive property of the second region.

**[0008]** In accordance with still another embodiment, a process for making a fibrous structure. The process comprises the step of depositing a plurality of filaments on to a three-dimensional molding member comprising a non-random repeating pattern such that a fibrous structure comprising one or more filament-forming materials and one or more active agents that are releasable from the filaments when exposed to conditions of intended use is produced. The fibrous structure further comprises at least a first region and a second region. Each of the first and second regions having at least one common intensive property. The at least one common intensive property of the first region differs in value from the at least one common intensive property of the second region.

**[0009]** While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter that is regarded as the present invention, it is believed that the invention will be more fully understood from the following description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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- <sup>5</sup> FIG. 1 is a known nonwoven substrate.
  - FIG. 2 is another known nonwoven substrate.
  - FIG. 3 is a schematic plan view of a portion of a fibrous structure.
  - FIG. 4 is a schematic cross-sectional view of the portion of the fibrous structure shown in FIG. 3 as taken along line 4-4.
  - FIG. 5 is a schematic plan view of an embodiment of a fibrous structure.
- FIG. 6 is a schematic cross-sectional view taken along line 6-6 of FIG. 5.
  - FIG. 7 is a schematic representation of an apparatus used to form fibrous structures.
  - FIG. 8 is a schematic representation of a die used on an apparatus as shown in FIG. 7.
  - FIG. 9 is a representative image of a molding member.
  - FIG. 10 illustrates representative images of molding members and the resulting fibrous structures.
- <sup>25</sup> FIG. 11A is a schematic view of equipment for measuring dissolution of a fibrous structure.
  - FIG. 11B is a schematic top view of FIG 11A.
  - FIG. 12 is a schematic view of equipment for measuring dissolution of a fibrous structure.
  - FIG. 13 is a cross-sectional view of a network region and a plurality of discrete zones of a fibrous structure as shown using a SEM micrograph.
- FIG. 14 shows a processed topography image of a network region and a plurality of discrete zones of a fibrous structure as shown using a SEM micrograph.
  - FIG. 15 illustrates a series of straight line regions of interest, drawn across the network region and discrete zones shown in FIG. 14.
- FIG. 16 illustrates a height profile plot along a straight line region of interest, drawn through a topography image, to show several elevation differential measurements.
  - FIG. 17 depicts a height profile plot along a straight line region of interest, drawn through a topography image, to show several transition region widths.

# **DETAILED DESCRIPTION**

# I. Definitions

- 50 [0011] As used herein, the following terms shall have the meaning specified thereafter:
  - [0012] "Filament" or "fiber" or "fibrous element" as used herein means an elongate particulate having a length greatly exceeding its diameter, i.e. a length to diameter ratio of at least about 10. A fibrous element may be a filament or a fiber. In one example, the fibrous element is a single fibrous element rather than a yarn comprising a plurality of fibrous elements. Fibrous elements may be spun from a filament-forming compositions also referred to as fibrous element-forming compositions via suitable spinning operations, such as meltblowing and/or spunbonding. Fibrous elements may be monocomponent and/or multicomponent. For example, the fibrous elements may comprise bicomponent fibers and/or filaments. The bicomponent fibers and/or filaments may be in any form, such as side-by-side, core and sheath, islands-in-the-sea and the like.

**[0013]** "Filament-forming composition" as used herein means a composition that is suitable for making a filament such as by meltblowing and/or spunbonding. The filament-forming composition comprises one or more filament-forming materials that exhibit properties that make them suitable for spinning into a filament. In one example, the filament-forming material comprises a polymer. In addition to one or more filament-forming materials, the filament-forming composition may comprise one or more additives, for example one or more active agents. In addition, the filament-forming composition may comprise one or more polar solvents, such as water, into which one or more, for example all, of the filament-forming materials and/or one or more, for example all, of the active agents are dissolved and/or dispersed.

**[0014]** "Filament-forming material" as used herein means a material, such as a polymer or monomers capable of producing a polymer that exhibits properties suitable for making a filament. In one example, the filament-forming material comprises one or more substituted polymers such as an anionic, cationic, zwitterionic, and/or nonionic polymer. In another example, the polymer may comprise a hydroxyl polymer, such as a polyvinyl alcohol ("PVOH") and/or a polysaccharide, such as starch and/or a starch derivative, such as an ethoxylated starch and/or acid-thinned starch. In another example, the polymer may comprise polyethylenes and/or terephthalates. In yet another example, the filament-forming material is a polar solvent-soluble material.

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[0015] "Additive" as used herein means any material present in a filament that is not a filament-forming material. In one example, an additive comprises an active agent. In another example, an additive comprises a processing aid. In still another example, an additive comprises a filler. In one example, an additive comprises any material present in the filament that its absence from the filament would not result in the filament losing its filament structure, in other words, its absence does not result in the filament losing its solid form. In another example, an additive, for example an active agent, comprises a non-polymer material.

[0016] "Conditions of intended use" as used herein means the temperature, physical, chemical, and/or mechanical conditions that a filament is exposed to when the filament is used for one or more of its designed purposes. For example, if a filament and/or a nonwoven web comprising a filament are designed to be used in a washing machine for laundry care purposes, the conditions of intended use will include those temperature, chemical, physical and/or mechanical conditions present in a washing machine, including any wash water, during a laundry washing operation. In another example, if a filament and/or a nonwoven web comprising a filament are designed to be used by a human as a shampoo for hair care purposes, the conditions of intended use will include those temperature, chemical, physical and/or mechanical conditions present during the shampooing of the human's hair. Likewise, if a filament and/or nonwoven web comprising a filament is designed to be used in a dishwashing operation, by hand or by a dishwashing machine, the conditions of intended use will include the temperature, chemical, physical and/or mechanical conditions present in a dishwashing water and/or dishwashing machine, during the dishwashing operation.

[0017] "Active agent" as used herein means an additive that produces an intended effect in an environment external to a filament and/or nonwoven web comprising the filament of the present, such as when the filament is exposed to conditions of intended use of the filament and/or nonwoven web comprising the filament. In one example, an active agent comprises an additive that treats a surface, such as a hard surface (i.e., kitchen countertops, bath tubs, toilets, toilet bowls, sinks, floors, walls, teeth, cars, windows, mirrors, dishes) and/or a soft surface (i.e., fabric, hair, skin, carpet, crops, plants,). In another example, an active agent comprises an additive that creates a chemical reaction (i.e., foaming, fizzing, coloring, warming, cooling, lathering, disinfecting and/or clarifying and/or chlorinating, such as in clarifying water and/or disinfecting water and/or chlorinating water). In yet another example, an active agent comprises an additive that treats an environment (i.e., deodorizes, purifies, perfumes air). In one example, the active agent is formed in situ, such as during the formation of the filament containing the active agent, for example the filament may comprise a water-soluble polymer (e.g., starch) and a surfactant (e.g., anionic surfactant), which may create a polymer complex or coacervate that functions as the active agent used to treat fabric surfaces.

**[0018]** "Fabric care active agent" as used herein means an active agent that when applied to fabric provides a benefit and/or improvement to the fabric. Non-limiting examples of benefits and/or improvements to fabric include cleaning (for example by surfactants), stain removal, stain reduction, wrinkle removal, color restoration, static control, wrinkle resistance, permanent press, wear reduction, wear resistance, pill removal, pill resistance, soil removal, soil resistance (including soil release), shape retention, shrinkage reduction, softness, fragrance, anti-bacterial, anti-viral, odor resistance, and odor removal.

**[0019]** "Dishwashing active agent" as used herein means an active agent that when applied to dishware, glassware, pots, pans, utensils, and/or cooking sheets provides a benefit and/or improvement to the dishware, glassware, plastic items, pots, pans and/or cooking sheets. Non-limiting example of benefits and/or improvements to the dishware, glassware, plastic items, pots, pans, utensils, and/or cooking sheets include food and/or soil removal, cleaning (for example by surfactants) stain removal, stain reduction, grease removal, water spot removal and/or water spot prevention, glass and metal care, sanitization, shining, and polishing.

**[0020]** "Hard surface active agent" as used herein means an active agent when applied to floors, countertops, sinks, windows, mirrors, showers, baths, and/or toilets provides a benefit and/or improvement to the floors, countertops, sinks, windows, mirrors, showers, baths, and/or toilets. Non-limiting example of benefits and/or improvements to the floors,

countertops, sinks, windows, mirrors, showers, baths, and/or toilets include food and/or soil removal, cleaning (for example by surfactants), stain removal, stain reduction, grease removal, water spot removal and/or water spot prevention, limescale removal, disinfection, shining, polishing, and freshening.

[0021] "Weight ratio" as used herein means the dry filament basis and/or dry detergent product basis-forming material (g or %) on a dry weight basis in the filament to the weight of additive, such as active agent(s) (g or %) on a dry weight basis in the filament.

**[0022]** "Hydroxyl polymer" as used herein includes any hydroxyl-containing polymer that can be incorporated into a filament, for example as a filament-forming material. In one example, the hydroxyl polymer includes greater than 10% and/or greater than 20% and/or greater than 25% by weight hydroxyl moieties.

[0023] "Biodegradable" as used herein means, with respect to a material, such as a filament as a whole and/or a polymer within a filament, such as a filament-forming material, that the filament and/or polymer is capable of undergoing and/or does undergo physical, chemical, thermal and/or biological degradation in a municipal solid waste composting facility such that at least 5% and/or at least 7% and/or at least 10% of the original filament and/or polymer is converted into carbon dioxide after 30 days as measured according to the OECD (1992) Guideline for the Testing of Chemicals 301B; Ready Biodegradability - CO<sub>2</sub> Evolution (Modified Sturm Test) Test incorporated herein by reference.

[0024] "Non-biodegradable" as used herein means, with respect to a material, such as a filament as a whole and/or a polymer within a filament, such as a filament-forming material, that the filament and/or polymer is not capable of undergoing physical, chemical, thermal and/or biological degradation in a municipal solid waste composting facility such that at least 5% of the original filament and/or polymer is converted into carbon dioxide after 30 days as measured according to the OECD (1992) Guideline for the Testing of Chemicals 301B; Ready Biodegradability - CO<sub>2</sub> Evolution (Modified Sturm Test) Test incorporated herein by reference.

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**[0025]** "Non-thermoplastic" as used herein means, with respect to a material, such as a filament as a whole and/or a polymer within a filament, such as a filament-forming material, that the filament and/or polymer exhibits no melting point and/or softening point, which allows it to flow under pressure, in the absence of a plasticizer, such as water, glycerin, sorbitol, urea and the like.

**[0026]** "Non-thermoplastic, biodegradable filament" as used herein means a filament that exhibits the properties of being biodegradable and non-thermoplastic as defined above.

**[0027]** "Non-thermoplastic, non-biodegradable filament" as used herein means a filament that exhibits the properties of being non-biodegradable and non-thermoplastic as defined above.

[0028] "Thermoplastic" as used herein means, with respect to a material, such as a filament as a whole and/or a polymer within a filament, such as a filament-forming material, that the filament and/or polymer exhibits a melting point and/or softening point at a certain temperature, which allows it to flow under pressure, in the absence of a plasticizer

**[0029]** "Thermoplastic, biodegradable filament" as used herein means a filament that exhibits the properties of being biodegradable and thermoplastic as defined above.

[0030] "Thermoplastic, non-biodegradable filament" as used herein means a filament that exhibits the properties of being non-biodegradable and thermoplastic as defined above.

**[0031]** "Polar solvent-soluble material" as used herein means a material that is miscible in a polar solvent. In one example, a polar solvent-soluble material is miscible in alcohol and/or water. In other words, a polar solvent-soluble material is a material that is capable of forming a stable (does not phase separate for greater than 5 minutes after forming the homogeneous solution) homogeneous solution with a polar solvent, such as alcohol and/or water at ambient conditions.

**[0032]** "Alcohol-soluble material" as used herein means a material that is miscible in alcohol. In other words, a material that is capable of forming a stable (does not phase separate for greater than 5 minutes after forming the homogeneous solution) homogeneous solution with an alcohol at ambient conditions.

[0033] "Water-soluble material" as used herein means a material that is miscible in water. In other words, a material that is capable of forming a stable (does not separate for greater than 5 minutes after forming the homogeneous solution) homogeneous solution with water at ambient conditions.

**[0034]** "Non-polar solvent-soluble material" as used herein means a material that is miscible in a non-polar solvent. In other words, a non-polar solvent-soluble material is a material that is capable of forming a stable (does not phase separate for greater than 5 minutes after forming the homogeneous solution) homogeneous solution with a non-polar solvent.

**[0035]** "Ambient conditions" as used herein means 73°F  $\pm$  4°F (about 23°C  $\pm$  2.2°C) and a relative humidity of 50%  $\pm$  10%.

**[0036]** "Weight average molecular weight" as used herein means the weight average molecular weight as determined using gel permeation chromatography according to the protocol found in Colloids and Surfaces A. Physico Chemical & Engineering Aspects, Vol. 162, 2000, pg. 107-121.

[0037] "Length" as used herein, with respect to a filament, means the length along the longest axis of the filament from one terminus to the other terminus. If a filament has a kink, curl or curves in it, then the length is the length along

the entire path of the filament.

conditions of intended use.

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[0038] "Diameter" as used herein, with respect to a filament, is measured according to the Diameter Test Method described herein. In one example, a filament can exhibit a diameter of less than 100  $\mu$ m and/or less than 75  $\mu$ m and/or less than 50  $\mu$ m and/or less than 25  $\mu$ m and/or less than 20  $\mu$ m and/or less than 15  $\mu$ m and/or less than 10  $\mu$ m and/or less than 10  $\mu$ m and/or less than 10  $\mu$ m and/or greater than 1  $\mu$ m and/or greater than 3  $\mu$ m.

[0039] "Triggering condition" as used herein in one example means anything, as an act or event, that serves as a stimulus and initiates or precipitates a change in the filament, such as a loss or altering of the filament's physical structure and/or a release of an additive, such as an active agent. In another example, the triggering condition may be present in an environment, such as water, when a filament and/or nonwoven web and/or film are added to the water. In other words, nothing changes in the water except for the fact that the filament and/or nonwoven and/or film are added to the water. [0040] "Morphology changes" as used herein with respect to a filament's morphology changing means that the filament experiences a change in its physical structure. Non-limiting examples of morphology changes for a filament include dissolution, melting, swelling, shrinking, breaking into pieces, exploding, lengthening, shortening, and combinations thereof. The filaments may completely or substantially lose their filament physical structure or they may have their morphology changed or they may retain or substantially retain their filament physical structure as they are exposed to

[0041] "Total level" as used herein, for example with respect to the total level of one or more active agents present in the filament and/or detergent product, means the sum of the weights or weight percent of all of the subject materials, for example active agents. In other words, a filament and/or detergent product may comprise 25% by weight on a dry filament basis and/or dry detergent product basis of an anionic surfactant, 15% by weight on a dry filament basis and/or dry detergent product basis of a nonionic surfactant, 10% by weight of a chelant, and 5% of a perfume so that the total level of active agents present in the filament is greater than 50%; namely 55% by weight on a dry filament basis and/or dry detergent product basis.

**[0042]** "Detergent product" as used herein means a solid form, for example a rectangular solid, sometimes referred to as a sheet, that comprises one or more active agents, for example a fabric care active agent, a dishwashing active agent, a hard surface active agent, and mixtures thereof. In one example, a detergent product can comprise one or more surfactants, one or more enzymes, one or more perfumes and/or one or more suds suppressors. In another example, a detergent product can comprise a builder and/or a chelating agent. In another example, a detergent product can comprise a bleaching agent.

**[0043]** "Web" as used herein means a collection of formed fibers and/or filaments, such as a fibrous structure, and/or a detergent product formed of fibers and/or filaments, such as continuous filaments, of any nature or origin associated with one another. In one example, the web is a rectangular solid comprising fibers and/or filaments that are formed via a spinning process, not a casting process.

[0044] "Nonwoven web" for purposes of the present disclosure as used herein and as defined generally by European Disposables and Nonwovens Association (EDANA) means a sheet of fibers and/or filaments, such as continuous filaments, of any nature or origin, that have been formed into a web by any means, and may be bonded together by any means, with the exception of weaving or knitting. Felts obtained by wet milling are not nonwoven webs. In one example, a nonwoven web means an orderly arrangement of filaments within a structure in order to perform a function. In one example, a nonwoven web is an arrangement comprising a plurality of two or more and/or three or more filaments that are inter-entangled or otherwise associated with one another to form a nonwoven web. In one example, a nonwoven web may comprise, in addition to the filaments, one or more solid additives, such as particulates and/or fibers.

**[0045]** "Particulates" as used herein means granular substances and/or powders. In one example, the filaments and/or fibers can be converted into powders.

[0046] "Equivalent diameter" is used herein to define a cross-sectional area and a surface area of an individual starch filament, without regard to the shape of the cross-sectional area. The equivalent diameter is a parameter that satisfies the equation  $S=\frac{1}{4}\pi D^2$ , where S is the filament's cross-sectional area (without regard to its geometrical shape),  $\pi=3.14159$ , and D is the equivalent diameter. For example, the cross-section having a rectangular shape formed by two mutually opposite sides "A" and two mutually opposite sides "B" can be expressed as:  $S=A\times B$ . At the same time, this cross-sectional area can be expressed as a circular area having the equivalent diameter D. Then, the equivalent diameter D can be calculated from the formula:  $S=\frac{1}{4}\pi D^2$ , where S is the known area of the rectangle. (Of course, the equivalent diameter of a circle is the circle's real diameter.) An equivalent radius is  $\frac{1}{2}$  of the equivalent diameter.

[0047] "Pseudo-thermoplastic" in conjunction with "materials" or "compositions" is intended to denote materials and compositions that by the influence of elevated temperatures, dissolution in an appropriate solvent, or otherwise can be softened to such a degree that they can be brought into a flowable state, in which condition they can be shaped as desired, and more specifically, processed to form starch filaments suitable for forming a fibrous structure. Pseudo-thermoplastic materials may be formed, for example, under combined influence of heat and pressure. Pseudo-thermoplastic materials differ from thermoplastic materials in that the softening or liquefying of the pseudo-thermoplastics is caused by softeners or solvents present, without which it would be impossible to bring them by any temperature or

pressure into a soft or flowable condition necessary for shaping, since pseudo thermoplastics do not "melt" as such. The influence of water content on the glass transition temperature and melting temperature of starch can be measured by differential scanning calorimetery as described by Zeleznak and Hoseny in "Cereal Chemistry", Vol. 64, No. 2, pp. 121-124, 1987. Pseudo-thermoplastic melt is a pseudo-thermoplastic material in a flowable state.

[0048] "Micro-geometry" and permutations thereof refers to relatively small (i.e., "microscopical") details of a fibrous structure, such as, for example, surface texture, without regard to the structure's overall configuration, as opposed to its overall (i.e., "macroscopical") geometry. Terms containing "macroscopical" or "macroscopically" refer to an overall geometry of a structure, or a portion thereof, under consideration when it is placed in a two-dimensional configuration, such as the X-Y plane. For example, on a macroscopical level, the fibrous structure, when it is disposed on a flat surface, comprises a relatively thin and flat sheet. On a microscopical level, however, the structure can comprise a plurality of first regions that form a first plane having a first elevation, and a plurality of domes or "pillows" dispersed throughout and outwardly extending from the framework region to form a second elevation.

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**[0049]** "Intensive properties" are properties which do not have a value dependent upon an aggregation of values within the plane of the fibrous structure. A common intensive property is an intensive property possessed by more than one region. Such intensive properties of the fibrous structure include, without limitation, density, basis weight, elevation, and opacity. For example, if a density is a common intensive property of two differential regions, a value of the density in one region can differ from a value of the density in the other region. Regions (such as, for example, a first region and a second region) are identifiable areas distinguishable from one another by distinct intensive properties.

**[0050]** "Glass transition temperature," Tg, is the temperature at which the material changes from a viscous or rubbery condition to a hard and relatively brittle condition.

**[0051]** "Machine direction" (or MD) is the direction parallel to the flow of the fibrous structure being made through the manufacturing equipment. "Cross-machine direction" (or CD) is the direction perpendicular to the machine direction and parallel to the general plane of the fibrous structure being made.

**[0052]** "X," "Y," and "Z" designate a conventional system of Cartesian coordinates, wherein mutually perpendicular coordinates "X" and "Y" define a reference X-Y plane, and "Z" defines an orthogonal to the X-Y plane. "Z-direction" designates any direction perpendicular to the X-Y plane. Analogously, the term "Z-dimension" means a dimension, distance, or parameter measured parallel to the Z-direction. When an element, such as, for example, a molding member curves or otherwise deplanes, the X-Y plane follows the configuration of the element.

[0053] "Substantially continuous" region refers to an area within which one can connect any two points by an uninterrupted line running entirely within that area throughout the line's length. That is, the substantially continuous region has a substantial "continuity" in all directions parallel to the first plane and is terminated only at edges of that region. The term "substantially," in conjunction with continuous, is intended to indicate that while an absolute continuity is preferred, minor deviations from the absolute continuity may be tolerable as long as those deviations do not appreciably affect the performance of the fibrous structure (or a molding member) as designed and intended.

[0054] "Substantially semi-continuous" region refers an area which has "continuity" in all, but at least one, directions parallel to the first plane, and in which area one cannot connect any two points by an uninterrupted line running entirely within that area throughout the line's length. The semi-continuous framework may have continuity only in one direction parallel to the first plane. By analogy with the continuous region, described above, while an absolute continuity in all, but at least one, directions is preferred, minor deviations from such a continuity may be tolerable as long as those deviations do not appreciably affect the performance of the fibrous structure.

**[0055]** "Discontinuous" regions refer to discrete, and separated from one another areas that are discontinuous in all directions parallel to the first plane.

[0056] "Flexibility" is the ability of a material or structure to deform under a given load without being broken, regardless of the ability or inability of the material or structure to return itself to its pre-deformation shape.

[0057] "Molding member" is a structural element that can be used as a support for the filaments that can be deposited thereon during a process of making a fibrous structure, and as a forming unit to form (or "mold") a desired microscopical geometry of a fibrous structure. The molding member may comprise any element that has the ability to impart a three-dimensional pattern to the structure being produced thereon, and includes, without limitation, a stationary plate, a belt, a cylinder/roll, a woven fabric, and a band.

**[0058]** "Melt-spinning" is a process by which a thermoplastic or pseudo-thermoplastic material is turned into fibrous material through the use of an attenuation force. Melt-spinning can include mechanical elongation, melt-blowing, spunbonding, and electro-spinning.

**[0059]** "Mechanical elongation" is the process inducing a force on a fiber thread by having it come into contact which a driven surface, such as a roll, to apply a force to the melt thereby making fibers.

**[0060]** "Melt-blowing" is a process for producing fibrous webs or articles directly from polymers or resins using high-velocity air or another appropriate force to attenuate the filaments. In a melt-blowing process the attenuation force is applied in the form of high speed air as the material exits the die or spinnerette.

[0061] "Spun-bonding" comprises the process of allowing the fiber to drop a predetermined distance under the forces

of flow and gravity and then applying a force via high velocity air or another appropriate source.

[0062] "Electro-spinning" is a process that uses electric potential as the force to attenuate the fibers.

**[0063]** "Dry-spinning," also commonly known as "solution-spinning," involves the use of solvent drying to stabilize fiber formation. A material is dissolved in an appropriate solvent and is attenuated via mechanical elongation, melt-blowing, spun-bonding, and/or electro-spinning. The fiber becomes stable as the solvent is evaporated.

**[0064]** "Wet-spinning" comprises dissolving a material in a suitable solvent and forming small fibers via mechanical elongation, melt-blowing, spun-bonding, and/or electro-spinning. As the fiber is formed it is run into a coagulation system normally comprising a bath filled with an appropriate solution that solidifies the desired material, thereby producing stable fibers.

[0065] "Melting temperature" means the temperature or the range of temperature at or above which the starch composition melts or softens sufficiently to be capable of being processed into starch filaments. It is to be understood that some starch compositions are pseudo-thermoplastic compositions and as such may not exhibit pure "melting" behavior.

[0066] "Processing temperature" means the temperature of the starch composition, at which temperature the starch filaments can be formed, for example, by attenuation.

[0067] ""Basis Weight" as used herein is the weight per unit area of a sample reported in gsm and is measured according to the Basis Weight Test Method described herein.

[0068] Fibrous structure" as used herein means a structure that comprises one or more fibrous filaments and/or fibers. In one example, a fibrous structure means an orderly arrangement of filaments and/or fibers within a structure in order to perform a function. Non-limiting examples of fibrous structures can include detergent products, fabrics (including woven, knitted, and non-woven), and absorbent pads (for example for diapers or feminine hygiene products). The fibrous structures of the present invention may be homogeneous or may be layered. If layered, the fibrous structures may comprise at least two and/or at least three and/or at least four and/or at least five layers, for example one or more fibrous element layers, one or more particle layers and/or one or more fibrous element/particle mixture layer.

[0069] As used herein, the articles "a" and "an" when used herein, for example, "an anionic surfactant" or "a fiber" is understood to mean one or more of the material that is claimed or described.

**[0070]** All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total composition unless otherwise indicated.

**[0071]** Unless otherwise noted, all component or composition levels are in reference to the active level of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources.

### II. Fibrous Structures

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[0072] As shown in FIGS. 3-4, a fibrous structure 20 can be formed from filaments having at least a first region (e.g., a network region 22) and a second region (e.g., discrete zones 24). Each of the first and second regions has at least one common intensive property, such as, for example, a basis weight or average density. The common intensive property of the first region can differ in value from the common intensive property of the second region. For example, the average density of the first region can be higher than the average density of the second region. FIG. 3 illustrates in plan view a portion of a fibrous structure 20 wherein the network region 22 is illustrated as defining hexagons, although it is to be understood that other preselected patterns can be used.

[0073] FIG. 4 is a cross-sectional view of fibrous structure 20 taken along line 4-4 of FIG. 3. As can be seen from the embodiment shown in FIG. 4, the network region 22 is essentially monoplanar. In one example, the network region is a macroscopically monoplanar, patterned, continuous network region. The second region of the fibrous structure 20 may comprise a plurality of discrete zones 24 dispersed throughout the entire network region 22 and essentially each is encircled by network region 22. The shape of the discrete zones 24 can be defined by the network region 22. As shown in FIG. 4, discrete zones 24, appear to extend from (protrude from) the plane formed by network region 22 toward an imaginary observer looking in the direction of arrow T. When viewed by an imaginary observer looking in the direction indicated by arrow B in FIG. 4, the second region comprises arcuate shaped voids which appear to be cavities or dimples. [0074] As shown in another embodiment, FIGS. 5-6, first and second regions 122 and 124 of the fibrous structure 120 can also differentiate in their respective micro-geometry. In FIGS. 5-6, for example, the first region 122 comprises a substantially continuous network forming a first plane at a first elevation when the fibrous structure 120 is disposed on a flat surface; and the second region 124 can comprise a plurality of discrete zones dispersed throughout the substantially continuous network. These discrete zones may, in some embodiments, comprise discrete protuberances, or "pillows," outwardly extending from the network region to form a second elevation greater than the first elevation, relative to the first plane. It is to be understood that pillows can also comprise a substantially continuous pattern and a substantially semi-continuous pattern.

[0075] In one embodiment, the substantially continuous network region can have a relatively high density, and the pillows have a relatively low density. In still other embodiments, the substantially continuous network region can have

a relatively low density, and the pillows can have a relatively high density. In certain embodiments, a fibrous structure may exhibit a basis weight of about 3000 gsm or less; in certain embodiments, a fibrous structure may exhibit a basis weight of about 1500 gsm or less; in certain embodiments, a fibrous structure may exhibit a basis weight of about 1000 gsm or less; in certain embodiments, a fibrous structure may exhibit a basis weight of about 700 gsm or less; in certain embodiments, a fibrous structure may exhibit a basis weight of about 500 gsm or less; in certain embodiments, a fibrous structure may exhibit a basis weight of about 300 gsm or less; in certain embodiments a fibrous structure may exhibit a basis weight of about 200 gsm or less; and in certain embodiments, a fibrous structure may exhibit a basis weight of about 150 or less as measured according to the Basis Weight Test Method described herein.

[0076] In other embodiments, a second region can comprise a semi-continuous network. A second region can comprise discrete areas, similar to those shown in FIGS. 5-6; and semi-continuous areas, extending in at least one direction as seen in the X-Y plane (i.e., a plane formed by the first region 122 of the fibrous structure 120 disposed on a flat surface). [0077] In the embodiments shown in FIGS. 5 and 6, the fibrous structure 120 comprises a third region 130 having at least one intensive property that is common with and differs in value from the intensive property of the first region 122 and the intensive property of the second region 124. For example, the first region 122 can have the common intensive property having a first value, the second region 124 can have the common intensive property having a second value, and the third region 130 can have the common intensive property having a third value, wherein the first value can be different from the second value, and the third value can be different from the second value and the first value. In one embodiment, such a third region can include a transition region 135 (see FIG. 4) located between the first region 122 and the second region 124. The transition region 135 is the area or region between which the network region and discrete zones transition.

**[0078]** When a fibrous structure 120 including at least three differential regions 122, 124, 130, as described herein, is disposed on a horizontal reference plane (e.g., the X-Y plane), the first region 122 defines the plane having the first elevation, and the second region 124 extends therefrom to define the second elevation. An embodiment is contemplated, in which the third region 130 defines a third elevation, wherein at least one of the first, second, and third elevations is different from at least one of the other elevations. For example, the third elevation can be intermediate the first and second elevations.

**[0079]** Suitable fibrous structures having a network region and a plurality of discrete zones can have predetermined elevations. For example, in certain embodiments, one of the network region or the discrete zones can have an elevation from about 50 microns to about 5000 microns; in certain embodiments, one of the network region or the discrete zones can have an elevation from about 100 microns to about 2000 microns; and in certain embodiments, one of the network region or the discrete zones can have an elevation from about 150 microns to about 1500 microns.

**[0080]** The following table shows, without limitation, some possible combinations of embodiments of the fibrous structure 120 comprising at least three regions having differential (i.e., high, medium, or low) intensive properties. All of these embodiments are included in the scope of the present disclosure.

INTENSIVE PROPERTIES		
HIGH	MEDIUM	LOW
Continuous	Discontinuous	Discontinuous
Continuous	Discontinuous	-
Continuous	-	Discontinuous
Semi-continuous	Semi-continuous	Semi-continuous
Semi-continuous	Semi-continuous	Discontinuous
Semi-continuous	Semi-continuous	-
Semi-continuous	Discontinuous	Semi-continuous
Semi-continuous	Discontinuous	Discontinuous
Semi-continuous	-	Semi-continuous
Discontinuous	Continuous	Discontinuous
Discontinuous	Continuous	-
Discontinuous	Semi-continuous	Semi-continuous
Discontinuous	Semi-continuous	Discontinuous
Discontinuous	Discontinuous	Continuous
Discontinuous	Discontinuous	Semi-continuous
Discontinuous	Discontinuous	Discontinuous
Discontinuous	-	Continuous
-	Continuous	Discontinuous

(continued)

INTENSIVE PROPERTIES		
HIGH	MEDIUM	LOW
-	Semi-continuous	Semi-continuous
-	Discontinuous	Continuous

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[0081] Suitable fibrous structures as described herein can have network regions and discrete zones having different (e.g., not the same) average densities. The average density for either the network region or the discrete zones can be from about 0.05 g/cc to about 0.80 g/cc, in certain embodiments, from about 0.10 g/cc to about 0.50 g/cc and in certain embodiments from about 0.15 g/cc to about 0.40 g/cc. In other embodiments, the average density of the network region can be from about 0.05 g/cc to about 0.15 g/cc and the average density of the discrete zones can be from about 0.15 g/cc to about 0.80 g/cc; or average density of the network region can be from about 0.07 g/cc to about 0.13 g/cc and the average density of the discrete zones can be from about 0.25 g/cc to about 0.70 g/cc; or the average density of the network region can from about 0.08 g/cc to about 0.12 g/cc and the average density of the discrete zones can from about 0.40 g/cc to about 0.60 g/cc. In other certain embodiments, the average density values can be vice-versa for each of the network region and the discrete zones. Considering the number of fibers underlying a unit area projected onto the portion of the fibrous structure under consideration, the ratio of the average density of the network region to the average density of the discrete zones can be greater than 1. In another embodiment, the ratio of the average density of the network region to the average density of the discrete zones can be greater than 1.

**[0082]** In certain embodiments, the basis weight of the network region to the basis weight to the discrete zones is from about 0.5 to about 1.5; and in certain embodiments, the basis weight of the network region to the basis weight of the discrete zones is from about 0.8 to about 1.2.

**[0083]** In certain embodiments, the network region can comprises from about 5% to about 95% of the total area of a fibrous structure; and in certain embodiments, from about 20% to about 40% of the total area of a fibrous structure. In certain embodiments, the plurality of discrete regions can comprise from about 5% to about 95% of the total area of a fibrous structure; and in certain embodiments, from about 60% to about 80% of the total area of a fibrous structure.

[0084] In certain embodiments, suitable fibrous structures can have a water content (% moisture) from 0% to about 20%; in certain embodiments, fibrous structures can have a water content from about 1% to about 15%; and in certain embodiments, fibrous structures can have a water content from about 5% to about 10%.

**[0085]** In certain embodiments, suitable fibrous structure can exhibit a geometric mean TEA of about 100 g\*in/in² or more, and/or about 150 g\*in/in² or more, and/or about 200 g\*in/in² or more, and/or about 300 g\*in/in² or more according to the Tensile Test Method described herein.

[0086] In certain embodiments, suitable fibrous structure can exhibit a geometric mean modulus of about of about 5000 g/cm or less, and/or 4000 g/cm or less, and/or about 3500 g/cm or less, and/or about 3000 g/cm or less, and/or about 2700 g/cm or less according to the Tensile Test Method described herein.

[0087] In certain embodiments, suitable fibrous structures as described herein can exhibit a geometric mean peak elongation of about 10% or greater, and/or about 20% or greater, and/or about 30% or greater, and/or about 50% or greater, and/or about 60% or greater, and/or about 65% or greater, and/or about 70% or greater as measured according to the Tensile Test Method described herein.

[0088] In certain embodiments, suitable fibrous structures as described herein can exhibit a geometric mean tensile strength of about 200 g/in or more, and/or about 300 g/in or more, and/or about 400 g/in or more, and/or about 500 g/in or more, and/or about 600 g/in or more as measure according to the Tensile Test Method described herein.

**[0089]** Other suitable arrangements of fibrous structures are described in U.S. Patent No. 4,637,859 and U.S. Patent Application Publication No. 2003/0203196.

**[0090]** Additional, non-limiting examples of other suitable fibrous structures are disclosed in U.S. Provisional Patent Application No. 61/583,018 (P&G Attorney Docket Number 12330P) filed concurrently with the present application and is hereby incorporated by reference herein.

[0091] The use of such fibrous structure as described herein as detergent products provides additional benefits from the prior art. By having at least two regions within the fibrous structure having different intensive properties, the fibrous structure can provide sufficient integrity prior to use, but during use (e.g., in washer) the fibrous structure can sufficiently dissolve and release the active agent. In addition, such fibrous structures are non-adhesive to any articles being washed (e.g., clothes), or washing machine surfaces, and such fibrous structures will not block the drainage unit of the washing machines.

# A. Filaments

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**[0092]** Filaments can include one or more filament-forming materials. In addition to the filament-forming materials, the filament may further comprise one or more active agents that are releasable from the filament, such as when the filament is exposed to conditions of intended use, wherein the total level of the one or more filament-forming materials present in the filament is less than 80% by weight on a dry filament basis and/or dry detergent product basis and the total level of the one or more active agents present in the filament is greater than 20% by weight on a dry filament basis and/or dry detergent product basis, is provided.

[0093] In another example, a filament may comprise one or more filament-forming materials and one or more active agents wherein the total level of filament-forming materials present in the filament can be from about 5% to less than 80% by weight on a dry filament basis and/or dry detergent product basis and the total level of active agents present in the filament can be greater than 20% to about 95% by weight on a dry filament basis and/or dry detergent product basis. [0094] In one example, a filament may comprise at least 10% and/or at least 15% and/or at least 20% and/or less than less than 80% and/or less than 75% and/or less than 65% and/or less than 60% and/or less than 55% and/or less than 50% and/or less than 45% and/or less than 40% by weight on a dry filament basis and/or dry detergent product basis of the filament-forming materials and greater than 20% and/or at least 35% and/or at least 40% and/or at least 45% and/or at least 50% and/or at least 60% and/or less than 95% and/or less than 90% and/or less than 85% and/or less than 80% and/or less than 75% by weight on a dry filament basis and/or dry detergent product basis of active agents. [0095] In one example, the filament can comprise at least 5% and/or at least 10% and/or at least 15% and/or at least 20% and/or less than 50% and/or less than 45% and/or less than 40% and/or less than 35% and/or less than 30% and/or less than 25% by weight on a dry filament basis and/or dry detergent product basis of the filament-forming materials and greater than 50% and/or at least 55% and/or at least 60% and/or at least 65% and/or at least 70% and/or less than 95% and/or less than 90% and/or less than 85% and/or less than 80% and/or less than 75% by weight on a dry filament basis and/or dry detergent product basis of active agents. In one example, the filament can comprise greater than 80% by weight on a dry filament basis and/or dry detergent product basis of active agents.

**[0096]** In another example, the one or more filament-forming materials and active agents are present in the filament at a weight ratio of total level of filament-forming materials to active agents of 4.0 or less and/or 3.5 or less and/or 3.0 or less and/or 2. 5 or less and/or 2.0 or less and/or 1.85 or less and/or less than 1.7 and/or less than 1.6 and/or less than 1.5 and/or less than 1.3 and/or less than 1.2 and/or less than 1 and/or less than 0.7 and/or less than 0.5 and/or less than 0.4 and/or less than 0.3 and/or greater than 0.1 and/or greater than 0.2.

**[0097]** In still another example, a filament may comprise from about 10% and/or from about 15% to less than 80% by weight on a dry filament basis and/or dry detergent product basis of a filament-forming material, such as polyvinyl alcohol polymer and/or a starch polymer, and greater than 20% to about 90% and/or to about 85% by weight on a dry filament basis and/or dry detergent product basis of an active agent. The filament may further comprise a plasticizer, such as glycerin and/or pH adjusting agents, such as citric acid.

**[0098]** In yet another example, a filament may comprise from about 10% and/or from about 15% to less than 80% by weight on a dry filament basis and/or dry detergent product basis of a filament-forming material, such as polyvinyl alcohol polymer and/or a starch polymer, and greater than 20% to about 90% and/or to about 85% by weight on a dry filament basis and/or dry detergent product basis of an active agent, wherein the weight ratio of filament-forming material to active agent is 4.0 or less. The filament may further comprise a plasticizer, such as glycerin and/or pH adjusting agents, such as citric acid.

[0099] In even another example, a filament may comprise one or more filament-forming materials and one or more active agents selected from the group consisting of: enzymes, bleaching agents, builder, chelants, sensates, dispersants, and mixtures thereof that are releasable and/or released when the filament is exposed to conditions of intended use. In one example, the filament comprises a total level of filament forming materials of less than 95% and/or less than 90% and/or less than 80% and/or less than 50% and/or less than 35% and/or to about 5% and/or to about 10% and/or to about 20% by weight on a dry filament basis and/or dry detergent product basis and a total level of active agents selected from the group consisting of: enzymes, bleaching agents, builder, chelants, and mixtures thereof of greater than 5% and/or greater than 10% and/or greater than 20% and/or greater than 35% and/or greater than 50% and/or greater than 65% and/or to about 95% and/or to about 90% and/or to about 80% by weight on a dry filament basis and/or dry detergent product basis. In one example, the active agent comprises one or more enzymes. In another example, the active agent comprises one or more builders. In still another example, the active agent comprises one or more chelants.

**[0100]** In yet another example, filaments may comprise active agents that may create health and/or safety concerns if they become airborne. For example, the filament may be used to inhibit enzymes within the filament from becoming airborne.

[0101] In one example, the filaments may be meltblown filaments. In another example, the filaments may be spunbond filaments. In another example, the filaments may be hollow filaments prior to and/or after release of one or more of its

active agents.

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**[0102]** Suitable filaments may be hydrophilic or hydrophobic. The filaments may be surface treated and/or internally treated to change the inherent hydrophilic or hydrophobic properties of the filament.

[0103] In one example, the filament exhibits a diameter of less than 100  $\mu$ m and/or less than 75  $\mu$ m and/or less than 30  $\mu$ m and/or less than 10  $\mu$ m and/or less than 5  $\mu$ m and/or less than 1  $\mu$ m as measured according to the Diameter Test Method described herein. In another example, the filament can exhibit a diameter of greater than 1  $\mu$ m as measured according to the Diameter Test Method described herein. The diameter of a filament may be used to control the rate of release of one or more active agents present in the filament and/or the rate of loss and/or altering of the filament's physical structure.

**[0104]** The filament may comprise two or more different active agents. In one example, the filament comprises two or more different active agents are compatible with one another. In another example, a filament may comprise two or more different active agents, wherein the two or more different active agents are incompatible with one another.

**[0105]** In one example, the filament may comprise an active agent within the filament and an active agent on an external surface of the filament, such as coating on the filament. The active agent on the external surface of the filament may be the same or different from the active agent present in the filament. If different, the active agents may be compatible or incompatible with one another.

[0106] In one example, one or more active agents may be uniformly distributed or substantially uniformly distributed throughout the filament. In another example, one or more active agents may be distributed as discrete regions within the filament. In still another example, at least one active agent is distributed uniformly or substantially uniformly throughout the filament and at least another active agent is distributed as one or more discrete regions within the filament. In still yet another example, at least one active agent is distributed as one or more discrete regions within the filament and at least another active agent is distributed as one or more discrete regions within the first discrete regions within the filament.

<sup>5</sup> **[0107]** The filaments may be used as discrete articles. In one example, the filaments may be applied to and/or deposited on a carrier substrate, for example a wipe, paper towel, bath tissue, facial tissue, sanitary napkin, tampon, diaper, adult incontinence article, washcloth, dryer sheet, laundry sheet, laundry bar, dry cleaning sheet, netting, filter paper, fabrics, clothes, undergarments, and the like.

**[0108]** In addition, a plurality of the filaments may be collected and pressed into a film thus resulting in the film comprising the one or more filament-forming materials and the one or more active agents that are releasable from the film, such as when the film is exposed to conditions of intended use.

**[0109]** In one example, a fibrous structure having such filaments can exhibit an average disintegration time of about 60 seconds (s) or less, and/or about 30 s or less, and/or about 10 s or less, and/or about 5 s or less, and/or about 2.0 s or less, and/or 1.5 s or less as measured according to the Dissolution Test Method described herein.

**[0110]** In one example, a fibrous structure having such filaments can exhibit an average dissolution time of about 600 seconds (s) or less, and/or about 400 s or less, and/or about 300 s or less, and/or about 200 s or less, and/or about 175 s or less as measured according to the Dissolution Test Method described herein.

**[0111]** In one example, a fibrous structure having such filaments can exhibit an average disintegration time per gsm of sample of about 1.0 second/gsm (s/gsm) or less, and/or about 0.5 s/gsm or less, and/or about 0.2 s/gsm or less, and/or about 0.1 s/gsm or less, and/or about 0.05 s/gsm or less, and/or about 0.03 s/gsm or less as measured according to the Dissolution Test Method described herein.

**[0112]** In one example, a fibrous structure having such filaments can exhibit an average dissolution time per gsm of sample of about 10 seconds/gsm (s/gsm) or less, and/or about 5.0 s/gsm or less, and/or about 3.0 s/gsm or less, and/or about 2.0 s/gsm or less, and/or about 1.8 s/gsm or less, and/or about 1.5 s/gsm or less as measured according to the Dissolution Test Method described herein.

# B. Filament-forming Material

**[0113]** A filament-forming material may include any suitable material, such as a polymer or monomers capable of producing a polymer that exhibits properties suitable for making a filament, such as by a spinning process.

**[0114]** In one example, the filament-forming material may comprise a polar solvent-soluble material, such as an alcohol-soluble material and/or a water-soluble material.

[0115] In another example, the filament-forming material may comprise a non-polar solvent-soluble material.

**[0116]** In still another example, the filament forming material may comprise a polar solvent-soluble material and be free (less than 5% and/or less than 3% and/or less than 1% and/or 0% by weight on a dry filament basis and/or dry detergent product basis) of non-polar solvent-soluble materials.

**[0117]** In yet another example, the filament-forming material may be a film-forming material. In still yet another example, the filament-forming material may be synthetic or of natural origin and it may be chemically, enzymatically, and/or

physically modified.

**[0118]** In even another example, the filament-forming material may comprise a polymer selected from the group consisting of: polymers derived from acrylic monomers such as the ethylenically unsaturated carboxylic monomers and ethylenically unsaturated monomers, polyvinyl alcohol, polyacrylates, polymethacrylates, copolymers of acrylic acid and methyl acrylate, polyvinylpyrrolidones, polyalkylene oxides, starch and starch derivatives, pullulan, gelatin, hydroxypropylmethylcelluloses, methycelluloses, and carboxymethycelluloses.

**[0119]** In still another example, the filament-forming material may comprises a polymer selected from the group consisting of: polyvinyl alcohol, polyvinyl alcohol derivatives, carboxylated polyvinylalcohol, sulfonated polyvinyl alcohol, starch, starch derivatives, cellulose derivatives, hemicellulose, hemicellulose derivatives, proteins, sodium alginate, hydroxypropyl methylcellulose, chitosan, chitosan derivatives, polyethylene glycol, tetramethylene ether glycol, polyvinyl pyrrolidone, hydroxymethyl cellulose, hydroxyethyl cellulose, and mixtures thereof.

[0120] In another example, the filament-forming material comprises a polymer is selected from the group consisting of: pullulan, hydroxypropylmethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, polyvinyl pyrrolidone, carboxymethyl cellulose, sodium alginate, xanthan gum, tragacanth gum, guar gum, acacia gum, Arabic gum, polyacrylic acid, methylmethacrylate copolymer, carboxyvinyl polymer, dextrin, pectin, chitin, levan, elsinan, collagen, gelatin, zein, gluten, soy protein, casein, polyvinyl alcohol, starch, starch derivatives, hemicellulose, hemicellulose derivatives, proteins, chitosan, chitosan derivatives, polyethylene glycol, tetramethylene ether glycol, hydroxymethyl cellulose, and mixtures thereof.

# i. Polar Solvent-soluble Materials

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**[0121]** Non-limiting examples of polar solvent-soluble materials include polar solvent-soluble polymers. The polar solvent-soluble polymers may be synthetic or natural original and may be chemically and/or physically modified. In one example, the polar solvent-soluble polymers exhibit a weight average molecular weight of at least 10,000 g/mol and/or at least 20,000 g/mol and/or at least 40,000 g/mol and/or at least 80,000 g/mol and/or at least 100,000 g/mol and/or at least 1,000,000 g/mol and/or at least 3,000,000 g/mol and/or at least 20,000,000 g/mol and/or to about 40,000,000 g/mol and/or to about 30,000,000 g/mol.

**[0122]** In one example, the polar solvent-soluble polymers are selected from the group consisting of: alcohol-soluble polymers, water-soluble polymers and mixtures thereof. Non-limiting examples of water-soluble polymers include water-soluble hydroxyl polymers, water-soluble thermoplastic polymers, water-soluble biodegradable polymers, water-soluble non-biodegradable polymers and mixtures thereof. In one example, the water-soluble polymer comprises polyvinyl alcohol. In another example, the water-soluble polymer comprises starch. In yet another example, the water-soluble polymer comprises polyvinyl alcohol and starch.

# a. Water-soluble Hydroxyl Polymers

**[0123]** Non-limiting examples of water-soluble hydroxyl polymers can include polyols, such as polyvinyl alcohol, polyvinyl alcohol derivatives, polyvinyl alcohol copolymers, starch, starch derivatives, starch copolymers, chitosan, chitosan derivatives, chitosan copolymers, cellulose derivatives such as cellulose ether and ester derivatives, cellulose copolymers, hemicellulose, hemicellulose derivatives, hemicellulose copolymers, gums, arabinans, galactans, proteins and various other polysaccharides and mixtures thereof.

[0124] In one example, a water-soluble hydroxyl polymer can include a polysaccharide.

**[0125]** "Polysaccharides" as used herein means natural polysaccharides and polysaccharide derivatives and/or modified polysaccharides. Suitable water-soluble polysaccharides include, but are not limited to, starches, starch derivatives, chitosan, chitosan derivatives, cellulose derivatives, hemicellulose, hemicellulose derivatives, gums, arabinans, galactans and mixtures thereof. The water-soluble polysaccharide may exhibit a weight average molecular weight of from about 10,000 to about 40,000,000 g/mol and/or greater than 1,000,000 g/mol and/or greater than 3,000,000 g/mol and/or greater than 3,000,000 g/mol and/or greater than 3,000,000 g/mol.

**[0126]** The water-soluble polysaccharides may comprise non-cellulose and/or non-cellulose derivative and/or non-cellulose copolymer water-soluble polysaccharides. Such non-cellulose water-soluble polysaccharides may be selected from the group consisting of: starches, starch derivatives, chitosan, chitosan derivatives, hemicellulose, hemicellulose derivatives, gums, arabinans, galactans and mixtures thereof.

[0127] In another example, a water-soluble hydroxyl polymer can comprise a non-thermoplastic polymer.

**[0128]** The water-soluble hydroxyl polymer may have a weight average molecular weight of from about 10,000 g/mol to about 40,000,000 g/mol and/or greater than 100,000 g/mol and/or greater than 3,000,000 g/mol and/or greater than 3,000,000 g/mol to about 40,000,000 g/mol. Higher and lower molecular weight water-soluble hydroxyl polymers may be used in combination with hydroxyl polymers having a certain desired weight average molecular weight.

**[0129]** Well known modifications of water-soluble hydroxyl polymers, such as natural starches, include chemical modifications and/or enzymatic modifications. For example, natural starch can be acid-thinned, hydroxy-ethylated, hydroxy-propylated, and/or oxidized. In addition, the water-soluble hydroxyl polymer may comprise dent corn starch.

[0130] Naturally occurring starch is generally a mixture of linear amylose and branched amylopectin polymer of D-glucose units. The amylose is a substantially linear polymer of D-glucose units joined by (1,4)- $\alpha$ -D links. The amylopectin is a highly branched polymer of D-glucose units joined by (1,4)- $\alpha$ -D links and (1,6)- $\alpha$ -D links at the branch points. Naturally occurring starch typically contains relatively high levels of amylopectin, for example, corn starch (64-80% amylopectin), waxy maize (93-100% amylopectin), rice (83-84% amylopectin), potato (about 78% amylopectin), and wheat (73-83% amylopectin). Though all starches are potentially useful herein, most are commonly practiced with high amylopectin natural starches derived from agricultural sources, which offer the advantages of being abundant in supply, easily replenishable and inexpensive.

**[0131]** As used herein, "starch" includes any naturally occurring unmodified starches, modified starches, synthetic starches and mixtures thereof, as well as mixtures of the amylose or amylopectin fractions; the starch may be modified by physical, chemical, or biological processes, or combinations thereof. The choice of unmodified or modified starch may depend on the end product desired. In one embodiment, the starch or starch mixture useful has an amylopectin content from about 20% to about 100%, more typically from about 40% to about 90%, even more typically from about 60% to about 85% by weight of the starch or mixtures thereof.

**[0132]** Suitable naturally occurring starches can include, but are not limited to, corn starch, potato starch, sweet potato starch, wheat starch, sago palm starch, tapioca starch, rice starch, soybean starch, arrow root starch, amioca starch, bracken starch, lotus starch, waxy maize starch, and high amylose corn starch. Naturally occurring starches particularly, corn starch and wheat starch, are the preferred starch polymers due to their economy and availability.

**[0133]** Polyvinyl alcohols herein can be grafted with other monomers to modify its properties. A wide range of monomers has been successfully grafted to polyvinyl alcohol. Non-limiting examples of such monomers include vinyl acetate, styrene, acrylamide, acrylic acid, 2-hydroxyethyl methacrylate, acrylonitrile, 1,3-butadiene, methyl methacrylate, methacrylic acid, maleic acid, itaconic acid, sodium vinylsulfonate, sodium allylsulfonate, sodium methylallyl sulfonate, sodium phenylallylether sulfonate, 2-acrylamido-methyl propane sulfonic acid (AMPs), vinylidene chloride, vinyl chloride, vinyl amine and a variety of acrylate esters.

[0134] In one example, the water-soluble hydroxyl polymer is selected from the group consisting of: polyvinyl alcohols, hydroxymethylcelluloses, hydroxypethylcelluloses, hydroxypropylme-thylcelluloses and mixtures thereof. A non-limiting example of a suitable polyvinyl alcohol includes those commercially available from Sekisui Specialty Chemicals America, LLC (Dallas, TX) under the CELVOL® trade name. A non-limiting example of a suitable hydroxypropylmethylcellulose includes those commercially available from the Dow Chemical Company (Midland, MI) under the METHOCEL® trade name including combinations with above mentioned polyvinyl alcohols.

# b. Water-soluble Thermoplastic Polymers

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**[0135]** Non-limiting examples of suitable water-soluble thermoplastic polymers include thermoplastic starch and/or starch derivatives, polylactic acid, polyhydroxyalkanoate, polycaprolactone, polyesteramides and certain polyesters, and mixtures thereof.

**[0136]** The water-soluble thermoplastic polymers may be hydrophilic or hydrophobic. The water-soluble thermoplastic polymers may be surface treated and/or internally treated to change the inherent hydrophilic or hydrophobic properties of the thermoplastic polymer.

[0137] The water-soluble thermoplastic polymers may comprise biodegradable polymers.

**[0138]** Any suitable weight average molecular weight for the thermoplastic polymers may be used. For example, the weight average molecular weight for a thermoplastic polymer can be greater than about 10,000 g/mol and/or greater than about 40,000 g/mol and/or greater than about 50,000 g/mol and/or less than about 500,000 g/mol and/or less than about 400,000 g/mol and/or less than about 200,000 g/mol.

# ii. Non-polar Solvent-soluble Materials

**[0139]** Non-limiting examples of non-polar solvent-soluble materials include non-polar solvent-soluble polymers. Non-limiting examples of suitable non-polar solvent-soluble materials include cellulose, chitin, chitin derivatives, polyolefins, polyesters, copolymers thereof, and mixtures thereof. Non-limiting examples of polyolefins include polypropylene, polyethylene and mixtures thereof. A non-limiting example of a polyester includes polyethylene terephthalate.

**[0140]** The non-polar solvent-soluble materials may comprise a non-biodegradable polymer such as polypropylene, polyethylene and certain polyesters.

**[0141]** Any suitable weight average molecular weight for the thermoplastic polymers may be used. For example, the weight average molecular weight for a thermoplastic polymer can be greater than about 10,000 g/mol and/or greater

than about 40,000 g/mol and/or greater than about 50,000 g/mol and/or less than about 500,000 g/mol and/or less than about 400,000 g/mol and/or less than about 200,000 g/mol.

# C. Active Agents

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[0142] Active agents are a class of additives that are designed and intended to provide a benefit to something other than the filament itself, such as providing a benefit to an environment external to the filament. Active agents may be any suitable additive that produces an intended effect under intended use conditions of the filament. For example, the active agent may be selected from the group consisting of: personal cleansing and/or conditioning agents such as hair care agents such as shampoo agents and/or hair colorant agents, hair conditioning agents, skin care agents, sunscreen agents, and skin conditioning agents; laundry care and/or conditioning agents such as fabric care agents, fabric conditioning agents, fabric softening agents, fabric anti-wrinkling agents, fabric care antistatic agents, fabric care stain removal agents, soil release agents, dispersing agents, suds suppressing agents, suds boosting agents, anti-foam agents, and fabric refreshing agents; liquid and/or powder dishwashing agents (for hand dishwashing and/or automatic dishwashing machine applications), hard surface care agents, and/or conditioning agents and/or polishing agents; other cleaning and/or conditioning agents such as antimicrobial agents, perfume, bleaching agents (such as oxygen bleaching agents, hydrogen peroxide, percarbonate bleaching agents, perborate bleaching agents, chlorine bleaching agents), bleach activating agents, chelating agents, builders, lotions, brightening agents, air care agents, carpet care agents, dye transferinhibiting agents, water-softening agents, water-hardening agents, pH adjusting agents, enzymes, flocculating agents, effervescent agents, preservatives, cosmetic agents, make-up removal agents, lathering agents, deposition aid agents, coacervate-forming agents, clays, thickening agents, latexes, silicas, drying agents, odor control agents, antiperspirant agents, cooling agents, warming agents, absorbent gel agents, anti-inflammatory agents, dyes, pigments, acids, and bases; liquid treatment active agents; agricultural active agents; industrial active agents; ingestible active agents such as medicinal agents, teeth whitening agents, tooth care agents, mouthwash agents, periodontal gum care agents, edible agents, dietary agents, vitamins, minerals; water-treatment agents such as water clarifying and/or water disinfecting agents, and mixtures thereof.

**[0143]** Non-limiting examples of suitable cosmetic agents, skin care agents, skin conditioning agents, hair care agents, and hair conditioning agents are described in CTFA Cosmetic Ingredient Handbook, Second Edition, The Cosmetic, Toiletries, and Fragrance Association, Inc. 1988, 1992.

**[0144]** One or more classes of chemicals may be useful for one or more of the active agents listed above. For example, surfactants may be used for any number of the active agents described above. Likewise, bleaching agents may be used for fabric care, hard surface cleaning, dishwashing and even teeth whitening. Therefore, one of ordinary skill in the art will appreciate that the active agents will be selected based upon the desired intended use of the filament and/or nonwoven made therefrom.

**[0145]** For example, if a filament and/or nonwoven made therefrom is to be used for hair care and/or conditioning then one or more suitable surfactants, such as a lathering surfactant could be selected to provide the desired benefit to a consumer when exposed to conditions of intended use of the filament and/or nonwoven incorporating the filament.

**[0146]** In one example, if a filament and/or nonwoven made therefrom is designed or intended to be used for laundering clothes in a laundry operation, then one or more suitable surfactants and/or enzymes and/or builders and/or perfumes and/or suds suppressors and/or bleaching agents could be selected to provide the desired benefit to a consumer when exposed to conditions of intended use of the filament and/or nonwoven incorporating the filament. In another example, if the filament and/or nonwoven made therefrom is designed to be used for laundering clothes in a laundry operation and/or cleaning dishes in a dishwashing operation, then the filament may comprise a laundry detergent composition or dishwashing detergent composition.

**[0147]** In one example, the active agent comprises a non-perfume active agent. In another example, the active agent comprises a non-surfactant active agent. In still another example, the active agent comprises a non-ingestible active agent, in other words an active agent other than an ingestible active agent.

# i. Surfactants

**[0148]** Non-limiting examples of suitable surfactants include anionic surfactants, cationic surfactants, nonionic surfactants, zwitterionic surfactants, amphoteric surfactants, and mixtures thereof. Co-surfactants may also be included in the filaments. For filaments designed for use as laundry detergents and/or dishwashing detergents, the total level of surfactants should be sufficient to provide cleaning including stain and/or odor removal, and generally ranges from about 0.5% to about 95%. Further, surfactant systems comprising two or more surfactants that are designed for use in filaments for laundry detergents and/or dishwashing detergents may include all-anionic surfactant systems, mixed-type surfactant systems comprising anionic-nonionic surfactant mixtures, or nonionic-cationic surfactant mixtures or low-foaming nonionic surfactants.

[0149] The surfactants herein can be linear or branched. In one example, suitable linear surfactants include those derived from agrochemical oils such as coconut oil, palm kernel oil, soybean oil, or other vegetable-based oils.

#### a. Anionic Surfactants

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**[0150]** Non-limiting examples of suitable anionic surfactants include alkyl sulfates, alkyl ether sulfates, branched alkyl sulfates, branched alkyl sulfates, branched alkyl alkoxylate sulfates, mid-chain branched alkyl aryl sulfonates, sulfated monoglycerides, sulfonated olefins, alkyl aryl sulfonates, primary or secondary alkane sulfonates, alkyl sulfosuccinates, acyl taurates, acyl isethionates, alkyl glycerylether sulfonate, sulfonated methyl esters, sulfonated fatty acids, alkyl phosphates, acyl glutamates, acyl sarcosinates, alkyl sulfoacetates, acylated peptides, alkyl ether carboxylates, acyl lactylates, anionic fluorosurfactants, sodium lauroyl glutamate, and combinations thereof.

**[0151]** Alkyl sulfates and alkyl ether sulfates suitable for use herein include materials with the respective formula  $ROSO_3M$  and  $RO(C_2H_4O)_xSO_3M$ , wherein R is alkyl or alkenyl of from about 8 to about 24 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Other suitable anionic surfactants are described in McCutcheon's Detergents and Emulsifiers, North American Edition (1986), Allured Publishing Corp. and McCutcheon's, Functional Materials, North American Edition (1992), Allured Publishing Corp.

**[0152]** In one example, anionic surfactants useful in the filaments can include  $C_9$ - $C_{15}$  alkyl benzene sulfonates (LAS),  $C_8$ - $C_{20}$  alkyl ether sulfates, for example alkyl poly(ethoxy) sulfates,  $C_8$ - $C_{20}$  alkyl sulfates, and mixtures thereof. Other anionic surfactants include methyl ester sulfonates (MES), secondary alkane sulfonates, methyl ester ethoxylates (MEE), sulfonated estolides, and mixtures thereof.

**[0153]** In another example, the anionic surfactant is selected from the group consisting of:  $C_{11}$ - $C_{18}$  alkyl benzene sulfonates ("LAS") and primary, branched-chain and random  $C_{10}$ - $C_{20}$  alkyl sulfates ("AS"),  $C_{10}$ - $C_{18}$  secondary (2,3) alkyl sulfates of the formula  $CH_3(CH_2)_x(CHOSO_3^-M^+)$   $CH_3$  and  $CH_3$  ( $CH_2$ ) $_y(CHOSO_3^-M^+)$   $CH_2CH_3$  where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the  $C_{10}$ - $C_{18}$  alpha-sulfonated fatty acid esters, the  $C_{10}$ - $C_{18}$  sulfated alkyl polyglycosides, the  $C_{10}$ - $C_{18}$  alkyl alkoxy sulfates ("AE $_x$ S") wherein x is from 1-30, and  $C_{10}$ - $C_{18}$  alkyl alkoxy carboxylates, for example comprising 1-5 ethoxy units, mid-chain branched alkyl sulfates as discussed in US 6,020,303 and US 6,060,443; mid-chain branched alkyl alkoxy sulfates as discussed in US 6,008,181 and US 6,020,303; modified alkylbenzene sulfonate (MLAS) as discussed in WO 99/05243, WO 99/05242 and WO 99/05244; methyl ester sulfonate (MES); and alpha-olefin sulfonate (AOS).

[0154] Other suitable anionic surfactants that may be used are alkyl ester sulfonate surfactants including sulfonated linear esters of  $C_8$ - $C_{20}$  carboxylic acids (i.e., fatty acids). Other suitable anionic surfactants that may be used include salts of soap,  $C_8$ - $C_{22}$  primary of secondary alkanesulfonates,  $C_8$ - $C_{24}$  olefinsulfonates, sulfonated polycarboxylic acids,  $C_8$ - $C_{24}$  alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (for example saturated and unsaturated  $C_{12}$ - $C_{18}$ - $C_{1$ 

[0155] Other exemplary anionic surfactants are the alkali metal salts of  $C_{10}$ - $C_{16}$  alkyl benzene sulfonic acids, preferably  $C_{11}$ - $C_{14}$  alkyl benzene sulfonic acids. In one example, the alkyl group is linear. Such linear alkyl benzene sulfonates are known as "LAS". Such surfactants and their preparation are described for example in U.S. Patent Nos. 2,220,099 and 2,477,383. IN another example, the linear alkyl benzene sulfonates include the sodium and/or potassium linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14. Sodium  $C_{11}$ - $C_{14}$  LAS, e.g.,  $C_{12}$  LAS, is a specific example of such surfactants.

**[0156]** Another exemplary type of anionic surfactant comprises linear or branched ethoxylated alkyl sulfate surfactants. Such materials, also known as alkyl ether sulfates or alkyl polyethoxylate sulfates, are those which correspond to the formula: R'-O-( $C_2H_4O$ )<sub>n</sub>- $SO_3M$  wherein R' is a  $C_8$ - $C_{20}$  alkyl group, n is from about 1 to 20, and M is a salt-forming cation. In a specific embodiment, R' is  $C_{10}$ - $C_{18}$  alkyl, n is from about 1 to 15, and M is sodium, potassium, ammonium, alkylammonium, or alkanolammonium. In more specific embodiments, R' is a  $C_{12}$ - $C_{16}$ , n is from about 1 to 6 and M is sodium. The alkyl ether sulfates will generally be used in the form of mixtures comprising varying R' chain lengths and varying degrees of ethoxylation. Frequently such mixtures will inevitably also contain some non-ethoxylated alkyl sulfate materials, i.e., surfactants of the above ethoxylated alkyl sulfate formula wherein n=0. Non-ethoxylated alkyl sulfates may also be added separately to the compositions and used as or in any anionic surfactant component which may be present. Specific examples of non-alkoyxylated, e.g., non-ethoxylated, alkyl ether sulfate surfactants are those produced by the sulfation of higher  $C_8$ - $C_{20}$  fatty alcohols. Conventional primary alkyl sulfate surfactants have the general formula: R''OSO $_3$ - $M^+$  wherein R'' is typically a  $C_8$ - $C_{20}$  alkyl group, which may be straight chain or branched chain, and M is a water-

solubilizing cation. In specific embodiments, R" is a  $C_{10}$ - $C_{15}$  alkyl group, and M is alkali metal, more specifically R" is  $C_{12}$ - $C_{14}$  alkyl and M is sodium. Specific, non-limiting examples of anionic surfactants useful herein include: a)  $C_{11}$ - $C_{18}$  alkyl benzene sulfonates (LAS); b)  $C_{10}$ - $C_{20}$  primary, branched-chain and random alkyl sulfates (AS); c)  $C_{10}$ - $C_{18}$  secondary (2,3)-alkyl sulfates having following formulae:

$$\begin{array}{ccc} \text{OSO}_3^{\text{-}}\text{M}^{\text{+}} & \text{OSO}_3^{\text{-}}\text{M}^{\text{+}} \\ \text{CH}_3(\text{CH}_2)_x(\text{CH})\text{CH}_3 & \text{or} & \text{CH}_3(\text{CH}_2)_y(\text{CH})\text{CH}_2\text{CH}_3 \end{array}$$

wherein M is hydrogen or a cation which provides charge neutrality, and all M units, whether associated with a surfactant or adjunct ingredient, can either be a hydrogen atom or a cation depending upon the form isolated by the artisan or the relative pH of the system wherein the compound is used, with non-limiting examples of suitable cations including sodium, potassium, ammonium, and mixtures thereof, and x is an integer of at least 7 and/or at least about 9, and y is an integer of at least 8 and/or at least 9; d)  $C_{10}$ - $C_{18}$  alkyl alkoxy sulfates (AE<sub>z</sub>S) wherein z, for example, is from 1-30; e)  $C_{10}$ - $C_{18}$  alkyl alkoxy carboxylates preferably comprising 1-5 ethoxy units; f) mid-chain branched alkyl sulfates as discussed in U.S. Patent Nos. 6,020,303 and 6,060,443; g) mid-chain branched alkyl alkoxy sulfates as discussed in U.S. Patent Nos. 6,008,181 and 6,020,303; h) modified alkylbenzene sulfonate (MLAS) as discussed in WO 99/05243, WO 99/05242, WO 99/05084, WO 99/05084, WO 99/050841, WO 99/07656, WO 00/23549, and WO 00/23548.; i) methyl ester sulfonate (MES); and j) alpha-olefin sulfonate (AOS).

# b. Cationic Surfactants

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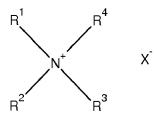
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[0157] Non-limiting examples of suitable cationic surfactants include, but are not limited to, those having the formula (I):



in which  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are each independently selected from (a) an aliphatic group of from 1 to 26 carbon atoms, or (b) an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulphate, and alkylsulphate radicals. In one example, the alkylsulphate radical is methosulfate and/or ethosulfate.

[0158] Suitable quaternary ammonium cationic surfactants of general formula (I) may include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride (BTAC), stearyltrimethylammonium chloride, cetylpyridinium chloride, octadecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, diodecyldimethylammonium chloride, diodecyldimethylammonium chloride, diodecyldimethylammonium chloride, diotadecyldimethylammonium chloride, distearyldimethylammonium chloride, tallowtrimethylammonium chloride, cocotrimethylammonium chloride, 2-ethylhexylstearyldimethylammonum chloride, dipalmitoylethyldimethylammonium chloride, PEG-2 oleylammonium chloride and salts of these, where the chloride is replaced by halogen, (e.g., bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, or alkylsulphate.

[0159] Non-limiting examples of suitable cationic surfactants are commercially available under the trade names AR-QUAD® from Akzo Nobel Surfactants (Chicago, IL).

**[0160]** In one example, suitable cationic surfactants include quaternary ammonium surfactants, for example that have up to 26 carbon atoms include: alkoxylate quaternary ammonium (AQA) surfactants as discussed in US 6,136,769; dimethyl hydroxyethyl quaternary ammonium as discussed in 6,004,922; dimethyl hydroxyethyl lauryl ammonium chloride; polyamine cationic surfactants as discussed in WO 98/35002, WO 98/35003, WO 98/35004, WO 98/35005, and WO 98/35006; cationic ester surfactants as discussed in US Patents Nos. 4,228,042, 4,239,660 4,260,529 and US 6,022,844; and amino surfactants as discussed in US 6,221,825 and WO 00/47708, for example amido propyldimethyl amine (APA).

**[0161]** Other suitable cationic surfactants include salts of primary, secondary, and tertiary fatty amines. In one embodiment, the alkyl groups of such amines have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. These amines are typically used in combination with an acid to provide the cationic species.

[0162] The cationic surfactant may include cationic ester surfactants having the formula:

$$R_{1}[O[(CH)_{n}O]_{b}] = \frac{R_{2}}{a} (X) \frac{R_{2}}{u} (CH_{2}) \frac{R_{2}}{m} (Y) \frac{R_{2}}{v} (CH_{2}) \frac{R_{2}}{t} R_{3} M^{-1}$$

wherein  $R_1$  is a  $C_5$ - $C_{31}$  linear or branched alkyl, alkenyl or alkaryl chain or  $M^-$  . $N^+(R_6R_7R_8)(CH_2)_s$ ; X and Y, independently, are selected from the group consisting of COO, OCO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCOO, OCOOH or NHCOO group;  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_6$ ,  $R_7$  and  $R_8$  are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxyalkenyl and alkaryl groups having from 1 to 4 carbon atoms; and  $R_5$  is independently H or a  $C_1$ - $C_3$  alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion. In one example,  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from  $CH_3$  and  $CH_2CH_2OH$ . In another example, M is selected from the group consisting of halide, methyl sulfate, sulfate, nitrate, chloride, bromide, or iodide.

[0163] The cationic surfactants may be chosen for use in personal cleansing applications. In one example, such cationic surfactants may be included in the filament and/or fiber at a total level by weight of from about 0.1% to about 10% and/or from about 0.5% to about 8% and/or from about 1% to about 5% and/or from about 1.4% to about 4%, in view of balance among ease-to-rinse feel, rheology and wet conditioning benefits. A variety of cationic surfactants including mono- and di-alkyl chain cationic surfactants can be used in the compositions. In one example, the cationic surfactants include mono-alkyl chain cationic surfactants in view of providing desired gel matrix and wet conditioning benefits. The mono-alkyl cationic surfactants are those having one long alkyl chain which has from 12 to 22 carbon atoms and/or from 16 to 22 carbon atoms and/or from 18 to 22 carbon atoms in its alkyl group, in view of providing balanced wet conditioning benefits. The remaining groups attached to nitrogen are independently selected from an alkyl group of from 1 to about 4 carbon atoms or an alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 4 carbon atoms. Such mono-alkyl cationic surfactants include, for example, mono-alkyl quaternary ammonium salts and mono-alkyl amines. Mono-alkyl quaternary ammonium salts include, for example, those having a non-functionalized long alkyl chain. Mono-alkyl amines include, for example, mono-alkyl amidoamines and salts thereof. Other cationic surfactants such as di-alkyl chain cationic surfactants may also be used alone, or in combination with the mono-alkyl chain cationic surfactants. Such di-alkyl chain cationic surfactants include, for example, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, and dicetyl dimethyl ammonium chloride.

[0164] In one example the cationic ester surfactants are hydrolyzable under the conditions of a laundry wash.

# c. Nonionic Surfactants

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**[0165]** Non-limiting examples of suitable nonionic surfactants include alkoxylated alcohols (AE's) and alkyl phenols, polyhydroxy fatty acid amides (PFAA's), alkyl polyglycosides (APG's), C<sub>10</sub>-C<sub>18</sub> glycerol ethers, and the like.

**[0166]** In one example, non-limiting examples of nonionic surfactants useful include:  $C_{12}$ - $C_{18}$  alkyl ethoxylates, such as, NEODOL® nonionic surfactants from Shell;  $C_6$ - $C_{12}$  alkyl phenol alkoxylates wherein the alkoxylate units are a mixture of ethyleneoxy and propyleneoxy units;  $C_{12}$ - $C_{18}$  alcohol and  $C_6$ - $C_{12}$  alkyl phenol condensates with ethylene oxide/propylene oxide block alkyl polyamine ethoxylates such as PLURONIC® from BASF;  $C_{14}$ - $C_{22}$  mid-chain branched alcohols, BA, as discussed in US 6,150,322;  $C_{14}$ - $C_{22}$  mid-chain branched alkyl alkoxylates, BAE<sub>x</sub>, wherein x is from 1-30, as discussed in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as discussed in U.S. 4,565,647 Llenado, issued January 26, 1986; specifically alkylpolyglycosides as discussed in US 4,483,780 and US 4,483,779; polyhydroxy detergent acid amides as discussed in US 5,332,528; and ether capped poly(oxyalkylated) alcohol surfactants as discussed in US 6,482,994 and WO 01/42408.

**[0167]** Examples of commercially available nonionic surfactants suitable include: Tergitol® 15-S-9 (the condensation product of  $C_{11}$ - $C_{15}$  linear alcohol with 9 moles ethylene oxide) and Tergitol® 24-L-6 NMW (the condensation product of  $C_{12}$ - $C_{14}$  primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Dow Chemical Company; Neodol® 45-9 (the condensation product of  $C_{14}$ - $C_{15}$  linear alcohol with 9 moles of ethylene oxide), Neodol® 23-3 (the condensation product of  $C_{12}$ - $C_{13}$  linear alcohol with 3 moles of ethylene oxide), Neodol® 45-7 (the condensation product of  $C_{14}$ - $C_{15}$  linear alcohol with 7 moles of ethylene oxide) and Neodol® 45-5 (the condensation product of  $C_{14}$ - $C_{15}$  linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company; Kyro® EOB (the condensation product of  $C_{13}$ - $C_{15}$  alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company; and Genapol LA 030 or O5O (the condensation product of  $C_{12}$ - $C_{14}$  alcohol with 3 or 5 moles of ethylene oxide) marketed

by Hoechst. The nonionic surfactants may exhibit an HLB range of from about 8 to about 17 and/or from about 8 to about 14. Condensates with propylene oxide and/or butylene oxides may also be used.

**[0168]** Non-limiting examples of semi-polar nonionic surfactants useful include: water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl moieties and hydroxyalkyl moieties containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl moieties and hydroxyalkyl moieties containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl moieties and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms. See WO 01/32816, US 4,681,704, and US 4,133,779.

**[0169]** Another class of nonionic surfactants that may be used include polyhydroxy fatty acid amide surfactants of the following formula:

$$R_2$$
— $C$ — $N$ — $Z$ ,
 $O$ 
 $R_1$ 

wherein  $R^1$  is H, or  $C_{1-4}$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof,  $R_2$  is  $C_{5-31}$  hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. In one example,  $R^1$  is methyl,  $R_2$  is a straight  $C_{11-15}$  alkyl or  $C_{15-17}$  alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction. Typical examples include the  $C_{12}$ - $C_{18}$  and  $C_{12}$ - $C_{14}$  N-methylglucamides

[0170] Alkylpolyaccharide surfactants may also be used as a nonionic surfactant.

**[0171]** Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are also suitable for use as a nonionic surfactant. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100 and X-102, all marketed by the Dow Chemical Company.

**[0172]** For automatic dishwashing applications, low foaming nonionic surfactants may be used. Suitable low foaming nonionic surfactants are disclosed in US 7,271,138 col. 7, line 10 to col. 7, line 60.

**[0173]** Examples of other suitable nonionic surfactants are the commercially-available Pluronic® surfactants, marketed by BASF, the commercially available Tetronic® compounds, marketed by BASF, and the commercially available Plurafac® surfactants, marketed by BASF.

# d. Zwitterionic Surfactants

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**[0174]** Non-limiting examples of zwitterionic or ampholytic surfactants include: derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants; betaines, including alkyl dimethyl betaine and cocodimethyl amidopropyl betaine,  $C_8$  to  $C_{18}$  (for example from  $C_{12}$  to  $C_{18}$ ) amine oxides and sulfo and hydroxy betaines, such as N-alkyl-N,N-dimethylammino-1-propane sulfonate where the alkyl group can be  $C_8$  to  $C_{18}$  and in certain embodiments from  $C_{10}$  to  $C_{14}$ .

#### e. Amphoteric Surfactants

[0175] Non-limiting examples of amphoteric surfactants include: aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain and mixtures thereof. One of the aliphatic substituents may contain at least about 8 carbon atoms, for example from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 at column 19, lines 18-35, for suitable examples of amphoteric surfactants.

# f. Co-surfactants

**[0176]** In addition to the surfactants described above, the filaments may also contain co-surfactants. In the case of laundry detergents and/or dishwashing detergents, they typically contain a mixture of surfactant types in order to obtain

broad-scale cleaning performance over a variety of soils and stains and under a variety of usage conditions. A wide range of these co-surfactants can be used in the filaments. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these co-surfactants, is given herein above, and may also be found in U.S. Pat. No. 3,664,961. In other words, the surfactant systems herein may also include one or more co-surfactants selected from nonionic, cationic, anionic, zwitterionic or mixtures thereof. The selection of co-surfactant may be dependent upon the desired benefit. The surfactant system may comprise from 0% to about 10%, or from about 0.1% to about 5%, or from about 1% to about 4% by weight of the composition of other co-surfactant(s).

# g. Amine-neutralized anionic surfactants

[0177] The anionic surfactants and/or anionic co-surfactants may exist in an acid form, which may be neutralized to form a surfactant salt. In one example, the filaments may comprise a surfactant salt form. Typical agents for neutralization include a metal counterion base such as hydroxides, eg, NaOH or KOH. Other agents for neutralizing the anionic surfactants and anionic co-surfactants in their acid forms include ammonia, amines, or alkanolamines. In one example, the neutralizing agent comprises an alkanolamine, for example an alkanolamine selected from the group consisting of: monoethanolamine, diethanolamine, triethanolamine, and other linear or branched alkanolamines known in the art; for example, 2-amino-1-propanol, 1-aminopropanol, monoisopropanolamine, or 1-amino-3-propanol. Amine neutralization may be done to a full or partial extent, e.g. part of the anionic surfactant mix may be neutralized with sodium or potassium and part of the anionic surfactant mix may be neutralized with amines or alkanolamines.

#### ii. Perfumes

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**[0178]** One or more perfume and/or perfume raw materials such as accords and/or notes may be incorporated into one or more of the filaments. The perfume may comprise a perfume ingredient selected from the group consisting of: aldehyde perfume ingredients, ketone perfume ingredients, and mixtures thereof.

**[0179]** One or more perfumes and/or perfumery ingredients may be included in the filaments. A wide variety of natural and synthetic chemical ingredients useful as perfumes and/or perfumery ingredients include but not limited to aldehydes, ketones, esters, and mixtures thereof. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. In one example, a finished perfume typically comprises from about 0.01% to about 2%, by weight on a dry filament basis and/or dry web material basis.

# iii. Perfume Delivery Systems

**[0180]** Certain perfume delivery systems, methods of making certain perfume delivery systems and the uses of such perfume delivery systems are disclosed in U.S. Patent Application Publication No. 2007/0275866. Non-limiting examples of perfume delivery systems include the following:

Polymer Assisted Delivery (PAD): This perfume delivery technology uses polymeric materials to deliver perfume materials. Classical coacervation, water soluble or partly soluble to insoluble charged or neutral polymers, liquid crystals, hot melts, hydrogels, perfumed plastics, microcapsules, nano- and micro-latexes, polymeric film formers, and polymeric absorbents, polymeric adsorbents, etc. are some examples. PAD includes but is not limited to:

a.) Matrix Systems: The fragrance is dissolved or dispersed in a polymer matrix or particle. Perfumes, for example, may be 1) dispersed into the polymer prior to formulating into the product or 2) added separately from the polymer during or after formulation of the product. Diffusion of perfume from the polymer is a common trigger that allows or increases the rate of perfume release from a polymeric matrix system that is deposited or applied to the desired surface (situs), although many other triggers are know that may control perfume release. Absorption and/or adsorption into or onto polymeric particles, films, solutions, and the like are aspects of this technology. Nano- or micro-particles composed of organic materials (e.g., latexes) are examples. Suitable particles include a wide range of materials including, but not limited to polyacetal, polyacrylate, polyacrylic, polyacrylonitrile, polyamide, polyaryletherketone, polybutadiene, polybutylene, polybutylene terephthalate, polychloroprene, poly ethylene, polyethylene terephthalate, polycarbonate, polychloroprene, polyhydroxyalkanoate, polyketone, polyester, polyethylene, polyetherimide, polyethersulfone, polyethylenechlorinates, polyimide, polysoprene, polylactic acid, polymethylpentene, polyphenylene oxide, polyphenylene sulfide, polyphthalamide, polypropylene, polystyrene, polysulfone, polyvinyl acetate, polyvinyl chloride, as well as polymers or copolymers based on acrylonitrile-butadiene, cellulose acetate, ethylene-vinyl acetate, ethylene vinyl alcohol, styrene-butadiene, vinyl acetate-ethylene, and mixtures thereof.

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"Standard" systems refer to those that are "pre-loaded" with the intent of keeping the pre-loaded perfume associated with the polymer until the moment or moments of perfume release. Such polymers may also suppress the neat product odor and provide a bloom and/or longevity benefit depending on the rate of perfume release. One challenge with such systems is to achieve the ideal balance between 1) in-product stability (keeping perfume inside carrier until you need it) and 2) timely release (during use or from dry situs). Achieving such stability is particularly important during in-product storage and product aging. This challenge is particularly apparent for aqueous-based, surfactantcontaining products, such as heavy duty liquid laundry detergents. Many "Standard" matrix systems available effectively become "Equilibrium" systems when formulated into aqueous-based products. One may select an "Equilibrium" system or a Reservoir system, which has acceptable in-product diffusion stability and available triggers for release (e.g., friction). "Equilibrium" systems are those in which the perfume and polymer may be added separately to the product, and the equilibrium interaction between perfume and polymer leads to a benefit at one or more consumer touch points (versus a free perfume control that has no polymer-assisted delivery technology). The polymer may also be pre-loaded with perfume; however, part or all of the perfume may diffuse during in-product storage reaching an equilibrium that includes having desired perfume raw materials (PRMs) associated with the polymer. The polymer then carries the perfume to the surface, and release is typically via perfume diffusion. The use of such equilibrium system polymers has the potential to decrease the neat product odor intensity of the neat product (usually more so in the case of pre-loaded standard system). Deposition of such polymers may serve to "flatten" the release profile and provide increased longevity. As indicated above, such longevity would be achieved by suppressing the initial intensity and may enable the formulator to use more high impact or low odor detection threshold (ODT) or low Kovats Index (KI) PRMs to achieve FMOT benefits without initial intensity that is too strong or distorted. It is important that perfume release occurs within the time frame of the application to impact the desired consumer touch point or touch points. Suitable micro-particles and micro-latexes as well as methods of making same may be found in USPA 2005/0003980 A1. Matrix systems also include hot melt adhesives and perfume plastics. In addition, hydrophobically modified polysaccharides may be formulated into the perfumed product to increase perfume deposition and/or modify perfume release. All such matrix systems, including for example polysaccharides and nanolatexes may be combined with other PDTs, including other PAD systems such as PAD reservoir systems in the form of a perfume microcapsule (PMC). Polymer Assisted Delivery (PAD) matrix systems may include those described in the following references: U.S. Patent Application Publication Nos. 2004/0110648 A1; 2004/0092414 A1; 2004/0091445 A1 and 2004/0087476 A1; and U.S. Patents 6,531,444; 6,024,943; 6,042,792; 6,051,540; 4,540,721 and 4,973,422.

Silicones are also examples of polymers that may be used as PDT, and can provide perfume benefits in a manner similar to the polymer-assisted delivery "matrix system". Such a PDT is referred to as silicone-assisted delivery (SAD). One may pre-load silicones with perfume, or use them as an equilibrium system as described for PAD. Suitable silicones as well as making same may be found in WO 2005/102261; U.S. Patent Application Publication No. 2005/0124530A1; U.S. Patent Application Publication No. 2005/0143282A1; and WO 2003/015736. Function-alized silicones may also be used as described in U.S. Patent Application Publication No. 2006/003913 A1. Examples of silicones include polydimethylsiloxane and polyalkyldimethylsiloxanes. Other examples include those with amine functionality, which may be used to provide benefits associated with amine-assisted delivery (AAD) and/or polymer-assisted delivery (PAD) and/or amine-reaction products (ARP). Other such examples may be found in U.S. Patent No. 4,911,852; and U.S. Patent Application Nos. 2004/0058845 A1; 2004/0092425 A1 and 2005/0003980 A1.

b.) Reservoir Systems: Reservoir systems are also known as a core-shell type technology, or one in which the fragrance is surrounded by a perfume release controlling membrane, which may serve as a protective shell. The material inside the microcapsule is referred to as the core, internal phase, or fill, whereas the wall is sometimes called a shell, coating, or membrane. Microparticles or pressure sensitive capsules or microcapsules are examples of this technology. Microcapsules of the current invention are formed by a variety of procedures that include, but are not limited to, coating, extrusion, spray-drying, interfacial, in-situ and matrix polymerization. The possible shell materials vary widely in their stability toward water. Among the most stable are polyoxymethyleneurea (PMU)-based materials, which may hold certain PRMs for even long periods of time in aqueous solution (or product). Such systems include but are not limited to urea-formaldehyde and/or melamine-formaldehyde. Stable shell materials include polyacrylate-based materials obtained as reaction product of an oil soluble or dispersible amine with a multifunctional acrylate or methacrylate monomer or oligomer, an oil soluble acid and an initiator, in presence of an anionic emulsifier comprising a water soluble or water dispersible acrylic acid alkyl acid copolymer, an alkali or alkali salt. Gelatinbased microcapsules may be prepared so that they dissolve quickly or slowly in water, depending for example on the degree of cross-linking. Many other capsule wall materials are available and vary in the degree of perfume diffusion stability observed. Without wishing to be bound by theory, the rate of release of perfume from a capsule, for example, once deposited on a surface is typically in reverse order of in-product perfume diffusion stability. As such, urea-formaldehyde and melamine-formaldehyde microcapsules for example, typically require a release mechanism other than, or in addition to, diffusion for release, such as mechanical force (e.g., friction, pressure, shear stress) that serves to break the capsule and increase the rate of perfume (fragrance) release. Other triggers include

melting, dissolution, hydrolysis or other chemical reaction, electromagnetic radiation, and the like. The use of pre-loaded microcapsules requires the proper ratio of in-product stability and in-use and/or on-surface (on-situs) release, as well as proper selection of PRMs. Microcapsules that are based on urea-formaldehyde and/or melamine-formaldehyde are relatively stable, especially in near neutral aqueous-based solutions. These materials may require a friction trigger which may not be applicable to all product applications. Other microcapsule materials (e.g., gelatin) may be unstable in aqueous-based products and may even provide reduced benefit (versus free perfume control) when in-product aged. Scratch and sniff technologies are yet another example of PAD. Perfume microcapsules (PMC) may include those described in the following references: U.S. Patent Application Publication Nos.: 2003/0125222 A1; 2003/215417 A1; 2003/216488 A1; 2003/158344 A1; 2003/165692 A1; 2004/071742 A1; 2004/071746 A1; 2004/072719 A1; 2004/072720 A1; 2006/0039934 A1; 2003/203829 A1; 2003/195133 A1; 2004/087477 A1; 2004/0106536 A1; and U.S. Patent Nos. 6,645,479 B1; 6,200,949 B1; 4,882,220; 4,917,920; 4,514,461; 6,106,875 and 4,234,627, 3,594,328 and US RE 32713, PCT Patent Application: WO 2009/134234 A1, WO 2006/127454 A2, WO 2010/079466 A2, WO 2010/079467 A2, WO 2010/079468 A2, WO 2010/084480 A2.

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[0181] Molecule-Assisted Delivery (MAD): Non-polymer materials or molecules may also serve to improve the delivery of perfume. Without wishing to be bound by theory, perfume may non-covalently interact with organic materials, resulting in altered deposition and/or release. Non-limiting examples of such organic materials include but are not limited to hydrophobic materials such as organic oils, waxes, mineral oils, petrolatum, fatty acids or esters, sugars, surfactants, liposomes and even other perfume raw material (perfume oils), as well as natural oils, including body and/or other soils. Perfume fixatives are yet another example. In one aspect, non-polymeric materials or molecules have a CLogP greater than about 2. Molecule-Assisted Delivery (MAD) may also include those described in U.S. Patent Nos. 7,119,060 and 5,506,201.

[0182] Fiber-Assisted Delivery (FAD): The choice or use of a situs itself may serve to improve the delivery of perfume. In fact, the situs itself may be a perfume delivery technology. For example, different fabric types such as cotton or polyester will have different properties with respect to ability to attract and/or retain and/or release perfume. The amount of perfume deposited on or in fibers may be altered by the choice of fiber, and also by the history or treatment of the fiber, as well as by any fiber coatings or treatments. Fibers may be woven and non-woven as well as natural or synthetic. Natural fibers include those produced by plants, animals, and geological processes, and include but are not limited to cellulose materials such as cotton, linen, hemp jute, flax, ramie, and sisal, and fibers used to manufacture paper and cloth. Fiber-Assisted Delivery may consist of the use of wood fiber, such as thermomechanical pulp and bleached or unbleached kraft or sulfite pulps. Animal fibers consist largely of particular proteins, such as silk, sinew, catgut and hair (including wool). Polymer fibers based on synthetic chemicals include but are not limited to polyamide nylon, PET or PBT polyester, phenol-formaldehyde (PF), polyvinyl alcohol fiber (PVOH), polyvinyl chloride fiber (PVC), polyolefins (PP and PE), and acrylic polymers. All such fibers may be pre-loaded with a perfume, and then added to a product that may or may not contain free perfume and/or one or more perfume delivery technologies. In one aspect, the fibers may be added to a product prior to being loaded with a perfume, and then loaded with a perfume by adding a perfume that may diffuse into the fiber, to the product. Without wishing to be bound by theory, the perfume may absorb onto or be adsorbed into the fiber, for example, during product storage, and then be released at one or more moments of truth or consumer touch points.

[0183] Amine Assisted Delivery (AAD): The amine-assisted delivery technology approach utilizes materials that contain an amine group to increase perfume deposition or modify perfume release during product use. There is no requirement in this approach to pre-complex or pre-react the perfume raw material(s) and amine prior to addition to the product. In one aspect, amine-containing AAD materials suitable for use herein may be non-aromatic; for example, polyalkylimine, such as polyethyleneimine (PEI), or polyvinylamine (PVAm), or aromatic, for example, anthranilates. Such materials may also be polymeric or non-polymeric. In one aspect, such materials contain at least one primary amine. This technology will allow increased longevity and controlled release also of low ODT perfume notes (e.g., aldehydes, ketones, enones) via amine functionality, and delivery of other PRMs, without being bound by theory, via polymer-assisted delivery for polymeric amines. Without technology, volatile top notes can be lost too quickly, leaving a higher ratio of middle and base notes to top notes. The use of a polymeric amine allows higher levels of top notes and other PRMS to be used to obtain freshness longevity without causing neat product odor to be more intense than desired, or allows top notes and other PRMs to be used more efficiently. In one aspect, AAD systems are effective at delivering PRMs at pH greater than about neutral. Without wishing to be bound by theory, conditions in which more of the amines of the AAD system are deprotonated may result in an increased affinity of the deprotonated amines for PRMs such as aldehydes and ketones, including unsaturated ketones and enones such as damascone. In another aspect, polymeric amines are effective at delivering PRMs at pH less than about neutral. Without wishing to be bound by theory, conditions in which more of the amines of the AAD system are protonated may result in a decreased affinity of the protonated amines for PRMs such as aldehydes and ketones, and a strong affinity of the polymer framework for a broad range of PRMs. In such an aspect, polymer-assisted delivery may be delivering more of the perfume benefit; such systems are a subspecies of AAD and

may be referred to as Amine- Polymer-Assisted Delivery or APAD. In some cases when the APAD is employed in a composition that has a pH of less than seven, such APAD systems may also be considered Polymer-Assisted Delivery (PAD). In yet another aspect, AAD and PAD systems may interact with other materials, such as anionic surfactants or polymers to form coacervate and/or co-acervates-like systems. In another aspect, a material that contains a heteroatom other than nitrogen, for example sulfur, phosphorus or selenium, may be used as an alternative to amine compounds. In yet another aspect, the aforementioned alternative compounds can be used in combination with amine compounds. In yet another aspect, a single molecule may comprise an amine moiety and one or more of the alternative heteroatom moieties, for example, thiols, phosphines and selenols. Suitable AAD systems as well as methods of making same may be found in U.S. Patent Application Publication Nos. 2005/0003980 A1; 2003/0199422 A1; 2003/0036489 A1; 2004/0220074 A1 and U.S. Patent No. 6,103,678.

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[0184] Cyclodextrin Delivery System (CD): This technology approach uses a cyclic oligosaccharide or cyclodextrin to improve the delivery of perfume. Typically a perfume and cyclodextrin (CD) complex is formed. Such complexes may be preformed, formed in-situ, or formed on or in the situs. Without wishing to be bound by theory, loss of water may serve to shift the equilibrium toward the CD-Perfume complex, especially if other adjunct ingredients (e.g., surfactant) are not present at high concentration to compete with the perfume for the cyclodextrin cavity. A bloom benefit may be achieved if water exposure or an increase in moisture content occurs at a later time point. In addition, cyclodextrin allows the perfume formulator increased flexibility in selection of PRMs. Cyclodextrin may be pre-loaded with perfume or added separately from perfume to obtain the desired perfume stability, deposition or release benefit. Suitable CDs as well as methods of making same may be found in U.S. Patent Application Publication Nos. 2005/0003980 A1 and 2006/0263313 A1 and U.S. Patent Nos. 5,552,378; 3,812,011; 4,317,881; 4,418,144 and 4,378,923.

[0185] Starch Encapsulated Accord (SEA): The use of a starch encapsulated accord (SEA) technology allows one to modify the properties of the perfume, for example, by converting a liquid perfume into a solid by adding ingredients such as starch. The benefit includes increased perfume retention during product storage, especially under non-aqueous conditions. Upon exposure to moisture, a perfume bloom may be triggered. Benefits at other moments of truth may also be achieved because the starch allows the product formulator to select PRMs or PRM concentrations that normally cannot be used without the presence of SEA. Another technology example includes the use of other organic and inorganic materials, such as silica to convert perfume from liquid to solid. Suitable SEAs as well as methods of making same may be found in U.S. Patent Application Publication No. 2005/0003980 A1 and U.S. Patent No. 6,458,754 B1.

Inorganic Carrier Delivery System (ZIC): This technology relates to the use of porous zeolites or other inorganic materials to deliver perfumes. Perfume-loaded zeolite may be used with or without adjunct ingredients used for example to coat the perfume-loaded zeolite (PLZ) to change its perfume release properties during product storage or during use or from the dry situs. Suitable zeolite and inorganic carriers as well as methods of making same may be found in U.S. Patent Application Publication No. 2005/0003980 A1 and U.S. Patent Nos. 5,858,959; 6,245,732 B1; 6,048,830 and 4,539,135. Silica is another form of ZIC. Another example of a suitable inorganic carrier includes inorganic tubules, where the perfume or other active material is contained within the lumen of the nano- or micro-tubules. In one aspect, the perfume-loaded inorganic tubule (or Perfume-Loaded Tubule or PLT) is a mineral nano- or micro-tubule, such as halloysite or mixtures of halloysite with other inorganic materials, including other clays. The PLT technology may also comprise additional ingredients on the inside and/or outside of the tubule for the purpose of improving in-product diffusion stability, deposition on the desired situs or for controlling the release rate of the loaded perfume. Monomeric and/or polymeric materials, including starch encapsulation, may be used to coat, plug, cap, or otherwise encapsulate the PLT. Suitable PLT systems as well as methods of making same may be found in U.S. Patent No. 5,651,976.

[0187] Pro-Perfume (PP): This technology refers to perfume technologies that result from the reaction of perfume materials with other substrates or chemicals to form materials that have a covalent bond between one or more PRMs and one or more carriers. The PRM is converted into a new material called a pro-PRM (i.e., pro-perfume), which then may release the original PRM upon exposure to a trigger such as water or light. Pro-perfumes may provide enhanced perfume delivery properties such as increased perfume deposition, longevity, stability, retention, and the like. Properfumes include those that are monomeric (non-polymeric) or polymeric, and may be pre-formed or may be formed insitu under equilibrium conditions, such as those that may be present during in-product storage or on the wet or dry situs. Nonlimiting examples of pro-perfumes include Michael adducts (e.g., beta-amino ketones), aromatic or non-aromatic imines (Schiff bases), oxazolidines, beta-keto esters, and orthoesters. Another aspect includes compounds comprising one or more beta-oxy or beta-thio carbonyl moieties capable of releasing a PRM, for example, an alpha, beta-unsaturated ketone, aldehyde or carboxylic ester. The typical trigger for perfume release is exposure to water; although other triggers may include enzymes, heat, light, pH change, autoxidation, a shift of equilibrium, change in concentration or ionic strength and others. For aqueous-based products, light-triggered pro-perfumes are particularly suited. Such photo-pro-perfumes (PPPs) include but are not limited to those that release coumarin derivatives and perfumes and/or pro-perfumes upon being triggered. The released pro-perfume may release one or more PRMs by means of any of the above mentioned triggers. In one aspect, the photo-pro-perfume releases a nitrogen-based pro-perfume when exposed to a light and/or moisture trigger. In another aspect, the nitrogen-based pro-perfume, released from the photo-pro-perfume, releases

one or more PRMs selected, for example, from aldehydes, ketones (including enones) and alcohols. In still another aspect, the PPP releases a dihydroxy coumarin derivative. The light-triggered pro-perfume may also be an ester that releases a coumarin derivative and a perfume alcohol. In one aspect the pro-perfume is a dimethoxybenzoin derivative as described in U.S. Patent Application Publication No. 2006/0020459 A1. In another aspect the pro-perfume is a 3', 5'-dimethoxybenzoin (DMB) derivative that releases an alcohol upon exposure to electromagnetic radiation. In yet another aspect, the pro-perfume releases one or more low ODT PRMs, including tertiary alcohols such as linalool, tetrahydrolinalool, or dihydromyrcenol. Suitable pro-perfumes and methods of making same can be found in U.S. Patent Nos. 7,018,978 B2; 6,987,084 B2; 6,956,013 B2; 6,861,402 B1; 6,544,945 B1; 6,093,691; 6,277,796 B1; 6,165,953; 6,316,397 B1; 6,437,150 B1; 6,479,682 B1; 6,096,918; 6,218,355 B1; 6,133,228; 6,147,037; 7,109,153 B2; 7,071,151 B2; 6,987,084 B2; 6,610,646 B2 and 5,958,870, as well as can be found in U.S. Patent Application Publication Nos. 2005/0003980 A1 and 2006/0223726 A1.

[0188] Amine Reaction Product (ARP): For purposes of the present application, ARP is a subclass or species of PP. One may also use "reactive" polymeric amines in which the amine functionality is pre-reacted with one or more PRMs to form an amine reaction product (ARP). Typically the reactive amines are primary and/or secondary amines, and may be part of a polymer or a monomer (non-polymer). Such ARPs may also be mixed with additional PRMs to provide benefits of polymer-assisted delivery and/or amine-assisted delivery. Nonlimiting examples of polymeric amines include polymers based on polyalkylimines, such as polyethyleneimine (PEI), or polyvinylamine (PVAm). Nonlimiting examples of monomeric (non-polymeric) amines include hydroxyl amines, such as 2-aminoethanol and its alkyl substituted derivatives, and aromatic amines such as anthranilates. The ARPs may be premixed with perfume or added separately in leave-on or rinse-off applications. In another aspect, a material that contains a heteroatom other than nitrogen, for example oxygen, sulfur, phosphorus or selenium, may be used as an alternative to amine compounds. In yet another aspect, the aforementioned alternative compounds can be used in combination with amine compounds. In yet another aspect, a single molecule may comprise an amine moiety and one or more of the alternative heteroatom moieties, for example, thiols, phosphines and selenols. The benefit may include improved delivery of perfume as well as controlled perfume release. Suitable ARPs as well as methods of making same can be found in U.S. Patent Application Publication No. 2005/0003980 A1 and U.S. Patent No. 6,413,920 B1.

### iv. Bleaching Agents

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[0189] Filaments may comprise one or more bleaching agents. Non-limiting examples of suitable bleaching agents include peroxyacids, perborate, percarbonate, chlorine bleaches, oxygen bleaches, hypohalite bleaches, bleach precursors, bleach activators, bleach catalysts, hydrogen peroxide, bleach boosters, photobleaches, bleaching enzymes, free radical initiators, peroxygen bleaches, and mixtures thereof.

**[0190]** One or more bleaching agents may be included in the filaments may be included at a level from about 1% to about 30% and/or from about 5% to about 20% by weight on a dry filament basis and/or dry web material basis. If present, bleach activators may be present in the filaments at a level from about 0.1% to about 60% and/or from about 0.5% to about 40% by weight on a dry filament basis and/or dry web material basis.

**[0191]** Non-limiting examples of bleaching agents include oxygen bleach, perborate bleach, percarboxylic acid bleach and salts thereof, peroxygen bleach, persulfate bleach, percarbonate bleach, and mixtures thereof. Further, non-limiting examples of bleaching agents are disclosed in U.S. Pat. No. 4,483,781, U.S. patent application Ser. No. 740,446, European Patent Application 0 133 354, U.S. Pat. No. 4,412,934, and U.S. Pat. No. 4,634,551.

**[0192]** Non-limiting examples of bleach activators (e.g., acyl lactam activators) are disclosed in U.S. Pat. Nos. 4,915,854; 4,412,934; 4,634,551; and 4,966,723.

[0193] In one example, the bleaching agent comprises a transition metal bleach catalyst, which may be encapsulated. The transition metal bleach catalyst typically comprises a transition metal ion, for example a transition metal ion from a transition metal selected from the group consisting of: Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(II), Fe(IV), Co(I), Co(II), Co(II), Ni(II), Ni(II), Ni(III), Cu(II), Cu(II), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(IVI), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(VI), W(VI), Pd(II), Ru(III), Ru(III), and Ru(IV). In one example, the transition metal is selected from the group consisting of: Mn(II), Mn(IV), Fe(II), Fe(III), Cr(II), Cr(III), Cr(IV), Cr(V), and Cr(VI). The transition metal bleach catalyst typically comprises a ligand, for example a macropolycyclic ligand, such as a cross-bridged macropolycyclic ligand. The transition metal ion may be coordinated with the ligand. Further, the ligand may comprise at least four donor atoms, at least two of which are bridgehead donor atoms. Non-limiting examples of suitable transition metal bleach catalysts are described in U.S. 5,580,485, U.S. 4,430,243; U.S. 4,728,455; U.S. 5,246,621; U.S. 5,244,594; U.S. 5,284,944; U.S. 5,194,416; U.S. 5,246,612; U.S. 5,256,779; U.S. 5,280,117; U.S. 5,274,147; U.S. 5,153,161; U.S. 5,227,084; U.S. 5,114,606; U.S. 5,114,611, EP 549,271 A1; EP 544,490 A1; EP 549,272 A1; and EP 544,440 A2. In one example, a suitable transition metal bleach catalyst comprises a manganese-based catalyst, for example disclosed in U.S. 5,576,282. In another example, suitable cobalt bleach catalysts are described, in U.S. 5,597,936 and U.S. 5,595,967. Such cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. 5,597,936,

and U.S. 5,595,967. In yet another, suitable transition metal bleach catalysts comprise a transition metal complex of ligand such as bispidones described in WO 05/042532 A1.

**[0194]** Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein (e.g., photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines (U.S. Pat. No. 4,033,718, incorporated herein by reference)), and/or preformed organic peracids, such as peroxycarboxylic acid or salt thereof, and/or peroxysulphonic acids or salts thereof. In one example, a suitable organic peracid comprises phthaloylimidoperoxy-caproic acid or salt thereof. When present, the photoactivated bleaching agents, such as sulfonated zinc phthalocyanine, may be present in the filaments at a level from about 0.025% to about 1.25% by weight on a dry filament basis and/or dry web material basis.

v. Brighteners

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[0195] Any optical brighteners or other brightening or whitening agents known in the art may be incorporated in the filaments at levels from about 0.01% to about 1.2% by weight on a dry filament basis and/or dry web material basis. Commercial optical brighteners which may be useful can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5-and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982). Specific nonlimiting examples of optical brighteners which are useful in the present compositions are those identified in U.S. Pat. No. 4,790,856 and U.S. Pat. No. 3,646,015.

# vi. Fabric Hueing Agents

[0196] Filaments may include fabric hueing agents. Non-limiting examples of suitable fabric hueing agents include small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.) classifications of Direct Blue, Direct Red, Direct Violet, Acid Blue, Acid Red, Acid Violet, Basic Blue, Basic Violet and Basic Red, or mixtures thereof. In another example, suitable polymeric dyes include polymeric dyes selected from the group consisting of fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA), dye-polymer conjugates formed from at least one reactive dye and a polymer selected from the group consisting of polymers comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and mixtures thereof. In still another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of Liquitint® (Milliken, Spartanburg, South Carolina, USA) Violet CT, carboxymethyl cellulose (CMC) conjugated with a reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC, alkoxylated triphenyl-methane polymeric colourants, alkoxylated thiophene polymeric colourants, and mixtures thereof.

[0197] Non-limiting examples of useful hueing dyes include those found in US 7,205,269; US 7,208,459; and US 7,674,757 B2. For example, fabric hueing dyes may be selected from the group consisting of: triarylmethane blue and violet basic dyes, methine blue and violet basic dyes, anthraquinone blue and violet basic dyes, azo dyes basic blue 16, basic blue 65, basic blue 66 basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48, oxazine dyes, basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141, Nile blue A and xanthene dye basic violet 10, an alkoxylated triphenylmethane polymeric colorant; an alkoxylated thiopene polymeric colorant; thiazolium dye; and mixtures thereof.

[0198] In one example, a fabric hueing dye includes the whitening agents found in WO 08/87497 A1. These whitening agents may be characterized by the following structure (I):

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(I)

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wherein  $R_1$  and  $R_2$  can independently be selected from:

a) [(CH<sub>2</sub>CR'HO)<sub>x</sub>(CH<sub>2</sub>CR"HO)<sub>y</sub>H]

wherein R' is selected from the group consisting of H,  $CH_3$ ,  $CH_2O(CH_2CH_2O)_zH$ , and mixtures thereof; wherein R" is selected from the group consisting of H,  $CH_2O(CH_2CH_2O)_zH$ , and mixtures thereof; wherein  $x + y \le 5$ ; wherein  $y \ge 1$ ; and wherein z = 0 to 5;

b)  $R_1$  = alkyl, aryl or aryl alkyl and  $R_2$  = [(CH<sub>2</sub>CR'HO)<sub>x</sub>(CH<sub>2</sub>CR"HO)<sub>y</sub>H] wherein R' is selected from the group consisting of H, CH<sub>3</sub>, CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>z</sub>H, and mixtures thereof; wherein R" is selected from the group consisting of H, CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>z</sub>H, and mixtures thereof; wherein x + y ≤ 10; wherein y ≥ 1; and wherein z = 0 to 5;

c)  $R_1 = [CH_2CH_2(OR_3)CH_2OR_4]$  and  $R_2 = [CH_2CH_2(OR_3)CH_2OR_4]$  wherein  $R_3$  is selected from the group consisting of H,  $(CH_2CH_2O)_zH$ , and mixtures thereof; and wherein z = 0 to 10; wherein  $R_4$  is selected from the group consisting of  $(C_1-C_{16})$  alkyl, aryl groups, and mixtures thereof; and

d) wherein R1 and R2 can independently be selected from the amino addition product of styrene oxide, glycidyl methyl ether, isobutyl glycidyl ether, isopropylglycidyl ether, t-butyl glycidyl ether, 2-ethylhexylgycidyl ether, and glycidylhexadecyl ether, followed by the addition of from 1 to 10 alkylene oxide units.

[0199] In another example, a suitable whitening agent may be characterized by the following structure (II):

40 CH<sub>3</sub>

$$N = \frac{1}{N}$$

$$N = \frac{1}{N$$

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(II)

wherein R' is selected from the group consisting of H,  $CH_3$ ,  $CH_2O(CH_2CH_2O)_zH$ , and mixtures thereof; wherein R" is selected from the group consisting of H,  $CH_2O(CH_2CH_2O)_zH$ , and mixtures thereof; wherein  $x + y \le 5$ ; wherein  $y \ge 1$ ; and wherein z = 0 to 5.

[0200] In yet another example, a suitable whitening agent may be characterized by the following structure (III):

**[0201]** This whitening agent is commonly referred to as "Violet DD". Violet DD is typically a mixture having a total of 5 EO groups. This structure is arrived by the following selection in Structure I of the following pendant groups shown in Table I below in "part a" above:

Table I R1 R2 R' R" Χ R' R" У Х У Н Н 3 1 Н 0 1 а Н b 2 1 Н Н Н Н 1 1 Н Н 1 1 Н Н 2 1 c=b d=a Н Н 0 1 Н Н 3 1

**[0202]** Further whitening agents of use include those described in US2008/34511 A1 (Unilever). In one example, the whitening agent comprises "Violet 13".

#### vii. Dye Transfer Inhibiting Agents

**[0203]** Filaments may include one or more dye transfer inhibiting agents that inhibit transfer of dyes from one fabric to another during a cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% and/or from about 0.01% to about 5% and/or from about 0.05% to about 2% by weight on a dry filament basis and/or dry web material basis.

#### viii. Chelating Agents

**[0204]** Filaments may contain one or more chelating agents, for example one or more iron and/or manganese and/or other metal ion chelating agents. Such chelating agents can be selected from the group consisting of: amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. If utilized, these chelating agents will generally comprise from about 0.1% to about 15% and/or from about 0.1% to about 10% and/or from about 0.1% to about 5% and/or from about 0.1% to about 3% by weight on a dry filament basis and/or dry web material basis.

**[0205]** The chelating agents may be chosen by one skilled in the art to provide for heavy metal (e.g. Fe) sequestration without negatively impacting enzyme stability through the excessive binding of calcium ions. Non-limiting examples of chelating agents are found in US 7445644, US 7585376 and US 2009/0176684A1.

**[0206]** Useful chelating agents include heavy metal chelating agents, such as diethylenetriaminepentaacetic acid (DTPA) and/or a catechol including, but not limited to, Tiron. In embodiments in which a dual chelating agent system is used, the chelating agents may be DTPA and Tiron.

[0207] DTPA has the following core molecular structure:

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$$HO_2C$$
 $N$ 
 $N$ 
 $CO_2H$ 
 $CO_2H$ 
 $CO_2H$ 

**[0208]** Tiron, also known as 1,2-diydroxybenzene-3,5-disulfonic acid, is one member of the catechol family and has the core molecular structure shown below:

HO<sub>3</sub>S OH OH SO<sub>3</sub>H

**[0209]** Other sulphonated catechols are of use. In addition to the disulfonic acid, the term "tiron" may also include mono- or di-sulfonate salts of the acid, such as, for example, the disodium sulfonate salt, which shares the same core molecular structure with the disulfonic acid.

**[0210]** Other chelating agents suitable for use herein can be selected from the group consisting of: aminocarboxylates, aminophosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. In one example, the chelating agents include but are not limited to: HEDP (hydroxyethanedimethylenephosphonic acid); MGDA (methylglycinediacetic acid); GLDA (glutamic-N,N-diacetic acid); and mixtures thereof.

**[0211]** Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove heavy metal ions from washing solutions by formation of soluble chelates; other benefits include inorganic film or scale prevention. Other suitable chelating agents for use herein are the commercial DEQUEST series, and chelants from Mon-santo, DuPont, and Nalco, Inc.

**[0212]** Aminocarboxylates useful as chelating agents include, but are not limited to, ethylenedi-aminetetracetates, N-(hydroxyethyl)ethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof. Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in the filaments, and include ethylenediaminetetrakis (methylenephosphonates). In one example, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Non-limiting examples of compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzenes

**[0213]** In one example, a biodegradable chelating agent comprises ethylenediamine disuccinate ("EDDS"), for example the [S,S] isomer as described in US 4,704,233. The trisodium salt of EDDS may be used. In another example, the magnesium salts of EDDS may also be used.

**[0214]** One or more chelating agents may be present in the filaments at a level from about 0.2% to about 0.7% and/or from about 0.3% to about 0.6% by weight on a dry filament basis and/or dry web material basis.

ix. Suds Suppressors

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**[0215]** Compounds for reducing or suppressing the formation of suds can be incorporated into the filaments. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. Pat. No. 4,489,455 and 4,489,574, and in front-loading-style washing machines.

**[0216]** A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). Examples of suds supressors include monocarboxylic fatty acid and soluble salts therein, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic  $C_{18}$ - $C_{40}$  ketones (e.g., stearone), N-alkylated amino triazines, waxy hydrocarbons preferably having a melting point below about 100 °C, silicone suds suppressors, and secondary alcohols. Suds supressors are described in U.S. Pat. No. 2,954,347; 4,265,779; 4,265,779; 3,455,839; 3,933,672; 4,652,392; 4,978,471; 4,983,316; 5,288,431; 4,639,489; 4,749,740; and 4,798,679; 4,075,118; European Patent Application No. 89307851.9; EP 150,872; and DOS 2,124,526.

**[0217]** For any filaments and/or fibrous structures comprising such filaments designed to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when

utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a lowsudsing laundry detergent for use in automatic laundry washing machines.

[0218] The filaments herein will generally comprise from 0% to about 10% by weight on a dry filament basis and/or dry web material basis of suds suppressors. When utilized as suds suppressors, for example monocarboxylic fatty acids, and salts therein, may be present in amounts up to about 5% and/or from about 0.5% to about 3% by weight on a dry filament basis and/or dry web material basis. When utilized, silicone suds suppressors are typically used in the filaments at a level up to about 2.0% by weight on a dry filament basis and/or dry web material basis, although higher amounts may be used. When utilized, monostearyl phosphate suds suppressors are typically used in the filaments at a level from about 0.1% to about 2% by weight on a dry filament basis and/or dry web material basis. When utilized, hydrocarbon suds suppressors are typically utilized in the filaments at a level from about 0.01% to about 5.0% by weight on a dry filament basis and/or dry web material basis, although higher levels can be used. When utilized, alcohol suds suppressors are typically used in the filaments at a level from about 0.2% to about 3% by weight on a dry filament basis and/or dry web material basis.

x. Suds Boosters

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**[0219]** If high sudsing is desired, suds boosters such as the  $C_{10}$ - $C_{16}$  alkanolamides can be incorporated into the filaments, typically at a level from 0% to about 10% and/or from about 1% to about 10% by weight on a dry filament basis and/or dry web material basis. The  $C_{10}$ - $C_{14}$  monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, water-soluble magnesium and/or calcium salts such as  $MgCl_2$ ,  $MgSO_4$ ,  $CaCl_2$ ,  $CaSO_4$  and the like, may be added to the filaments at levels from about 0.1 % to about 2% by weight on a dry filament basis and/or dry web material basis to provide additional suds.

xi. Softening Agents

**[0220]** One or more softening agents may be present in the filaments. Non-limiting examples of suitable softening agents include quaternary ammonium compounds for example a quaternary ammonium esterquat compound, silicones such as polysiloxanes, clays such as smectite clays, and mixture thereof.

**[0221]** In one example, the softening agents comprise a fabric softening agent. Non-limiting examples of fabric softening agents include impalpable smectite clays, such as those described in U.S. 4,062,647, as well as other fabric softening clays known in the art. When present, the fabric softening agent may be present in the filaments at a level from about 0.5% to about 10% and/or from about 0.5% to about 5% by weight on a dry filament basis and/or dry web material basis. Fabric softening clays may be used in combination with amine and/or cationic softening agents such as those disclosed in U.S. 4,375,416, and U.S. 4,291,071. Cationic softening agents may also be used without fabric softening clays.

xii. Conditioning Agents

**[0222]** Filaments may include one or more conditioning agents, such as a high melting point fatty compound. The high melting point fatty compound may have a melting point of about 25°C or greater, and may be selected from the group consisting of: fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. Such fatty compounds that exhibit a low melting point (less than 25°C) are not intended to be included as a conditioning agent. Non-limiting examples of the high melting point fatty compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

**[0223]** One or more high melting point fatty compounds may be included in the filaments at a level from about 0.1% to about 40% and/or from about 1% to about 30% and/or from about 1.5% to about 16% and/or from about 1.5% to about 8% by weight on a dry filament basis and/or dry web material basis. The conditioning agents may provide conditioning benefits, such as slippery feel during the application to wet hair and/or fabrics, softness and/or moisturized feel on dry hair and/or fabrics.

**[0224]** Filaments may contain a cationic polymer as a conditioning agent. Concentrations of the cationic polymer in the filaments, when present, typically range from about 0.05% to about 3% and/or from about 0.075% to about 2.0% and/or from about 0.1% to about 1.0% by weight on a dry filament basis and/or dry web material basis. Non-limiting examples of suitable cationic polymers may have cationic charge densities of at least 0.5 meq/gm and/or at least 0.9 meq/gm and/or at least 1.2 meq/gm and/or at least 1.5 meq/gm at a pH of from about 3 to about 9 and/or from about 4 to about 8. In one example, cationic polymers suitable as conditioning agents may have cationic charge densities of less than 7 meq/gm and/or less than 5 meq/gm at a pH of from about 3 to about 9 and/or from about 4 to about 8. Herein, "cationic charge density" of a polymer refers to the ratio of the number of positive charges on the polymer to the molecular

weight of the polymer. The weight average molecular weight of such suitable cationic polymers will generally be between about 10,000 and 10 million, in one embodiment between about 50,000 and about 5 million, and in another embodiment between about 100,000 and about 3 million.

**[0225]** Suitable cationic polymers for use in the filaments may contain cationic nitrogen-containing moieties such as quaternary ammonium and/or cationic protonated amino moieties. Any anionic counterions may be used in association with the cationic polymers so long as the cationic polymers remain soluble in water and so long as the counterions are physically and chemically compatible with the other components of the filaments or do not otherwise unduly impair product performance, stability or aesthetics of the filaments. Non-limiting examples of such counterions include halides (e.g., chloride, fluoride, bromide, iodide), sulfates and methylsulfates.

[0226] Non-limiting examples of such cationic polymers are described in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C. (1982)).

**[0227]** Other suitable cationic polymers for use in such filaments may include cationic polysaccharide polymers, cationic guar gum derivatives, quaternary nitrogen-containing cellulose ethers, cationic synthetic polymers, cationic copolymers of etherified cellulose, guar and starch. When used, the cationic polymers herein are soluble in water. Further, suitable cationic polymers for use in the filaments are described in U.S. 3,962,418, U.S. 3,958,581, and U.S. 2007/0207109A1, which are all incorporated herein by reference.

**[0228]** Filaments may include a nonionic polymer as a conditioning agent. Polyalkylene glycols having a molecular weight of more than about 1000 are useful herein. Useful are those having the following general formula:

wherein R<sup>95</sup> is selected from the group consisting of: H, methyl, and mixtures thereof.

**[0229]** Silicones may be included in the filaments as conditioning agents. The silicones useful as conditioning agents typically comprise a water insoluble, water dispersible, non-volatile, liquid that forms emulsified, liquid particles. Suitable conditioning agents for use in the composition are those conditioning agents characterized generally as silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicones, and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof, or those conditioning agents which otherwise form liquid, dispersed particles in the aqueous surfactant matrix herein. Such conditioning agents should be physically and chemically compatible with the essential components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

**[0230]** The concentration of the conditioning agents in the filaments may be sufficient to provide the desired conditioning benefits. Such concentration can vary with the conditioning agent, the conditioning performance desired, the average size of the conditioning agent particles, the type and concentration of other components, and other like factors.

[0231] The concentration of the silicone conditioning agents typically ranges from about 0.01% to about 10% by weight on a dry filament basis and/or dry web material basis. Non-limiting examples of suitable silicone conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584, U.S. Pat. Nos. 5,104,646; 5,106,609; 4,152,416; 2,826,551; 3,964,500; 4,364,837; 6,607,717; 6,482,969; 5,807,956; 5,981,681; 6,207,782; 7,465,439; 7,041,767; 7,217,777; US Patent Application Nos. 2007/0286837A1; 2005/0048549A1; 2007/0041929A1; British Pat. No. 849,433; German Patent No. DE 10036533, which are all incorporated herein by reference; Chemistry and Technology of Silicones, New York: Academic Press (1968); General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76; Silicon Compounds, Petrarch Systems, Inc. (1984); and in Encyclopedia of Polymer Science and Engineering, vol. 15, 2d ed., pp 204-308, John Wiley & Sons, Inc. (1989).

[0232] In one example, filaments may also comprise from about 0.05% to about 3% by weight on a dry filament basis and/or dry web material basis of at least one organic conditioning oil as a conditioning agent, either alone or in combination with other conditioning agents, such as the silicones (described herein). Suitable conditioning oils include hydrocarbon oils, polyolefins, and fatty esters. Also suitable for use in the compositions herein are the conditioning agents described by the Procter & Gamble Company in U.S. Pat. Nos. 5,674,478, and 5,750,122. Also suitable for use herein are those conditioning agents described in U.S. Pat. Nos. 4,529,586, 4,507,280, 4,663,158, 4,197,865, 4,217, 914, 4,381,919, and 4,422, 853, which are all incorporated herein by reference.

# xiii. Humectants

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**[0233]** Filaments may contain one or more humectants. The humectants herein are selected from the group consisting of polyhydric alcohols, water soluble alkoxylated nonionic polymers, and mixtures thereof. The humectants, when used, may be present in the filaments at a level from about 0.1% to about 20% and/or from about 0.5% to about 5% by weight

on a dry filament basis and/or dry web material basis.

xiv. Suspending Agents

[0234] Filaments may further comprise a suspending agent at concentrations effective for suspending water-insoluble material in dispersed form in the compositions or for modifying the viscosity of the composition. Such concentrations of suspending agents range from about 0.1% to about 10% and/or from about 0.3% to about 5.0% by weight on a dry filament basis and/or dry web material basis.

**[0235]** Non-limiting examples of suitable suspending agents include anionic polymers and nonionic polymers (e.g., vinyl polymers, acyl derivatives, long chain amine oxides, and mixtures thereof, alkanol amides of fatty acids, long chain esters of long chain alkanol amides, glyceryl esters, primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms). Examples of suspending agents are described in U.S. Pat. No. 4,741,855.

15 xv. Enzymes

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**[0236]** One or more enzymes may be present in the filaments. Non-limiting examples of suitable enzymes include proteases, amylases, lipases, cellulases, carbohydrases including mannanases and endoglucanases, pectinases, hemicellulases, peroxidases, xylanases, phopholipases, esterases, cutinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, penosanases, malanases, glucanases, arabinosidases, hyaluraonidases, chrondroitinases, laccases, and mixtures thereof.

**[0237]** Enzymes may be included in the filaments for a variety of purposes, including but not limited to removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. In one example, the filaments may include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Selections of the enzymes utilized are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to other additives, such as active agents, for example builders, present within the filaments. In one example, the enzyme is selected from the group consisting of: bacterial enzymes (for example bacterial amylases and/or bacterial proteases), fungal enzymes (for example fungal cellulases), and mixtures thereof.

[0238] When present in the filaments, the enzymes may be present at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the filament and/or fiber. Stated otherwise, the filaments can typically comprise from about 0.001% to about 5% and/or from about 0.01% to about 3% and/or from about 0.01% to about 1% by weight on a dry filament basis and/or dry web material basis.

[0239] One or more enzymes may be applied to the filament and/or fibrous structure after the filament and/or fibrous structure are produced.

**[0240]** A range of enzyme materials and means for their incorporation into the filament-forming composition, which may be a synthetic detergent composition, is also disclosed in WO 9307263 A; WO 9307260 A; WO 8908694 A; U.S. Pat. Nos. 3,553,139; 4,101,457; and U.S. Pat. No. 4,507,219.

xvi. Enzyme Stabilizing System

[0241] When enzymes are present in the filaments and/or fibers, an enzyme stabilizing system may also be included in the filaments. Enzymes may be stabilized by various techniques. Non-limiting examples of enzyme stabilization techniques are disclosed and exemplified in U.S. Pat. Nos. 3,600,319 and 3,519,570; EP 199,405, EP 200,586; and WO 9401532 A.

[0242] In one example, the enzyme stabilizing system may comprise calcium and/or magnesium ions.

[0243] The enzyme stabilizing system may be present in the filaments at a level of from about 0.001% to about 10% and/or from about 0.005% to about 8% and/or from about 0.01% to about 6% by weight on a dry filament basis and/or dry web material basis. The enzyme stabilizing system can be any stabilizing system which is compatible with the enzymes present in the filaments. Such an enzyme stabilizing system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of enzymes. Such enzyme stabilizing systems may, for example, comprise calcium ion, magnesium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems.

xvii. Builders

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**[0244]** Filaments may comprise one or more builders. Non-limiting examples of suitable builders include zeolite builders, aluminosilicate builders, silicate builders, phosphate builders, citric acid, citrates, nitrilo triacetic acid, nitrilo triacetate, polyacrylates, acrylate/maleate copolymers, and mixtures thereof.

[0245] In one example, a builder selected from the group consisting of: aluminosilicates, silicates, and mixtures thereof, may be included in the filaments. The builders may be included in the filaments to assist in controlling mineral, especially calcium and/or magnesium hardness in wash water or to assist in the removal of particulate soils from surfaces. Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following general Formula I an anhydride form:  $x(M_2O) \cdot ySiO_2 \cdot zM'O$  wherein M is Na and/or K, M' is Ca and/or Mg; y/x is 0.5 to 2.0 and z/x is 0.005 to 1.0 as taught in U.S. Pat. No. 5,427,711.

[0246] Non-limiting examples of other suitable builders that may be included in the filaments include phosphates and polyphosphates, for example the sodium salts thereof; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; organic mono-, di-, tri-, and tetracarboxylates for example water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These builders may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, for example sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing filaments.

**[0247]** Still other builders may be selected from polycarboxylates, for example copolymers of acrylic acid, copolymers of acrylic acid and maleic acid, and copolymers of acrylic acid and/or maleic acid and other suitable ethylenic monomers with various types of additional functionalities.

**[0248]** Builder level can vary widely depending upon end use. In one example, the filaments may comprise at least 1% and/or from about 1% to about 30% and/or from about 1% to about 20% and/or from about 1% to about 10% and/or from about 2% to about 5% by weight on a dry fiber basis of one or more builders.

xviii. Clay Soil Removal/Anti-Redeposition Agents

**[0249]** Filaments may contain water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. Such water-soluble ethoxylated amines may be present in the filaments at a level of from about 0.01% to about 10.0% and/or from about 0.01% to about 7% and/or from about 0.1% to about 5% by weight on a dry filament basis and/or dry web material basis of one or more water-soluble ethoxylates amines. Non-limiting examples of suitable clay soil removal and antiredeposition agents are described in U.S. Pat. Nos. 4,597,898; 548,744; 4,891,160; European Patent Application Nos. 111,965; 111,984; 112,592; and WO 95/32272.

xix. Polymeric Soil Release Agent

**[0250]** Filaments may contain polymeric soil release agents, hereinafter "SRAs." If utilized, SRA's will generally comprise from about 0.01% to about 10.0% and/or from about 0.1% to about 5% and/or from about 0.2% to about 3.0% by weight on a dry filament basis and/or dry web material basis.

**[0251]** SRAs typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with SRA to be more easily cleaned in later washing procedures.

[0252] SRAs can include, for example, a variety of charged, e.g., anionic or even cationic (see U.S. Pat. No. 4,956,447), as well as non-charged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products. Non-limiting examples of SRAs are described in U.S. Pat. Nos. 4,968,451; 4,711,730; 4,721,580; 4,702,857; 4,877,896; 3,959,230; 3,893,929; 4,000,093; 5,415,807; 4,201,824; 4,240,918; 4,525,524; 4,201,824; 4,579,681; and 4,787,989; European Patent Application 0 219 048; 279,134 A; 457,205 A; and DE 2,335,044.

xx. Polymeric Dispersing Agents

**[0253]** Polymeric dispersing agents can advantageously be utilized in the filaments at levels from about 0.1% to about 7% and/or from about 0.1% to about 5% and/or from about 0.5% to about 4% by weight on a dry filament basis and/or dry web material basis, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing

agents may include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. For example, a wide variety of modified or unmodified polyacrylates, polyacrylate/mealeates, or polyacrylate/methacrylates are highly useful. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition. Non-limiting examples of polymeric dispersing agents are found in U.S. Pat. No. 3,308,067, European Patent Application No. 66915, EP 193,360, and EP 193,360.

xxi. Alkoxylated Polyamine Polymers

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**[0254]** Alkoxylated polyamines may be included in the filaments for providing soil suspending, grease cleaning, and/or particulate cleaning. Such alkoxylated polyamines include but are not limited to ethoxylated polyethyleneimines, ethoxylated hexamethylene diamines, and sulfated versions thereof. Polypropoxylated derivatives of polyamines may also be included in the filaments. A wide variety of amines and polyaklyeneimines can be alkoxylated to various degrees, and optionally further modified to provide the abovementioned benefits. A useful example is 600g/mol polyethyleneimine core ethoxylated to 20 EO groups per NH and is available from BASF.

xxii. Alkoxylated Polycarboxylate Polymers

**[0255]** Alkoxylated polycarboxylates such as those prepared from polyacrylates may be included in the filaments to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula - (CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub> wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10% by weight on a dry filament basis and/or dry web material basis.

xxiii. Amphilic Graft Co-Polymers

[0256] Filaments may include one or more amphilic graft co-polymers. An example of a suitable amphilic graft co-polymer comprises (i) a polyethyelene glycol backbone; and (ii) and at least one pendant moiety selected from polyvinyl acetate, polyvinyl alcohol and mixtures thereof. A non-limiting example of a commercially available amphilic graft co-polymer is Sokalan HP22, supplied from BASF.

xxiv. Dissolution Aids

**[0257]** Filaments may incorporate dissolution aids to accelerate dissolution when the filament contains more the 40% surfactant to mitigate formation of insoluble or poorly soluble surfactant aggregates that can sometimes form or surfactant compositions are used in cold water. Non-limiting examples of dissolution aids include sodium chloride, sodium sulfate, potassium chloride, potassium sulfate, magnesium chloride, and magnesium sulfate.

xxv. Buffer Systems

[0258] Filaments may be formulated such that, during use in an aqueous cleaning operation, for example washing clothes or dishes, the wash water will have a pH of between about 5.0 and about 12 and/or between about 7.0 and 10.5. In the case of a dishwashing operation, the pH of the wash water typically is between about 6.8 and about 9.0. In the case of washing clothes, the pH of the was water typically is between 7 and 11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art. These include the use of sodium carbonate, citric acid or sodium citrate, monoethanol amine or other amines, boric acid or borates, and other pH-adjusting compounds well known in the art.

**[0259]** Filaments useful as "low pH" detergent compositions can be included and are especially suitable for the surfactant systems and may provide in-use pH values of less than 8.5 and/or less than 8.0 and/or less than 7.0 and/or less than 7.0 and/or to about 5.0.

[0260] Dynamic in-wash pH profile filaments can be included. Such filaments may use wax-covered citric acid particles in conjunction with other pH control agents such that (i) 3 minutes after contact with water, the pH of the wash liquor is greater than 10; (ii) 10mins after contact with water, the pH of the wash liquor is less than 9.5; (iii) 20mins after contact with water, the pH of the wash liquor is less than 9.0; and (iv) optionally, wherein, the equilibrium pH of the wash liquor is in the range of from above 7.0 to 8.5.

# xxvi. Heat Forming Agents

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[0261] Filaments may contain a heat forming agent. Heat forming agents are formulated to generate heat in the presence of water and/or oxygen (e.g., oxygen in the air, etc.) and to thereby accelerate the rate at which the fibrous structure degrades in the presence of water and/or oxygen, and/or to increase the effectiveness of one or more of the actives in the filament. The heat forming agent can also or alternatively be used to accelerate the rate of release of one or more actives from the fibrous structure. The heat forming agent is formulated to undergo an exothermic reaction when exposed to oxygen (i.e., oxygen in the air, oxygen in the water, etc.) and/or water. Many different materials and combination of materials can be used as the heat forming agent. Non-limiting heat forming agents that can be used in the fibrous structure include electrolyte salts (e.g., aluminum chloride, calcium chloride, calcium sulfate, cupric chloride, cuprous chloride, ferric sulfate, magnesium chloride, magnesium sulfate, manganese chloride, manganese sulfate, potassium chloride, potassium sulfate, sodium acetate, sodium chloride, sodium carbonate, sodium sulfate, etc.), glycols (e.g., propylene glycol, dipropylenenglycol, etc.), lime (e.g., quick lime, slaked lime, etc.), metals (e.g., chromium, copper, iron, magnesium, manganese, etc.), metal oxides (e.g., aluminum oxide, iron oxide, etc.), polyalkyleneamine, polyalkyleneimine, polyvinyl amine, zeolites, gycerin, 1,3, propanediol, polysorbates esters (e.g., Tweens 20, 60, 85, 80), and/or poly glycerol esters (e.g., Noobe, Drewpol and Drewmulze from Stepan). The heat forming agent can be formed of one or more materials. For example, magnesium sulfate can singularly form the heat forming agent. In another non-limiting example, the combination of about 2-25 weight percent activated carbon, about 30-70 weight percent iron powder and about 1-10 weight percent metal salt can form the heat forming agent. As can be appreciated, other or additional materials can be used alone or in combination with other materials to form the heat forming agent. Non-limiting examples of materials that can be used to form the heat forming agent used in a fibrous structure are disclosed in U.S. Pat. Nos. 5,674,270 and 6,020,040; and in U.S. Patent Application Publication Nos. 2008/0132438 and 2011/0301070.

#### xxvii. Degrading Accelerators

[0262] Filaments may contain a degrading accelerators used to accelerate the rate at which a fibrous structure degrades in the presence of water and/or oxygen. The degrading accelerator, when used, is generally designed to release gas when exposed to water and/or oxygen, which in turn agitates the region about the fibrous structure so as to cause acceleration in the degradation of a carrier film of the fibrous structure. The degrading accelerator, when used, can also or alternatively be used to accelerate the rate of release of one or more actives from the fibrous structure; however, this is not required. The degrading accelerator, when used, can also or alternatively be used to increase the effectivity of one or more of the actives in the fibrous structure; however, this is not required. The degrading accelerator can include one or more materials such as, but not limited to, alkali metal carbonates (e.g. sodium carbonate, potassium carbonate, etc.), alkali metal hydrogen carbonates (e.g., sodium hydrogen carbonate, potassium hydrogen carbonate, etc.), ammonium carbonate, etc. The water soluble strip can optionally include one or more activators that are used to activate or increase the rate of activation of the one or more degrading accelerators in the fibrous structure. As can be appreciated, one or more activators can be included in the fibrous structure even when no degrading accelerator exists in the fibrous structure; however, this is not required. For instance, the activator can include an acidic or basic compound, wherein such acidic or basic compound can be used as a supplement to one or more actives in the fibrous structure when a degrading accelerator is or is not included in the fibrous structure. Non-limiting examples of activators, when used, that can be included in the fibrous structure include organic acids (e.g., hydroxy-carboxylic acids [citric acid, tartaric acid, malic acid, lactic acid, gluconic acid, etc.], saturated aliphatic carboxylic acids [acetic acid, succinic acid, etc.], unsaturated aliphatic carboxylic acids [e.g., fumaric acid, etc.]. Non-limiting examples of materials that can be used to form degrading accelerators and activators used in a fibrous structure are disclosed in U.S. Patent Application Publication No. 2011/0301070.

# III. Release of Active Agent

**[0263]** One or more active agents may be released from the filament when the filament is exposed to a triggering condition. In one example, one or more active agents may be released from the filament or a part of the filament when the filament or the part of the filament loses its identity, in other words, loses its physical structure. For example, a filament loses its physical structure when the filament-forming material dissolves, melts or undergoes some other transformative step such that the filament structure is lost. In one example, the one or more active agents are released from the filament when the filament's morphology changes.

**[0264]** In another example, one or more active agents may be released from the filament or a part of the filament when the filament or the part of the filament alters its identity, in other words, alters its physical structure rather than loses its physical structure. For example, a filament alters its physical structure when the filament-forming material swells, shrinks, lengthens, and/or shortens, but retains its filament-forming properties.

**[0265]** In another example, one or more active agents may be released from the filament with the filament's morphology not changing (not losing or altering its physical structure).

[0266] In one example, the filament may release an active agent upon the filament being exposed to a triggering condition that results in the release of the active agent, such as by causing the filament to lose or alter its identity as discussed above. Non-limiting examples of triggering conditions include exposing the filament to solvent, a polar solvent, such as alcohol and/or water, and/or a non-polar solvent, which may be sequential, depending upon whether the filament-forming material comprises a polar solvent-soluble material and/or a non-polar solvent-soluble material; exposing the filament to heat, such as to a temperature of greater than 75°F and/or greater than 100°F and/or greater than 150°F and/or greater than 212°F; exposing the filament to cold, such as to a temperature of less than 40°F and/or less than 32°F and/or less than 0°F; exposing the filament to a force, such as a stretching force applied by a consumer using the filament; and/or exposing the filament to a chemical reaction; exposing the filament to a condition that results in a phase change; exposing the filament to a pH change and/or a pressure change and/or temperature change; exposing the filament to one or more chemicals that result in the filament releasing one or more of its active agents; exposing the filament to ultrasonics; exposing the filament to light and/or certain wavelengths; exposing the filament to a different ionic strength; and/or exposing the filament to an active agent released from another filament.

**[0267]** In one example, one or more active agents may be released from the filaments when a nonwoven web comprising the filaments is subjected to a triggering step selected from the group consisting of: pre-treating stains on a fabric article with the nonwoven web; forming a wash liquour by contacting the nonwoven web with water; tumbling the nonwoven web in a dryer; heating the nonwoven web in a dryer; and combinations thereof.

IV. Filament-Forming Composition

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**[0268]** The filaments are made from a filament-forming composition. The filament-forming composition can be a polar-solvent-based composition. In one example, the filament-forming composition can be an aqueous composition comprising one or more filament-forming materials and one or more active agents.

**[0269]** The filament-forming composition may be processed at a temperature of from about 50°C to about 100°C and/or from about 65°C to about 95°C and/or from about 70°C to about 90°C when making filaments from the filament-forming composition.

**[0270]** In one example, the filament-forming composition may comprise at least 20% and/or at least 30% and/or at least 40% and/or at least 45% and/or at least 50% to about 90% and/or to about 85% and/or to about 80% and/or to about 75% by weight of one or more filament-forming materials, one or more active agents, and mixtures thereof. The filament-forming composition may comprise from about 10% to about 80% by weight of a polar solvent, such as water. **[0271]** The filament-forming composition may exhibit a Capillary Number of at least 1 and/or at least 3 and/or at least 5 such that the filament-forming composition can be effectively polymer processed into a hydroxyl polymer fiber.

**[0272]** The Capillary number is a dimensionless number used to characterize the likelihood of this droplet breakup. A larger capillary number indicates greater fluid stability upon exiting the die. The Capillary number is defined as follows:

$$Ca = \frac{V * \eta}{\sigma}$$

V is the fluid velocity at the die exit (units of Length per Time),

η is the fluid viscosity at the conditions of the die (units of Mass per Length\*Time),

 $\sigma$  is the surface tension of the fluid (units of mass per Time<sup>2</sup>). When velocity, viscosity, and surface tension are expressed in a set of consistent units, the resulting Capillary number will have no units of its own; the individual units will cancel out.

**[0273]** The Capillary number is defined for the conditions at the exit of the die. The fluid velocity is the average velocity of the fluid passing through the die opening. The average velocity is defined as follows:

$$V = \frac{Vol'}{Area}$$

Vol' = volumetric flowrate (units of Length<sup>3</sup> per Time)
Area = cross-sectional area of the die exit (units of Length<sup>2</sup>).

[0274] When the die opening is a circular hole, then the fluid velocity can be defined as

$$V = \frac{Vol'}{\pi * R^2}$$

5 R is the radius of the circular hole (units of length).

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**[0275]** The fluid viscosity will depend on the temperature and may depend of the shear rate. The definition of a shear thinning fluid includes a dependence on the shear rate. The surface tension will depend on the makeup of the fluid and the temperature of the fluid.

[0276] In a fiber spinning process, the filaments need to have initial stability as they leave the die. The Capillary number is used to characterize this initial stability criterion. At the conditions of the die, the Capillary number should be greater than 1 and/or greater than 4.

**[0277]** In one example, the filament-forming composition exhibits a Capillary Number of from at least 1 to about 50 and/or at least 3 to about 50 and/or at least 5 to about 30.

[0278] In one example, the filament-forming composition may comprise one or more release agents and/or lubricants. Non-limiting examples of suitable release agents and/or lubricants include fatty acids, fatty acid salts, fatty alcohols, fatty esters, sulfonated fatty acid esters, fatty amine acetates and fatty amides, silicones, aminosilicones, fluoropolymers and mixtures thereof.

**[0279]** In one example, the filament-forming composition may comprise one or more antiblocking and/or detackifying agents. Non-limiting examples of suitable antiblocking and/or detackifying agents include starches, modified starches, crosslinked polyvinylpyrrolidone, crosslinked cellulose, microcrystalline cellulose, silica, metallic oxides, calcium carbonate, talc and mica.

**[0280]** Active agents may be added to the filament-forming composition prior to and/or during filament formation and/or may be added to the filament after filament formation. For example, a perfume active agent may be applied to the filament and/or nonwoven web are formed. In another example, an enzyme active agent may be applied to the filament and/or nonwoven web comprising the filament after the filament and/or nonwoven web are formed. In still another example, one or more particulate active agents, such as one or more ingestible active agents, such as bismuth subsalicylate, which may not be suitable for passing through the spinning process for making the filament, may be applied to the filament and/or nonwoven web comprising the filament after the filament and/or nonwoven web are formed.

V. Method for Making a Filament

[0281] Filaments may be made by any suitable process. A non-limiting example of a suitable process for making the filaments is described below.

[0282] In one example, a method for making a filament comprises the steps of: a. providing a filament-forming composition comprising one or more filament-forming materials and one or more active agents; and b. spinning the filament-forming composition into one or more filaments comprising the one or more filament-forming materials and the one or more active agents that are releasable from the filament when exposed to conditions of intended use, wherein the total level of the one or more filament-forming materials present in the filament is less than 65% and/or 50% or less by weight on a dry filament basis and/or dry detergent product basis and the total level of the one or more active agents present in the filament is greater than 35% and/or 50% or greater by weight on a dry filament basis and/or dry detergent product basis.

**[0283]** In one example, during the spinning step, any volatile solvent, such as water, present in the filament-forming composition is removed, such as by drying, as the filament is formed. In one example, greater than 30% and/or greater than 40% and/or greater than 50% of the weight of the filament-forming composition's volatile solvent, such as water, is removed during the spinning step, such as by drying the filament being produced.

**[0284]** The filament-forming composition may comprise any suitable total level of filament-forming materials and any suitable level of active agents so long as the filament produced from the filament-forming composition comprises a total level of filament-forming materials in the filament of from about 5% to 50% or less by weight on a dry filament basis and/or dry detergent product basis and a total level of active agents in the filament of from 50% to about 95% by weight on a dry filament basis and/or dry detergent product basis.

[0285] In one example, the filament-forming composition may comprise any suitable total level of filament-forming materials and any suitable level of active agents so long as the filament produced from the filament-forming composition comprises a total level of filament-forming materials in the filament of from about 5% to 50% or less by weight on a dry filament basis and/or dry detergent product basis and a total level of active agents in the filament of from 50% to about 95% by weight on a dry filament basis and/or dry detergent product basis, wherein the weight ratio of filament-forming material to additive is 1 or less.

[0286] In one example, the filament-forming composition comprises from about 1% and/or from about 5% and/or from

about 10% to about 50% and/or to about 40% and/or to about 30% and/or to about 20% by weight of the filament-forming composition of filament-forming materials; from about 1% and/or from about 5% and/or from about 10% to about 50% and/or to about 40% and/or to about 30% and/or to about 20% by weight of the filament-forming composition of active agents; and from about 20% and/or from about 25% and/or from about 30% and/or from about 40% and/or to about 80% and/or to about 50% by weight of the filament-forming composition of a volatile solvent, such as water. The filament-forming composition may comprise minor amounts of other active agents, such as less than 10% and/or less than 5% and/or less than 3% and/or less than 1% by weight of the filament-forming composition of plasticizers, pH adjusting agents, and other active agents.

**[0287]** The filament-forming composition is spun into one or more filaments by any suitable spinning process, such as meltblowing and/or spunbonding. In one example, the filament-forming composition is spun into a plurality of filaments by meltblowing. For example, the filament-forming composition may be pumped from an extruder to a meltblown spinnerette. Upon exiting one or more of the filament-forming holes in the spinnerette, the filament-forming composition is attenuated with air to create one or more filaments. The filaments may then be dried to remove any remaining solvent used for spinning, such as the water.

[0288] Filaments may be collected on a molding member, such as a patterned belt to form a fibrous structure.

### VI. Detergent Product

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[0289] Detergent products comprising one or more active agents can exhibit novel properties, features, and/or combinations thereof compared to known detergent products comprising one or more active agents.

### A. Fibrous Structure

**[0290]** In one example, a detergent product may comprise a fibrous structure, for example a web. One or more, and/or a plurality of filaments may form a fibrous structure by any suitable process known in the art. The fibrous structure may be used to deliver the active agents from the filaments when the fibrous structure is exposed to conditions of intended use of the filaments and/or the fibrous structure.

**[0291]** Even though fibrous structures may be in solid form, the filament-forming composition used to make the filaments may be in the form of a liquid.

[0292] In one example, a fibrous structure may comprise a plurality of identical or substantially identical from a compositional perspective filaments. In another example, the fibrous structure may comprise two or more different filaments. Non-limiting examples of differences in the filaments may be physical differences such as differences in diameter, length, texture, shape, rigidness, elasticity, and the like; chemical differences such as crosslinking level, solubility, melting point, Tg, active agent, filament-forming material, color, level of active agent, level of filament-forming material, presence of any coating on filament, biodegradable or not, hydrophobic or not, contact angle, and the like; differences in whether the filament loses its physical structure when the filament is exposed to conditions of intended use; differences in whether the filament's morphology changes when the filament is exposed to conditions of intended use; and differences in rate at which the filament releases one or more of its active agents when the filament is exposed to conditions of intended use. In one example, two or more filaments within the fibrous structure may comprise the same filament-forming material, but have different active agents. This may be the case where the different active agents may be incompatible with one another, for example an anionic surfactant (such as a shampoo active agent) and a cationic surfactant (such as a hair conditioner active agent).

**[0293]** In another example, a fibrous structure may comprise two or more different layers (in the z-direction of the fibrous structure of filaments that form the fibrous structure. The filaments in a layer may be the same as or different from the filaments of another layer. Each layer may comprise a plurality of identical or substantially identical or different filaments. For example, filaments that may release their active agents at a faster rate than others within the fibrous structure may be positioned to an external surface of the fibrous structure.

**[0294]** In another example, a fibrous structure may exhibit different regions, such as different regions of basis weight, density and/or caliper. In yet another example, the fibrous structure may comprise texture on one or more of its surfaces. A surface of the fibrous structure may comprise a pattern, such as a non-random, repeating pattern. The fibrous structure may be embossed with an emboss pattern. In another example, the fibrous structure may comprise apertures. The apertures may be arranged in a non-random, repeating pattern.

[0295] In one example, a fibrous structure may comprise discrete regions of filaments that differ from other parts of the fibrous structure.

[0296] Non-limiting examples of use of a fibrous structure include, but are not limited to a laundry dryer substrate, washing machine substrate, washcloth, hard surface cleaning and/or polishing substrate, floor cleaning and/or polishing substrate, as a component in a battery, baby wipe, adult wipe, feminine hygiene wipe, bath tissue wipe, window cleaning substrate, oil containment and/or scavenging substrate, insect repellant substrate, swimming pool chemical substrate,

food, breath freshener, deodorant, waste disposal bag, packaging film and/or wrap, wound dressing, medicine delivery, building insulation, crops and/or plant cover and/or bedding, glue substrate, skin care substrate, hair care substrate, air care substrate, water treatment substrate and/or filter, toilet bowl cleaning substrate, candy substrate, pet food, livestock bedding, teeth whitening substrates, carpet cleaning substrates, and other suitable uses of the active agents.

[0297] A fibrous structure may be used as is or may be coated with one or more active agents.

[0298] In another example, a fibrous structure may be pressed into a film, for example by applying a compressive force and/or heating the fibrous structure to convert the fibrous structure into a film. The film would comprise the active agents that were present in the filaments. The fibrous structure may be completely converted into a film or parts of the fibrous structure may remain in the film after partial conversion of the fibrous structure into the film. The films may be used for any suitable purposes that the active agents may be used for including, but not limited to the uses exemplified for the fibrous structure.

#### B. Methods of Use of the Detergent Product

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[0299] The nonwoven webs or films comprising one or more fabric care active agents may be utilized in a method for treating a fabric article. The method of treating a fabric article may comprise one or more steps selected from the group consisting of: (a) pre-treating the fabric article before washing the fabric article; (b) contacting the fabric article with a wash liquor formed by contacting the nonwoven web or film with water; (c) contacting the fabric article with the nonwoven web or film in a dryer; (d) drying the fabric article in the presence of the nonwoven web or film in a dryer; and (e) combinations thereof.

[0300] In some embodiments, the method may further comprise the step of pre-moistening the nonwoven web or film prior to contacting it to the fabric article to be pre-treated. For example, the nonwoven web or film can be pre-moistened with water and then adhered to a portion of the fabric comprising a stain that is to be pre-treated. Alternatively, the fabric may be moistened and the web or film placed on or adhered thereto. In some embodiments, the method may further comprise the step of selecting of only a portion of the nonwoven web or film for use in treating a fabric article. For example, if only one fabric care article is to be treated, a portion of the nonwoven web or film may be cut and/or torn away and either placed on or adhered to the fabric or placed into water to form a relatively small amount of wash liquor which is then used to pre-treat the fabric. In this way, the user may customize the fabric treatment method according to the task at hand. In some embodiments, at least a portion of a nonwoven web or film may be applied to the fabric to be treated using a device. Exemplary devices include, but are not limited to, brushes and sponges. Any one or more of the aforementioned steps may be repeated to achieve the desired fabric treatment benefit.

## VII. Method of Making Fibrous Structure

[0301] The following methods were used in forming inventive examples 1-8 described herein. Fibrous structures were formed by means of a small-scale apparatus, a schematic representation of which is shown in FIG. 7. A pressurized tank, suitable for batch operation was filled with a suitable material for spinning. The pump used was a Zenith®, type PEP II, having a capacity of 5.0 cubic centimeters per revolution (cc/rev), manufactured by Parker Hannifin Corporation, Zenith Pumps division, of Sanford, N.C., USA. The material flow to a die was controlled by adjusting the number of revolutions per minute (rpm) of the pump. Pipes connected the tank, the pump, and the die.

[0302] The die in FIG. 8 had several rows of circular extrusion nozzles spaced from one another at a pitch P (FIG. 8) of about 1.524 millimeters (about 0.060 inches). The nozzles had individual inner diameters of about 0.305 millimeters (about 0.012 inches) and individual outside diameters of about 0.813 millimeters (about 0.032 inches). Each individual nozzle was encircled by an annular and divergently flared orifice to supply attenuation air to each individual melt capillary. The material extruded through the nozzles was surrounded and attenuated by generally cylindrical, humidified air streams supplied through the orifices.

**[0303]** Attenuation air can be provided by heating compressed air from a source by an electrical-resistance heater, for example, a heater manufactured by Chromalox, Division of Emerson Electric, of Pittsburgh, Pa., USA. An appropriate quantity of steam was added to saturate or nearly saturate the heated air at the conditions in the electrically heated, thermostatically controlled delivery pipe. Condensate was removed in an electrically heated, thermostatically controlled, separator.

[0304] The embryonic fibers were dried by a drying air stream having a temperature from about 149° C. (about 300° F.) to about 315° C. (about 600° F.) by an electrical resistance heater (not shown) supplied through drying nozzles and discharged at an angle of about 90 degrees relative to the general orientation of the non-thermoplastic embryonic fibers being extruded. The dried embryonic fibers were collected on a collection device, such as, for example, a movable foraminous belt or molding member. The addition of a vacuum source directly under the formation zone may be used to aid collection of the fibers.

[0305] Table 1 below sets forth an example of a filament-forming composition for making filaments and/or a fibrous

structure suitable for use as a laundry detergent. This mixture was made and placed in the pressurized tank in FIG. 8.

## TABLE 1

	Filament-forming composition (i.e., premix) (%)	Filament-Forming Composition (%)	Filament (i.e., components remaining upon drying)(%)	Percent by weigh on a dry filament basis (%)
C12-15 AES	28.45	11.38	11.38	28.07
C11.8 HLAS	12.22	4.89	4.89	12.05
MEA	7.11	2.85	2.85	7.02
N67HSAS	4.51	1.81	1.81	4.45
Glycerol	3.08	1.23	1.23	3.04
PE-20, Polyethyleneimine Ethoxylate, PEI 600 E20	3.00	1.20	1.20	2.95
Ethoxylated/ Propoxylated Polyethyleneimine	2.95	1.18	1.18	2.91
Brightener 15	2.20	0.88	0.88	2.17
Amine Oxide	1.46	0.59	0.59	1.44
Sasol 24,9 Nonionic Surfactant	1.24	0.50	0.50	1.22
DTPA (Chelant)	1.08	0.43	0.43	1.06
Tiron (Chelant)	1.08	0.43	0.43	1.06
Celvol 523 PVOH <sup>1</sup>	0.000	13.20	13.20	32.55
Water	31.63	59.43		

[0306] The dry embryonic filaments may be collected on a molding member as described above. The construction of the molding member will provide areas that are air-permeable due to the inherent construction. The filaments that are used to construct the molding member will be non-permeable while the void areas between the filaments will be permeable. Additionally a pattern may be applied to the molding member to provide additional non-permeable areas which may be continuous, discontinuous, or semi-continuous in nature. A vacuum used at the point of lay down is used to help deflect fibers into the presented pattern. An example of one of these molding members is shown in FIG. 9.

[0307] Base spinning conditions were achieved with a fibrous web being collected on the collecting molding member. These were passed beneath the die and samples were collected after the vacuum. This process was repeated and samples collected with eight molding members of varying design. Representative pictures of the molding member and the resulting fibrous structures are shown in FIG. 10 (e.g., Inventive Examples 1-8 described herein). These fibrous structures may then be further processed.

[0308] Processes for forming the fibrous structure are further described in U.S. Patent No. 4,637,859.

In addition to the techniques described herein in forming regions within the fibrous structures having a different properties (e.g., average densities), other techniques can also be applied to provide suitable results. One such example includes embossing techniques to form such regions. Suitable embossing techniques are described in U.S. Patent Application Publication Nos. 2010/0297377, 2010/0295213, 2010/0295206, 2010/0028621, and 2006/0278355.

## **Test Methods**

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[0310] Unless otherwise specified, all tests described herein including those described under the Definitions section and the following test methods are conducted on samples that have been conditioned at a temperature of 23°C ± 1C° and a relative humidity of  $50\% \pm 2\%$  for a minimum of 2 hours prior to testing. All tests are conducted under the same

environmental conditions. Do not test samples that have defects such as wrinkles, tears, holes, and like. Samples conditioned as described herein are considered dry samples (such as "dry filaments") for purposes. Further, all tests are conducted in such conditioned room.

## 5 Basis Weight Test Method

**[0311]** Basis weight of a nonwoven structure and/or a dissolving fibrous structure is measured on stacks of twelve usable units using a top loading analytical balance with a resolution of  $\pm$  0.001 g. The balance is protected from air drafts and other disturbances using a draft shield. A precision cutting die, measuring 3.500 in  $\pm$  0.0035 in by 3.500 in  $\pm$  0.0035 in is used to prepare all samples.

**[0312]** With a precision cutting die, cut the samples into squares. Combine the cut squares to form a stack twelve samples thick. Measure the mass of the sample stack and record the result to the nearest 0.001 g.

[0313] The Basis Weight is calculated in lbs/3000 ft<sup>2</sup> or g/m<sup>2</sup> as follows:

Basis Weight = (Mass of stack) / [(Area of 1 square in stack) x (Number of squares in stack)]

For example,

Basis Weight (lbs/3000 ft<sup>2</sup>) = [[Mass of stack (g) / 453.6 (g/lbs)] / [12.25 (in<sup>2</sup>) / 144 (in<sup>2</sup>/ft<sup>2</sup>)  $\times$  12]]  $\times$  3000

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Basis Weight 
$$(g/m^2)$$
 = Mass of stack  $(g) / [79.032 (cm^2) / 10,000 (cm^2/m^2) \times 12]$ 

[0314] Report result to the nearest 0.1 lbs/3000 ft<sup>2</sup> or 0.1 g/m<sup>2</sup>. Sample dimensions can be changed or varied using a similar precision cutter as mentioned above, so as at least 100 square inches of sample area in stack.

## Water Content Test Method

<sup>35</sup> **[0315]** The water (moisture) content present in a filament and/or fiber and/or nonwoven web is measured using the following Water Content Test Method.

[0316] A filament and/or nonwoven or portion thereof ("sample") in the form of a pre-cut sheet is placed in a conditioned room at a temperature of  $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$  and a relative humidity of  $50\% \pm 2\%$  for at least 24 hours prior to testing. Each sample has an area of at least 4 square inches, but small enough in size to fit appropriately on the balance weighing plate. Under the temperature and humidity conditions mentioned above, using a balance with at least four decimal places, the weight of the sample is recorded every five minutes until a change of less than 0.5% of previous weight is detected during a 10 minute period. The final weight is recorded as the "equilibrium weight". Within 10 minutes, the samples are placed into the forced air oven on top of foil for 24 hours at  $70^{\circ}\text{C} \pm 2^{\circ}\text{C}$  at a relative humidity of  $4\% \pm 2\%$  for drying. After the 24 hours of drying, the sample is removed and weighed within 15 seconds. This weight is designated as the "dry weight" of the sample.

[0317] The water (moisture) content of the sample is calculated as follows:

The % Water (moisture) in sample for 3 replicates is averaged to give the reported % Water (moisture) in sample. Report results to the nearest 0.1%.

## **Dissolution Test Method**

Apparatus and Materials (also, see FIGS. 11 and 12):

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600 mL Beaker 240

Magnetic Stirrer 250 (Labline Model No. 1250 or equivalent)

Magnetic Stirring Rod 260 (5 cm)

Thermometer (1 to 100°C +/- 1 °C)

Cutting Die -- Stainless Steel cutting die with dimensions 3.8 cm x 3.2 cm

**[0319]** Timer (0-3,600 seconds or 1 hour), accurate to the nearest second. Timer used should have sufficient total time measurement range if sample exhibits dissolution time greater than 3,600 seconds. However, timer needs to be accurate to the nearest second.

Polaroid 35 mm Slide Mount 270 (commercially available from Polaroid Corporation or equivalent) -)

35 mm Slide Mount Holder 280 (or equivalent)

<sup>25</sup> **[0320]** City of Cincinnati Water or equivalent having the following properties: Total Hardness = 155 mg/L as CaCO<sub>3</sub>; Calcium content = 33.2 mg/L; Magnesium content = 17.5 mg/L; Phosphate content = 0.0462.

## **Test Protocol**

30 [0321] Equilibrate samples in constant temperature and humidity environment of 23°C ± 1 °C and 50%RH ± 2% for at least 2 hours.

[0322] Measure the basis weight of the sample materials using Basis Weight Method defined herein.

**[0323]** Cut three dissolution test specimens from nonwoven structure sample using cutting die  $(3.8 \text{ cm} \times 3.2 \text{ cm})$ , so it fits within the 35 mm slide mount 270 which has an open area dimensions  $24 \times 36 \text{ mm}$ .

[0324] Lock each specimen in a separate 35 mm slide mount 270.

[0325] Place magnetic stirring rod 260 into the 600 mL beaker 240.

**[0326]** Turn on the city water tap flow (or equivalent) and measure water temperature with thermometer and, if necessary, adjust the hot or cold water to maintain it at the testing temperature. Testing temperature is  $15^{\circ}C \pm 1^{\circ}C$  water. Once at testing temperature, fill beaker 240 with 500 mL  $\pm$  5 mL of the  $15^{\circ}C \pm 1^{\circ}C$  city water.

[0327] Place full beaker 240 on magnetic stirrer 250, turn on stirrer 250, and adjust stir speed until a vortex develops and the bottom of the vortex is at the 400 mL mark on the beaker 240.

[0328] Secure the 35 mm slide mount 270 in the alligator clamp 281 of the 35 mm slide mount holder 280 such that the long end 271 of the slide mount 270 is parallel to the water surface. The alligator clamp 281 should be positioned in the middle of the long end 271 of the slide mount 270. The depth adjuster 285 of the holder 280 should be set so that the distance between the bottom of the depth adjuster 285 and the bottom of the alligator clip 281 is ~11 +/- 0.125 inches. This set up will position the sample surface perpendicular to the flow of the water. A slightly modified example of an arrangement of a 35 mm slide mount and slide mount holder are shown in FIGS. 1-3 of U.S. Patent No. 6,787,512.

[0329] In one motion, drop the secured slide and clamp into the water and start the timer. The sample is dropped so that the sample is centered in the beaker. Disintegration occurs when the nonwoven structure breaks apart. Record this as the disintegration time. When all of the visible nonwoven structure is released from the slide mount, raise the slide out of the water while continuing the monitor the solution for undissolved nonwoven structure fragments. Dissolution occurs when all nonwoven structure fragments are no longer visible. Record this as the dissolution time.

**[0330]** Three replicates of each sample are run and the average disintegration and dissolution times are recorded. Average disintegration and dissolution times are in units of seconds.

[0331] The average disintegration and dissolution times are normalized for basis weight by dividing each by the sample basis weight as determined by the Basis Weight Method defined herein. Basis weight normalized disintegration and dissolution times are in units of seconds/gsm of sample (s/(g/m²)).

# Average Density Test Method

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**[0332]** Fibrous structures can comprise network regions and pluralities of discrete zones which have characteristic densities. A cross-sectional, SEM micrograph of such a fibrous structure is shown in FIG. 13. The regions of the fibrous structure are illustrated in the micrograph by the zones comprising different caliper or thickness. These caliper differences are one of the factors responsible for the superior performance characteristics of these fibrous structures.

**[0333]** The regions with higher caliper are lower in structure density and these are typically referred to as "pillows". The regions with lower caliper are higher in structure density and these are typically referred to as "knuckles."

[0334] The density of the regions within a fibrous structure is measured by first cutting for a length of at least 2-3 knuckle and pillow regions with a previously unused single edge PTFE-treated razor blade such as the GEM® razor blades available from Ted Pella Inc. Only one cut is made per razor blade. Each cross-sectioned sample is mounted on a SEM sample holder, secured by carbon paste, then plunged and frozen in liquid nitrogen. The sample is transferred to an SEM chamber at - 90°C, coated with Gold/Palladium for 60 seconds and analyzed using a commercially available SEM equipped with a cryo-system such as a Hitachi S-4700 with Alto cryo system and PCI (Passive Capture Imaging) software for image analysis or an equivalent SEM system and equivalent software. All samples are evaluated while frozen to ensure their original size and shape under vacuum while in the scanning electron microscope.

[0335] Pillow and knuckle thickness or network regions and discrete zone thickness are determined using image analysis software associated with the SEM equipment. As the measurements are the thickness of a sample, such analysis software is standard for all SEM equipment. Measurements are taken where the thickness of the region or zone are at their respective local maximum values. Thickness values for at least 2 individual, separate network regions (or discrete zone) are recorded and then averaged and reported as the average network region thickness. The average thickness is measured in units of microns.

**[0336]** Separately, the basis weight of the sample being measured for density is determined using the basis weight method defined herein. The basis weight as measured in gsm (g/m²) is calculated using the Basis Weight Method and used to calculate the region density.

**[0337]** Below is an example for calculating the average network density and average discrete zone density for a sample with a basis weight of  $100 \text{ g/m}^2$ , a network region average thickness of 625 micron, and a discrete zone average thickness of 311 micron.

Average network density 
$$\left(\frac{g}{cc}\right) = \frac{basis\ weight}{network\ thickness} = \frac{100\frac{g}{m^2}}{625 \times 10^{-6} m} \times \frac{m^2}{1 \times 10^6 cc} = 0.16\frac{g}{cc}$$

Average discrete zone density 
$$\left(\frac{g}{cc}\right) = \frac{basis\ weight}{discrete\ zone\ thickness} = \frac{100\frac{g}{m^2}}{311\times10^{-6}\ m} \times \frac{m^2}{1\times10^6\ cc} = 0.32\frac{g}{cc}$$

## 40 Diameter Test Method

**[0338]** The diameter of a discrete filament or a filament within a nonwoven web or film is determined by using a Scanning Electron Microscope (SEM) or an Optical Microscope and an image analysis software. A magnification of 200 to 10,000 times is chosen such that the filaments are suitably enlarged for measurement. When using the SEM, the samples are sputtered with gold or a palladium compound to avoid electric charging and vibrations of the filament in the electron beam. A manual procedure for determining the filament diameters is used from the image (on monitor screen) taken with the SEM or the optical microscope. Using a mouse and a cursor tool, the edge of a randomly selected filament is sought and then measured across its width (i.e., perpendicular to filament direction at that point) to the other edge of the filament. A scaled and calibrated image analysis tool provides the scaling to get actual reading in μm. For filaments within a nonwoven web or film, several filament are randomly selected across the sample of the nonwoven web or film using the SEM or the optical microscope. At least two portions the nonwoven web or film (or web inside a product) are cut and tested in this manner. Altogether at least 100 such measurements are made and then all data are recorded for statistical analysis. The recorded data are used to calculate average (mean) of the filament diameters, standard deviation of the filament diameters, and median of the filament diameters.

[0339] Another useful statistic is the calculation of the amount of the population of filaments that is below a certain upper limit. To determine this statistic, the software is programmed to count how many results of the filament diameters are below an upper limit and that count (divided by total number of data and multiplied by 100%) is reported in percent as percent below the upper limit, such as percent below 1 micrometer diameter or %-submicron, for example. We denote

the measured diameter (in  $\mu m$ ) of an individual circular filament as di.

**[0340]** In case the filaments have non-circular cross-sections, the measurement of the filament diameter is determined as and set equal to the hydraulic diameter which is four times the cross-sectional area of the filament divided by the perimeter of the cross-section of the filament (outer perimeter in case of hollow filaments). The number-average diameter, alternatively average diameter is calculated as:

$$d_{num} = \frac{\sum_{i=1}^{n} d_i}{n}$$

Tensile Test Method: Elongation, Tensile Strength, TEA and Modulus

[0341] Elongation, Tensile Strength, TEA and Tangent Modulus are measured on a constant rate of extension tensile tester with computer interface (a suitable instrument is the EJA Vantage from the Thwing-Albert Instrument Co. Wet Berlin, NJ) using a load cell for which the forces measured are within 10% to 90% of the limit of the cell. Both the movable (upper) and stationary (lower) pneumatic jaws are fitted with smooth stainless steel faced grips, 25.4 mm in height and wider than the width of the test specimen. An air pressure of about 60 psi is supplied to the jaws.

**[0342]** Eight usable units of nonwoven structure and/or dissolving fibrous structure are divided into two stacks of four samples each. The samples in each stack are consistently oriented with respect to machine direction (MD) and cross direction (CD). One of the stacks is designated for testing in the MD and the other for CD. Using a one inch precision cutter (Thwing Albert JDC-1-10, or similar) cut 4 MD strips from one stack, and 4 CD strips from the other, with dimensions of 1.00 in  $\pm$  0.01 in wide by 3.0 - 4.0 in long. Each strip of one usable unit thick will be treated as a unitary specimen for testing.

**[0343]** Program the tensile tester to perform an extension test, collecting force and extension data at an acquisition rate of 20 Hz as the crosshead raises at a rate of 2.00 in/min (5.08 cm/min) until the specimen breaks. The break sensitivity is set to 80%, i.e., the test is terminated when the measured force drops to 20% of the maximum peak force, after which the crosshead is returned to its original position.

**[0344]** Set the gauge length to 1.00 inch. Zero the crosshead and load cell. Insert at least 1.0 in of the unitary specimen into the upper grip, aligning it vertically within the upper and lower jaws and close the upper grips. Insert the unitary specimen into the lower grips and close. The unitary specimen should be under enough tension to eliminate any slack, but less than 5.0 g of force on the load cell. Start the tensile tester and data collection. Repeat testing in like fashion for all four CD and four MD unitary specimens.

[0345] Program the software to calculate the following from the constructed force (g) verses extension (in) curve: Tensile Strength is the maximum peak force (g) divided by the sample width (in) and reported as g/in to the nearest 1 g/in.

[0346] Adjusted Gauge Length is calculated as the extension measured at 3.0 g of force (in) added to the original gauge length (in).

**[0347]** Elongation is calculated as the extension at maximum peak force (in) divided by the Adjusted Gauge Length (in) multiplied by 100 and reported as % to the nearest 0.1 %

**[0348]** Total Energy (TEA) is calculated as the area under the force curve integrated from zero extension to the extension at the maximum peak force (g\*in), divided by the product of the adjusted Gauge Length (in) and specimen width (in) and is reported out to the nearest 1 g\*in/in².

**[0349]** Replot the force (g) verses extension (in) curve as a force (g) verses strain curve. Strain is herein defined as the extension (in) divided by the Adjusted Gauge Length (in).

[0350] Program the software to calculate the following from the constructed force (g) verses strain curve:

[0351] Tangent Modulus is calculated as the slope of the linear line drawn between the two data points on the force (g) versus strain curve, where one of the data points used is the first data point recorded after 28 g force, and the other data point used is the first data point recorded after 48 g force. This slope is then divided by the specimen width (2.54 cm) and reported to the nearest 1 g/cm.

**[0352]** The Tensile Strength (g/in), Elongation (%), Total Energy (g\*in/in²) and Tangent Modulus (g/cm) are calculated for the four CD unitary specimens and the four MD unitary specimens. Calculate an average for each parameter separately for the CD and MD specimens.

## Calculations:

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Geometric Mean Tensile = Square Root of [MD Tensile Strength (g/in) x CD Tensile Strength (g/in)

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Geometric Mean Peak Elongation = Square Root of [MD Elongation (%) x CD Elongation (%)]

Geometric Mean TEA = Square Root of [MD TEA  $(g*in/in^2)$  x CD TEA  $(g*in/in^2)$ ]

Geometric Mean Modulus = Square Root of [MD Modulus (g/cm) x CD Modulus (g/cm)]

Total Dry Tensile Strength (TDT) = MD Tensile Strength (g/in) + CD Tensile Strength (g/in)

Total TEA = MD TEA  $(g*in/in^2)$  + CD TEA  $(g*in/in^2)$ 

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Total Modulus = MD Modulus (g/cm) + CD Modulus (g/cm)

Tensile Ratio = MD Tensile Strength (g/in) / CD Tensile Strength (g/in)

Topographic Measurements of Differential Density Fibrous Structures

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[0354] Topographic measurements of differential density fibrous structures are obtained via computer-controlled fringeprojection optical profilometry. Optical profilometer systems measure the physical dimensions of the test surface, resulting in a map of surface height elevation (z), versus lateral displacement in the x-y plane. A suitable optical profilometer instrument will have a field of view and x-y resolution such that the acquired images possess at least 10 pixels linearly across the narrowest feature being measured. A suitable instrument is a GFM Mikrocad system, running OD-SCAD software version 4 or 6, or equivalent, available from GFMessthechnik GmbH, Teltow, Germany.

[0355] If necessary in order to make samples suitably reflective for accurate measurement of the surface features, the surface to be measured is lightly sprayed with a very fine white powder spray. Preferably this spray is NORD-TEST Developer U 89, available from Helling GmbH, Heidgraben, Germany, which is sold for the detection of cracks in metal objects and welds. Samples should be equilibrated at 23°C  $\pm$  2 °C and 50%  $\pm$  2% relative humidity for at least 2 hours immediately prior to applying such a spray, and for at least 2 hours after spraying. Care is taken to deposit only the minimum amount of white spray needed to create a thin reflective white coating.

[0356] Samples should be equilibrated at 23°C ± 2°C and 50% ± 2% relative humidity for at least 2 hours immediately prior to acquiring measurements.

[0357] The area of the fibrous structure to be measured is restricted solely to areas possessing regions with different densities and excluding other areas or zones that might be present. The sample is placed with the surface area to be measured facing upward, underneath and normal to, the profilometer's projection head. The instrument manufacturer's instructions are followed, and optimized illumination and reflection requirements are achieved as outlined by the manufacturer. Digital images are then captured and stored.

[0358] Any portion of the image that is not part of the area to be measured should be cropped out of the captured image. Such cropping must occur prior to any further image processing, filtering or measurement analysis. The size of the resultant cropped image may vary between samples and images, depending upon the dimensions of the patterned area of that sample.

[0359] Prior to making measurements, the images are processed in the instrument software, in order to lightly smooth noise in the images, and to reduce irregularity or waviness due to the sample's overall shape. This noise filtering processing includes the removal of invalid pixel values (those black pixels having a grey value at the dark limit of the grayscale range), and the removal of spike values or outlier peaks (those very bright pixels identified by the software as statistical outli-ers). A polynomial high-pass filter is then utilized with settings of: n=8, difference. For samples with very small features where it is difficult to clearly observe the pattern features, it may be useful to also apply a Fourier filter (for example: a 5mm wave filter, fine structure result). When such a Fourier filter is used, it removes features larger than

the filter length as noise, and consequently reduces variability, lowering the statistical standard deviation around the topography measurements. It is therefore essential that the size of the filter used is larger than any features of interest so as not to filter out said features. Processed images such as the topography image shown in FIG. 14, can be displayed, analyzed and measured. Figure 14 was cropped then flattened via filtering with a polynomial (n=8 difference) filter to remove irregularity due to the sample's overall waviness.

**[0360]** Measurements are then made from the processed topography images to yield the spatial parameters of elevation differential (E), and transition region width (T). These measurements are achieved by using the instrument software to draw straight line regions of interest within a topography image of the sample's x-y surface, and to then generate height profile plots along these straight lines. The straight line regions of interest are drawn such that they sample several different locations within each image, crossing continuous regions and the center of adjacent discrete zones. The lines are drawn so that they bisect each transition region between continuous and discrete zones at an angle perpendicular to the long axis of the transition region, as shown in FIG. 15. As shown in FIG. 15, a series of straight line regions of interest, drawn across the continuous and discrete zones, bisecting each transition region at an angle perpendicular to the long axis of the transition region. The parameters (E) and (T) are then measured from the height profile plots generated from these straight line regions of interest.

[0361] In a height profile plot, the plot's x-axis represents the length of the line, and the y-axis represents the vertical elevation of the surface perpendicular to the sample's planar surface. The elevation differential (E) is measured in micrometers as the vertical straight-line distance from the apex of a peak to the lowest point of an adjacent recess, on a height profile plot as shown in FIG. 16. As illustrated in FIG. 16, the height profile plot along a straight line region of interest, drawn through a topography image, shows several elevation differential (E) measurements. Typically this represents the maximum vertical elevation differential between the surface of a continuous region and an adjacent discrete zone, or vice versa. The transition region width (T) is measured in micrometers as the x-axis width of the curve across the central sixty percent (60%) of the elevation differential (E), on a height profile plot as shown in FIG. 17. As illustrated in FIG. 17, the height profile plot along a straight line region of interest, drawn through a topography image, shows several transition region widths (T). Typically, this represents the rate of transition from a continuous region to an adjacent discrete zone, or vice versa.

**[0362]** Where a sample has discrete zones which appear to fall into two or more distinct classes, as determined by visually observing their overall shape, size, elevation, and density, then separate values of (E) and (T) are to be determined for each discrete zone class and adjacent continuous region pairing.

[0363] If the sample visibly appears to have more than one pattern of discrete zones in different locations on the product, then each pattern is to have its values of (E) and (T) determined separately from the other pattern(s).

**[0364]** If a sample has a first region and an adjacent second region, wherein the first and second regions visibly appear to differ in their surface elevation, then the product is to have values of (E) and (T) measured from these regions. In this case all the method instructions given herein are to be followed and the first and second regions substituted for both the continuous region and the discrete zones named in this method.

[0365] For each pattern to be tested, five replicate product samples are imaged, and from each replicate sample measurements are made of at least ten elevation differentials (E) for each class of discrete zone, and ten transition region widths (T) for each class of discrete zone. This is repeated for each planar surface of each sample. Values of (E) and (T) are reported from the planar surface possessing the largest value of (E). For each parameter calculated for a specific pattern and discrete zone class, the values from each of the five replicate samples are averaged together to give the final value for each parameter.

### Examples

**[0366]** Provided below are Inventive Examples 1-8. As illustrated the average thickness and average density of the network region and the discrete zones can vary. Also shown, Inventive Example 2 illustrates a sample having multiple regions and provides an average thickness and average density for each of those regions.

			Average	Average	Average		Ratio of
		Basis	Network	Network	Discrete Zone	Average	Network/
Inventive		weight	Thickness	Density	Thickness	Discrete Zone	Discrete Zone
Examples	Region	(gsm)	(microns)	(g/cc)	(microns)	Density (g/cc)	Density
1		100	313.0	0.32	775.0	0.13	2.5

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(continued)

	Inventive Examples	Region	Basis weight (gsm)	Average Network Thickness (microns)	Average Network Density (g/cc)	Average Discrete Zone Thickness (microns)	Average Discrete Zone Density (g/cc)	Ratio of Network/ Discrete Zone Density
•		region 1		1108.0	0.10			
		region 2		674.0	0.17			
	2	region 3	114.3			284	0.40	
		region 4				357	0.32	
		region 5				251	0.46	
	3		94.7	552.0	0.17	307.5	0.31	0.6
	4		108.7	312.5	0.35	552.3	0.20	1.8
	5		100	401.8	0.25	539.5	0.19	1.3
	6		100	336.0	0.30	465.7	0.21	1.4
	7		100	208.3	0.48	364.8	0.27	1.8
	8		86.6	458.6	0.19	278.1	0.31	0.6

[0367] Provided below are MD Tensile Strength, MD Peak Elongation, MD TEA, and MD Modulus values for Inventive Examples 3, 4 and 8.

Inventive Examples	Basis Weight	Thickness	MD Tensile Strength	MD Peak Elongation	MD TEA	MD Modulus
	gsm	microns	g/in	%	g*in/in <sup>2</sup>	g/cm
3	94.7	463.7	644	64.1	318	2302
4	108.7	477.5	688	68.5	372	2793
8	86.6	417.8	636	65.2	324	3017

[0368] Provided below are CD Tensile Strength, CD Peak Elongation, CD TEA and CD Modulus values for Inventive Examples 3, 4 and 8.

	Inventive Examples	Basis Weight	Thickness	CD Tensile Strength	CD Peak Elongation	CD TEA	CD Modulus
		gsm	microns	g/in	%	g*in/in <sup>2</sup>	g/cm
	3	94.7	463.7	579	84.2	359	1059
	4	108.7	477.5	629	74.2	362	1853
Ī	8	86.6	417.8	589	83.7	376	2305

**[0369]** Provided below are geometric mean tensile strength, geometric peak elongation, geometric mean TEA and geometric mean modulus values for Inventive Examples 3, 4 and 8.

Inventive Examples	Basis Weight	Thickness	Geometric Mean Tensile Strength	Geometric Mean Peak Elongation	Geometric Mean TEA	Geometric Mean Modulus
	gsm	microns	g/in	%	g*in/in <sup>2</sup>	g/cm
3	94.7	463.7	611	73.5	338	1562
4	108.7	477.5	658	71.3	367	2275

(continued)

Inventive Examples	Basis Weight	Thickness	Geometric Mean Tensile Strength	Geometric Mean Peak Elongation	Geometric Mean TEA	Geometric Mean Modulus
	gsm	microns	g/in	%	g*in/in <sup>2</sup>	g/cm
8	86.6	417.8	612	73.9	349	2637

**[0370]** Provided below is profilometry data relating to Inventive Examples 1-8, including for example elevation differentials (E) and transition region widths (T).

[			· · · · · · · · · · · · · · · · · · ·		
Inventive Examples	Region	Prof	filometry		
		Elevation Differential (E)	Transition Region Widths (T)		
		microns	microns		
1		817	2600		
	region 6	1160			
2	region 7	1294			
2	region 8	1408			
	region 9		1900		
3		684	2800		
4		479	2400		
5		229	1400		
6		168	1300		
7		298	1700		
8		177	700		

[0371] Moisture content data is provided below for Inventive Examples 2, 3 and 8.

Inventive Examples	Moisture Content (%)
2	7.5
3	8.1
8	7.5

[0372] Dissolution and disintegration times for Inventive Examples 2-4 and 8 are provided below according to the Dissolution Test Method described herein.

Inventive Examples	Basis weight (gsm)	Disintegration time (s)	Dissolution time (s)	Basis weight normalized disintegration time (s/gsm)	Basis weight normalized dissolution time (s/gsm)
2	114.3	0.8	167.3	0.007	1.46
3	94.7	1.3	63.3	0.014	0.67
4	108.7	1.2	63.1	0.011	0.58
8	86.6	1.3	87.7	0.015	1.01

**[0373]** The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

[0374] For clarity purposes, the total "% wt" values do not exceed 100% wt.

**[0375]** The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

[0376] Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

[0377] While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

## **Claims**

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- 1. A fibrous structure comprising filaments wherein the filaments comprise one or more filament-forming materials and one or more active agents that are releasable from the filament when exposed to conditions of intended use, the fibrous structure further comprising:
  - a) a continuous network region, wherein the network region comprises a first average density; and
  - b) a plurality of discrete zones comprising a second average density, wherein the discrete zones being dispersed throughout the network region, and wherein the first average density and the second average density are different; and
  - c) a transition region between the network region and the discrete zones; and
  - wherein the active agent is selected from the group consisting of: skin benefit agents, medical agents, lotions, fabric care agents, dishwashing agents, carpet care agents, surface care agents, hair care agents, air care agents, teeth whitening agents, tooth care agents, mouthwash agents, and periodontal gum care agents; and wherein the filament-forming material comprises a polymer, and wherein the polymer is a water-soluble hydroxyl polymer.
- 40 2. The fibrous structure according to claim 1, wherein the first average density is from 0.05 g/cc to 0.80 g/cc.
  - **3.** The fibrous structure according to any of the preceding claims, wherein the second average density is from 0.05 g/cc to 0.80 g/cc.
- **45 4.** The fibrous structure according to any of the preceding claims, wherein the continuous network region is a macroscopically monoplanar, patterned, continuous network region.
  - **5.** The fibrous structure according to any of the preceding claims, wherein the total level of the one or more filament-forming materials present in the filaments is less than 80% by weight on a dry filament basis and the total level of the one or more active agents present in the filaments is greater than 20% by weight on a dry filament basis.
  - **6.** The fibrous structure according to any of the preceding claims wherein the fibrous structure exhibits a basis weight of 3000 gsm or less as measured according to the Basis Weight Test Method described herein.
- 7. The fibrous structure according to claim 6 wherein the fibrous structure exhibits a basis weight of 1500 gsm or less as measured according to the Basis Weight Test Method described herein.
  - 8. The fibrous structure according to any of the preceding claims wherein the one or more active agents comprises a

surfactant.

- 9. The fibrous structure according to any of the preceding claims wherein the fibrous structure comprises two or more different active agents.
- 10. The fibrous structure according to any of the preceding claims exhibits a water content of from 0% to 20% as measured according to the Water Content Test Method described herein.
- 11. The fibrous structure according to any of the preceding claims, wherein at least some of the filaments exhibit a diameter of less than 50  $\mu$ m as measured according to the Diameter Test Method described herein.
  - 12. The fibrous structure according to any of the preceding claims wherein the fibrous structure exhibits a geometric mean tensile strength of 200 g/in or more as measured according to the Tensile Test Method described herein.
- 15 13. The fibrous structure according to any of the preceding claims wherein the fibrous structure exhibits a basis weight normalized disintegration time of 1.0 seconds/gsm or less as measured according to the Dissolution Test Method described herein.
  - 14. The fibrous structure according to any of the preceding claims wherein the fibrous structure exhibits a basis weight normalized dissolution time of 10 seconds/gsm or less as measured according to the Dissolution Test Method described herein.
  - 15. The fibrous structure according to any of the preceding claims wherein the water-soluble hydroxyl polymer is selected from polyvinyl alcohol, polyvinyl alcohol derivatives, polyvinyl alcohol copolymers, starch, starch derivatives, starch copolymers, chitosan, chitosan derivatives, chitosan copolymers, cellulose derivatives such as cellulose ether and ester derivatives, cellulose co-polymers, hemicellulose, hemicellulose derivatives, hemicellulose copolymers, gums, arabinans, galactans, proteins and various other polysaccharides and mixtures thereof.

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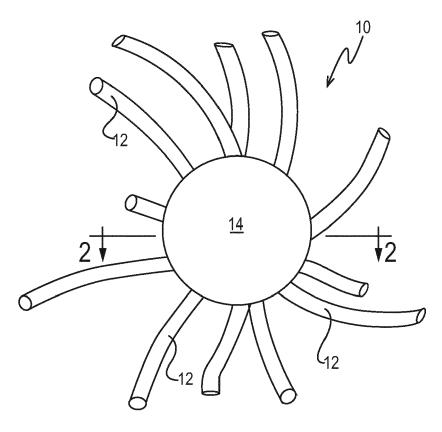


Fig. 1 (PRIOR ART)

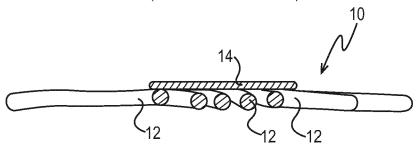


Fig. 2 (PRIOR ART)

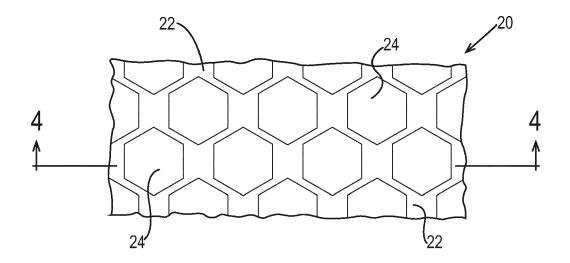
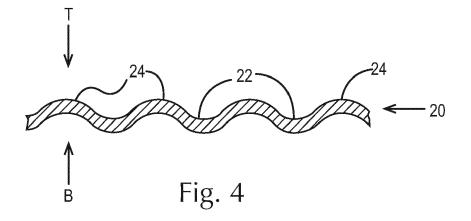


Fig. 3



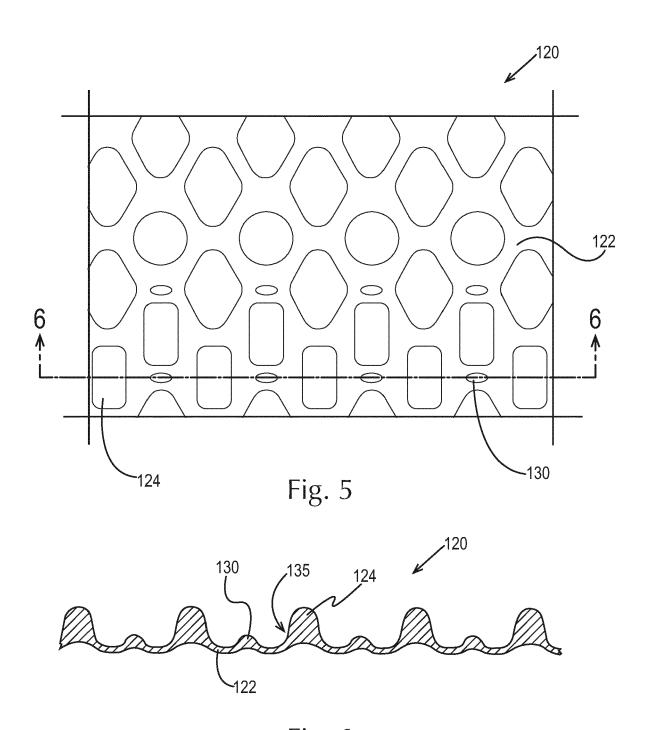


Fig. 6

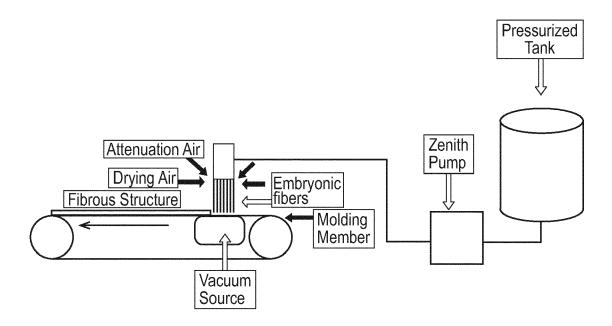


Fig. 7

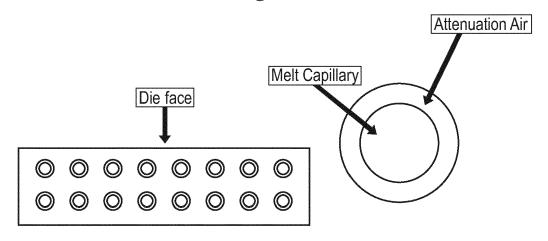


Fig. 8

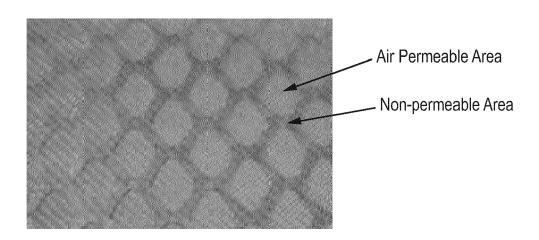


Fig. 9

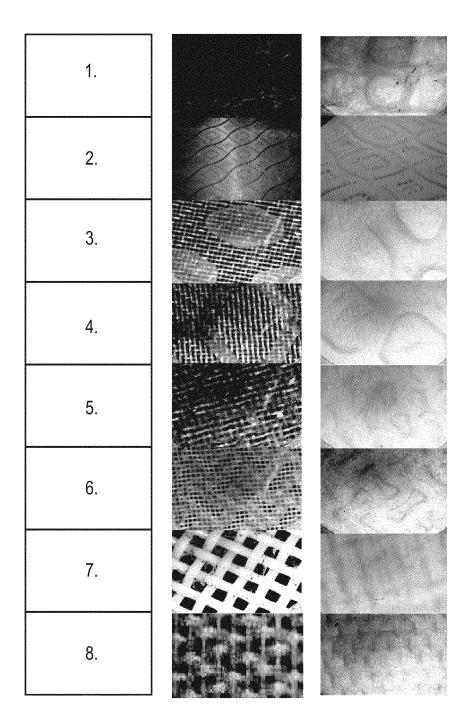
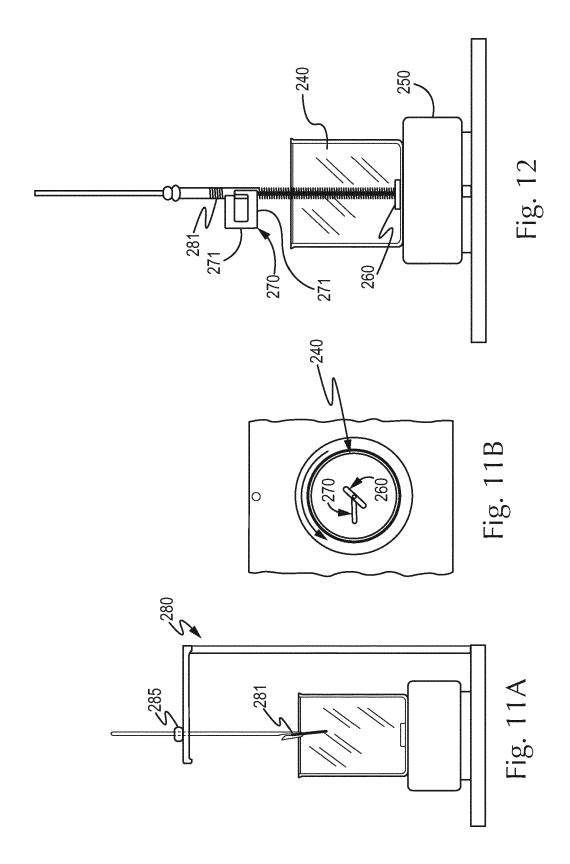


Fig. 10



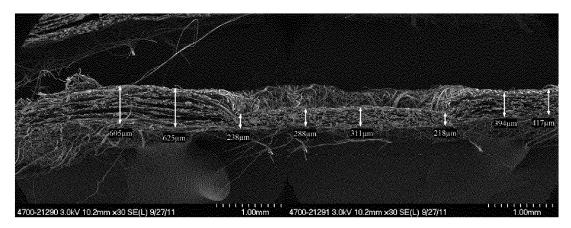
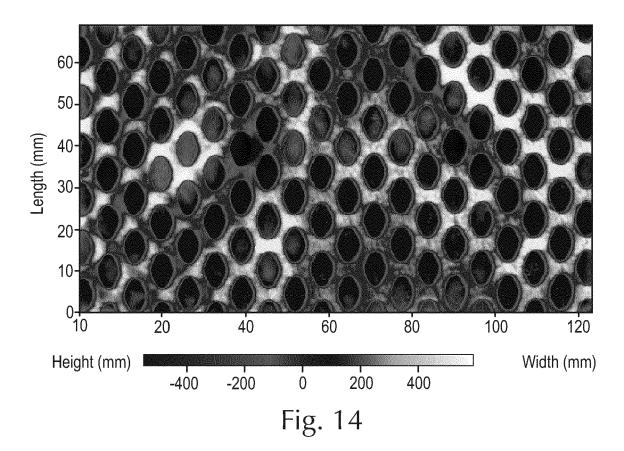
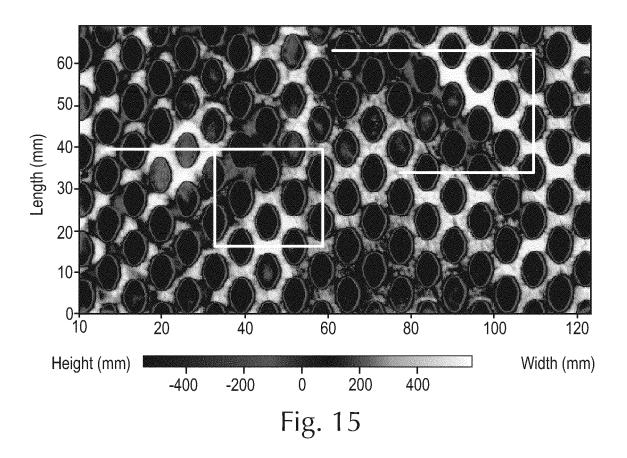
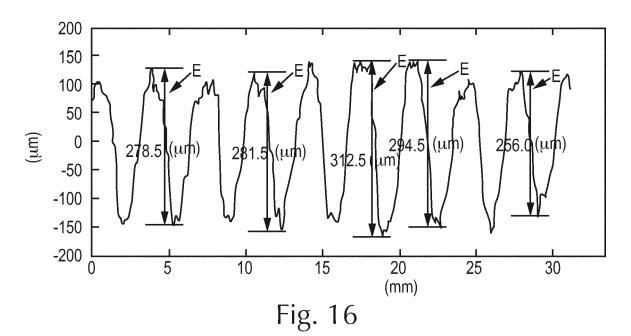
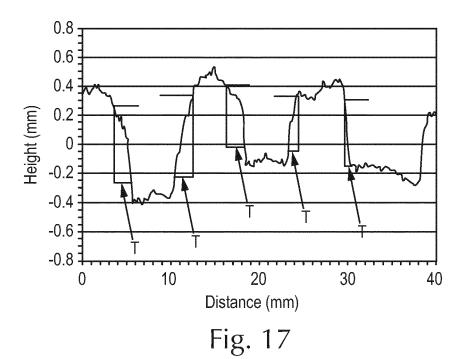


Fig. 13











# **EUROPEAN SEARCH REPORT**

**Application Number** 

EP 18 15 8889

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I	DOCUMENTS CONSID	ERED TO BE RELEVANT		
Category	Citation of document with ir of relevant pass	ndication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	CO [US]) 30 May 200 * page 3, line 10 -		1-15	INV. D01F1/10 D04H1/736 C11D17/04
A	US 4 070 218 A (WEB 24 January 1978 (19 * column 2, line 9 * column 3, line 40 * column 4, line 1 * examples *	78-01-24) - line 21 *	1-15	
4	WO 02/064875 A2 (PR 22 August 2002 (200 * page 25, line 3 - * page 37, line 1 - * claim 6 *	line 29 *	1-15	
A	AL) 12 February 200	WU MARGARET M [US] ET 9 (2009-02-12) - paragraph [0013] *	1-15	TECHNICAL FIELDS SEARCHED (IPC) D01F D04H
A	EP 0 394 028 A2 (MI [US]) 24 October 19 * page 2, line 14 - * example 1 *		1-15	C11D D21F
	The present search report has I	peen drawn up for all claims  Date of completion of the search	<u> </u> 	Examiner
	The Hague	9 July 2018	Fio	occo, Marco
X : parti Y : parti docu A : tech O : non-	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anot ment of the same category nological background written disclosure mediate document	L : document cited f	cument, but publiste in the application or other reasons	shed on, or

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 18 15 8889

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-07-2018

	Patent document cited in search report		Publication date		Patent family member(s)		Publication date
	WO 03044153	A1	30-05-2003	AR AU BR CA CN EP JP KR MX TW US	037204 555190 2002336747 0213868 2463838 1589320 1444320 2005509734 20040063151 PA04004546 I295320 2003100236 03044153	T A1 A A1 A A1 A A A B A1	27-10-2004 15-05-2012 10-06-2003 31-08-2004 30-05-2003 02-03-2005 11-08-2004 14-04-2005 12-07-2004 10-09-2004 01-04-2008 29-05-2003
	US 4070218	Α	24-01-1978	US US	3973068 4070218		03-08-1976 24-01-1978
	WO 02064875	A2	22-08-2002	AU US WO	2002253937 2002150431 02064875	A1	28-08-2002 17-10-2002 22-08-2002
	US 2009041820	A1	12-02-2009	NON	E		
	EP 0394028	A2	24-10-1990	AU BR DE DE EP JP JP US	617639 9001855 69013386 69013386 0394028 2912674 H0319951 4933229	A D1 T2 A2 B2 A	28-11-1991 18-06-1991 24-11-1994 11-05-1995 24-10-1990 28-06-1999 29-01-1991 12-06-1990
FORM P0459							

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#### REFERENCES CITED IN THE DESCRIPTION

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## Patent documents cited in the description

- US 4637859 A [0089] [0308]
- US 20030203196 A [0089]
- US 61583018 A [0090]
- US 6020303 A [0153] [0156] [0166]
- US 6060443 A [0153] [0156]
- US 6008181 A [0153] [0156]
- WO 9905243 A [0153] [0156]
- WO 9905242 A [0153] [0156]
- WO 9905244 A [0153] [0156]
- US 2220099 A [0155]
- US 2477383 A [0155]
- WO 9905082 A [0156]
- WO 9905084 A [0156]
- WO 9905241 A [0156]
- WO 9907656 A [0156]
- WO 0023549 A [0156]
- WO 0023548 A [0156]
- US 6136769 A [0160]
- US 6004922 A [0160]
- WO 9835002 A [0160]
- WO 9835003 A [0160]
- WO 9835004 A [0160]
- WO 9835005 A [0160]
- WO 9835006 A [0160]
- US 4228042 A [0160]
- US 4239660 A [0160] US 4260529 A [0160]
- US 6022844 A [0160]
- US 6221825 B [0160]
- WO 0047708 A [0160]
- US 6150322 A [0166]
- US 6153577 A [0166]
- US 6093856 A [0166]
- US 4565647 A, Llenado [0166]
- US 4483780 A [0166]
- US 4483779 A [0166]
- US 5332528 A [0166]
- US 6482994 B [0166]
- WO 0142408 A [0166]
- WO 0132816 A [0168]
- US 4681704 A [0168]
- US 4133779 A [0168]
- US 7271138 B [0172]
- US 3929678 A [0174] [0175]
- US 3664961 A [0176]
- US 20070275866 A [0180]
- US 20050003980 A1 [0180] [0183] [0184] [0185] [0186] [0187] [0188]
- US 20040110648 A1 [0180]

- US 20040092414 A1 [0180]
- US 20040091445 A1 [0180]
- US 20040087476 A1 [0180]
- US 6531444 B [0180]
- US 6024943 A [0180]
- US 6042792 A [0180]
- US 6051540 A [0180]
- US 4540721 A [0180]
- US 4973422 A [0180]
- WO 2005102261 A [0180]
- US 20050124530 A1 [0180]
- US 20050143282 A1 [0180]
- WO 2003015736 A [0180]
- US 2006003913 A1 [0180]
- US 4911852 A [0180]
- US 20040058845 A1 [0180]
- US 20040092425 A1 [0180]
- US 20030125222 A1 [0180]
- US 2003215417 A1 [0180]
- US 2003216488 A1 [0180]
- US 2003158344 A1 [0180]
- US 2003165692 A1 [0180]
- US 2004071742 A1 [0180]
- US 2004071746 A1 [0180]
- US 2004072719 A1 [0180]
- US 2004072720 A1 [0180] US 20060039934 A1 [0180]
- US 2003203829 A1 [0180]
- US 2003195133 A1 [0180]
- US 2004087477 A1 [0180]
- US 20040106536 A1 [0180]
- US 6645479 B1 [0180]
- US 6200949 B1 [0180]
- US 4882220 B1 [0180]
- US 4917920 B1 [0180]
- US 4514461 B1 [0180]
- US 6106875 B1 [0180]
- US 4234627 A [0180]
- US 3594328 A [0180]
- US RE32713 E [0180]
- WO 2009134234A1 PCT [0180]
- WO 2006127454 A2 [0180]
- WO 2010079466 A2 [0180]
- WO 2010079467 A2 [0180]
- WO 2010079468 A2 [0180]
- WO 2010084480 A2 [0180] US 7119060 B [0181]
- US 5506201 A [0181]
- US 20030199422 A1 [0183]

•	US 20030036489 A1	[0183]
---	-------------------	--------

- US 20040220074 A1 [0183]
- US 6103678 A [0183]
- US 20060263313 A1 [0184]
- US 5552378 A [0184]
- US 3812011 A [0184]
- US 4317881 A [0184]
- US 4418144 A [0184]
- US 4378923 A [0184]
- US 6458754 B1 **[0185]**
- US 5858959 A [0186]
- US 6245732 B1 [0186]
- US 6048830 B1 [0186]
- US 4539135 B1 [0186]
- US 5651976 A **[0186]**
- US 20060020459 A1 [0187]
- US 7018978 B2 [0187]
- US 6987084 B2 [0187]
- US 6956013 B2 [0187]
- US 6861402 B1 [0187]
- US 6544945 B1 [0187]
- US 6093691 B1 [0187]
- US 6277796 B1 [0187]
- US 6165953 B1 [0187]
- US 6316397 B1 [0187]
- US 6437150 B1 [0187]
- US 6479682 B1 [0187]
- US 6096918 B1 [0187]
- US 6218355 B1 [0187]
- US 6133228 B1 [0187]
- US 6147037 B1 [0187]
- US 7109153 B2 [0187]
- US 7071151 B2 [0187]
- US 6610646 B2 [0187]
- US 5958870 B2 [0187]
- US 20060223726 A1 [0187]
- US 6413920 B1 [0188]
- US 4483781 A [0191]
- US 740446 A [0191]
- EP 0133354 A [0191]
- US 4412934 A [0191] [0192]
- US 4634551 A [0191] [0192]
- US 4915854 A [0192]
- US 4966723 A [0192]
- US 5580485 A [0193]
- US 4430243 A [0193]
- US 4728455 A [0193]
- US 5246621 A [0193]
- US 5244594 A [0193]
- US 5284944 A [0193]
- US 5194416 A [0193]
- US 5246612 A [0193]
   US 5256779 A [0193]
- US 5280117 A [0193]
- 03 3260117 A [0193]
- US 5274147 A [0193]
   US 5153161 A [0193]
- US 5227084 A [0193]
- US 5114606 A **[0193]**

- US 5114611 A [0193]
- EP 549271 A1 [0193]
- EP 544490 A1 [0193]
- EP 549272 A1 **[0193]**
- EP 544440 A2 [0193]
  US 5576282 A [0193]
- . UC 5507026 A [0402]
- US 5597936 A [0193]
- US 5595967 A [0193]
- WO 05042532 A1 **[0193]**
- US 4033718 A **[0194]**
- US 4790856 A [0195]
- US 3646015 A [0195]
- US 7205269 B [0197]
- US 7208459 B [0197]
- US 7674757 B2 [0197]
- WO 0887497 A1 [0198]
- US 200834511 A1, Unilever [0202]
- US 7445644 B [0205]
- US 7585376 B [0205]
- US 20090176684 A1 [0205]
- US 3812044 A, Connor [0212]
- US 4704233 A **[0213]**
- US 4489455 A **[0215]**
- US 4489574 A [0215]
- US 2954347 A [0216]
- US 4265779 A [0216]
- US 3455839 A **[0216]**
- US 3433639 A [UZ 16]
- US 3933672 A [0216]
   US 4652392 A [0216]
- US 4978471 A [0216]
- US 4983316 A [0216]
- US 5288431 A [0216]
- US 4639489 A [0216]
- US 4749740 A [0216]
- US 4798679 A [0216]US 4075118 A [0216]
- EP 89307851 A [0216]
- EP 150872 A **[0216]**
- EP DOS2124526 A [0216]
- US 4062647 A [0221]
- US 4375416 A [0221]
- US 4291071 A [0221]
- US 3962418 A [0227]
- US 3958581 A [0227]
- US 20070207109 A1 [0227]
- US 34584 A [0231]
- US 5104646 A [0231]
- US 5106609 A [0231]
- US 4152416 A [0231]
- US 2826551 A [0231]
   US 3964500 A [0231]
- US 4364837 A [0231]
- US 6607717 B [0231]
- US 6482969 B [0231]
- US 5807956 A [0231]
- US 5981681 A [0231]
   US 6207782 B [0231]
- US 7465439 B [0231]

- US 7041767 B [0231]
- US 7217777 B [0231]
- US 20070286837 A1 [0231]
- US 20050048549 A1 [0231]
- US 20070041929 A1 [0231]
- GB 849433 A [0231]
- DE 10036533 [0231]
- US 5674478 A [0232]
- US 5750122 A [0232]
- US 4529586 A [0232]
- US 4507280 A [0232]
- US 4663158 A [0232]
- US 4197865 A [0232]
- US 4217914 A [0232]
- US 4381919 A [0232]
- US 4422853 A [0232]
- US 4741855 A [0235]
- WO 9307263 A [0240]
- WO 9307260 A [0240]
- WO 8908694 A [0240]
- 110 0550400 17 **[02-10**
- US 3553139 A [0240]
- US 4101457 A [0240]
- US 4507219 A **[0240]**
- US 3600319 A [0241]
- US 3519570 A [0241]
- EP 199405 A **[0241]**
- EP 200586 A [0241]
- WO 9401532 A [0241]
- US 5427711 A [0245]
- US 4597898 A [0249]
- US 548744 A [0249]
- US 4891160 A [0249]
- EP 111965 A [0249]
   EP 111984 A [0249]
- EP 112592 A [0249]

- WO 9532272 A [0249]
- US 4956447 A [0252]
- US 4968451 A [0252]
- US 4711730 A [0252]
- US 4721580 A [0252]
- US 4702857 A [0252]
- US 4877896 A **[0252]**
- US 3959230 A [0252]
- US 3893929 A [0252]
- US 4000093 A [0252]
- US 5415807 A [0252]
- US 4201824 A [0252]
- US 4240918 A [0252]
- US 4525524 A [0252]
- US 4579681 A [0252]
- US 4787989 A [0252]
- EP 0219048 A [0252]
- EP 279134 A [0252]
- EP 457205 A [0252]
- DE 2335044 **[0252]**
- US 3308067 A [0253]
- EP 66915 A [0253]
- EP 193360 A [0253]
- WO 9108281 A [0255]
- WO 9001815 A [0255]
- US 5674270 A [0261]
- US 6020040 A [0261]
- US 20080132438 A [0261]
- US 20110301070 A [0261] [0262]
- US 20100297377 A [0309]
- US 20100295213 A [0309]
- US 20100295206 A [0309]
- US 20100028621 A [0309]
- US 20060278355 A [0309]
  US 6787512 B [0328]
- Non-patent literature cited in the description
- Colloids and Surfaces A. Physico Chemical & Engineering Aspects, 2000, vol. 162, 107-121 [0036]
- ZELEZNAK; HOSENY. Cereal Chemistry, 1987, vol. 64 (2), 121-124 [0047]
- CTFA Cosmetic Ingredient Handbook. The Cosmetic, Toiletries, and Fragrance Association, Inc, 1988
  [0143]
- McCutcheon's Detergents and Emulsifiers. Allured Publishing Corp, 1986 [0151]
- McCutcheon's, Functional Materials. Allured Publishing Corp, 1992 [0151]
- M. ZAHRADNIK. The Production and Application of Fluorescent Brightening Agents. John Wiley & Sons, 1982 [0195]

- Kirk Othmer Encyclopedia of Chemical Technology.
   John Wiley & Sons, Inc, 1979, vol. 7, 430-447 [0216]
- International Cosmetic Ingredient Dictionary. 1993
   [0222]
- CTFA Cosmetic Ingredient Handbook. 1992 [0222]
- CTFA Cosmetic Ingredient Dictionary. The Cosmetic, Toiletry, and Fragrance Association, Inc, 1982 [0226]
- Chemistry and Technology of Silicones. Academic Press, 1968 [0231]
- Encyclopedia of Polymer Science and Engineering.
   John Wiley & Sons, Inc, 1989, vol. 15, 204-308 [0231]