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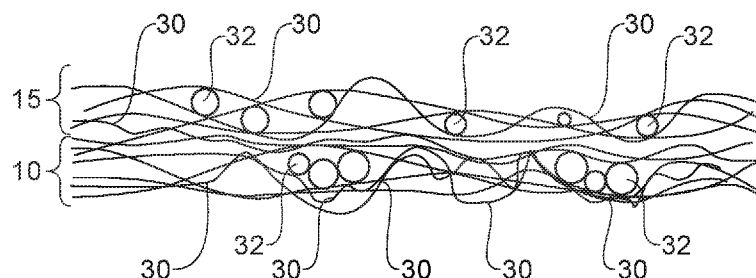


FIG. 1

(57) Abstract: The present invention relates to a process for laundering fabrics using a detergent composition and a fibrous water-soluble unit dose in the rinse cycle.



15484-WO JC

1

PROCESS OF LAUNDERING FABRICS

FIELD OF THE INVENTION

The present invention relates to a process for laundering fabrics using a detergent
5 composition in combination with an acid delivery system.

BACKGROUND OF THE INVENTION

Laundry wash processes are designed to eliminate soils from fabrics. Some soils cannot
be removed under certain pH conditions. For example, mustard stains are known to be more
10 readily removed under alkaline pH conditions. In contrast, tea is more readily removed under
acidic pH conditions. This creates an issue when formulating a detergent and rinse combination.

Additionally, because both detergents and rinse agents are handled by everyday consumers,
there are limits as to the concentration of acids and bases that may be used.

Therefore, there is an on-going need for a method of removing stains that enables the
15 removal of stains in both acidic pH conditions and alkaline pH conditions.

Additionally, there is an on-going need for a method of reducing the rinse liquor to lower
acidic pH conditions safely to help eliminate stains that are more readily removed in low pH
conditions.

It was surprisingly found that the process according to the present invention provided
20 allows for one to remove stains under both alkaline and acidic rinse conditions in one cycle.
Additionally, it was surprisingly found that the process according to the present invention provided
allows for one to achieve acidic rinse liquor conditions that result in statistically better removal of
certain stains.

25 SUMMARY OF THE INVENTION

Described herein is a process of laundering fabrics. The process of laundering fabrics comprising
the steps of;

- a. combining fabrics with a wash liquor, wherein the wash liquor comprises a detergent;
- b. washing the fabrics in the wash liquor using an automatic wash operation, a manual wash operation of a mixture thereof, preferably an automatic wash operation, wherein the process of washing the fabrics comprises a rinse cycle comprising a rinse liquor, wherein the rinse liquor comprises a concentrated acid delivery source in the form of a fibrous water-soluble unit dose;

15484-WO JC

2

- c. separating the fabrics and the wash liquor from one another; and
- d. drying the fabrics.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a cross-sectional view of an example of a multi-ply fibrous structure.

FIG. 2 is a perspective view of an example of a water-soluble unit dose article.

- 5 FIG. 3 is a micro-CT scan image showing a cross-sectional view of the example of a water-soluble unit dose article taken along line 3-3.

FIG. 4 is a magnified view of a portion of FIG. 3.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process of reducing the pH of a rinse liquor below a pH of 5. The present invention further relates to A process of laundering fabrics, comprising the steps of;

- a. combining fabrics with a wash liquor, wherein the wash liquor comprises a detergent;
- b. washing the fabrics in the wash liquor using an automatic wash operation, a manual wash operation of a mixture thereof, preferably an automatic wash operation, wherein the process of washing the fabrics comprises a rinse cycle comprising a rinse liquor, wherein the rinse liquor comprises a concentrated acid delivery source in the form of a fibrous water-soluble unit dose;
- c. separating the fabrics and the wash liquor from one another; and
- d. drying the fabrics.

Those skilled in the art will know how to make the wash liquor. Without wishing to be bound by theory, addition of the laundry detergent composition to water will cause the laundry detergent composition to dissolve and create the wash liquor.

The wash liquor can be created automatically in the drum of an automatic washing machine or can be made in a manual wash operation.

The laundry detergent composition may be comprised in a water-soluble unit dose article, wherein the water-soluble unit dose article comprises a water-soluble film. The laundry detergent composition may be a liquid detergent or a powder detergent. The laundry detergent composition may be a fibrous detergent or in the form of sheets. The detergent will combine with the water

15484-WO JC

3

creating the main wash liquor. The wash liquor can be created automatically in the drum of an automatic washing machine or can be made in a manual wash operation. When made in the drum of an automatic washing machine, traditionally, the fabrics to be washed and the water-soluble unit dose article are added to the drum and the door of the washing machine closed. The washing machine then automatically adds water to the drum to create the wash liquor.

Preferably the wash liquor comprises between 1L and 64L, preferably between 2L and 32L, more preferably between 3L and 20L of water. The laundry detergent composition is described in more detail below.

The wash liquor also comprises a concentrated acid delivery source. The concentrated acid delivery source comprises a water-soluble fibrous unit dose article comprising acid described in more detail below.

The process further comprises washing the fabrics in the wash liquor using an automatic wash operation, a manual wash operation of a mixture thereof, preferably an automatic wash operation.

Those skilled in the art will know how to wash fabrics in an automatic wash operation, a manual wash operation or a mixture thereof.

Preferably, the wash liquor is at a temperature of between 5°C and 90°C, preferably between 10°C and 60°C, more preferably between 12°C and 45°C, most preferably between 15°C and 40°C.

Preferably, washing the fabrics in the wash liquor takes between 5 minutes and 50 minutes, preferably between 5 minutes and 40 minutes, more preferably between 5 minutes and 30 minutes, even more preferably between 5 minutes and 20 minutes, most preferably between 6 minutes and 18 minutes to complete.

Preferably, the wash liquor comprises between 1kg and 20 kg, preferably between 3kg and 15kg, most preferably between 5 and 10 kg of the fabrics.

The wash liquor may comprise water of any hardness preferably varying between 0 gpg to 40gpg. A lower water hardness is termed soft water whereas a higher water hardness is termed hard water.

The step of washing the fabrics in the wash liquor using an automated wash operation comprising a rinse cycle. The rinse cycle comprising a rinse liquor, wherein the rinse liquor comprises a concentrated acid delivery source in the form of a fibrous water-soluble unit dose.

15484-WO JC

4

Preferably the rinse liquor comprises between 1L and 64L, preferably between 2L and 32L, more preferably between 3L and 20L of water. The concentrated acid delivery source in the form of a fibrous water-soluble unit dose is described in more detail below.

Preferably, the rinse liquor is at a temperature of between 5°C and 90°C, preferably between 10°C and 60°C, more preferably between 12°C and 45°C, most preferably between 15°C and 40°C.

Preferably, rinsing the fabrics in the rinse liquor takes between 5 minutes and 50 minutes, preferably between 5 minutes and 40 minutes, more preferably between 5 minutes and 30 minutes, even more preferably between 5 minutes and 20 minutes, most preferably between 6 minutes and 18 minutes to complete.

Preferably, the rinse liquor comprises between 1kg and 20 kg, preferably between 3kg and 15kg, most preferably between 5 and 10 kg of the fabrics.

The rinse liquor may comprise water of any hardness preferably varying between 0 gpg to 40gpg. A lower water hardness is termed soft water whereas a higher water hardness is termed hard water.

The process may further comprise separating the fabrics and the rinse liquor from one another.

The fabrics and the rinse liquor are separated from one another following washing of the fabrics. Such separation may involve removing the fabrics from the rinse liquor, or draining the rinse liquor away from the fabrics. In an automatic washing machine operation it is preferred that the rinse liquor is draining away from the fabrics. In the avoidance of doubt, some of the wash liquor and some of the rinse liquor may remain soaked into the fabrics following separation of the fabrics and the main wash liquor and the main rinse liquor, i.e. the fabrics remain wet. With respect to the present invention the fabrics and rinse liquor are deemed separated from one another once the fabric is separate from the main volume of the rinse liquor or the main volume of the rinse liquor has been drained away, despite some residual rinse liquor possibly remaining soaked into the fabrics.

The process may further comprise drying the fabrics.

Those skilled in the art will be aware of suitable means to dry the fabrics. The fabrics may be dried on a line at room temperature, in an automatic drying machine or a mixture thereof. Those skilled in the art will know at what point the fabrics are deemed dry as opposed to wet.

Laundry detergent composition

15484-WO JC

5

The process according to the present invention comprises the step of diluting a laundry detergent composition. The laundry detergent composition may have a pH greater than 6 or less than 6.

The laundry detergent composition having a pH greater than 6 may be a powder, a liquid, a water-soluble unit dose article or a mixture thereof, preferably a water-soluble unit dose comprising a liquid composition.

5 The solid laundry detergent composition may comprise solid particulates or may be a single homogenous solid. Preferably, the solid laundry detergent composition comprises particles. This means the solid laundry detergent composition comprises individual solid particles as opposed to the solid being a single homogenous solid. The particles may be free-flowing or may be compacted, preferably free-flowing.

10 The term 'liquid laundry detergent composition' refers to any laundry detergent composition comprising a liquid capable of wetting and treating a fabric, and includes, but is not limited to, liquids, gels, pastes, dispersions and the like. The liquid composition can include solids or gases in suitably subdivided form, but the liquid composition excludes forms which are non-fluid overall, such as powders, tablets or granules.

The water-soluble unit dose article is described in more detail below.

The laundry detergent composition comprises between 0.01% to 5%, more preferably from 0.03% to 1%, most preferably from 0.05% to 0.5% by weight of the laundry detergent composition of an oligoamine or salt thereof. The oligoamine or salt thereof is described in more detail below.

The laundry detergent composition preferably comprises a non-soap surfactant. More preferably, the non-soap surfactant is selected from non-soap anionic surfactant, non-ionic surfactant, amphoteric surfactant, cationic surfactant, or a mixture thereof. The laundry detergent composition preferably comprises between 10% and 60%, more preferably between 20% and 55% by weight of the laundry detergent composition of the non-soap surfactant.

Preferably, the non-soap anionic surfactant comprises linear alkylbenzene sulphonate, alkoxylated alkyl sulphate, alkyl sulfate, or a mixture thereof. Preferably, the alkyl sulphate is an ethoxylated alkyl sulphate.

Preferably, the laundry detergent composition comprises between 5% and 50%, preferably between 15% and 45%, more preferably between 25% and 40%, most preferably between 30% and 40% by weight of the detergent composition of the non-soap anionic surfactant.

Preferably, the non-soap anionic surfactant comprises linear alkylbenzene sulphonate and alkoxylated alkyl sulphate, wherein the ratio of linear alkylbenzene sulphonate to alkoxylated alkyl sulphate preferably the weight ratio of linear alkylbenzene sulphonate to ethoxylated alkyl sulphate

15484-WO JC

6

is from 1:2 to 20:1, preferably from 1.1:1 to 15:1, more preferably from 1.2:1 to 10:1, even more preferably from 1.3:1 to 5:1, most preferably from 1.4:1 to 3:1.

Preferably, the laundry detergent composition comprises between 0% and 10%, preferably between 0.01% and 8%, more preferably between 0.1% and 6%, most preferably between 0.15% and 4% by weight of the laundry detergent composition of a non-ionic surfactant. The non-ionic surfactant is preferably selected from alcohol alkoxylate, an oxo-synthesized alcohol alkoxylate, Guerbet alcohol alkoxylates, alkyl phenol alcohol alkoxylates or a mixture thereof.

Preferably, the laundry preferably liquid laundry detergent composition comprises between 1.5% and 20%, more preferably between 2% and 15%, even more preferably between 3% and 10%, most preferably between 4% and 8% by weight of the laundry detergent composition of soap, preferably a fatty acid salt, more preferably an amine neutralized fatty acid salt, wherein preferably the amine is an alkanolamine more preferably selected from monoethanolamine, diethanolamine, triethanolamine or a mixture thereof, more preferably monoethanolamine.

The laundry detergent composition preferably comprises an ingredient selected from the list comprising cationic polymers, polyester terephthalates, amphiphilic graft co-polymers, carboxymethylcellulose, enzymes, perfumes, encapsulated perfumes, bleach or a mixture thereof. Without wishing to be bound by theory it is believed further addition of these materials can further facilitate malodor reduction.

The laundry detergent composition may comprise an adjunct ingredient, wherein the adjunct ingredient is selected from non-aqueous solvents, water, hueing dyes, aesthetic dyes, enzymes, cleaning polymers, builders like fatty acid, bleach, dispersants, dye transfer inhibitor polymers, fluorescent whitening agent, opacifier, antifoam or a mixture thereof.

Preferably, the laundry detergent composition comprises a chelant, wherein the chelant is preferably selected from phosphonates, aminocarboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents, or mixtures thereof, more preferably an additional chelating agent selected from DTPA (diethylenetriaminepentaacetic acid), HEDP (hydroxyethanediphosphonic acid), EDDS (ethylenediamine disuccinate (EDDS), DTPMP (diethylene triamine penta (methylene phosphonic acid)), EDTMP (ethylene diamine tetra(methylene phosphonic acid)), Tiron® (1,2-dihydroxybenzene-3,5-disulfonic acid), HPNO (2-pyridinol-N-oxide), MGDA (methylglycinediacetic acid), GLDA (glutamic-N,N-diacetic acid), any suitable derivative thereof, salts thereof, and mixtures thereof.

The laundry detergent composition may comprise an antioxidant. Without wishing to be bound by theory, it is believed that antioxidants may help to improve malodor control and/or cleaning performance of the compositions, particularly in combination with the oligoamines of the

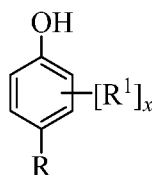
15484-WO JC

7

present disclosure. Antioxidants may also help to reduce yellowing that may be associated with amines, allowing the amines to be formulated at a relatively higher level.

The laundry detergent composition may comprise a hindered phenol antioxidant in an amount of from 0.001% to 2%, preferably from 0.01% to 0.5%, by weight of the laundry detergent composition.

Suitable antioxidants may include alkylated phenols, having the general formula:



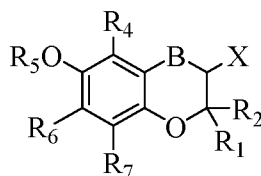
wherein R is C₁-C₂₂ linear alkyl or C₃-C₂₂ branched alkyl, each (1) having optionally therein one or more ester (-CO₂-) or ether (-O-) links, and (2) optionally substituted by an organic group comprising an alkyleneoxy or polyalkyleneoxy group selected from EO (ethoxy), PO (propoxy), BO (butoxy), and mixtures thereof, more preferably from EO alone or from EO/PO mixtures; R may preferably be methyl, branched C₃-C₆ alkyl, or C₁-C₆ alkoxy, preferably methoxy; R¹ is a C₃-C₆ branched alkyl, preferably tert-butyl; x is 1 or 2.

Preferred types of alkylated phenols having this formula may include hindered phenolic compounds. As used herein, the term “hindered phenol” is used to refer to a compound comprising a phenol group with either (a) at least one C₃ or higher branched alkyl, preferably a C₃-C₆ branched alkyl, preferably tert-butyl, attached at a position ortho to at least one phenolic -OH group, or (b) substituents independently selected from the group consisting of a C₁-C₆ alkoxy, preferably methoxy, a C₁-C₂₂ linear alkyl or C₃-C₂₂ branched alkyl, preferably methyl or branched C₃-C₆ alkyl, or mixtures thereof, at each position ortho to at least one phenolic -OH group. If a phenyl ring comprises more than one -OH group, the compound is a hindered phenol provided at least one such -OH group is substituted as described immediately above. Where any R group in the structure above comprises three or more contiguous monomers, that antioxidant is defined herein as a “polymeric hindered phenol antioxidant.” Compositions according to the present disclosure may include a hindered phenol antioxidant. A preferred hindered phenol antioxidant includes 3,5-di-tert-butyl-4-hydroxytoluene (BHT).

A further class of hindered phenol antioxidants that may be suitable for use in the composition is a benzofuran or benzopyran derivative having the formula:

15484-WO JC

8



wherein R₁ and R₂ are each independently alkyl or R₁ and R₂ can be taken together to form a C₅-C₆ cyclic hydrocarbyl moiety; B is absent or CH₂; R₄ is C₁-C₆ alkyl; R₅ is hydrogen or -C(O)R₃ wherein R₃ is hydrogen or C₁-C₁₉ alkyl; R₆ is C₁-C₆ alkyl; R₇ is hydrogen or C₁-C₆ alkyl; X is -CH₂OH, or -CH₂A wherein A is a nitrogen-comprising unit, phenyl, or substituted phenyl. Preferred nitrogen-comprising A units include amino, pyrrolidino, piperidino, morpholino, piperazino, and mixtures thereof.

Suitable hindered phenol antioxidants may include: 2,6-bis(1,1-dimethylethyl)-4-methylphenol; 3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid, methyl ester; 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, octadecyl ester; or mixtures thereof.

Commercially available antioxidants that may be suitable include BHT, RALOX 35TM, and/or TINOGARD TSTM.

Additional antioxidants may be employed. Examples of suitable antioxidants for use in the composition include, but are not limited to, the group consisting of α-, β-, γ-, δ-tocopherol, ethoxyquin, 2,2,4-trimethyl-1,2-dihydroquinoline, 2,6-di-tert-butyl hydroquinone, tert-butyl hydroxyanisole, lignosulphonic acid and salts thereof, and mixtures thereof. It is noted that ethoxyquin (1,2-dihydro-6-ethoxy-2,2,4-trimethylquinoline) is marketed under the name RaluquinTM by the company RaschigTM. Other types of antioxidants that may be used in the composition are 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (TroloxTM) and 1,2-benzisothiazoline-3-one (Proxel GXLTM). Antioxidants such as tocopherol sorbate, butylated hydroxyl benzoic acids and their salts, gallic acid and its alkyl esters, uric acid and its salts, sorbic acid and its salts, and dihydroxyfumaric acid and its salts may also be useful.

The use of non-yellowing antioxidants, such as non-yellowing hindered phenol antioxidants, may be preferred. Antioxidants that form such yellow by-products may be avoided if they lead to perceptible negative attributes in the consumer experience (such as deposition of yellow by-products on fabric, for example). The skilled artisan is able to make informed decisions regarding the selection of antioxidants to employ.

The liquid laundry detergent composition described above preferably has a pH between 6 and 10, more preferably between 6.5 and 8.9, most preferably between 7 and 8, wherein the pH of the liquid laundry detergent composition is measured as a neat pH. For assessment of liquid laundry detergent pH, wash liquor pH, or rinse liquor pH, a 50 ml aliquot may be sampled from a

15484-WO JC

9

North America top loader machine which has an approximate volume of 64 Liters. Additionally, if the detergent is a solid laundry detergent, the solid laundry detergent preferably has a pH between 6 and 10, more preferably between 6.5 and 8.9, most preferably between 7 and 8, wherein the pH of the solid laundry detergent composition is measured as a 10% dilution in demineralized water at 20°C.

Concentrated acid delivery source:

The concentrated acid delivery source comprises of a fibrous water-soluble unit dose comprising an active agent as described below. As used herein, the phrases “water-soluble unit dose article,” “water-soluble fibrous structure”, and “water-soluble fibrous element” mean that the unit dose article, fibrous structure, and fibrous element are miscible in water. In other words, the unit dose article, fibrous structure, or fibrous element is capable of forming a homogeneous solution with water at ambient conditions. “Ambient conditions” as used herein means $23^{\circ}\text{C} \pm 1.0^{\circ}\text{C}$ and a relative humidity of $50\% \pm 2\%$. The fibrous water-soluble unit dose article may contain insoluble materials, which are dispersible in aqueous wash conditions to a suspension mean particle size that is less than about 20 microns, or less than about 50 microns.

The fibrous water-soluble unit dose article may include any of the disclosures found in U.S. Patent Application No. 15/880,594 filed on January 26, 2018; U.S. Patent Application No. 15/880,599 filed January 26, 2018; and U.S. Patent Application No. 15/880,604 filed January 26, 2018; incorporated by reference in their entirety.

These fibrous water-soluble unit dose articles can be dissolved under various wash conditions, e.g., low temperature, low water and/or short wash cycles or cycles where consumers have been overloading the machine, especially with items having high water absorption capacities, while providing sufficient delivery of active agents for the intended effect on the target consumer substrates (with similar performance as today’s liquid products). Furthermore, the fibrous water-soluble unit dose articles described herein can be produced in an economical manner by spinning fibers comprising active agents. The fibrous water-soluble unit dose articles described herein also have improved cleaning performance.

The surface of the fibrous water-soluble unit dose article may comprise a printed area. The printed area may cover between about 10% and about 100% of the surface of the article. The area of print may comprise inks, pigments, dyes, bluing agents or mixtures thereof. The area of print may be opaque, translucent or transparent. The area of print may comprise a single color or multiple colors. The printed area may be on more than one side of the article and contain instructional text and/or graphics. The surface of the fibrous water-soluble unit dose article may

15484-WO JC

10

comprise an aversive agent, for example a bittering agent. Suitable bittering agents include, but are not limited to, naringin, sucrose octacetate, quinine hydrochloride, denatonium benzoate, or mixtures thereof. Any suitable level of aversive agent may be used. Suitable levels include, but are not limited to, 1 to 5000ppm, or even 100 to 2500ppm, or even 250 to 2000ppm.

5 The fibrous water-soluble unit dose may utilize the acid as the bittering agent, preferably citric acid and salts thereof. The citric acid may be combined with any one of the bittering agents previously stated. The citric acid may be used as the bittering agent within the article while a different bittering agent is used on the surface of the article.

10 The fibrous water-soluble unit dose articles may exhibit a thickness of greater than 0.01 mm and/or greater than 0.05 mm and/or greater than 0.1 mm and/or to about 100 mm and/or to about 50 mm and/or to about 20 mm and/or to about 10 mm and/or to about 5 mm and/or to about 2 mm and/or to about 0.5 mm and/or to about 0.3 mm as measured by the Thickness Test Method described herein.

15 The fibrous water-soluble unit dose articles may have basis weights of from about 500 grams/m² to about 5,000 grams/m², or from about 1,000 grams/m² to about 4,000 grams/m², or from about 1,500 grams/m² to about 3,500 grams/m², or from about 2,000 grams/m² to about 3,000 grams/m², as measured according to the Basis Weight Test Method described herein.

20 The fibrous water-soluble unit dose article may exhibit different regions, such as different regions of basis weight, density, caliper, and/or wetting characteristics. The fibrous water-soluble unit dose article may be compressed at the point of edge sealing. The fibrous water-soluble unit dose article may comprise texture on one or more of its surfaces. A surface of the fibrous water-soluble unit dose article may comprise a pattern, such as a non-random, repeating pattern. The fibrous water-soluble unit dose article may comprise apertures. The fibrous water-soluble unit dose article may comprise a fibrous structure having discrete regions of fibrous elements that differ
25 from other regions of fibrous elements in the structure. The fibrous water-soluble unit dose article may be used as is or it may be coated with one or more active agents.

30 The fibrous water-soluble unit dose article may comprise one or more plies. The fibrous water-soluble unit dose article may comprise at least two and/or at least three and/or at least four and/or at least five plies. The fibrous plies can be fibrous structures. Each ply may comprise one or more layers, for example one or more fibrous element layers, one or more particle layers, and/or one or more fibrous element/particle mixture layers. The layer(s) may be sealed. In particular, particle layers and fibrous element/particle mixture layers may be sealed, such that the particles do not leak out. The fibrous water-soluble unit dose articles may comprise multiple plies, where each ply comprises two layers, where one layer is a fibrous element layer and one layer is a fibrous

15484-WO JC

11

element/particle mixture layer, and where the multiple plies are sealed (e.g., at the edges) together. Sealing may inhibit the leakage of particles as well as help the unit dose article maintain its original structure. However, upon addition of the water-soluble unit dose article to water, the unit dose article dissolves and releases the particles into the wash liquor.

5 The fibrous water-soluble unit dose may be in the form of any three-dimensional structure. The fibrous water-soluble unit dose article can be perforated. The article can also be cut or shaped into various sizes for different intended uses. For example, fibrous the water-soluble unit dose may be in the form of a square, a rounded square, a kite, a rectangle, a triangle, a circle, an ellipse, and mixtures thereof.

10 The water-soluble unit dose articles disclosed herein comprise a water-soluble fibrous structure and one or more particles. The water-soluble fibrous structure may comprise a plurality of fibrous elements, for example a plurality of filaments. The one or more particles, for example one or more active agent-containing particles, may be distributed throughout the structure. The water-soluble unit dose article may comprise a plurality of two or more and/or
15 three or more fibrous elements that are inter-entangled or otherwise associated with one another to form a fibrous structure and one or more particles, which may be distributed throughout the fibrous structure.

 The fibrous water-soluble unit dose article may comprise a water-soluble fibrous structure and a plurality of particles distributed throughout the structure, where the water-soluble
20 fibrous structure comprises a plurality of identical or substantially identical, from a compositional perspective, fibrous elements. The water-soluble fibrous structure may comprise two or more different fibrous elements. Non-limiting examples of differences in the fibrous elements may be physical differences, such as differences in diameter, length, texture, shape, rigidity, elasticity, and the like; chemical differences, such as crosslinking level, solubility,
25 melting point, Tg, active agent, filament-forming material, color, level of active agent, basis weight, level of filament-forming material, presence of any coating on fibrous element, biodegradable or not, hydrophobic or not, contact angle, and the like; differences in whether the fibrous element loses its physical structure when the fibrous element is exposed to conditions of intended use; differences in whether the fibrous element's morphology changes when the fibrous
30 element is exposed to conditions of intended use; and differences in rate at which the fibrous element releases one or more of its active agents when the fibrous element is exposed to conditions of intended use. Two or more fibrous elements within the fibrous structure may comprise different active agents. This may be the case where the different active agents may be incompatible with one another, for example an anionic surfactant and a cationic polymer. When

15484-WO JC

12

using different fibrous elements, the resulting structure may exhibit different wetting, imbibitions, and solubility characteristics.

Fibrous Structure

Fibrous structures comprise one or more fibrous elements. The fibrous elements can be associated with one another to form a structure. Fibrous structures can include particles within and or on the structure. Fibrous structures can be homogeneous, layered, unitary, zoned, or as otherwise desired, with different active agents defining the various aforesaid portions.

A fibrous structure can comprise one or more layers, the layers together forming a ply.

Fibrous Elements

The fibrous elements may be water-soluble. The fibrous elements may comprise one or more filament-forming materials and/or one or more active agents, such as a surfactant. The one or more active agents may be releasable from the fibrous element, such as when the fibrous element and/or fibrous structure comprising the fibrous element is exposed to conditions of intended use.

The fibrous elements of the present invention may be spun from a filament-forming composition, also referred to as fibrous element-forming compositions, via suitable spinning process operations, such as meltblowing, spunbonding, electro-spinning, and/or rotary spinning.

“Filament-forming composition” and/or “fibrous element-forming composition” as used herein means a composition that is suitable for making a fibrous element of the present invention 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 fibrous element. The filament-forming material may comprise a polymer. In addition to one or more filament-forming materials, the filament-forming composition may comprise one or more active agents, for example, a surfactant. 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 prior to spinning a fibrous element, such as a filament from the filament-forming composition.

The filament-forming composition may comprise two or more different filament-forming materials. Thus, the fibrous elements may be monocomponent (one type of filament-forming material) and/or multicomponent, such as bicomponent. The two or more different filament-forming materials may be randomly combined to form a fibrous element. The two or more different filament-forming materials may be orderly combined to form a fibrous element, such as a core and sheath bicomponent fibrous element, which is not considered a random mixture of

15484-WO JC

13

different filament-forming materials for purposes of the present disclosure. Bicomponent fibrous elements may be in any form, such as side-by-side, core and sheath, islands-in-the-sea and the like.

The fibrous elements may be substantially free of alkylalkoxylated sulfate. Each fibrous element may comprise from about 0%, or from about 0.1%, or from about 5%, or from about 10%,
5 or from about 15%, or from about 20%, or from about 25%, or from about 30%, or from about 35%, or from about 40% to about 0.2%, or to about 1%, or to about 5%, or to about 10%, or to about 15%, or to about 20%, or to about 25%, or to about 30%, or to about 35% or to about 40%, or to about 50% by weight on a dry fibrous element basis of an alkylalkoxylated sulfate. The amount of alkylalkoxylated sulfate in each of the fibrous elements is sufficiently small so as not
10 to affect the processing stability and film dissolution thereof. Alkylalkoxylated sulfates, when dissolved in water, may undergo a highly viscous hexagonal phase at certain concentration ranges, e.g., 30-60% by weight, resulting in a gel-like substance. Therefore, if incorporated into the fibrous elements in a significant amount, alkylalkoxylated sulfates may significantly slow down the dissolution of the fibrous water-soluble unit dose articles in water, and worse yet, result in
15 undissolved solids afterwards. Correspondingly, most of such surfactants are formulated into the particles.

The fibrous elements may each contain at least one filament-forming material and an active agent, preferably a surfactant. The surfactant may have a relatively low hydrophilicity, as such a surfactant is less likely to form a viscous, gel-like hexagonal phase when being diluted. By using
20 such a surfactant in forming the filaments, gel-formation during wash may be effectively reduced, which in turn may result in faster dissolution and low or no residues in the wash. The surfactant can be selected, for example, from the group consisting of unalkoxylated C₆-C₂₀ linear or branched alkyl sulfates (AS), C₆-C₂₀ linear alkylbenzene sulfonates (LAS), and combinations thereof. The surfactant may be a C₆-C₂₀ linear alkylbenzene sulfonates (LAS). LAS surfactants are well known
25 in the art and can be readily obtained by sulfonating commercially available linear alkylbenzenes. Exemplary C₆-C₂₀ linear alkylbenzene sulfonates that can be used include alkali metal, alkaline earth metal or ammonium salts of C₆-C₂₀ linear alkylbenzene sulfonic acids, such as the sodium, potassium, magnesium and/or ammonium salts of C₁₁-C₁₈ or C₁₁-C₁₄ linear alkylbenzene sulfonic acids. The sodium or potassium salts of C₁₂ linear alkylbenzene sulfonic acids, for example, the
30 sodium salt of C₁₂ linear alkylbenzene sulfonic acid, i.e., sodium dodecylbenzene sulfonate, may be used as the first surfactant.

The fibrous element may comprise at least about 5%, and/or at least about 10%, and/or at least about 15%, and/or at least about 20%, and/or less than about 80%, and/or less than about 75%, and/or less than about 65%, and/or less than about 60%, and/or less than about 55%, and/or

15484-WO JC

14

less than about 50%, and/or less than about 45%, and/or less than about 40%, and/or less than about 35%, and/or less than about 30%, and/or less than about 25% by weight on a dry fibrous element basis and/or dry fibrous structure basis of the filament-forming material and greater than about 20%, and/or at least about 35%, and/or at least about 40%, and/or at least about 45%, and/or at least about 50%, and/or at least about 55%, and/or at least about 60%, and/or at least about 65%, and/or at least about 70%, and/or less than about 95%, and/or less than about 90%, and/or less than about 85%, and/or less than about 80%, and/or less than about 75% by weight on a dry fibrous element basis and/or dry fibrous structure basis of an active agent, preferably surfactant. The fibrous element may comprise greater than about 80% by weight on a dry fibrous element basis and/or dry fibrous structure basis of surfactant.

Preferably, each fibrous element may be characterized by a sufficiently high total surfactant content, e.g., at least about 30%, or at least about 40%, or at least about 50%, or at least about 60%, or at least about 70%, by weight on a dry fibrous element basis and/or dry fibrous structure basis of the first surfactant.

The total level of filament-forming materials present in the fibrous element may be from about 5% to less than about 80% by weight on a dry fibrous element basis and/or dry fibrous structure basis and the total level of surfactant present in the fibrous element may be greater than about 20% to about 95% by weight on a dry fibrous element basis and/or dry fibrous structure basis.

One or more of the fibrous elements may comprise at least one additional surfactant selected from the group consisting of other anionic surfactants (i.e., other than AS and LAS), nonionic surfactants, zwitterionic surfactants, amphoteric surfactants, cationic surfactants, and combinations thereof.

Other suitable anionic surfactants include C₆-C₂₀ linear or branched alkyl sulfonates, C₆-C₂₀ linear or branched alkyl carboxylates, C₆-C₂₀ linear or branched alkyl phosphates, C₆-C₂₀ linear or branched alkyl phosphonates, C₆-C₂₀ alkyl N-methyl glucose amides, C₆-C₂₀ methyl ester sulfonates (MES), and combinations thereof.

Suitable nonionic surfactants include alkoxyated fatty alcohols. The nonionic surfactant may be selected from ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)_nOH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of *n* is from about 5 to about 15. Non-limiting examples of nonionic surfactants useful herein include: C₈-C₁₈ alkylethoxylates, such as, NEODOL[®] nonionic surfactants from Shell; C₆-C₁₂ alkyl phenol

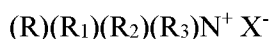
15484-WO JC

15

alkoxylates where the alkoxylate units may be ethyleneoxy units, propyleneoxy units, or a mixture thereof; C₁₂-C₁₈ alcohol and C₆-C₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic[®] from BASF; C₁₄-C₂₂ mid-chain branched alcohols, BA; C₁₄-C₂₂ mid-chain branched alkylalkoxylates, BAE_x, wherein *x* is from 1 to 30; alkylpolysaccharides; specifically alkylpolyglycosides; polyhydroxy fatty acid amides; and ether capped poly(oxyalkylated) alcohol surfactants. Suitable nonionic deterative surfactants also include alkyl polyglucoside and alkylalkoxylated alcohol. Suitable nonionic surfactants also include those sold under the tradename Lutensol[®] from BASF.

Non-limiting examples of cationic surfactants include: the quaternary ammonium surfactants, which can have up to 26 carbon atoms include: alkoxylate quaternary ammonium (AQA) surfactants; dimethyl hydroxyethyl quaternary ammonium; dimethyl hydroxyethyl lauryl ammonium chloride; polyamine cationic surfactants; cationic ester surfactants; and amino surfactants, e.g., amido propyldimethyl amine (APA). Suitable cationic deterative surfactants also include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

Suitable cationic deterative surfactants are quaternary ammonium compounds having the general formula:



wherein, R is a linear or branched, substituted or unsubstituted C₆₋₁₈ alkyl or alkenyl moiety, R₁ and R₂ are independently selected from methyl or ethyl moieties, R₃ is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, suitable anions include: halides, for example chloride; sulfate; and sulfonate. Suitable cationic deterative surfactants are mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly suitable cationic deterative surfactants are mono-C₈₋₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C₁₀₋₁₂ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

Suitable examples of zwitterionic surfactants include: derivatives of secondary and tertiary amines, including derivatives of heterocyclic secondary and tertiary amines; derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds; betaines, including alkyl dimethyl betaine, cocodimethyl amidopropyl betaine, and sulfo and hydroxy betaines; C₈ to C₁₈ (e.g., from C₁₂ to C₁₈) amine oxides; N-alkyl-N,N-dimethylamino-1-propane sulfonate, where the alkyl group can be C₈ to C₁₈.

15484-WO JC

16

Suitable amphoteric surfactants include aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight or branched-chain and where one of the aliphatic substituents contains at least about 8 carbon atoms, or from about 8 to about 18 carbon atoms, and at least one of the aliphatic substituents contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. Suitable amphoteric surfactants also include sarcosinates, glycinate, taurinate, and mixtures thereof.

The fibrous elements may comprise a surfactant system containing only anionic surfactants, e.g., either a single anionic surfactant or a combination of two or more different anionic surfactants. Alternatively, the fibrous elements may include a composite surfactant system, e.g., containing a combination of one or more anionic surfactants with one or more nonionic surfactants, or a combination of one or more anionic surfactants with one or more zwitterionic surfactants, or a combination of one or more anionic surfactants with one or more amphoteric surfactants, or a combination of one or more anionic surfactants with one or more cationic surfactants, or a combination of all the above-mentioned types of surfactants (i.e., anionic, nonionic, amphoteric and cationic).

In general, fibrous elements are elongated particulates having a length greatly exceeding average diameter, e.g., a length to average diameter ratio of at least about 10. A fibrous element may be a filament or a fiber. Filaments are relatively longer than fibers. A filament may have a length of greater than or equal to about 5.08 cm (2 in.), and/or greater than or equal to about 7.62 cm (3 in.), and/or greater than or equal to about 10.16 cm (4 in.), and/or greater than or equal to about 15.24 cm (6 in.). A fiber may have a length of less than about 5.08 cm (2 in.), and/or less than about 3.81 cm (1.5 in.), and/or less than about 2.54 cm (1 in.).

The one or more filament-forming materials and active agents may be present in the fibrous element at a weight ratio of total level of filament-forming materials to active agents of about 2.0 or less, and/or about 1.85 or less, and/or less than about 1.7, and/or less than about 1.6, and/or less than about 1.5, and/or less than about 1.3, and/or less than about 1.2, and/or less than about 1, and/or less than about 0.7, and/or less than about 0.5, and/or less than about 0.4, and/or less than about 0.3, and/or greater than about 0.1, and/or greater than about 0.15, and/or greater than about 0.2. The one or more filament-forming materials and active agents may be present in the fibrous element at a weight ratio of total level of filament-forming materials to active agents of about 0.2 to about 0.7.

The fibrous element may comprise from about 10% to less than about 80% by weight on a dry fibrous element basis and/or dry fibrous structure basis of a filament-forming material, such

15484-WO JC

17

as polyvinyl alcohol polymer, starch polymer, and/or carboxymethylcellulose polymer, and greater than about 20% to about 90% by weight on a dry fibrous element basis and/or dry fibrous structure basis of an active agent, such as surfactant. The fibrous element may further comprise a plasticizer, such as glycerin, and/or additional pH adjusting agents, such as citric acid. The fibrous element
5 may have a weight ratio of filament-forming material to active agent of about 2.0 or less. The filament-forming material may be selected from the group consisting of polyvinyl alcohol, starch, carboxymethylcellulose, polyethylene oxide, and other suitable polymers, especially hydroxyl-containing polymers and their derivatives. The filament-forming material may range in weight average molecular weight from about 100,000 g/mol to about 3,000,000 g/mol. It is believed that
10 in this range, the filament-forming material may provide extensional rheology, without being so elastic that fiber attenuation is inhibited in the fiber-making process.

The one or more active agents may be releasable and/or released when the fibrous element and/or fibrous structure comprising the fibrous element is exposed to conditions of intended use. The one or more active agents in the fibrous element may be selected from the group consisting of
15 surfactants, organic polymeric compounds, and mixtures thereof.

The fibrous elements may exhibit a diameter of less than about 300 μm , and/or less than about 75 μm , and/or less than about 50 μm , and/or less than about 25 μm , and/or less than about 10 μm , and/or less than about 5 μm , and/or less than about 1 μm as measured according to the Diameter Test Method described herein. The fibrous elements may exhibit a diameter of greater
20 than about 1 μm as measured according to the Diameter Test Method described herein. The diameter of a fibrous element may be used to control the rate of release of one or more active agents present in the fibrous element and/or the rate of loss and/or altering of the fibrous element's physical structure.

The fibrous element may comprise two or more different active agents, which are
25 compatible or incompatible with one another. The fibrous element may comprise an active agent within the fibrous element and an active agent on an external surface of the fibrous element, such as an active agent coating on the fibrous element. The active agent on the external surface of the fibrous element may be the same or different from the active agent present in the fibrous element. If different, the active agents may be compatible or incompatible with one another. The one or
30 more active agents may be uniformly distributed or substantially uniformly distributed throughout the fibrous element. The one or more active agents may be distributed as discrete regions within the fibrous element.

Active Agents

15484-WO JC

18

The fibrous water-soluble unit dose articles described herein may contain one or more active agents. The active agents may be present in the fibrous elements in the form of distinct particles, in the form of or integrated into particles, or as a premix in the article. Premixes for example, may be slurries of active agents that are combined with aqueous absorbents.

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The active agent may be an acid in the form of an active agent acid or an acid. Examples of acids suitable for use include, but are not limited to, organic acids selected from the group consisting of acetic acid, adipic acid, aspartic acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, citric acid, benzoic acid, formic acid, glutaric acid, glutonic acid, hydroxyethyliminodiacetic acid, iminodiacetic acid, lactic acid, maleic acid, malic acid, malonic acid, oxydiacetic acid, oxydisuccinic acid, succinic acid, sulfamic acid, tartaric acid, tartaric-disuccinic acid, tartaric-monosuccinic acid, their salts or mixtures thereof, either alone or in combination. Preferably, the acid is citric acid, lactic acid, acetic acid, and/or tartaric acid, and more preferably citric acid.

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In certain aspects, the acid comprises a coating. The coating can help prevent the active agent from prematurely dissolving. A preferred acid is citric acid and preferred coatings include maltodextrin, waxes, citrate, sulfate, zeolites, anti-caking agents such as silicon dioxide or other desiccants. Preferred combinations include citric acid coated with maltodextrin (available under the tradename Citric Acid DC), citric acid coated with citrate (available under the tradename CITROCOAT® N), or citric acid coated with silicon dioxide (available under the tradename Citric Acid S40).

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The active agent acid may be incorporated into the fibrous water-soluble unit dose composition at a level of from about 5% to about 90%, preferably from about 10% to about 80%, preferably from about 15% to about 75%, preferably from about 40% to about 70%, preferably from about 60% to about 70%, by weight of the fibrous water-soluble unit dose article, such as, for example, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, or 80% by weight of the fibrous water-soluble unit dose article. The active agent acid may be incorporated as distinct particles, a encapsulated particles, as particles in a slurry, as part of the fibers, or as a mixture thereof.

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The fibrous water-soluble unit dose may comprise one or more additional organic acids. The additional organic acid may be in the form of an organic carboxylic acid or polycarboxylic acid. Examples of organic acids that may be used include: acetic acid, adipic acid, aspartic acid, benzoic acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, citric acid, formic

15484-WO JC

19

acid, glycolic acid, benzoic acid, gluconic acid, glutaric acid, hydroxyethyliminodiacetic acid, iminodiacetic acid, lactic acid, maleic acid, malic acid, malonic acid, oxydiacetic acid, oxydisuccinic acid, succinic acid, sulfamic acid, tartaric acid, tartaric-disuccinic acid, tartaric-monosuccinic acid, their salts or mixtures thereof. In some aspects, the composition comprises
5 organic acids that can also serve as detergent builders, such as citric acid.

The water soluble unit dose may further comprise acids with a pKa of from about 1.0 to about 5.0. Suitable acids within this pKa range can be found but not limited to those in the CRC Handbook of Chemistry and Physics, 99th edition, Taylor & Francis.

The organic acid may be a water-soluble or water-miscible acid. In some aspects, the
10 organic acid has a solubility in water at 20°C of at least about 10g acid / 100ml water, or at least about 30g acid / 100ml water, or at least about 50g acid / 100ml water, or at least about 70g acid / 100ml water, or at least about 85g / 100ml water. In some aspects, the composition is substantially free of fatty acid.

The organic acid may be a low-weight acid, for example, an acid having a molecular weight of
15 less than 210 g/mole. In some aspects, the organic acid has no more than nine carbon atoms, alternatively no more than six carbon atoms. The organic acid in the detergent composition may have no more than four carbon atoms, or no more than three carbon atoms, or fewer than three carbon atoms. Specific examples of organic acids having fewer than three carbon atoms include formic acid and acetic acid.

20 FIG. 1 shows a first ply 10 and a second ply 15 associated with the first ply 10, wherein the first ply 10 and the second ply 15 each comprises a plurality of fibrous elements 30, in this case filaments, and a plurality of particles 32 (active agent acid here in the form of citric acid). In the second ply 15, the particles 32 are dispersed randomly, in the x, y, and z axes, and in the first ply, the particles 32 are in pockets.

25 FIG. 2 is a perspective view of a fibrous water-soluble unit dose 60.

FIG. 3 is a micro-CT scan image showing a cross-sectional view of an example of the fibrous water-soluble unit dose article of FIG. 2 taken along line 3-3. The fibrous water-soluble unit dose having a fibrous element layer and a fibrous element/particle mixture layer. The fibrous water-soluble unit dose comprises a plurality of fibrous elements 30, in this case filaments, and a
30 plurality of particles 32. The multiply, multilayer article is sealed at the edges 64, so that the particles do not leak out. The outer surfaces of the article are fibrous element layers. As shown in

15484-WO JC

20

FIG. 3, the particles 32 do not agglomerate between the fibers and can be seen as individual particles.

FIG. 4 is a magnified view 62 of a portion of FIG. 3. As shown in FIG. 4, the sealing edge 64 of the fibrous water-soluble unit dose 60 comprises of one or more particles 32 of citric acid.

Fabric softeners are traditionally not buffered to reduce the rinse liquor pH. As such, one of ordinary skill in the art would expect the use of the fibrous water-soluble unit dose comprising citric acid to have a greater efficacy for stain removal versus when used with an acidic fabric treatment composition as described below.

10 Fabric Treatment Composition

The fabric treatment compositions may be an acidic fabric treatment composition such as one described in United States Patent Application No. 62/756,672 filed on November 7, 2018 (first inventor Delaney, Sarah Ann); herein incorporated by reference.

. As described in more detail below, the compositions may include acetic acid, which may be in the form of vinegar. The acetic acid may be part of an organic acid system. The compositions may provide cleaning, softness, and/or freshness benefits to a target fabric. For example, it is believed that the acetic acid and/or other organic acids may remove mineral deposits that may build up on fabrics, particularly those washed in hard water, resulting in improved softness.

The fabric treatment compositions are liquid compositions. The liquid composition may be of relatively low viscosity, even similar to that of water. Consumers may desire such low-viscosity compositions due to an association with purity, natural-ness, and/or simplicity. The compositions may be characterized by a viscosity of from about 1 to about 200, or to about 150, or to about 100, or to about 75 cps, or to about 50 cps, or to about 30 cps, or to about 20 cps, or to about 15 cps, or to about 10 cps. As used herein, viscosity is determined by the method provided in the Test Methods section below.

The fabric treatment compositions described below are acidic compositions. The fabric treatment compositions of the present disclosure may be characterized by a pH of less than 7, or less than about 6, or less than about 5, or less than about 4, or less than about 3. The fabric treatment compositions of the present disclosure may be characterized by a pH of from about 1, or from about 1.5, or from about 2, to about 6, or to about 5, or to about 4, or to about 3, or to about 2.5. The compositions may have a pH of from about 2 to about 4, or to about 3.

15484-WO JC

21

In addition to the organic acids described below, the compositions may comprise additional pH adjusting agents, such as buffer agents and/or neutralizing agents, such as caustic materials (e.g., NaOH).

The compositions of the present disclosure may be characterized by a Reserve Acidity measurement. Without being limited by theory, the Reserve Acidity measurement is found to be the best measure of the acidifying power of a composition, or the ability of a composition to provide a target acidic wash or rinse pH when added at high dilution into tap water as opposed to pure or distilled water. The Reserve Acidity may be controlled by the level of formulated organic acid along with the neat product pH as well as, in some aspects, other buffers. The compositions of the present disclosure may have a Reserve Acidity to pH 4.0 of at least about 1, or at least about 3, or at least about 5. The compositions described may have a Reserve Acidity to pH 4.0 of from about 3 to about 10, or from about 4 to about 7. As used herein, "Reserve Acidity" refers to the grams of NaOH per 100 g of product required to attain a pH of 4.0. The Reserve Acidity measurement as used herein is based upon titration (at standard temperature and pressure) of a 1% product solution in distilled water to an end point of pH 4.00, using standardized NaOH solution.

The fabric treatment compositions of the present disclosure may be substantially transparent. Such compositions may signal purity and/or natural origins (and consequently, lack of synthetic ingredients) to the consumer. The compositions may be characterized by a percent transmittance (%T) of at least about 50%, or at least about 60%, or at least about 70%, or at least about 80%, or at least about 90%, or at least about 95% of light using a 1 centimeter cuvette, at a wavelength of 410-800 nanometers, or 570-690 nanometers, where the composition is substantially free of dyes. For purposes of this disclosure, as long as one wavelength in the visible light range has greater than 50% transmittance, it is considered to be substantially transparent/translucent.

The disclosed compositions may be isotropic at 22°C. As used herein, "isotropic" means a clear mixture, having a % transmittance of greater than 50% at a wavelength of 570 nm measured via a standard 10 mm pathlength cuvette with a Beckman DU spectrophotometer, in the absence of dyes. The percent transmittance is determined according to the method provided in the Test Methods section below.

15484-WO JC

22

Alternatively, transparency of the composition may be measured as having an absorbency in the visible light wavelength (from about 410 to 800 nm) of less than 0.3, which is in turn equivalent to at least 50% transmittance using the cuvette and wavelengths noted above.

The fabric treatment composition may be present in a single phase. The compositions may be stable according to the Stability method presented in the Test Methods section below.

Organic Acid(s)

The fabric treatment compositions may include one or more organic acids. The fabric treatment compositions may include an organic acid system, which may comprise the one or more organic acids. The composition may include at least two organic acids. The organic acid system may comprise at least acetic acid and a second organic acid, such as citric acid. The organic acids of the present disclosure may have a molecular weight of less than about 80 Daltons.

The fabric treatment compositions may include from about 1% to about 40%, by weight of the composition of the organic acid system. The organic acid system may be present at a level of from about 1%, or from about 2%, or from about 3%, or from about 5%, or from about 10%, or from about 15%, or from about 20%, to about 40%, or to about 35%, or to about 30%, or to about 25%, or to about 20%, by weight of the fabric treatment compositions.

The fabric treatment compositions may comprise acetic acid. It is believed that acetic acid helps to remove certain residues from fabrics, leaving them cleaner and/or softer. Acetic acid may be present at a level of from about 0.05%, or from about 0.1%, or from about 0.15%, or from about 0.2% to about 5%, or to about 3%, or to about 2%, or to about 1%, or to about 0.5%, or to about 0.3%, by weight of the composition.

The acetic acid may be provided as vinegar. Thus, the fabric treatment compositions of the present disclosure may comprise vinegar. The vinegar may be present at a level of from about 0.5%, or from about 1%, or from about 1.5%, or from about 2%, to about 20%, or to about 15%, or to about 10%, or to about 5%, or to about 4%, or to about 3%, by weight of the composition. Vinegar suitable for use in a domestic kitchen typically comprises about 4% to about 5%, by weight of the vinegar, of acetic acid, although more concentrated forms may be available.

15484-WO JC

23

Due to the significant odor of acetic acid, relatively low levels of acetic acid and/or vinegar may be desired, although a certain minimum amount may still be desired to give a performance benefit. While white vinegar typically contains about 4% to about 5% of acetic acid, the compositions of the present disclosure may include acetic acid at a relatively lower level. When the level of acetic acid or vinegar is low, the performance of composition may be improved with the addition of a second organic acid, such as citric acid.

The fabric treatment compositions and/or the organic acid systems of the present disclosure may comprise at least a second organic acid in addition to acetic acid / vinegar. Suitable second organic acids may include citric acid, lactic acid, adipic acid, aspartic acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, glutaric acid, hydroxyethyliminodiacetic acid, iminodiacetic acid, maleic acid, malic acid, malonic acid, oxydiacetic acid, oxydisuccinic acid, succinic acid, sulfamic acid, tartaric acid, tartaric-discsuccinic acid, tartaric-monosuccinic acid, or mixtures thereof. The fabric treatment composition may include citric acid. It may be preferred to select a second organic acid that can also function as a builder during usage, such as citric acid.

The second organic acid may be present at a greater level than the acetic acid. The second organic acid may be present in the fabric treatment composition at a level of from about 1%, or from about 2%, or from about 3%, or from about 5%, or from about 10%, or from about 15%, or from about 20%, to about 40%, or to about 35%, or to about 30%, or to about 25%, or to about 20%, by weight of the fabric treatment compositions. The acetic acid and the second organic acid, for example citric acid, may be present in a weight ratio of from about 1:300, or from about 1:250, or from about 1:225, or from about 1:200, to about 1:1, or to about 1:10, or to about 1:50, or to about 1:100. It may be desirable to have relatively more of the second organic acid compared to the acetic acid in order to improve performance while minimizing undesirable odor.

Fragrance Materials

The fabric treatment compositions may include fragrance material(s). The fragrance materials are added to provide aesthetically pleasing scent to the liquid product composition, to a treatment liquor, and/or to fabrics treated with the composition. The compositions of the present disclosure may include from about 0.1% to about 20%, or from about 0.2% to about 10%, or from about 0.3% to about 5%, by weight of the composition, of fragrance materials.

15484-WO JC

24

Non-limiting examples of fragrance materials include, but are not limited to, aldehydes, ketones, esters, and the like. Other examples include 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.

- 5 Finished perfumes can comprise extremely complex mixtures of such ingredients.

Tested Compositions for Examples:

The tests below compare multiple detergents, rinses, and the concentrated acid delivery source described herein, alone and in combinations. Specifically, the use of 9 elements Low pH Formula Detergent, a Mid-pH (pH of 8.5) formula detergent, and Platinum Advanced Shirt & Laundry Detergent when using both an acid rinse (9 Elements Rinse) and the concentrated acid delivery system of the present invention.

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Table 1: Detergent Compositions

Detergent	Ingredients/ Composition
9 Elements Detergent Formulation	HLAS, Nonionic surfactant, amine oxide, citric acid, sodium hydroxide, acetic acid, biobased propylene glycol, perfume, deionized water.
Mid-pH Detergent Formulation	Sodium Dodecyl Benzene Sulfonate at 6.8%; C12-C14 EO 9at 10.8%; Citric acid at 1%; NaOH at 1%; DI Water to Balance.

- 9 Elements detergent compositions are further described in United States Patent Application No. 62/756,855 filed on November 7, 2018 (first named inventor Delaney, Sarah Ann; herein incorporated by reference.

Platinum Advanced Shirt & Laundry Detergent is Product number: 8930 from manufacturer Fabritec International, Inc. located at 8145 Holton Drive, Suite 110 in Florence, KY 41042 USA having a listed phone number of (859) 781-8200.

- 9 Elements rinse which comprises of the following composition: Citric Acid, Vinegar (6% Acetic acid), Sodium Hydroxide, 1,2 propanediol, perfume, and deionized water. 9

15484-WO JC

25

Elements rinse is described in United States Patent Application No. 62/756,672 filed on November 7, 2018 (first inventor Delaney, Sarah Ann); herein incorporated by reference.

The concentrated acid delivery system described above is exemplified by the table below having the following composition according to the present disclosure.

Table 2: Concentrated Acid Delivery Source Composition

Name	Citrocoat Particle (%)	Web (%)	Finished Pad (g)	Finished Pad (%)
Raw Material				
NaAS (from fiber)	0.00%	21.56%	0.80	6.63%
NaLAS (from fiber & particle)	0.00%	43.11%	1.60	13.26%
Citrocoat (from particle)	100.00%	0.00%	8.38	69.23%
PVOH 505 (from fiber)	0.00%	29.33%	1.09	9.03%
PEOn10 (from fiber)	0.00%	2.60%	0.10	0.80%
PEOn60k (from fiber)	0.00%	0.40%	0.01	0.12%
Misc & Moisture	0.00%	3.00%	0.11	0.92%
Web TOTAL	100.00%	100.00%	12.10	100.00%
Charm TOTAL			12.10	100.00%
Pad/Dose			1.00	
Surfactant/Dose (g)			2.41	
PVOH/Dose (g)			1.20	
Dose Wt			12.10	
%LAS			67%	
6" x 1 m Weight (g) (193 OK)			130	
Total Product Basis Wt (GSM) (ET4-3333)			2574	

LAS is linear alkylbenzenesulfonate having an average aliphatic carbon chain length C₁₁-C₁₂ supplied by Stepan, Northfield, Illinois, USA or Huntsman Corp. HLAS is acid form.

AS is a C₁₂₋₁₄ sulfate, supplied by Stepan, Northfield, Illinois, USA, and/or a mid-branched alkyl sulfate.

PEG-PVAc polymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the

15484-WO JC

26

polyethylene oxide to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units. Available from BASF (Ludwigshafen, Germany).

Ethoxylated Polyethylenimine (PE20) is a 600 g/mol molecular weight polyethylenimine core with 20 ethoxylate groups per -NH. Available from BASF (Ludwigshafen, Germany).

5 Citrocoat (NF5000) is available from Jungbunzlauer (Basel, Switzerland).

PVOH and Celvol® are available from Sekisui Specialty Chemicals America, LLC located in Dallas Texas.

Determination of pH

Unless otherwise stated herein, the pH of the composition is defined as the neat pH of the composition at $20 \pm 2^\circ\text{C}$. Any meter capable of measuring pH to ± 0.01 pH units is suitable. Orion meters (Thermo Scientific, Clintonpark –Keppekouter, Ninovesteenweg 198, 9320 Erembodegem –Aalst, Belgium) or equivalent are acceptable instruments. The pH meter should be equipped with a suitable glass electrode with calomel or silver/silver chloride reference. An example includes Mettler DB 115. The electrode should be stored in the manufacturer's recommended electrolyte solution. The pH is measured according to the standard procedure of the pH meter manufacturer. Furthermore, the manufacturer's instructions to set up and calibrate the pH assembly should be followed.

Table 3: pH data for various combinations of detergent, detergent plus rinse, and detergent plus rinse plus Power Tab as sampled from a traditional top loading washing machine:

	Water pH without added component	1 Minute Wash pH	3 Minute Wash pH	5 Minute Wash pH	1 Minute Rinse pH	2 Minute Rinse pH
Elements Detergent	8.11	6.57	6.58	6.65	7.84	8.04
Mid pH Detergent	7.93	8.23	8.2	8.11	7.95	7.97
Platinum Detergent	7.93	9.99	10.02	10.03	8.39	8.3
Elements Detergent plus Elements Rinse	7.95	6.28	6.33	6.42	5.43	5.44
Mid pH Detergent plus rinse	7.96	8.15	8.17	8.21	5.36	5.41
Platinum Detergent plus rinse	8.15	10.04	10.04	10.01	5.7	5.69
Elements plus rinse plus Concentrated Acid Delivery Source	8.07	6.41	6.51	6.9	4.64	4.64

15484-WO JC

27

Mid pH Detergent plus Rinse and Concentrated Acid Delivery Source	8.01	8.16	8.28	8.23	4.53	4.53
Platinum Detergent plus Rinse and Concentrated Acid Delivery Source	7.98	10	10.01	10.01	4.72	4.78

As shown in the table above, the water pH was measured for each sample. pH measurements were then taken at various stages including at approximately 1 minute into the washing cycle, at approximately 3 minutes into the washing cycle, at approximately 5 minutes into the washing cycle, at approximately 1 minutes into the rinse cycle, and at approximately 2 minutes into the rinse cycle. All measurements were taken of water, wash liquor, or rinse liquor only. No fabrics were in the machine.

Without being bound by theory, it has been found that one can improve the cleaning efficacy of a wash and rinse cycle by reducing the pH of the rinse cycle below a pH of 5.3 such as, for example a pH between 3 and 5.3, a pH between 4 and 5, or a pH between 4.5 and 4.9. This may be accomplished via a process that utilizes one or more of the fibrous water-soluble unit dose article having an active comprising an acid. As shown in the table below, the addition of the fibrous water-soluble unit dose reduces the pH of the rinse cycle to below 5 when combined with a low pH rinse composition. Without being bound by theory, it is believed that by using a high pH detergent followed by a low pH rinse composition and a water-soluble fibrous unit dose article, one can effectively remove high pH stains such as mustard while additionally removing low pH stains such as tea. As shown in the pH curves and the stain data below, one can achieve this combination of stain removal even without the use of the pH rinse composition.

Without being bound by theory, it has been found that one may safely reach pH levels below 5 in a rinse cycle thereby more efficaciously removing stains by combining a low pH rinse composition with a water-soluble fibrous unit dose article. Due to the restriction in amounts of capacity of a rinse drawer space and restrictions on the concentration of acid in a liquid softener, one cannot achieve the targeted rinse cycle pH of less than 5.5 without the use of a water-soluble unit dose article. As shown in the table above and the stain data below, the addition of the fibrous water-soluble unit dose allows for one to achieve new pH levels that significantly increase the stain removal efficacy for a particular set of stains.

Stain Removal

15484-WO JC

28

Stain Removal testing is conducted in Front Loader HE machines, in line with the guidance provided by ASTM4265-14 Standard Guide for Evaluating Stain Removal Performance in Home Laundering. Technical stain swatches of cotton CW120 containing 22 stains were purchased. The stained swatches were washed in conventional North American washing machines (Whirlpool®) using 7 grains per gallon hardness, selecting the normal cycle at 86F, using each of the respective detergent compositions listed in the table below. It is noted that the volume for a standard front loading HE washing machine is approximately 18 Liters. Image analysis was used to compare each stain to an unstained fabric control. Software converted images taken into standard colorimetric values and compared these to standards based on the commonly used Macbeth Colour Rendition Chart, assigning each stain a colorimetric value (Stain Level). Eight replicates of each were prepared. The stain removal index was then calculated according to the formula shown below.

Stain removal from the swatches was measured as follows:

$$\text{Stain Removal Index (SRI)} = \frac{\Delta E_{\text{initial}} - \Delta E_{\text{washed}}}{\Delta E_{\text{initial}}} \times 100$$

$\Delta E_{\text{initial}}$ = Stain level before washing

ΔE_{washed} = Stain level after washing

STAIN REMOVAL

Example. Effect of reducing rinse liquor pH in an already-low pH rinse environment via addition of 9-Elements PowerTab on top of 9-Elements Rinse formulation

This example demonstrates the improved stain removal efficacy achieved via adding the 9-Elements PowerTab citric acid formulation (the concentrated acid delivery source) in the Rinse, on top of the 9-Elements citric acid liquid rinse formulation, which enables superior stain cleaning versus the rinse alone. As excess acid is added into the rinse step of the laundry cycle, the ability of citric acid to act as a builder scavenging metals in the rinse enables stain removal of metal-sensitive stains to continue beyond the wash part of the cycle.

In order to assess the impact of Acid Rinse alone in varying detergent contexts versus 9 Elements Rinse AND 9 Elements PowerTabs (the concentrated acid delivery source) in those same analogous contexts, 53mL of Acid rinse formulation was added to the rinse, or combined 53mL of Acid Rinse plus one PowerTab respectively. Results are provided in the tables below:

15484-WO JC

29

Table 4: Stain Removal results in Front Loader HE machines and Cotton Fabrics

	Platinum Detergent +9 Elements Rinse	Platinum Detergent + 9 Elements Rinse + Concentrated Acid Delivery Source	HSD
Soy Milk	7.3	9.4	1.72
Lipton Tea	35.9	43.1	5.48

As shown in the table above, the addition of a concentrated acid delivery source to the rinse cycle results in a significant increase in stain removal efficacy. The delta is greater than the Honestly Significant Difference at a 95% confidence interval.

Table 5: Stain Removal results in Front Loader HE machines and Cotton Fabrics

	Mid pH Detergent +9 Elements Rinse	Mid pH Detergent + 9 Elements Rinse + Concentrated Acid Delivery Source	HSD
Soy Milk	6.9	9.9	1.72
Lipton Tea	42.2	52	5.48

As shown in the table above, the addition of a concentrated acid delivery source to the rinse cycle results in a significant increase in stain removal efficacy. The delta is greater than the Honestly Significant Difference at a 95% confidence interval.

Table 6: Stain Removal results in Front Loader HE machines and Cotton Fabrics

	9 Elements Detergent +9 Elements Rinse	9 Elements Detergent + 9 Elements Rinse + Concentrated Acid Delivery Source	HSD
Soy Milk	9.3	11.6	1.72
Chocolate Sauce	68.4	75	4.72
Animal Blood	71.7	74.8	2.57

15484-WO JC

30

As shown in the table above, the addition of a concentrated acid delivery source to the rinse cycle results in a significant increase in stain removal efficacy. The delta is greater than the Honestly Significant Difference at a 95% confidence interval.

As shown in Tables a/b/c, the addition of a PowerTab formulation into an already low-pH rinse (arrived at via addition of 9 Elements liquid rinse addition), enables increased Stain Removal, namely in Soy Milk stains. Depending on the detergent in-wash composition, the additional inclusion of the PowerTab on top of the 9 Elements rinse enables other stain removal improvements like Tea, Animal Blood, or Chocolate Sauce stains at a 95% confidence interval.

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.”

Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, 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.

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.

15484-WO JC

31

CLAIMS

What is claimed is:

1. A process of laundering fabrics, comprising the steps of;
 - a. combining fabrics with a wash liquor, wherein the wash liquor comprises a detergent;
 - b. washing the fabrics in the wash liquor using an automatic wash operation, a manual wash operation of a mixture thereof, preferably an automatic wash operation, wherein the process of washing the fabrics comprises a rinse cycle comprising a rinse liquor, wherein the rinse liquor comprises a concentrated acid delivery source in the form of a fibrous water-soluble unit dose;
 - c. separating the fabrics and the wash liquor from one another;
 - d. drying the fabrics.
2. The process of laundering fabrics according to any preceding claims;
 - a. wherein the fabrics are washed in the wash liquor at a temperature of between 10°C and 60°C, preferably between 10°C and 45°C, more preferably between 10°C and 35°C;
 - b. wherein the wash operation in step b takes between 5 minutes and 60 minutes, preferably between 5 minutes and 45 minutes, more preferably between 5 minutes and 30 minutes;
 - c. or a mixture thereof.
3. The process of laundering fabrics according to any preceding claims, wherein the rinse cycle further comprises a low pH rinse product.
4. The process of laundering fabrics according to any preceding claims, wherein the laundry detergent composition is a liquid and wherein the liquid laundry detergent composition has a pH between 6 and 10, more preferably between 6.5 and 8.9, most preferably between 7 and 8, wherein the pH of the liquid laundry detergent composition is measured as a neat pH.
5. The process of laundering fabrics according to any of claims 1-3, wherein the laundry detergent composition is a liquid and wherein the liquid laundry detergent composition

has a pH between 2 and 6, more preferably between 2 and 5, most preferably between 3 and 4, wherein the pH of the liquid laundry detergent composition is measured as a neat pH.

6. The process of laundering fabrics according to any of the preceding claims, wherein the fibrous water-soluble unit dose comprises an active agent acid selected from the group consisting acetic acid, adipic acid, aspartic acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, citric acid, formic acid, glutaric acid, gluconic acid, hydroxyethyliminodiacetic acid, iminodiacetic acid, lactic acid, maleic acid, malic acid, malonic acid, oxydiacetic acid, oxydisuccinic acid, succinic acid, sulfamic acid, tartaric acid, tartaric-disuccinic acid, tartaric-monosuccinic acid, their salts or mixtures thereof, either alone or in combination.
7. The process of laundering fabrics according to claim 6, wherein the active agent acid is citric acid and sodium citrate.
8. The process of laundering fabrics according to any of the preceding claims, wherein the fibrous water-soluble unit dose comprises a citric acid comprises a coating.
9. The process of laundering fabrics according to any of claims 6-8, wherein the citric acid serves as a bittering agent within the fibrous water-soluble unit dose article.
10. The process of laundering fabrics according to any of the preceding claims, wherein the fibrous water-soluble fibrous unit dose comprises a bittering agent on an outer surface.
11. The process of laundering fabrics according to any of the preceding claims, wherein the fibrous water-soluble unit dose comprises an active agent, wherein the active agent comprises from about 50% to 70% by weight of the water-soluble unit dose.
12. The process of laundering fabrics according to any of the preceding claims, wherein the fibrous water-soluble unit dose comprises a soluble fibrous structure, wherein the soluble fibrous structure forms a pouch which encases an active agent.
13. The process of laundering fabrics according to claim 12, wherein the active agent is commingled with the soluble fibrous structure to form a coform structure.
14. The process of laundering fabrics according to any of claims 12-13, wherein the soluble fibrous structure comprises fibrous elements having a surfactant therein.

15. The process of laundering fabrics according to any of the preceding claims, wherein the composition of the fibrous water-soluble unit dose comprises of 50% or greater of bio-based materials.
16. The process of laundering fabrics according to any of claims 12-15, wherein the fibrous structure comprises fibrous elements comprising starch.
17. The process of laundering fabrics according to any of the preceding claims, wherein the process of washing the fabrics further comprises reducing the pH of the rinse liquor to a pH between 2 and 5.3, preferably to a pH between 3 and 5, more preferably to a pH between 4 and 5.

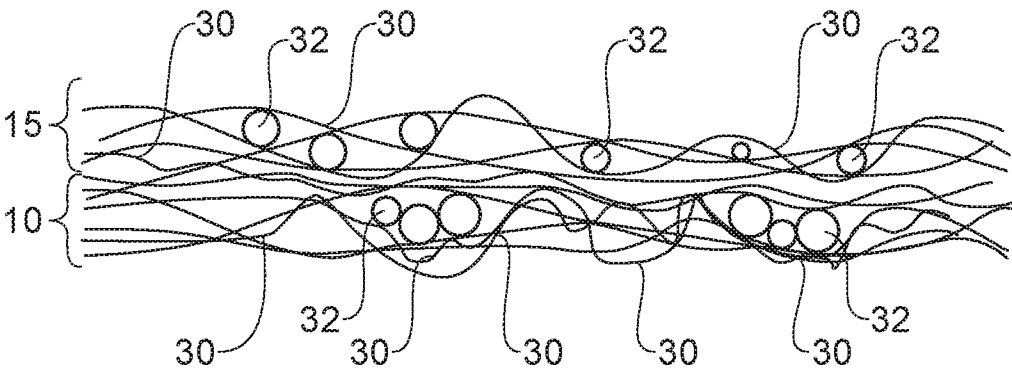


FIG. 1

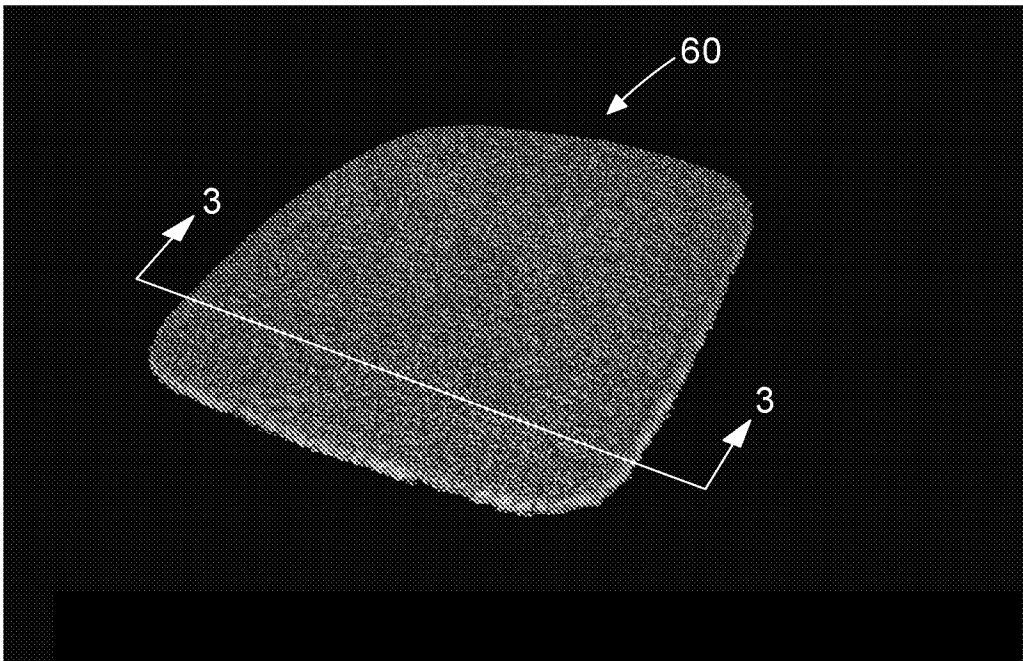


FIG. 2

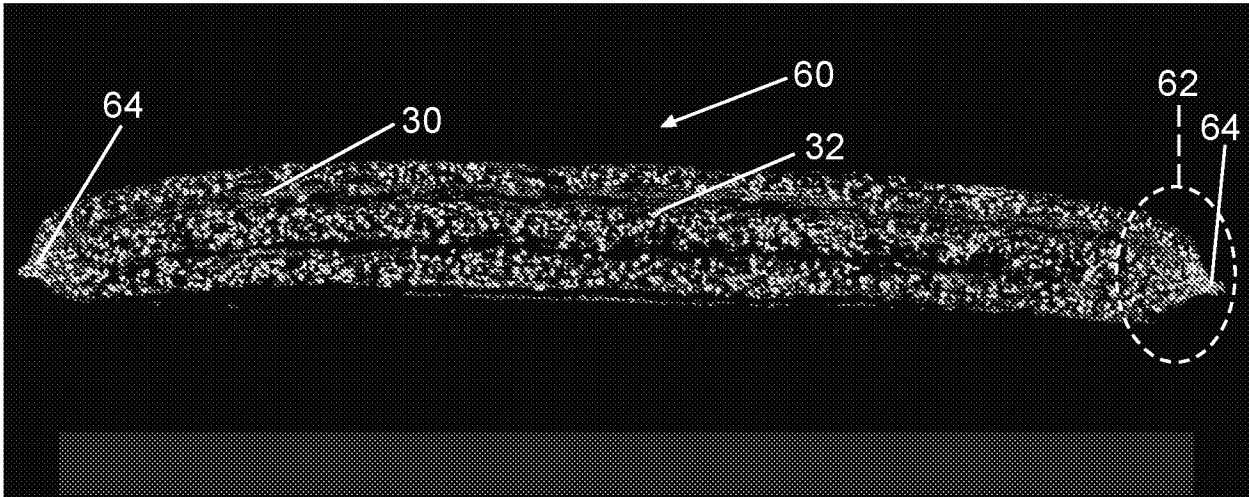


FIG. 3

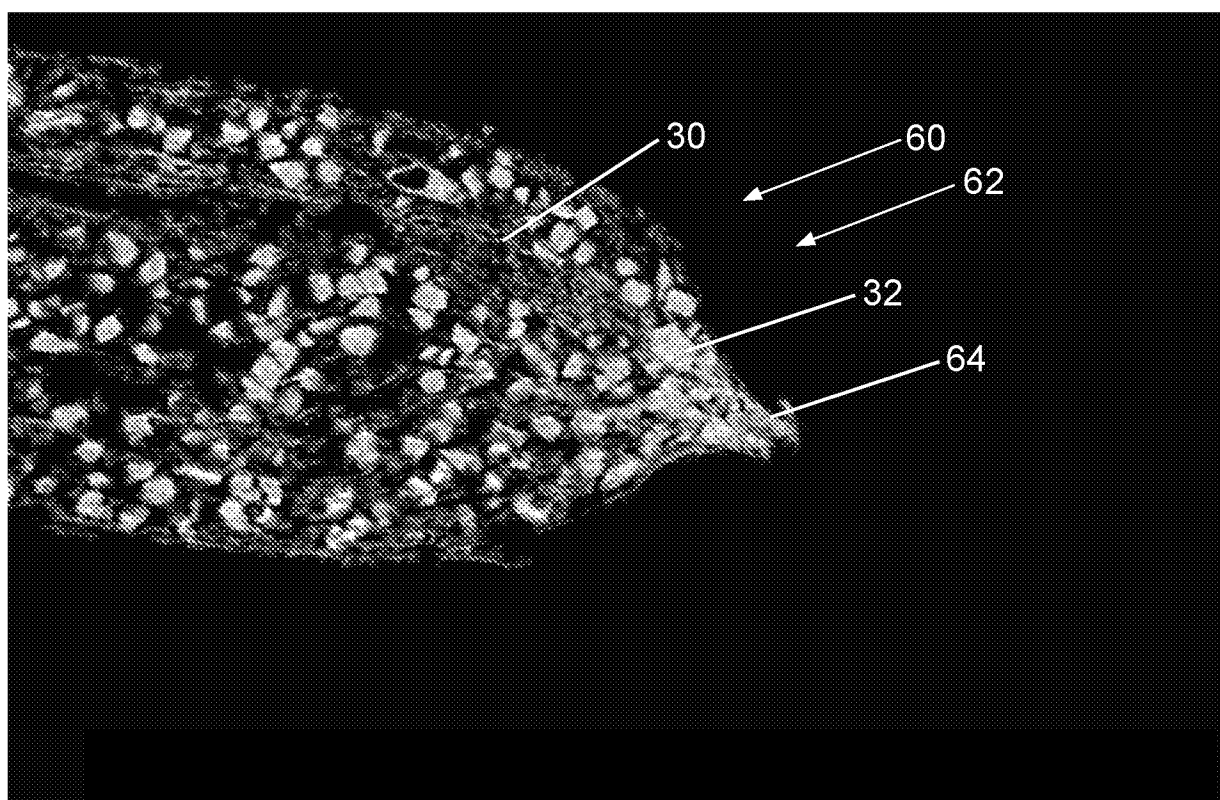


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/023562

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D11/00 C11D17/04 C11D3/20 C11D3/22 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2005/061685 A1 (PROCTER & GAMBLE [US]; SADLOWSKI EUGENE STEVEN [US] ET AL.) 7 July 2005 (2005-07-07) claims 1, 16; example II -----	1-17
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Y	WO 2006/005919 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB] ET AL.) 19 January 2006 (2006-01-19) claims 1, 5, 8, 9; example 5 ----- -/-	1-17
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 June 2020		Date of mailing of the international search report 23/06/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

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