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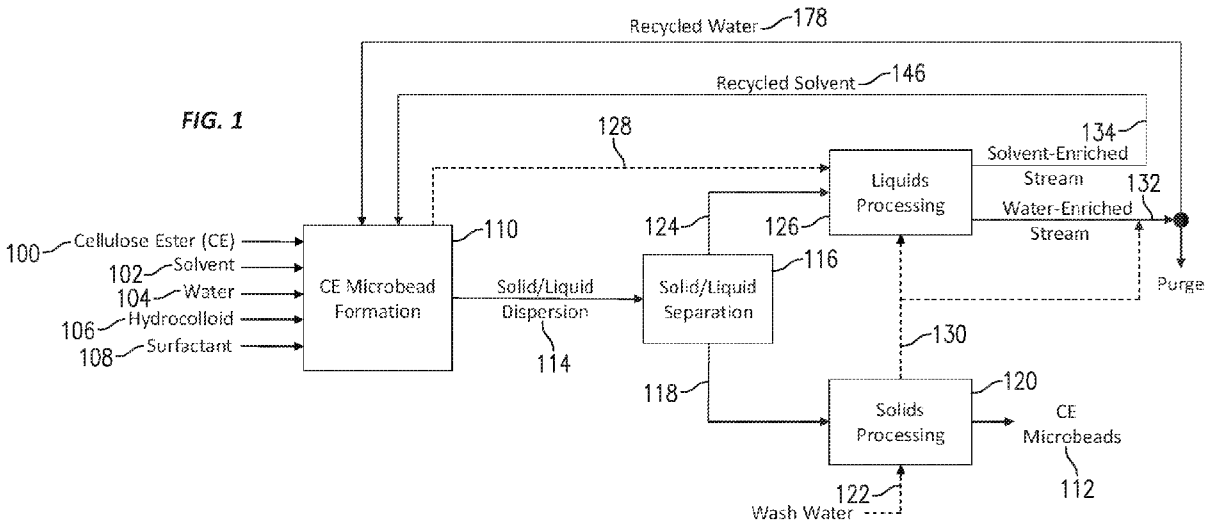
(54) **Title:** METHODS OF MAKING CELLULOSE ESTER MICROBEADS WITH SOLVENT REMOVAL PRIOR TO MICROBEAD HARDENING

FIG. 1



(57) **Abstract:** Methods of making cellulose ester (CE) microbeads are provided. The CE microbeads are produced by forming initial CE microparticles suspended in a Equid phase, and converting the microparticles to hardened CE microbeads. The produced microbeads are biodegradable, and have enhanced solidity, sphericity, and smoothness.

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METHODS OF MAKING CELLULOSE ESTER MICROBEADS WITH SOLVENT REMOVAL PRIOR TO MICROBEAD HARDENING

BACKGROUND

[0001] Microbeads are typically spheroidal plastic particles having a diameter of less than 1 millimeter (mm). These particles are sometimes included in consumer products, such as personal care and cosmetic products. Many of these microbead-containing products are designed to be applied and then washed or rinsed from the user's body. When the microbead-containing products are washed or rinsed from the user's body, the particles are flushed down the drain and received at municipal water treatment facilities. In the past, many known microbeads had been formed from plastic or polymeric materials, such as polyethylene, polypropylene, polymethyl methacrylate, nylon, polyurethane, and the like. These materials generally have limited biodegradability. In addition, the small size of the particles limits their ability to be captured at the water treatment facilities, such that the particles may be discharged from the facilities and into larger bodies of water (e.g., rivers, seas, and oceans). Once in these larger bodies of water, the plastic or polymeric microbeads may be ingested by wildlife or cause other environmental concerns. Thus, the possibility of producing microbead particles from more environmentally friendly materials has recently been explored. However, consumers tend to have high expectations when it comes to the personal care and/or cosmetic products they use, including those containing micron-sized particles. For example, consumers expect these personal care and cosmetic products to exhibit certain optical properties that allow the products to blend in with natural skin color and readily hide any undesirable blemishes.

[0002] Thus, it is desirable to develop biodegradable microbeads that meet environmental and consumer expectation standards, particularly regarding optical properties for personal care and cosmetic products.

SUMMARY

[0003] Provided herein is a method of making cellulose ester (CE) microbeads. The method comprises (a) combining a CE dope and an aqueous mixture to form an initial emulsion comprising a dispersed phase and a continuous phase, wherein the CE dope comprises a CE dissolved in a solvent, (b) converting at least a portion of the initial emulsion into a dispersion

comprising a solid phase and a liquid phase, wherein the solid phase comprises pre-hardened microparticles comprising at least a portion of the CE and at least a portion of the solvent, and the liquid phase comprises at least a portion of the solvent and at least a portion of the aqueous mixture, (c) removing at least some of the solvent from the liquid phase to form a removed solvent and a solvent-depleted dispersion comprising the pre-hardened CE microparticles, and (d) converting at least a portion of the pre-hardened CE microparticles in the solvent-depleted dispersion into hardened CE microbeads.

[0004] Also provided herein is a method of making cellulose ester (CE) microbeads. The method comprises (a) providing a CE dope comprising a CE dissolved in a solvent, (b) combining at least a portion of the CE dope with an aqueous mixture to produce an initial emulsion, (c) converting at least a portion of the initial emulsion into a dispersion comprising a solid phase and a liquid phase, wherein the solid phase comprises pre-hardened CE microparticles comprising at least a portion of the CE and at least a portion of the solvent, and the liquid phase comprises at least a portion of the solvent and at least a portion of the aqueous mixture, (d) removing at least a portion of solvent from the liquid phase to form a solvent-depleted dispersion comprising the pre-hardened CE microparticles, (e) separating at least a portion of the solvent-depleted dispersion from the hardened CE microbeads to define a separated solvent-enriched stream, and (f) recycling at least a portion of the separated solvent-enriched stream for use in the solvent of step (a) or the aqueous mixture of step (b).

[0005] Also provided herein is a method of making cellulose ester (CE) microbeads. The method comprises (a) combining a CE dope and an aqueous mixture to form an initial emulsion, (b) converting at least a portion of the initial emulsion into a dispersion comprising a solid phase and a liquid phase, wherein the solid phase comprises pre-hardened CE microparticles comprising at least a portion of the CE and at least a portion of the solvent, and the liquid phase comprises at least a portion of the solvent and at least a portion of the aqueous mixture, (c) removing at least a portion of the solvent from the liquid phase to form a removed solvent and a solvent-depleted dispersion comprising the pre-hardened CE microparticles, and (d) contacting at least a portion of the solvent-depleted dispersion with a drowning liquid to thereby form a hardened dispersion comprising hardened CE microbeads and the drowning liquid, wherein a volume ratio of the drowning liquid to the solvent-depleted dispersion is less than 2.5:1.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 is a schematic diagram of an example process for making cellulose ester microbeads.

[0007] FIG. 2 is a more detailed schematic diagram of an example process for making cellulose ester microbeads.

[0008] FIG. 3 is a schematic diagram of an alternative process for making cellulose ester microbeads by serialized particle formation.

[0009] FIG. 4 is a schematic diagram of an alternative process for making cellulose ester microbeads by separated dope and aqueous mixture formation, and combined emulsion/dispersion formation and particle hardening.

[0010] FIG. 5 is a schematic diagram of an alternative process for making cellulose ester microbeads by combined emulsion/dispersion formation.

[0011] FIG. 6 is a schematic diagram of an alternative process for making cellulose ester microbeads by combined emulsion/dispersion formation and particle hardening.

[0012] FIG. 7 is a schematic diagram of an alternative process for making cellulose ester microbeads by solvent flashing prior to particle hardening.

DETAILED DESCRIPTION

[0013] The present disclosure is directed to compositions and processes for making hardened cellulose ester (CE) microbeads that exhibit superior optical properties. The processes disclosed herein enable the solidity of the produced microbeads to be controlled such that they exhibit desirable tactile and optical qualities. For example, the CE microbeads may have enhanced solidity, sphericity, and smoothness, low moisture content, and/or low free acid content. These qualities, along with the biodegradability of CE, make the CE microbeads produced herein desirable for use in personal care products, cosmetics, and the like.

[0014] The present invention may be understood more readily by reference to the following detailed description and the examples provided therein. It is to be understood that this

disclosure is not limited to the specific methods, formulations, and conditions described, as such may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects of the disclosed embodiments only and is not intended to be limiting.

[0015] Values may be expressed as "about" or "approximately" a given number. Similarly, ranges may be expressed herein as from "about" one particular value and/or to "about" or another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect.

[0016] As used herein, the terms "a," "an," and "the" mean one or more.

[0017] As used herein, the term "and/or," when used in a list of two or more items, means that any one of the listed items can be employed by itself or any combination of two or more of the listed items can be employed. For example, if a composition is described as containing components A, B, and/or C, the composition can contain A alone; B alone; C alone; A and B in combination; A and C in combination, B and C in combination; or A, B, and C in combination.

[0018] As used herein, the terms "comprising," "comprises," and "comprise" are open-ended transition terms used to transition from a subject recited before the term to one or more elements recited after the term, where the element or elements listed after the transition term are not necessarily the only elements that make up the subject.

[0019] As used herein, the terms "having," "has," and "have" have the same open-ended meaning as "comprising," "comprises," and "comprise" provided above.

[0020] As used herein, the terms "including," "includes," and "include" have the same open-ended meaning as "comprising," "comprises," and "comprise" provided above.

[0021] As used herein, a "mixed cellulose ester" shall denote a cellulose ester having at least two different ester substituents on a single cellulose ester polymer chain.

[0022] "Degree of Substitution" is used to describe the average substitution level of the substituents per anhydroglucose unit ("AGU"). Generally, conventional cellulose contains three hydroxyl groups in each AGU that can be substituted. Therefore, the DS can have a value between 0 and 3. However, low molecular weight cellulose mixed esters can have a total degree of substitution slightly above 3 from end group contributions. Low molecular weight cellulose mixed esters are discussed in more detail subsequently in this disclosure. Because DS is a statistical mean value, a value of 1 does not assure that every AGU has a single substituent. In some cases, there can be unsubstituted anhydroglucose units, some with two and some with three substituents, and more often than not the value will be a noninteger. Total DS is defined as the average number of all substituents per anhydroglucose unit. The degree of substitution per AGU can also refer to a particular substituent, such as, for example, hydroxyl, acetyl, butyryl, or propionyl. Additionally, the degree of substitution can specify a given hydroxyl based on the carbon unit of the anhydroglucose unit.

[0023] When the degree of substitution refers to hydroxyl, i.e., DS_{OH}, the reference is to the average hydroxyl groups per anhydroglucose that are not substituted. As a result, DS_{OH} is not used in the calculation of the total degree of substitution.

[0024] The present description uses numerical ranges to quantify certain parameters relating to the invention. It should be understood that when numerical ranges are provided, such ranges are to be construed as providing literal support for claim limitations that only recite the lower value of the range as well as claim limitations that only recite the upper value of the range. For example, a disclosed numerical range of 10 to 100 provides literal support for a claim reciting "greater than 10" (with no upper bounds) and a claim reciting "less than 100" (with no lower bounds).

[0025] The present description uses specific numerical values to quantify certain parameters relating to the invention, where the specific numerical values are not expressly part of a numerical range. It should be understood that each specific numerical value provided herein is to be construed as providing literal support for a broad, intermediate, and narrow range. The broad range associated with each specific numerical value is the numerical value plus and minus 60 percent of the numerical value, rounded to two significant digits. The intermediate range associated with each specific numerical value is the numerical value plus and minus 30 percent of the numerical value, rounded to two significant digits. The narrow

range associated with each specific numerical value is the numerical value plus and minus 15 percent of the numerical value, rounded to two significant digits. For example, if the specification describes a specific temperature of 62 °F, such a description provides literal support for a broad numerical range of 25 °F to 99 °F (62 °F +/- 37 °F), an intermediate numerical range of 43 °F to 81 °F (62 °F +/- 19 °F), and a narrow numerical range of 53 °F to 71 °F (62 °F +/- 9 °F). These broad, intermediate, and narrow numerical ranges should be applied not only to the specific values, but should also be applied to differences between these specific values. Thus, if the specification describes a first pressure of 110 psia and a second pressure of 48 psia (a difference of 62 psi), the broad, intermediate, and narrow ranges for the pressure difference between these two streams would be 25 to 99 psi, 43 to 81 psi, and 53 to 71 psi, respectively.

[0026] Throughout this application, where patents or publications are referenced, the disclosures of these references in their entireties are intended to be incorporated by reference into this application, to the extent they are not inconsistent with the present invention, in order to more fully describe the state of the art to which the invention pertains.

[0027] Referring now to FIG. 1, cellulose ester (CE) 100, solvent 102, water 104, hydrocolloid 106, and surfactant 108 may be combined in one or more units to make CE microbeads 112. In the illustrated example, CE 100, solvent 102, water 104, hydrocolloid 106, and surfactant 108 are combined at unit 110 to form an initial emulsion therein. The initial emulsion includes a dispersed phase and a continuous phase. The dispersed phase includes at least a portion of CE 100 and at least a portion of solvent 102. The continuous phase includes at least a portion of water 104, at least a portion of hydrocolloid 106, and at least a portion of surfactant 108.

[0028] Once combined, the initial emulsion may be agitated at unit 110 to form a pre-hardened dispersion including a sold phase and a liquid phase. The solid phase includes initial microparticles including at least a portion of CE 100 and at least a portion of solvent 102. The liquid phase includes at least a portion of water 104, at least a portion of hydrocolloid 106, and at least a portion of surfactant 108. Additional water 104 (i.e., a drowning liquid/extractant) may be added to the pre-hardened dispersion to increase the concentration of water around the initial microparticles. An initial hardening dispersion including the initial microparticles and the drowning liquid is formed therefrom. The initial hardening dispersion may be agitated at

unit 110 to promote the transfer of solvent from the initial microparticles to the drowning liquid. This solvent transfer facilitates hardening of the initial microparticles to produce hardened CE microbeads 112, which are entrained in a solvent-ladened drowning liquid.

[0029] CE microbeads 112 may be recovered from this dispersion 114 first by processing at a solid/liquid separation unit 116. A solid stream 118 including CE microbeads 112 may be channeled to a solids processing unit 120, where CE microbeads 112 are washed with water 122 and then dried to recover CE microbeads 112, as will be described in more detail below. A liquid stream 124 formed from the solvent-ladened drowning liquid may be channeled to a liquids processing unit 126. Optionally, an excess liquid stream 128 channeled from unit 110 and a wash water stream 130 from unit 120 may also be received at unit 126 for processing therein.

[0030] At unit 126, the liquids received therein may be separated into at least a water-enriched stream 132 and a solvent-enriched stream 134. In some embodiments, water-enriched stream 132 may be recovered and at least a portion of which utilized in unit 110, for example. In addition, solvent-enriched stream 134 may be recycled and utilized as at least a portion of the solvent for forming CE microbeads 112 in unit 110. Re-utilization of the recovered water and/or solvent facilitates improving the economics of the CE microbead formation processes described herein.

[0031] As used herein, the term "enriched" refers to having a concentration of a specific component that is greater than the concentration of that component in a reference material or stream.

CELLULOSE ESTERS

[0032] CE 100 can be cellulose diacetate ("CDA"), a mixed cellulose ester ("MCE"), or combinations of CDA and one or more MCEs. MCEs include, for example, cellulose acetate butyrate ("CAB") and cellulose acetate propionate ("CAP").

[0033] Generally, the cellulose esters described herein, such as CE 100, can be produced by any method known in the art. Examples of processes for producing cellulose esters are taught in Kirk-Othmer, Encyclopedia of Chemical Technology, 5th Edition, Vol. 5, Wiley-Interscience, New York (2004), pp. 394-444, the disclosure of which is incorporated by

reference in its entirety. Cellulose, the starting material for producing cellulose esters, can be obtained in different grades and from sources such as, for example, cotton linters, softwood pulp, hardwood pulp, corn fiber and other agricultural sources, and bacterial celluloses.

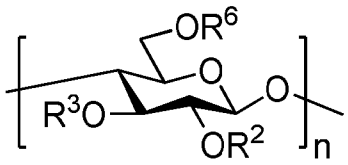
[0034] One method of producing cellulose esters is by esterification. In such a method, the cellulose is mixed with the appropriate organic acids, acid anhydrides, and/or catalysts and then converted to a cellulose triester. Ester hydrolysis is then performed by adding a water-acid mixture to the cellulose triester, which can be filtered to remove any gel particles or fibers. Water is added to the mixture to precipitate out the cellulose ester. The cellulose ester can then be washed with water to remove reaction by-products followed by dewatering and drying.

[0035] Acylating reagents suitable for use herein can include, but are not limited to, alkyl or aryl carboxylic anhydrides, carboxylic acid halides, and/or carboxylic acid esters containing the above-described alkyl or aryl groups suitable for use in the acyl substituents of the substituted cellulose esters described herein. Examples of suitable carboxylic anhydrides include, but are not limited to, acetic anhydride, propionic anhydride, butyric anhydride, pivaloyl anhydride, benzoic anhydride, and naphthoyl anhydride. Examples of carboxylic acid halides include, but are not limited to, acetyl, propionyl, butyryl, pivaloyl, benzoyl, and naphthoyl chlorides or bromides. Examples of carboxylic acid esters include, but are not limited to, acetyl, propionyl, butyryl, pivaloyl, benzoyl and naphthoyl methyl esters. In one or more embodiments, the acylating reagent can be one or more carboxylic anhydrides selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, pivaloyl anhydride, benzoyl anhydride, and naphthoyl anhydride.

[0036] In various embodiments, the cellulose triesters that are hydrolyzed can have three substituents selected independently from alkanoyls having from 2 to 12 carbon atoms. Examples of cellulose triesters include cellulose triacetate, cellulose tripropionate, cellulose tributyrate, or mixed triesters of cellulose, such as cellulose acetate propionate and cellulose acetate butyrate. These cellulose triesters can be prepared by a number of methods known to those skilled in the art. For example, cellulose triesters can be prepared by heterogeneous acylation of cellulose in a mixture of carboxylic acid and anhydride in the presence of a catalyst, such as H_2SO_4. Cellulose triesters can also be prepared by the homogeneous acylation of cellulose dissolved in an appropriate solvent such as LiCl/DMAc or LiCl/NMP.

[0037] After esterification of the cellulose to the triester, part of the acyl substituents can be removed by hydrolysis or by alcoholysis to give a secondary cellulose ester. Secondary cellulose esters can also be prepared directly with no hydrolysis by using a limiting amount of acylating reagent. This process is particularly useful when the reaction is conducted in a solvent that will dissolve cellulose.

[0038] The cellulose esters thus prepared generally comprise the following structure:



where R^2, R^3, and R^6 are hydrogen (with the proviso that R^2, R^3, and R^6 are not hydrogen simultaneously), alkyl-acyl groups, and/or aryl-acyl groups (such as those described above) bound to the cellulose via an ester linkage.

[0039] The degree of polymerization ("DP") of the cellulose esters prepared by these methods can be at least 10. In other embodiments, the DP of the cellulose esters can be at least 50, at least 100, or at least 250. In other embodiments, the DP of the cellulose esters can be in the range of from about 5 to about 100, or in the range of from about 10 to about 50.

[0040] Acylating reagents suitable for use herein can include, but are not limited to, alkyl or aryl carboxylic anhydrides, carboxylic acid halides, and/or carboxylic acid esters containing the above-described alkyl or aryl groups suitable for use in the acyl substituents of the substituted cellulose esters described herein. Examples of suitable carboxylic anhydrides include, but are not limited to, acetic anhydride, propionic anhydride, butyric anhydride, pivaloyl anhydride, benzoic anhydride, and naphthoyl anhydride. Examples of carboxylic acid halides include, but are not limited to, acetyl, propionyl, butyryl, pivaloyl, benzoyl, and naphthoyl chlorides or bromides. Examples of carboxylic acid esters include, but are not limited to, acetyl, propionyl, butyryl, pivaloyl, benzoyl and naphthoyl methyl esters. In one or more embodiments, the acylating reagent can be one or more carboxylic anhydrides selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, pivaloyl anhydride, benzoyl anhydride, and naphthoyl anhydride.

[0041] The present application discloses, in a first aspect, a mixed ester cellulose ester ("MCE"), comprising: (1) a plurality of acetyl substituents; (2) a plurality of propionyl substituents; and (3) a plurality of hydroxyl substituents, wherein: the MCE has an average degree of substitution for the acetyl substituents ("DSAc") from 0.1 to 2.3, the MCE has an average degree of substitution for the propionyl substituents ("DSPr") from 0.1 to 1.2, and the MCE has an average degree of substitution for the hydroxyl substituents ("DSOH") from 0.6 to 2.8.

[0042] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DSAc is at least 0.1, at least 0.2, at least 0.3, at least 0.4, at least 0.5, at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.6, at least 1.7, at least 1.8, at least 1.9, or at least 2.0. Additionally, or in the alternative, the DSAc is less than 2.3, less than 2.2, less than 2.1, less than 2.0, less than 1.9, less than 1.8, less than 1.7, less than 1.6, less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, less than 0.8, less than 0.7, less than 0.5, less than 0.4, or less than 0.3.

[0043] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DSAc is from 0.6 to 2.2, or 0.6 to 2.1, or 0.6 to 2.0, or 0.6 to 1.9, or 0.6 to 1.8, or 0.7 to 2.3, or 0.7 to 2.2, or 0.7 to 2.1, or 0.7 to 2.0, or 0.7 to 1.9, or 0.8 to 2.3, or 0.8 to 2.2, or 0.8 to 2.1, or 0.8 to 2.0, or 0.8 to 1.9, or 0.9 to 2.3, or 0.9 to 2.2, or 0.9 to 2.1, or 0.9 to 2.0, or 0.9 to 1.9, or 1.0 to 2.3 or 1.0 to 2.2, or 1.0 to 2.1, or 1.0 to 2.0, or 1.0 to 1.9, or 1.1 to 2.3, or 1.1 to 2.2, or 1.1 to 2.1, or 1.1 to 2.0, or 1.1 to 1.9, , or 1.2 to 2.3 or 1.2 to 2.2, or 1.2 to 2.1, or 1.2 to 2.0, or 1.2 to 1.9, or 0.6 to 1.5, or 0.6 to 1.3, or 0.6 to 1.1, or 0.6 to 0.9 or 0.7 to 1.5, or 0.7 to 1.3, or 0.7 to 1.1, or 0.7 to 0.9.

[0044] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DS_{Pr} is at least 0.1, at least 0.2, at least 0.3, at least 0.4, at least 0.5, at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, or at least 1.4. Additionally, or in the alternative, the DS_{Pr} is less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, less than 0.8, less than 0.7, less than 0.5, less than 0.4, or less than 0.3.

[0045] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DS_{Pr} is from 0.1 to 0.9, or 0.1 to 0.85, or 0.1 to 0.8, or 0.1 to 0.75, or 0.1 to 0.7, or 0.1 to 0.6 or 0.1 to 0.5, or 0.1 to 0.4, or 0.15 to 0.95, or 0.15 to 0.9, or 0.15 to 0.85, or 0.15 to 0.8, or 0.15 to 0.75, or 0.15 to 0.7, or 0.15 to 0.65, or 0.2 to 0.95, or 0.2 to 0.9, or 0.2 to 0.85, or 0.2 to 0.8, or 0.2 to 0.75, or 0.2 to 0.7, or 0.2 to 0.65, 0.25 to 0.95, or 0.25 to 0.9, or 0.25 to 0.85, or 0.25 to 0.8, or 0.25 to 0.75, or 0.25 to 0.7, or 0.25 to 0.65, or 0.3 to 0.95, or 0.3 to 0.9, or 0.3 to 0.85, or 0.3 to 0.8, or 0.3 to 0.75, or 0.3 to 0.7, or 0.3 to 0.65, or 0.35 to 0.95, or 0.35 to 0.9, or 0.35 to 0.85, or 0.35 to 0.8, or 0.35 to 0.75, or 0.35 to 0.7, or 0.35 to 0.65, or 0.4 to 0.95, or 0.4 to 0.9, or 0.4 to 0.85, or 0.4 to 0.8, or 0.4 to 0.75, or 0.4 to 0.7, or 0.4 to 0.65, or 0.45 to 0.95, or 0.45 to 0.9, or 0.45 to 0.85, or 0.45 to 0.8, or 0.45 to 0.75, or 0.45 to 0.7, or 0.45 to 0.65, or 0.5 to 0.95, or 0.5 to 0.9, or 0.5 to 0.85, or 0.5 to 0.8, or 0.5 to 0.75, or 0.5 to 0.7, or 0.5 to 0.65, or 0.1 to 0.9, or 0.1 to 0.85, or 0.1 to 0.8.

[0046] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DSOH is at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.6, at least 1.7, at least 1.8, at least 1.9, at least 2.0, at least 2.1, at least 2.2, at least 2.3, at least 2.4, at least 2.5, or at least 2.6. Additionally, or in the alternative, the DSOH is less than 2.8, less than 2.7, less than 2.6, less than 2.5, less than 2.4, less than 2.3, less than 2.2, less than 2.1, less than 2.0, less than 1.9, less than 1.8, less than 1.7, less than 1.6, less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, or less than 0.8.

[0047] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DSOH is from 0.5 to 1.5, or 0.5 to 1.45, or 0.5 to 1.40, or 0.5 to 1.35, or 0.5 to 1.30, or 0.5 to 1.25, or 0.5 to 1.2, or 0.5 to 1.15, or 0.5 to 1.1, or 0.5 to 1.05, or 0.5 to 1.0, or 0.5 to 0.95 or 0.5 to 0.9, or 0.55 to 1.5, or 0.55 to 1.45, or 0.55 to 1.40, or 0.55 to 1.35, or 0.55 to 1.30, or 0.55 to 1.25, or 0.55 to 1.2, or 0.55 to 1.15, or 0.55 to 1.1, or 0.55 to 1.05, or 0.55 to 1.0, or 0.55 to 0.95 or 0.55 to 0.9, or 0.6 to 1.5, or 0.6 to 1.45, or 0.6 to 1.40, or 0.6 to 1.35, or 0.6 to 1.30, or 0.6 to 1.25, or 0.6 to 1.2, or 0.6 to 1.15, or 0.6 to 1.1, or 0.6 to 1.05, or 0.6 to 1.0, or 0.6 to 0.95 or 0.6 to 0.9, or 0.65 to 1.5, or 0.65 to 1.45, or 0.65 to 1.40, or 0.65 to 1.35, or 0.65 to 1.30, or 0.65 to 1.25, or 0.65 to 1.2, or 0.65 to 1.15, or 0.65 to 1.1, or 0.65 to 1.05, or 0.65 to 1.0, or 0.65 to 0.95 or 0.65 to 0.9, or 0.7 to 1.5, or 0.7 to 1.45, or 0.7

to 1.40, or 0.7 to 1.35, or 0.7 to 1.30, or 0.7 to 1.25, or 0.7 to 1.2, or 0.7 to 1.15, or 0.7 to 1.1, or 0.7 to 1.05, or 0.7 to 1.0, or 0.7 to 0.95 or 0.7 to 0.9.

[0048] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the sum of DSPr and DSAc is from 1.9 to 2.44, or 1.9 to 2.0, or 1.9 to 2.1, or 1.9 to 2.2, or 1.9 to 2.3, or 2.0 to 2.44, or 2.0 to 2.1, or 2.0 to 2.2, or 2.0 to 2.3, or 2.1 to 2.44, or 2.1 to 2.2, or 2.1 to 2.3, or 2.2 to 2.44, or 2.2 to 2.3.

[0049] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the mixed cellulose ester has a ratio of hydroxyl substituents to acetyl substituents of at least 0.4:1, at least 0.5:1, at least 0.6:1, at least 0.7:1, at least 0.8:1, at least 0.9:1, at least 1:1, at least 1.1:1, at least 1.2:1, at least 1.3:1, at least 1.4:1, at least 1.5:1, at least 1.6:1, at least 1.7:1, at least 1.8:1, at least 1.9:2, or at least 2:1. Additionally, in the alternative, the mixed cellulose ester has a ratio of hydroxyl substituents to acetyl substituents of less than 2:1, less than 1.9:1, less than 1.8:1, less than 1.7:1, less than 1.6:1, less than 1.5:1, less than 1.4:1, less than 1.3:1, less than 1.2:1, less than 1.1:1, or less than 1:1.

[0050] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the MCE has a ratio of hydroxyl substituents to propionyl substituents of at least 0.4:1, at least 0.5:1, at least 0.6:1, at least 0.7:1, at least 0.8:1, at least 0.9:1, at least 1:1, at least 1.1:1, at least 1.2:1, at least 1.3:1, at least 1.4:1, at least 1.5:1, at least 1.6:1, at least 1.7:1, at least 1.8:1, at least 1.9:2, or at least 2:1. Additionally, or in the alternative, the MCE has a ratio of hydroxyl substituents to propionyl substituents of less than 2:1, less than 1.9:1, less than 1.8:1, less than 1.7:1, less than 1.6:1, less than 1.5:1, less than 1.4:1, less than 1.3:1, less than 1.2:1, less than 1.1:1, or less than 1:1.

[0051] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the MCE exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 56 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0052] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the MCE exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 60 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0053] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, the MCE has a weight average molecular weight in the range of from 5,000 to 100,000 Da, or 5,000 to 50,000 Da, or 5,000 to 25,000 Da, or 15,000 to 100,000 Da, or 15,000 to 50,000 Da, or 15,000 to 25,000 Da, or 50,000 to 100,000 Da, or 75,000 to 100,000 Da, or 15,000 to 250,000 Da.

[0054] The present application discloses, in a second aspect, a mixed cellulose ester ("MCE"), comprising: (1) a plurality of acetyl substituents; (2) a plurality of propionyl substituents; and (3) a plurality of hydroxyl substituents, wherein: the MCE has an average degree of substitution for the acetyl substituents ("DS_{Ac}") from 0.1 to 1.2, the MCE has an average degree of substitution for the propionyl substituents ("DS_{Pr}") from 0.1 to 1.4, and the MCE has an average degree of substitution for the hydroxyl substituents ("DS_{OH}") from 0.7 to 2.8.

[0055] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DSAc is at least 0.1, at least 0.2, at least 0.3, at least 0.4, at least 0.5, at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.6, at least 1.7, at least 1.8, at least 1.9, or at least 2.0. Additionally, or in the alternative, the DSAc is less than 2.3, less than 2.2, less than 2.1, less than 2.0, less than 1.9, less than 1.8, less than 1.7, less than 1.6, less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, less than 0.8, less than 0.7, less than 0.5, less than 0.4, or less than 0.3.

[0056] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DSAc is from 0.6 to 0.7, or 0.6 to 0.8, or 0.6 to 0.9, or 0.6 to 1.0, or 0.6 to 1.1, or 0.7 to 0.9, or 0.7 to 1.0, or 0.7 to 1.1, or 0.7 to 1.2, or 0.8 to 0.9, or 0.8 to

1.0, or 0.8 to 1.1, or 0.8 to 1.2, or 0.9 to 1.0, or 0.9 to 1.1, or 0.9 to 1.2, or 1.0 to 1.1, or 1.0 to 1.2, or 1.1 to 1.2.

[0057] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DSPr is at least 0.1, at least 0.2, at least 0.3, at least 0.4, at least 0.5, at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, or at least 1.4. Additionally, or in the alternative, the DSPr is less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, less than 0.8, less than 0.7, less than 0.5, less than 0.4, or less than 0.3.

[0058] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DS_{Pr} is from 1.05 to 1.35, or 1.05 to 1.3, or 1.05 to 1.25, or 1.05 to 1.2, or 1.05 to 1.15, or 1.05 to 1.1, or 1.1 to 1.4, or 1.1 to 1.35, or 1.1 to 1.3, or 1.1 to 1.25, or 1.1 to 1.2, or 1.1 to 1.15, or 1.15 to 1.4, or 1.15 to 1.35, or 1.15 to 1.3, or 1.15 to 1.25, or 1.15 to 1.2, or 1.2 to 1.4, or 1.2 to 1.35, or 1.2 to 1.3, or 1.2 to 1.25, or 1.25 to 1.4, or 1.25 to 1.35, or 1.25 to 1.3, or 1.3 to 1.4, or 1.3 to 1.35.

[0059] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DSOH is at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.6, at least 1.7, at least 1.8, at least 1.9, at least 2.0, at least 2.1, at least 2.2, at least 2.3, at least 2.4, at least 2.5, or at least 2.6. Additionally, or in the alternative, the DSOH is less than 2.8, less than 2.7, less than 2.6, less than 2.5, less than 2.4, less than 2.3, less than 2.2, less than 2.1, less than 2.0, less than 1.9, less than 1.8, less than 1.7, less than 1.6, less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, or less than 0.8.

[0060] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DSOH is from 0.7 to 1.35, or 0.7 to 1.3, or 0.7 to 1.25, or 0.7 to 1.2, or 0.7 to 1.15, or 0.7 to 1.1, or 0.7 to 1.05, or 0.7 to 1.0, or 0.7 to 0.95, or 0.7 to 0.9, or 0.7 to 0.85, or 0.7 to 0.8, or 0.7 to 0.75, or 0.75 to 1.4, or 0.75 to 1.35, or 0.75 to 1.3, or 0.75 to 1.25, or 0.75 to 1.2, or 0.75 to 1.15, or 0.75 to 1.1, or 0.75 to 1.05, or 0.75 to 1.0, or 0.75 to 0.95, or 0.8 to 1.4, or 0.8 to 1.35, or 0.8 to 1.3, or 0.8 to 1.25, or 0.8 to 1.2, or 0.8 to 1.15, or 0.8 to 1.1, or 0.8 to 1.05, or 0.85 to 1.4, or 0.85 to 1.35, or 0.85 to 1.3, or 0.85 to 1.25, or 0.85

to 1.2, or 0.85 to 1.15, or 0.85 to 1.1, or 0.85 to 1.05, or 0.9 to 1.4, or 0.9 to 1.35, or 0.9 to 1.3, or 0.9 to 1.25, or 0.9 to 1.2, or 0.9 to 1.15, or 0.9 to 1.1, or 0.9 to 1.05.

[0061] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the sum of DSPr and DSAc is from 1.65 to 2.3, or 1.65 to 2.2, or 1.65 to 2.1, or 1.65 to 2.0, or 1.65 to 1.9, or 1.65 to 1.8, or 1.7 to 2.3, or 1.7 to 2.2, or 1.7 to 2.1, or 1.7 to 2.0, or 1.7 to 1.9, or 1.7 to 1.8, or 1.75 to 2.3, or 1.75 to 2.2, or 1.75 to 2.1, or 1.75 to 2.0, or 1.75 to 1.9, or 1.8 to 2.3, or 1.8 to 2.2, or 1.8 to 2.1, or 1.8 to 2.0, or 1.8 to 1.9, or 1.9 to 2.3, or 1.9 to 2.2, or 1.9 to 2.1, or 1.9 to 2.0, or 2.0 to 2.3, or 2.0 to 2.2, or 2.0 to 2.1.

[0062] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the DS_{OH} is from 0.6 to 0.7, or 0.7 to 1.35, or 0.7 to 1.3, or 0.7 to 1.25, or 0.7 to 1.2, or 0.7 to 1.15, or 0.7 to 1.1, or 0.7 to 1.05, or 0.7 to 1.0, or 0.7 to 0.95, or 0.7 to 0.9, or 0.7 to 0.85, or 0.7 to 0.8, or 0.7 to 0.75, or 0.75 to 1.4, or 0.75 to 1.35, or 0.75 to 1.3, or 0.75 to 1.25, or 0.75 to 1.2, or 0.75 to 1.15, or 0.75 to 1.1, or 0.75 to 1.05, or 0.75 to 1.0, or 0.75 to 0.95, or 0.8 to 1.4, or 0.8 to 1.35, or 0.8 to 1.3, or 0.8 to 1.25, or 0.8 to 1.2, or 0.8 to 1.15, or 0.8 to 1.1, or 0.8 to 1.05, or 0.85 to 1.4, or 0.85 to 1.35, or 0.85 to 1.3, or 0.85 to 1.25, or 0.85 to 1.2, or 0.85 to 1.15, or 0.85 to 1.1, or 0.85 to 1.05, or 0.9 to 1.4, or 0.9 to 1.35, or 0.9 to 1.3, or 0.9 to 1.25, or 0.9 to 1.2, or 0.9 to 1.15, or 0.9 to 1.1, or 0.9 to 1.05.

[0063] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the mixed cellulose ester has a ratio of hydroxyl substituents to acetyl substituents of at least 0.4:1, at least 0.5:1, at least 0.6:1, at least 0.7:1, at least 0.8:1, at least 0.9:1, at least 1:1, at least 1.1:1, at least 1.2:1, at least 1.3:1, at least 1.4:1, at least 1.5:1, at least 1.6:1, at least 1.7:1, at least 1.8:1, at least 1.9:2, or at least 2:1. Additionally, in the alternative, the mixed cellulose ester has a ratio of hydroxyl substituents to acetyl substituents of less than 2:1, less than 1.9:1, less than 1.8:1, less than 1.7:1, less than 1.6:1, less than 1.5:1, less than 1.4:1, less than 1.3:1, less than 1.2:1, less than 1.1:1, or less than 1:1.

[0064] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the MCE has a ratio of hydroxyl substituents to propionyl substituents of at least 0.4:1, at least 0.5:1, at least 0.6:1, at least 0.7:1, at least 0.8:1, at least 0.9:1, at least 1:1, at least 1.1:1, at least 1.2:1, at least 1.3:1, at least 1.4:1, at least 1.5:1, at least 1.6:1, at least 1.7:1, at least 1.8:1, at least 1.9:2, or at least 2:1. Additionally, or in the

alternative, the MCE has a ratio of hydroxyl substituents to propionyl substituents of less than 2:1, less than 1.9:1, less than 1.8:1, less than 1.7:1, less than 1.6:1, less than 1.5:1, less than 1.4:1, less than 1.3:1, less than 1.2:1, less than 1.1:1, or less than 1:1.

[0065] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the MCE exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 56 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0066] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, wherein the MCE exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 60 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0067] In one embodiment or in combination with any other embodiment, class or subclass of this second aspect, the MCE has a weight average molecular weight in the range of from 5,000 to 100,000 Da, or 5,000 to 50,000 Da, or 5,000 to 25,000 Da, or 15,000 to 100,000 Da, or 15,000 to 50,000 Da, or 15,000 to 25,000 Da, or 50,000 to 100,000 Da, or 75,000 to 100,000 Da, or 15,000 to 250,000 Da.

[0068] The present application, in a third aspect, also discloses a mixed cellulose ester ("MCE"), comprising: (1) a plurality of acetyl substituents; (2) a plurality of butyryl substituents; and (3) a plurality of hydroxyl substituents, wherein: the MCE has an average degree of substitution for the acetyl substituents ("DS_{Ac}") from 0.1 to 2.4, the MCE has an average degree of substitution for the butyryl substituents ("DS_{Bu}") from 0.1 to 1.4, and the MCE has an average degree of substitution for the hydroxyl substituents ("DS_{OH}") from 0.6 to 2.8.

[0069] In one embodiment or in combination with any other embodiment, class or subclass of this first aspect, wherein the DS_{Ac} is at least 0.1, at least 0.2, at least 0.3, at least 0.4, at least 0.5, at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.6, at least 1.7, at least 1.8, at least 1.9, or at least 2.0. Additionally, or in the alternative, the DS_{Ac} is less than 2.3, less than 2.2, less than 2.1, less than 2.0, less than 1.9, less than 1.8, less than 1.7, less than 1.6, less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, less than 0.8, less than 0.7, less than 0.5, less than 0.4, or less than 0.3.

[0070] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the DS_{Ac} is from 0.9 to 2.4, 0.9 to 2.3, or 0.9 to 2.2, or 0.9 to 2.1, or 0.9 to 2.0, or 0.9 to 1.9, or 0.9 to 1.8, or 0.9 to 1.7, or 0.9 to 1.6, or 0.9 to 1.4, 0.9 to 1.3, or 0.9 to 1.2, or 0.9 to 1.1, or 0.9 to 1.0, or 0.92 to 2.4, 0.92 to 2.3, or 0.92 to 2.2, or 0.92 to 2.1, or 0.92 to 2.0, or 0.92 to 1.9, or 0.92 to 1.8, or 0.92 to 1.7, or 0.92 to 1.6, or 0.92 to 1.4, 0.92 to 1.3, or 0.92 to 1.2, or 0.92 to 1.1, or 0.92 to 1.0, or 0.94 to 2.4, 0.94 to 2.3, or 0.94 to 2.2, or 0.94 to 2.1, or 0.94 to 2.0, or 0.94 to 1.9, or 0.94 to 1.8, or 0.94 to 1.7, or 0.94 to 1.6, or 0.94 to 1.4, 0.94 to 1.3, or 0.94 to 1.2, or 0.94 to 1.1, or 0.94 to 1.0, or 0.96 to 2.4, 0.96 to 2.3, or 0.96 to 2.2, or 0.96 to 2.1, or 0.96 to 2.0, or 0.96 to 1.9, or 0.96 to 1.8, or 0.96 to 1.7, or 0.96 to 1.6, or 0.96 to 1.4, 0.96 to 1.3, or 0.96 to 1.2, or 0.96 to 1.1, or 0.96 to 1.0, or 0.98 to 2.4, 0.98 to 2.3, or 0.98 to 2.2, or 0.98 to 2.1, or 0.98 to 2.0, or 0.98 to 1.9, or 0.98 to 1.8, or 0.98 to 1.7, or 0.98 to 1.6, 0.98 to 1.4, 0.98 to 1.3, or 0.98 to 1.2, or 0.98 to 1.1, or 0.98 to 1.0, or 1.0 to 2.4, 1.0 to 2.3, or 1.0 to 2.2, or 1.0 to 2.1, or 1.0 to 2.0, or 1.0 to 1.9, or 1.0 to 1.8, or 1.0 to 1.7, or 1.0 to 1.6, or 1.0 to 1.4, or 1.0 to 1.3, 1.0 to 1.2, or 1.0 to 1.1, or 1.1 to 2.4, or 1.1 to 2.3, or 1.1 to 2.2, or 1.1 to 2.1, or 1.1 to 2.0, or 1.1 to 1.9, or 1.1 to 1.8, or 1.1 to 1.7, or 1.1 to 1.6, 1.1 to 1.4, or 1.1 to 1.3, or 1.1 to 1.2, or 1.2 to 2.4, or 1.2 to 2.3, or 1.2 to 2.2, or 1.2 to 2.1, or 1.2 to 2.0, or 1.2 to 1.9, or 1.2 to 1.8, or 1.2 to 1.7, or 1.2 to 1.6, or 1.2 to 1.4, or 1.2 to 1.3, or 1.3 to 2.4, or 1.3 to 2.3, or 1.3 to 2.2, or 1.3 to 2.1, or 1.3 to 2.0, or 1.3 to 1.9, or 1.3 to 1.8, or 1.3 to 1.7, or 1.3 to 1.6, or 1.3 to 1.4, or 1.4 to 2.4, or 1.4 to 2.3, or 1.4 to 2.2, or 1.4 to 2.1, or 1.4 to 2.0, or 1.4 to 1.9, or 1.4 to 1.8, or 1.4 to 1.7, or 1.4 to 1.6, or 1.5 to 2.4, or 1.5 to 2.3, or 1.5 to 2.2, or 1.5 to 2.1, or 1.5 to 2.0, or 1.5 to 1.9, or 1.5 to 1.8, or 1.5 to 1.7, or 1.5 to 1.6, or 1.6 to 2.4, or 1.6 to 2.3, or 1.6 to 2.2, or 1.6 to 2.1, or 1.6 to 2.0, or 1.6 to 1.9, or 1.6 to 1.8, or 1.6 to 1.7, or 1.7 to 2.4, or 1.7 to 2.3, or 1.7 to 2.2, or 1.7 to 2.1, or 1.7 to 2.0, or 1.7 to 1.9, or 1.7 to 1.8, or 1.8 to 2.3, or 1.8 to 2.1, or 1.8 to 2.0, or 1.8 to 1.9, or 1.9 to 2.3, or 1.9 to 2.2, or 1.9 to

2.1, or 1.9 to 2.0, or 2.0 to 2.4, or 2.0 to 2.3, or 2.0 to 2.2, or 2.0 to 2.1, or 2.1 to 2.4, or 2.1 to 2.3, or 2.1 to 2.2, or 2.2 to 2.3.

[0071] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the DSBu is at least 0.1, at least 0.2, at least 0.3, at least 0.4, at least 0.5, at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, or at least 1.4. Additionally, or in the alternative, the DSBu is less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, less than 0.8, less than 0.7, less than 0.5, less than 0.4, or less than 0.3.

[0072] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the DS_{Bu} is from 0.1 to 1.35, or 0.1 to 1.3, or 0.1 to 1.25, or 0.1 to 1.2, or 0.1 to 1.15, or 0.1 to 1.1, or 0.1 to 1.0, or 0.1 to 0.8, or 0.1 to 0.6, or 0.2 to 1.35, or 0.2 to 1.3, or 0.2 to 1.25, or 0.2 to 1.2, or 0.2 to 1.15, or 0.2 to 1.1, or 0.2 to 1.0, or 0.2 to 0.8, or 0.2 to 0.6, or 0.2 to 0.4, or 0.3 to 1.35, or 0.3 to 1.3, or 0.3 to 1.25, or 0.3 to 1.2, or 0.3 to 1.15, or 0.3 to 1.1, or 0.3 to 1.0, or 0.3 to 0.8, or 0.3 to 0.6, or 0.3 to 0.5, or 0.4 to 1.35, or 0.4 to 1.3, or 0.4 to 1.25, or 0.4 to 1.2, or 0.4 to 1.15, or 0.4 to 1.1, or 0.4 to 1.0, or 0.4 to 0.8, or 0.4 to 0.6, or 0.5 to 1.35, or 0.5 to 1.3, or 0.5 to 1.25, or 0.5 to 1.2, or 0.5 to 1.15, or 0.5 to 1.1, or 0.5 to 1.0, or 0.5 to 0.8, or 0.5 to 0.7, or 0.6 to 1.35, or 0.6 to 1.3, or 0.6 to 1.25, or 0.6 to 1.2, or 0.6 to 1.15, or 0.6 to 1.1, or 0.6 to 1.0, or 0.6 to 0.8, or 0.7 to 1.35, or 0.7 to 1.3, or 0.7 to 1.25, or 0.7 to 1.2, or 0.7 to 1.15, or 0.7 to 1.1, or 0.7 to 1.0, or 0.8 to 1.35, or 0.8 to 1.3, or 0.8 to 1.25, or 0.8 to 1.2, or 0.8 to 1.15, or 0.8 to 1.1, or 0.8 to 1.0, or 0.9 to 1.35, or 0.9 to 1.3, or 0.9 to 1.25, or 0.9 to 1.2, or 0.9 to 1.15, or 0.9 to 1.1, or 1.0 to 1.35, or 1.0 to 1.3, or 1.0 to 1.25, or 1.0 to 1.2, or 1.0 to 1.15, or 1.0 to 1.1, or 1.05 to 1.35, or 1.05 to 1.3, or 1.05 to 1.25, or 1.05 to 1.2, or 1.05 to 1.15, or 1.05 to 1.1, or 1.1 to 1.4, or 1.1 to 1.35, or 1.1 to 1.3, or 1.1 to 1.25, or 1.1 to 1.2, or 1.1 to 1.15, or 1.15 to 1.4, or 1.15 to 1.35, or 1.15 to 1.3, or 1.15 to 1.25, or 1.15 to 1.2, or 1.2 to 1.4, or 1.2 to 1.35, or 1.2 to 1.3, or 1.2 to 1.25, or 1.25 to 1.4, or 1.25 to 1.35, or 1.25 to 1.3, or 1.3 to 1.4, or 1.3 to 1.35.

[0073] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the DS_{OH} is at least 0.6, at least 0.7, at least 0.8, at least 0.9, at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.6, at least 1.7, at least 1.8, at least 1.9, at least 2.0, at least 2.1, at least 2.2, at least 2.3, at least 2.4, at least 2.5, or at least 2.6. Additionally, or in the alternative, the DS_{OH} is less than 2.8, less than 2.7, less than

2.6, less than 2.5, less than 2.4, less than 2.3, less than 2.2, less than 2.1, less than 2.0, less than 1.9, less than 1.8, less than 1.7, less than 1.6, less than 1.5, less than 1.4, less than 1.3, less than 1.2, less than 1.1, less than 1.0, less than 0.9, or less than 0.8.

[0074] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the DSOH is from 0.5 to 1.0, or 0.5 to 0.95, or 0.5 to 0.9, or 0.5 to 0.85, or 0.5 to 0.8, or 0.5 to 0.75, or 0.5 to 0.7, or 0.5 to 0.65, or 0.5 to 0.6, or 0.5 to 0.55, or 0.55 to 1.0, or 0.55 to 0.95, or 0.55 to 0.9, or 0.55 to 0.85, or 0.55 to 0.8, or 0.55 to 0.75, or 0.55 to 0.7, or 0.55 or 0.65, or 0.55 to 0.6, or 0.6 to 0.65, or 0.6 to 0.7, or 0.6 to 0.75, or 0.6 to 0.8, or 0.6 to 0.85, or 0.6 to 0.9, or 0.6 to 0.95, or 0.6 to 1.0, or 0.65 to 0.7, or 0.65 to 0.75, or 0.65 to 0.8, or 0.65 to 0.85, or 0.65 to 0.9, or 0.65 to 0.95, or 0.65 to 1.0.

[0075] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the sum of DSBu and DSAc is from 1.65 to 2.3, or 1.65 to 2.2, or 1.65 to 2.1, or 1.65 to 2.0, or 1.65 to 1.9, or 1.65 to 1.8, or 1.7 to 2.3, or 1.7 to 2.2, or 1.7 to 2.1, or 1.7 to 2.0, or 1.7 to 1.9, or 1.7 to 1.8, or 1.75 to 2.3, or 1.75 to 2.2, or 1.75 to 2.1, or 1.75 to 2.0, or 1.75 to 1.9, or 1.8 to 2.3, or 1.8 to 2.2, or 1.8 to 2.1, or 1.8 to 2.0, or 1.8 to 1.9, or 1.9 to 2.3, or 1.9 to 2.2, or 1.9 to 2.1, or 1.9 to 2.0, 2.0 to 2.4, or 2.0 to 2.3, or 2.0 to 2.2, or 2.0 to 2.1.

[0076] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the mixed cellulose ester has a ratio of hydroxyl substituents to acetyl substituents of at least 0.4:1, at least 0.5:1, at least 0.6:1, at least 0.7:1, at least 0.8:1, at least 0.9:1, at least 1:1, at least 1.1:1, at least 1.2:1, at least 1.3:1, at least 1.4:1, at least 1.5:1, at least 1.6:1, at least 1.7:1, at least 1.8:1, at least 1.9:2, or at least 2:1. Additionally, in the alternative, the mixed cellulose ester has a ratio of hydroxyl substituents to acetyl substituents of less than 2:1, less than 1.9:1, less than 1.8:1, less than 1.7:1, less than 1.6:1, less than 1.5:1, less than 1.4:1, less than 1.3:1, less than 1.2:1, less than 1.1:1, or less than 1:1.

[0077] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the mixed cellulose ester has a ratio of hydroxyl substituents to butyryl substituents of at least 0.4:1, at least 0.5:1, at least 0.6:1, at least 0.7:1, at least 0.8:1, at least 0.9:1, at least 1:1, at least 1.1:1, at least 1.2:1, at least 1.3:1, at least 1.4:1, at least 1.5:1, at least 1.6:1, at least 1.7:1, at least 1.8:1, at least 1.9:2, or at least 2:1. Additionally, or in the alternative, the mixed cellulose ester has a ratio of hydroxyl substituents to butyryl substituents

of less than 2:1, less than 1.9:1, less than 1.8:1, less than 1.7:1, less than 1.6:1, less than 1.5:1, less than 1.4:1, less than 1.3:1, less than 1.2:1, less than 1.1:1, or less than 1:1.

[0078] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the MCE exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 56 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0079] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, wherein the MCE exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 60 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0080] In one embodiment or in combination with any other embodiment, class or subclass of this third aspect, the MCE has a weight average molecular weight in the range of from 5,000 to 100,000 Da, or 5,000 to 50,000 Da, or 5,000 to 25,000 Da, or 15,000 to 100,000 Da, or 15,000 to 50,000 Da, or 15,000 to 25,000 Da, or 50,000 to 100,000 Da, or 75,000 to 100,000 Da, or 15,000 to 250,000 Da.

[0081] In one embodiment or in combination with any embodiment mentioned herein, the CE 100 can be the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect, including any class or subclass of these aspects.

SOLVENT SYSTEM

[0082] The solvent system, such as solvent 102, is generally capable of solubilizing CE to produce the dispersed/solid phase of an emulsion/dispersion as described herein. In one embodiment or in combination with any embodiment mentioned herein, solvent 102 may consist of a single solvent component, or may be a solvent system including a plurality of

solvent components. The plurality of solvent components may include at least two solvent components, at least three solvent components, or three total solvent components.

[0083] In one embodiment or in combination with any embodiment mentioned herein, solvent 102 includes at least one, at least two, or all three of a C1-C4 alkyl acetate, a C1-C4 alcohol, and water. The C1-C4 alkyl acetate may include one or more of methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, and sec-butyl acetate. The C1-C4 alcohol may include one or more of methanol, ethanol, propanols (e.g., isopropanol, n-propanol, and isopropyl alcohol), and butanols (e.g., n-butanol, isobutanol, sec-butanol, and tert-butanol).

[0084] In one embodiment or in combination with any embodiment mentioned herein, when solvent 102 includes more than one solvent component, the C1-C4 alkyl acetate may be present in one or more of the following amounts: (1) at least 10, 25, 50, 60, or 70 weight percent; (2) not more than 99, 95, 90, 85, or 80 weight percent; and (3) in the range of 10-99, 25-95, 50-90, or 70-85 weight percent.

[0085] In one embodiment or in combination with any embodiment mentioned herein, when solvent 102 includes more than one solvent component, the C1-C4 alcohol is present in one or more of the following amounts: (1) at least 1, 2, 4, 6, 8, or 10 weight percent; (2) not more than 80, 60, 40, 30, 20, or 15 weight percent; and (3) in the range or 1-80, 2-60, 4-40, 6-30, 8-20, or 10-15 weight percent.

[0086] In one embodiment or in combination with any embodiment mentioned herein, when solvent 102 includes more than one solvent component, the water is present in one or more of the following amounts: (1) at least 1, 2, 4, 6, or 8 weight percent; (2) not more than 50, 25, 20, or 15 weight percent; and (3) in the range of 1-50, 2-25, 4-30, 6-20, or 8-15 weight percent.

[0087] In one embodiment or in combination with any embodiment mentioned herein, solvent 102 includes at least one, at least two, or all three of ethyl acetate, n-propanol, and water. In such an embodiment, ethyl acetate is present in an amount in the range of 50-90, 55-90, 60-90, 65-90, 65-85, 70-85, or 75-85 weight percent, n-propanol is present in an amount in

the range of 4-40, 5-35, 6-30, 7-25, 8-20, 10-20, or 10-15 weight percent, and water is present in an amount in the range of 4-30, 5-25, 6-20, 7-15, 8-12, or 9-12 weight percent.

[0088] Surprisingly, it has been found that water contributes and/or enables certain mixed cellulose esters to be solubilized. Particularly, it has been found that water contributes and/or enables mixed cellulose esters having high degrees of biodegradability, such as those associated with DS_{OH} values greater than a determined threshold, to be solubilized. These findings are disclosed in the EXPERIMENTS section below.

HYDROCOLLOID

[0089] Hydrocolloids as described herein, such as hydrocolloid 106, are used as a colloidal protector and/or viscosity builder. In one embodiment or in combination with any embodiment mentioned herein, hydrocolloid 106 is a lyophilic colloid. For example, hydrocolloid 106 may include at least one of a gelatin, a natural gum, a protein, or a cellulose derivative. The cellulose derivative may include one or both of methyl cellulose, and carboxy methyl cellulose.

[0090] The hydrocolloid, such as carboxy methyl cellulose, may be selected based on a desired viscosity of the resulting aqueous mixture. In one embodiment or in combination with any embodiment mentioned herein, a "low" viscosity hydrocolloid has a viscosity in a range between 10-50 cps, a "medium" viscosity hydrocolloid has a viscosity in a range between 400-800 cps, and a "high" viscosity hydrocolloid has a viscosity in a range between 1500-3000 cps.

SURFACTANT SYSTEM

[0091] In one embodiment or in combination with any embodiment mentioned herein, surfactant 108 includes two or more individual emulsifiers. The individual emulsifiers may be differentiated from each other based on their Hydrophilic-Lipophilic Balance (HLB) numbers. For example, when surfactant 108 includes two individual emulsifiers, the emulsifiers may include a lower-HLB emulsifier, and a higher-HLB emulsifier.

[0092] In one embodiment or in combination with any embodiment mentioned herein, the HLB number of the higher-HLB emulsifier is at least 6, 8, 10, 12, 14, 16, or 18, and the HLB number of the lower-HLB emulsifier not more than 12, 10, 8, 6, or 4.

[0093] In one embodiment or in combination with any embodiment mentioned herein, the HLB number of the higher-HLB emulsifier is greater than the HLB number of the lower-HLB emulsifier by at least one of the following: (1) at least 2, 4, 8, 10, 12, or 14; (2) not more than 25, 20, or 15; or (3) in the range of 2-25, 8-20, or 12-15.

[0094] In one embodiment or in combination with any embodiment mentioned herein, the lower-HLB emulsifier is a glycerol ester of stearic acid. In one embodiment or in combination with any embodiment mentioned herein, the higher-HLB emulsifier is a secondary alcohol ethoxylate.

[0095] In one embodiment or in combination with any embodiment mentioned herein, surfactant 108 further includes a third emulsifier. The third emulsifier has an HLB number greater than the HLB number of the lower-HLB emulsifier. In one embodiment or in combination with any embodiment mentioned herein, the third emulsifier is a polyethylene glycol ester of stearic acid.

[0096] When the surfactant 108 is formed from all three emulsifiers, the lower-HLB emulsifier and the third emulsifier may be present in a ratio that is at least 0.25:1, 0.5:1, 0.75:1, 1:1, 1.25:1, 1.5:1, 1.75:1, or 2:1 and/or not more than 5:1, 4:1, 3:1, 2:1, 1.75:1, 1.5:1, or 1.25:1. The lower-HLB emulsifier and the third emulsifier may define a combined emulsifier. In addition, the higher-HLB emulsifier and the combined emulsifier may be present in surfactant 108 in a ratio that is at least 0.25:1, 0.5:1, 0.75:1, 1:1, 1.25:1, 1.5:1, 1.75:1, or 2:1 and/or not more than 5:1, 4:1, 3:1, 2:1, 1.75:1, 1.5:1, or 1.25:1.

[0097] Referring now to FIG. 2, the illustrated process for making CE microbeads 112 includes separate formation of a CE dope 136 and an aqueous mixture 138. CE dope 136 and aqueous mixture 138 are then combined to form CE microbeads 112. For example, CE dope 136 may be formed at unit 140, and aqueous mixture 138 may be formed at unit 142. CE dope 136 and aqueous mixture 138 may then be combined at unit 144 to form an emulsion and/or dispersion, as will be described in more detail below.

[0098] In one embodiment or in combination with any embodiment mentioned herein, CE dope 136 is formed from CE 100, solvent 102, water 104, and, in some embodiments, recycled solvent 146 derived from solvent-enriched stream 134.

[0099] In one embodiment or in combination with any embodiment mentioned herein, CE 100 is present in CE dope in one or more of: (1) at least 1, 2, 4, 6, 8, or 10 weight percent; (2) not more than 80, 60, 40, 30, 20, or 15 weight percent; and (3) in the range 1-80, 2-60, 4-40, 6-30, 8-20, or 10-15 weight percent.

[0100] In one embodiment or in combination with any embodiment mentioned herein, when solvent 102 includes a C1-C4 alkyl acetate, the C1-C4 alkyl acetate is present in CE dope 136 in one or more of the following amounts: (1) at least 10, 25, 50, 60, or 65 weight percent; (2) not more than 95, 90, 85, 80 or 75 weight percent; and (3) in the range 10-95, 25-90, 50-85, or 65-75 weight percent.

[0101] In one embodiment or in combination with any embodiment mentioned herein, when solvent 102 includes a C1-C4 alcohol, the C1-C4 alcohol is present in CE dope 136 in one or more of the following amounts: (1) at least 1, 2, 4, 6, or 8 weight percent; (2) not more than 50, 25, 20, or 15 weight percent; and (3) in the range of 1-50, 2-25, 4-30, 6-20, or 8-15 weight percent.

[0102] In one embodiment or in combination with any other embodiment, the ratio of solvent to CE used in the dissolving to form CE dope 136 is at least 1:1, 2:1, 3:1, 4:1, or 5:1 and/or not more than 100:1, 50:1, 25:1, or 10:1.

[0103] In one embodiment or in combination with any embodiment mentioned herein, when solvent 102 includes water, the water is present in CE dope 136 in one or more of the following amounts: (1) at least 0.5, 1, 2, 4, or 6 weight percent; (2) not more than 40, 25, 15, or 10 weight percent; and (3) in the range of 0.5-40, 1-25, 2-15, 4-20, or 6-10 weight percent.

[0104] In one particular embodiment, CE dope 136 is formed from CE 100, solvent 102 including ethyl acetate and n-propanol, and water 104. In such an embodiment, CE is present in CE dope 136 in an amount in the range of 6-30, 7-25, 8-20, 9-20, 10-15, or 12-15 weight percent, ethyl acetate is present in CE dope 136 in an amount in the range of 50-85, 55-85, 60-85, 65-85, 70-85, or 75-85 weight percent, n-propanol is present in CE dope 136 in an amount in the range of 4-30, 6-25, 8-20, 10-20, or 12-15 weight percent, and water is present in CE dope 136 in an amount in the range of 4-20, 5-18, 6-16, 7-14, or 8-12 weight percent.

[0105] In one embodiment or in combination with any embodiment mentioned herein, CE 100, solvent 102, and water 104 are combined at unit 140 until substantially homogeneous to produce CE dope 136. In one embodiment or in combination with any embodiment mentioned herein, these components are mixed at room temperature (e.g., at least 15, 20, 25, or 30 °C and/or not more than 45, 40, 35, 30, 25, or 20 °C) for a duration of at least 1, 2, 5, 10, 15, 20, 25, 30, 45, 60, 120, or 240 minutes and/or for as long as is needed to produce the substantially homogeneous mixture.

[0106] In one embodiment or in combination with any embodiment mentioned herein, aqueous mixture 138 is formed from water 104, hydrocolloid 106, surfactant 108, and, in some embodiments, recycled solvent 146 derived from solvent-enriched stream 134. Optionally, additional solvent 148 may be added to units 140 and/or 142 as needed to maintain concentration(s) of solvent components at suitable levels.

[0107] In one embodiment or in combination with any embodiment mentioned herein, the ratio of the recycled solvent portion to the fresh solvent portion used in said units 140 and/or 142 is at least 2.5:1, 10:1, 25:1, 50:1, 75:1, 90:1, 95:1, or 99:1 by weight and/or not more 1000:1, 500:1, 200:1 or 100:1 by weight.

[0108] In one embodiment or in combination with any embodiment mentioned herein, the compositional make-up of the recycled solvent varies from the composition make-up of said fresh solvent by not more than 10, 5, 2, or 1 weight percent total.

[0109] In one embodiment or in combination with any embodiment mentioned herein, the fresh solvent and the recycled solvent portion have substantially the same composition.

[0110] In one embodiment or in combination with any embodiment mentioned herein, water is present in aqueous mixture 138 in one or more of the following amounts: (1) at least 40, 60, 70, 80, or 85 weight percent; (2) not more than 99, 97, 95, 94, or 92 weight percent; and (3) in the range of 40-99, 70-95, or 85-92 weight percent.

[0111] In one embodiment or in combination with any embodiment mentioned herein, the hydrocolloid is present in aqueous mixture 138 in one or more of the following amounts: (1) at least 0.001, 0.005, 0.01, 0.05, or 0.1 weight percent; (2) not more than 15, 10, 5, 2, or 1 weight percent; and (3) in the range of 0.001-15, 0.01-5, or 0.1-2 weight percent.

[0112] In one embodiment or in combination with any embodiment mentioned herein, the surfactant is present in aqueous mixture 138 in one or more of the following amounts: (1) at least 0.005, 0.01, 0.05, 0.1, or 0.5 weight percent; (2) not more than 15, 10, 5, 2, or 1.5 weight percent; and (3) in the range of 0.005-15, 0.05-5, or 0.5-1.5 weight percent.

[0113] As described above, the surfactant described herein may include a higher-HLB emulsifier and a lower-HLB emulsifier. In such embodiments, the higher-HLB emulsifier and the lower-HLB emulsifier are present in aqueous mixture 138 in a high-to-low HLB emulsifier ratio in the range of at least 0.25:1, 0.5:1, 1:1, 1.5:1, or 1.75:1 and/or not more than 10:1, 5:1, 3:1, or 2.5:1 and/or in the range of 0.25:1-10:1, 0.5:1-5:1, or 1:1-3:1.

[0114] Referring again to FIG. 2, in some embodiments, additional solvent 148 and/or recycled solvent 146 is received at unit 142. In such embodiments, the solvent used to form CE dope 136 and aqueous mixture 138 is a common C1-C4 alkyl acetate. Using the at least one common component in the solvent systems received at units 140 and 142 facilitates simplification of separation, recovery, and re-use of the solvent as described herein.

[0115] In one embodiment or in combination with any embodiment mentioned herein, when the aqueous mixture 138 include a C1-C4 alkyl acetate, the C1-C4 alkyl acetate is present in aqueous mixture 138 in one or more of the following amounts: (1) at least 1, 2, 4, 6, or 8 weight percent; (2) not more than 50, 40, 30, 20, or 15 weight percent; and (3) in the range of 1-50, 2-40, or 6-20 weight percent.

[0116] In one embodiment or in combination with any embodiment mentioned herein, the C1-C4 alkyl acetate is present in aqueous mixture 138 in an amount, by weight percent, that is within 25, 20, 15, 10, 5, or 2 weight percent of the solubility, by weight percent, of the C1-C4 alkyl acetate in water at 20°C.

[0117] The C1-C4 alkyl acetate may be one or both of methyl acetate and ethyl acetate. In one embodiment or in combination with any embodiment mentioned herein, when the C1-C4 alkyl acetate is ethyl acetate, ethyl acetate is present in aqueous mixture in an amount in the range of 2-25, 4-20, 6-15, or 8-10 weight percent. In one embodiment or in combination with any embodiment mentioned herein, when the C1-C4 alkyl acetate is methyl acetate, methyl

acetate is present in aqueous mixture in an amount in the range of 5-50, 10-40, 15-35, or 20-30 weight percent.

[0118] In one particular embodiment, aqueous mixture 138 is formed from water 104, hydrocolloid 106, surfactant 108, and a C1-C4 alkyl acetate. In such an embodiment, water is present in aqueous mixture 138 in an amount in the range of 70-95, 75-95, 80-95, 85-95, or 87.5-92.5 weight percent, the hydrocolloid is present in aqueous mixture 138 in an amount in the range of 0.01-5, 0.1-4, 0.5-3, 0.6-2, 0.7-1, or 0.8-0.9 weight percent, the surfactant is present in aqueous mixture 138 in an amount in the range of 0.05-5, 0.1-5, 0.1-4, 0.5-3, 0.6-2, 0.7-1, or 0.8-1 weight percent, and the C1-C4 alkyl acetate is present in aqueous mixture 138 in an amount in the range of 2-40, 3-35, 4-30, 5-25, 5-20, 5-15, 5-10, or 6-10 weight percent.

[0119] In one embodiment or in combination with any embodiment mentioned herein, water 104, hydrocolloid 106, surfactant 108, and optionally a C1-C4 alkyl acetate are combined at unit 142 to produce aqueous mixture 138. In one embodiment or in combination with any embodiment mentioned herein, these components are mixed at a temperature of at least 15, 20, 25, 30, 35, 40, 45, or 50 °C and/or not more than 100, 75, 50, 40, 35, 30, 25, or 20 °C, for a duration of at least 1, 2, 5, 10, 15, 20, 25, 30, 45, 60, 120, or 240 minutes and/or for as long as is needed to produce a substantially homogeneous mixture, depending on the viscosity of the hydrocolloid used.

EMULSION/DISPERSION FORMATION

[0120] Once formed, CE dope 136 and aqueous mixture 138 may be combined at unit 144 to produce an emulsion and/or a dispersion, as described above.

[0121] In one embodiment or in combination with any embodiment mentioned herein, a ratio of CE dope 136 to aqueous mixture 138 combined at unit 144 to form the initial emulsion is at least 0.05:1 to 10:1, 0.1:1 to 5:1, 0.2:1 to 2:1, or 0.4:1 to 0.8:1.

[0122] In one embodiment or in combination with any embodiment mentioned herein, the initial emulsion comprises water in an amount of at least 10, 20, 30, 40, 50, or 60 weight percent and/or not more than 90, 80, 70, 60, 50, or 40 weight percent.

[0123] Once combined, the initial emulsion is converted into a pre-hardened dispersion including the solid phase and the liquid phase. This conversion may be carried out by at least one of shearing, spraying (ultrasonic or electro), and membrane emulsion.

[0124] In one embodiment or in combination with any embodiment mentioned herein, the combined CE dope and aqueous mixture is recirculated through a high shear mixer to disperse the solid phase within the liquid phase, and to facilitate hardening of the solid phase to produce the initial microparticles. This shearing may be performed as CE dope 136 and aqueous mixture 138 are fed to unit 144 and/or may be performed after predetermined quantities of CE dope 136 and aqueous mixture 138 are within unit 144.

[0125] In one embodiment or in combination with any embodiment mentioned herein, the combined CE dope and aqueous mixture is recirculated through the high shear mixer for at least 1, 2, 3, 4, or 5 residence times and/or for not more than 20, 15, 10, 9, or 8 residence times based on the total volume of the high shear mixer used. In addition, the high shear mixing is performed for a duration of at least 1, 2, 5, 10, 15, 20, 25, 30, 45, 60, 120, or 240 minutes and/or for as long as is needed to recirculate the volume of the mixture for the predetermined number of residence times.

[0126] To produce initial microparticles that will form the CE microbeads as described herein, agitation of the combined CE dope and aqueous mixture is performed at unit 144. The agitation performed at unit 144 may be quantified by at least one of the following: (1) impeller tip speed, (2) impeller Reynolds number, and (3) power to mass ratio. In one embodiment or in combination with any embodiment mentioned herein, the high shear mixing is performed at an impeller tip speed of at least 25, 50, 75, 100, 150, 200, 250, or 300 cm/s and/or not more than 1000, 500, 400, 300, 200, or 100 cm/s. In one embodiment or in combination with any embodiment mentioned herein, the high shear mixing is performed at an impeller Reynolds number of at least 500, 1000, 1500, 2000, 3000, 4000, 5000, or 6000 and/or not more than 15000, 10000, 8000, 6000, 5000, 4000, or 3000. In one embodiment or in combination with any embodiment mentioned herein, the high shear mixing is performed at a power to mass ratio of at least 0.01, 0.02, 0.03, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 or 3.0 and/or not more than 10.0, 7.5, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0 0.5, or 0.1.

[0127] As used herein, terms such as "solid," "solid phase," "particles," and "microparticles" refer to semi-solid materials that do not lose their discrete nature (i.e., flowing together) when an aqueous/continuous phase surrounding the material is removed.

HARDENING WITH EXTRACTANT

[0128] A pre-hardened dispersion 150 formed at unit 144, and including the initial microparticles (i.e., solid phase), may be channeled to a hardening unit 152 to convert the initial particles to hardened CE microbeads 112. At unit 152, the initial microparticles contained within pre-hardened dispersion 150 are contacted with an extractant 154 (i.e., a drowning liquid) to produce a hardened dispersion 156. That is, the contacting step facilitates de-solventizing and hardening the initial microparticles into CE microbeads. In one embodiment or in combination with any embodiment mentioned herein, the extractant is water. Alternatively, the extractant may be methanol, ethanol, and combinations thereof.

[0129] In one embodiment or in combination with any embodiment mentioned herein, the pre-hardened dispersion and the extractant are combined at unit 152 at an extractant-to-dispersion weight ratio of at least 0.5:1, 1:1, 1.5:1, 2:1, or 1.5:1 and/or not more than 10:1, 8:1, 6:1, 4:1, or 3:1.

[0130] In one embodiment or in combination with any embodiment mentioned herein, the weight ratio of extractant to pre-hardened particles used in the contacting step is at least 2:1, 5:1, 10:1, 20:1. 30:1, or 40:1 and/or not more than 200:1, 100:1, 80:1. 60:1, or 50:1.

[0131] As a result, in one embodiment or in combination with any embodiment mentioned herein, hardened dispersion 156 has water in one or more of the following amounts: (1) at least 25, 50, 60, 70, 80, 85, or 90 weight percent; (2) not more than 99, 97.5, 95, 92.5, 90, 80, 70, 60, or 50 weight percent; and (3) in the range of 50-99, 70-95, or 80-92.5 weight percent.

[0132] In one embodiment or in combination with any embodiment mentioned herein, hardened dispersion 156 has water in a weight concentration that is at least 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 times greater than and/or not more than 100, 70, 50, 25, 15, 10, 5, or 2.5 times greater than the weight concentration of water in the initial emulsion.

[0133] In one embodiment or in combination with any embodiment mentioned herein, hardening of the microparticles is carried out under agitation. The agitation performed at unit 152 may be quantified by at least one of the following: (1) impeller tip speed, (2) impeller Reynolds number, and (3) power to mass ratio. In one embodiment or in combination with any embodiment mentioned herein, the converting/hardening is performed at an impeller tip speed of at least 25, 50, 75, 100, 150, 200, 250, or 300 cm/s and/or not more than 1000, 500, 400, 300, 200, or 100 cm/s. In one embodiment or in combination with any embodiment mentioned herein, the converting/hardening is performed at an impeller Reynolds number of at least 500, 1000, 1500, 2000, 3000, 4000, 5000, or 6000 and/or not more than 15000, 10000, 8000, 6000, 5000, 4000, or 3000. In one embodiment or in combination with any embodiment mentioned herein, the converting/hardening is performed at a power to mass ratio of at least 0.01, 0.02, 0.03, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 or 3.0 and/or not more than 10.0, 7.5, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0 0.5, or 0.1.

[0134] In addition, the converting/hardening is performed for a time period of at least 0.1, 0.5, 1, 2, 4, 6, 8, 10, or 20 minutes and/or not more than 12, 8, 6, 4, or 2 hours, and at a temperature of at least 0, 5, or 10 °C and/or not more than 100, 75, 50, or 25 °C.

[0135] In one embodiment or in combination with any embodiment mentioned herein, the converting/hardening is performed in a single vessel, or in multiple vessels. Multiple vessels may be needed based on the output of CE microbeads to be produced and the volumetric capacity of available vessels used for the hardening. In embodiments where multiple vessels are used, a first portion of pre-hardened dispersion 150 may be received at a first hardening unit, and a second portion of pre-hardened dispersion may be received at a second hardening unit. Flow communication may then be provided between the separate hardening units to enhance mass transfer such that desolventization of the initial microparticles is accelerated.

[0136] In one embodiment or in combination with any embodiment mentioned herein, pre-hardened dispersion 150 has a solids content of at least 0.5, 1, 2, 3, or 4 and/or not more than 40, 30, 20, 10, or 6 weight percent.

[0137] As a result of the hardening, in one embodiment or in combination with any embodiment mentioned herein, hardened dispersion 156 has a solids content of at least 0.05, 0.1, 0.5, or 1 weight percent and/or not more than 20, 10, 5, 2, or 1 weight percent.

[0138] In one embodiment or in combination with any embodiment mentioned herein, the solids content of the pre-hardened dispersion is at least 1.5, 2, 3, or 4 and/or not more than 20, 10, 8, or 6 times greater than the solids content of the hardened dispersion. In other words, at unit 152, solvent is extracted from the initial microparticles to produce hardened dispersion 156 including hardened CE microbeads 112 and a solvent-laden drowning liquid.

CE MICROBEAD ISOLATION/SEPARATION

[0139] CE microbeads 112 may be isolated and recovered from hardened dispersion 156 using any suitable technique at unit 158. In one embodiment or in combination with any embodiment mentioned herein, the isolating may be performed by at least one, at least two, or all three of the following: (1) flashing one or more liquid components away from the hardened CE microbeads; (2) filtering the hardened CE microbeads away from one or more liquid components; and (3) centrifuging, redispersing, and drying the hardened microbeads.

[0140] Solids processing and/or CE microbead isolation may be performed in a single unit, as illustrated in FIG. 1, or may be performed in multiple units, as illustrated in FIG. 2. Referring to FIG. 2, a wet solids stream 160 and a separated mother liquor stream 162 are discharged from unit 158. Wet solids stream 160 contains the hardened CE microbeads and residual liquid. In one embodiment or in combination with any embodiment mentioned herein, wet solids stream 160 has a solids content of at least 10, 20, 25, 30, 35, 40, or 45 weight percent and/or not more than 60, 65, 50, 45, or 40 weight percent. This enables wet solids stream 160 to be conveyed to downstream units with reduced clogging and processing concerns.

[0141] Wet solids stream 160 may then, optionally, be processed in a wash unit 164, and a second solid/liquid separation unit 166. At unit 164, the hardened CE microbeads are washed with water 122 to produce a washed solids stream 168. Washed solids stream 168 is then processed at unit 166 by at least one, at least two, or all three of the following: (1) flashing one or more liquid components away from the hardened CE microbeads; (2) filtering the hardened CE microbeads away from one or more liquid components; and (3) centrifuging, redispersing, and drying the hardened microbeads. This second solid/liquid separation step facilitates reducing the solvent content in the liquid around the hardened CE microbeads.

[0142] A wash liquor 130 may be recovered from the second solid/liquid separation step and then recycled for use as at least a portion of the aqueous mixture in unit 142 and/or for use as at least a portion of the drowning liquid in unit 152.

[0143] In one embodiment or in combination with any embodiment mentioned herein, at least 1, 5, or 10 weight percent and/or not more than 90, 50, 20, or 10 weight percent of aqueous mixture 138 is the recycled wash liquor.

[0144] In one embodiment or in combination with any embodiment mentioned herein, at least 1, 5, or 10 weight percent and/or not more than 90, 50, 20, or 10 weight percent of drowning liquid 154 used in unit 152 is the recycled wash liquor.

[0145] A wet solids stream 172 discharged from unit 166 is then received at a drying unit 170. In one embodiment or in combination with any embodiment mentioned herein, drying is performed at unit 170 under agitation and with the addition of heat. Such agitation facilitates reducing agglomeration of the recovered CE microbeads 112. Properties of the recovered CE microbeads 112 are described in more detail below.

[0146] In one embodiment or in combination with any embodiment mentioned herein, drying unit 170 is a rotary cone dryer.

LIQUIDS PROCESSING AND RECYCLE

[0147] Separated mother liquor stream 162 discharged from unit 158 may be processed to recover water and/or solvent. The recovered water and/or solvent may then be recycled to one or more of the units shown in FIG. 2 to enhance the economic efficiency of the microbeads formation processes described herein.

[0148] The liquid processing may be performed in a single unit, as illustrated in FIG. 1, or may be performed in multiple units, as illustrated in FIG. 2. Referring to FIG. 2, mother liquor stream 162 contains at least a portion of the water and at least a portion of the solvent introduced at units 140 and/or 142, for example. Mother liquor stream 162 may also contain residual amounts of the hydrocolloid, surfactant, and any components used in the making of the mixed cellulose esters.

[0149] Mother liquor stream 162 may be heated 174 and then separated at unit 176 into at least two separate streams, such as solvent-enriched stream 134 and water-enriched (solvent-depleted) stream 132. Mother liquor stream 162 may be separated using any suitable technique at unit 176. In one embodiment or in combination with any embodiment mentioned herein, the liquids separation may be performed by distillation and the like.

[0150] In one embodiment or in combination with any embodiment mentioned herein, water-enriched stream 132 includes one or more of the following: (1) water; (2) a surfactant; (3) a hydrocolloid; and (4) a C1-C4 alkyl acetate.

[0151] Accordingly, water-enriched stream 132 may be cooled 181 and then recycled to one or more units illustrated in FIG. 2. For example, the composition of water-enriched stream 132 enables it to be recycled to at least one of unit 142 as stream 178 for use in the forming of aqueous mixture 138, and/or to unit 152 as stream 180 for use in de-solventizing the initial microparticles, thereby reducing water usage required for such processes. Any excess not required by these processes may be purged from the system and subjected to wastewater treatment, for example.

[0152] In one embodiment or in combination with any embodiment mentioned herein, the ratio of recycled water in stream 180 used in the hardening step to recycled water in stream 178 used in forming aqueous mixture 138 is at least 1:1, 1.5:1, 2:1, 3:1, 4:1 and/or not more than 20:1, 10:1, 8:1, or 6:1.

[0153] In one embodiment or in combination with any embodiment mentioned herein, the ratio of recycled water in stream 180 used in the hardening step to purge water is at least 1:1, 1.5:1, 2:1, 3:1, 4:1 and/or not more than 20:1, 10:1, 8:1, or 6:1.

[0154] In one embodiment or in combination with any embodiment mentioned herein, at least 75, 90, 95, 98, 99, or 100 weight percent of the extractant used in unit 152 is recycled water recovered downstream from unit 152, such as water contained in water-enriched stream 132 that is recycled to unit 152.

[0155] In one embodiment or in combination with any embodiment mentioned herein, fresh water 154 is added to unit 152 for use in the hardening step.

[0156] In one embodiment or in combination with any embodiment mentioned herein, wherein the ratio of the total amount of added fresh water to purge water is at least 0.25:1 0.5:1, 0.75:1, or 0.9:1 and/or not more than 4:1, 2:1, 1.5:1, 1.25:1, or 1.1:1.

[0157] In one embodiment or in combination with any embodiment mentioned herein, solvent-enriched stream 134 includes one or more of: (1) a C1-C4 alkyl acetate; (2) a C1-C4 alcohol; and (3) water.

[0158] Accordingly, solvent-enriched stream 134 may be recycled to one or more units illustrated in FIG. 2. For example, the composition of solvent-enriched stream 134 enables it to be recycled to at least one of unit 140 for use as a portion of the solvent in the forming of CE dope 136, and/or to unit 142 for use in the forming of aqueous mixture 138. Any excess not required by these processes may be purged from the system.

[0159] In one embodiment or in combination with any embodiment mentioned herein, at least 75, 90, 95, 98, 99, or 100 weight percent of the solvent used in unit 140 used to form CE dope 136 is recycled solvent 146.

[0160] In one embodiment or in combination with any embodiment mentioned herein, fresh water 104 is added to unit 142 for use in forming aqueous mixture 138.

[0161] In one embodiment or in combination with any embodiment mentioned herein, the ratio of the combined amount of water in streams 178 and 180 to the total amount of added fresh water 104 in unit 142 is at least 2:1, 4:1, 6:1, or 8:1.

[0162] In one embodiment or in combination with any embodiment mentioned herein, aqueous mixture 138 includes an azeotrope of water and C1-C4 alkyl acetate, and/or of water and C1-C4 alcohol, derived from water-enriched stream 132.

[0163] Hydroxyl is generally a strong hydrogen bonder. Thus, the opportunity for hydrogen bonding increases as the DSOH of a given substance increases. The cosolvent alcohol of the solvent system described herein is also a strong hydrogen bonder. Surprisingly however, the ability of the cosolvent alcohol to hydrogen bond was found to decrease as the number of carbons (i.e., C1-C4) increases. Accordingly, lower carbon number binary solvent systems that did not contain water were found to be capable of dissolving cellulose esters having a DS_{OH}

greater than a biodegradability threshold (e.g., DS_{OH} of greater than 0.8). In contrast, higher carbon number binary solvent systems that did not contain water were found to not be capable of dissolving cellulose esters having a DS_{OH} greater than the same biodegradability threshold. Accordingly, it has been found that the presence of a strong hydrogen bonder (i.e., water) with essentially no steric hindrance in solvent systems containing higher carbon number alcohols facilitates dissolution of the mixed CEs described herein in the solvent systems.

[0164] In one embodiment or in combination with any embodiment mentioned herein, recycled solvent 146 contains water in an amount of at least 1, 2, 4, 6, or 8 weight percent and/or not more than 50, 40, 30, 20, or 10 weight percent.

[0165] In one embodiment or in combination with any embodiment mentioned herein, recycled solvent 146 contains at least one azeotrope, wherein the azeotrope contains water and another component.

[0166] In one embodiment or in combination with any embodiment mentioned herein, the azeotrope in recycled solvent 146 may be a water/alcohol azeotrope, a water/alkyl acetate azeotrope, or both a water/alcohol azeotrope and a water/alkyl acetate azeotrope.

[0167] In one embodiment or in combination with any embodiment mentioned herein, recycled solvent 146 contains a plurality of azeotropes. In one embodiment or in combination with any embodiment mentioned herein, the plurality of azeotropes include a plurality of binary azeotropes. In one embodiment or in combination with any embodiment mentioned herein, the components of the solvent system are selected such that recycled solvent 146 does not contain any ternary azeotropes, thereby simplifying recovery and recycling of said solvent.

[0168] In one embodiment or in combination with any embodiment mentioned herein, solvent-enriched stream 134 contains less than 10 weight percent, less than 1 weight percent, less than 0.1 weight percent, or 0.0 weight percent of a ternary azeotrope.

[0169] In one embodiment or in combination with any embodiment mentioned herein, recycled solvent 146 contains three total binary azeotropes, such as a water/alcohol azeotrope, a water/alkyl acetate azeotrope, and an alcohol/alkyl acetate azeotrope.

[0170] Per block flow diagram shown in FIG.2 and ASPEN model mass fractions in TABLE A, Separated Mother Liquor Stream 162 from Solid/Liquid Separation 158 feeds column Solvent/Extractant Separation 176 with optional (pre)Heat 174. The column Solvent/Extract Separation 176 bottoms Water Enriched Stream 132 at the mass fractions shown in TABLE A flows through Cool(er) 181 as Recycled Water 178 stream to Aqueous Mixture Formation 142, as Recycled Extractant 180 stream to Particle Hardening 152, and as a Water Purge stream. The Water Purge stream is required to prevent accumulation of Hydrocolloid 106 and Surfactant 108 in the entire system. Solvent Enriched Stream 134 flows from the top of the column Solvent/Extract Separation 176 as Recycled Solvent 146 to Dope Formation 140 and possibly to Aqueous Mixture Formation 142. TABLE A ASPEN run is for one particular embodiment. There is essentially complete recovery of Solvent 102 and recycle back to the process in Recycled Solvent stream 146. There is about 98% recovery of Solvent 148 and recycle back to the process in Recycled Solvent stream 146. About 16% of the water in the Hardened Dispersion 156 feed to Solid Liquid Separation 158 must be purged from the system in the Water Purge stream to prevent significant accumulation of Hydrocolloid 106 and Surfactant 108 in the process.

[0171] TABLE A – Aspen Model for Solvent and Water Recovery System and Balance of Recycle Streams and Purge.

	Separated Mother Liquor Stream	Water Enriched Stream	Recycled Water	Recycled Extractant	Water Purge	Recycled Solvent
	162	134	178	180		146
Mass Fractions						
Solvent 102	0.086945	4.31E-13	4.31E-13	4.31E-13	4.31E-13	0.807219
Solvent 148	0.013661	0.000306	0.000306	0.000306	0.000306	0.124297
Water	0.891288	0.990609	0.990609	0.990609	0.990609	0.068484
Hydrocolloid 106	0.002389	0.002677	0.002677	0.002677	0.002677	1.27E-103
CE 100	0.000642	0.000719	0.000719	0.000719	0.000719	3.40E-104
Surfactant 108	0.005076	0.005689	0.005689	0.005689	0.005689	4.82E-37
Relative Mass Flow						
Solvent 102	8.26448	3.66E-11	6.79E-12	2.37E-11	6.07E-12	8.26448
Solvent 148	1.30E+00	0.025970	4.82E-03	0.0168372	0.0043086	1.27258
Water	8.47E+01	84.0199	1.56E+01	54.4721	13.9393	0.701152
Hydrocolloid 106	2.27E-01	0.227057	4.22E-02	0.147207	0.0376699	1.30E-102
CE 100	0.060997	0.0609968	0.0113314	0.0395457	0.0101197	3.48E-103
Surfactant 108	0.482496	0.482496	0.089633	0.312814	0.0800486	4.94E-36

ADDITIONAL EMBODIMENTS

[0172] Referring now to FIG. 3, CE microbeads 112 are produced by serialized particle formation. In the example embodiment, particle formation begins at unit 142, in which water 104, hydrocolloid 106, surfactant 108, and, in some embodiments, recycled solvent 146 derived from solvent-enriched stream 134 is combined to form aqueous mixture 138.

[0173] Aqueous mixture 138 is discharged from unit 142 and received at a dispersion formation unit 182. At unit 182, aqueous mixture 138 is combined with CE 100, solvent 102, and, optionally, recycled solvent 146 derived from solvent-enriched stream 134. Thus, rather

than forming CE dope 136 and aqueous mixture 138 in separate units, aqueous mixture 138, CE 100, and solvent 102 are combined in a common unit to form the initial emulsion.

[0174] In one embodiment or in combination with any embodiment mentioned herein, aqueous mixture 138, CE 100, and solvent 102 are agitated in unit 182 the combined CE dope and aqueous mixture is recirculated through a high shear mixer to disperse the solid phase within the liquid phase of the initial emulsion, and to facilitate hardening of the solid phase to produce the initial microparticles.

[0175] To produce the initial microparticles, agitation of the combined aqueous mixture 138, CE 100, and solvent 102 is performed at unit 182. The agitation performed at unit 182 may be quantified by at least one of the following: (1) impeller tip speed, (2) impeller Reynolds number, and (3) power to mass ratio. In one embodiment or in combination with any embodiment mentioned herein, the high shear mixing is performed at an impeller tip speed of at least 25, 50, 75, 100, 150, 200, 250, or 300 cm/s and/or not more than 1000, 500, 400, 300, 200, or 100 cm/s. In one embodiment or in combination with any embodiment mentioned herein, the high shear mixing is performed at an impeller Reynolds number of at least 500, 1000, 1500, 2000, 3000, 4000, 5000, or 6000 and/or not more than 15000, 10000, 8000, 6000, 5000, 4000, or 3000. In one embodiment or in combination with any embodiment mentioned herein, the high shear mixing is performed at a power to mass ratio of at least 0.01, 0.02, 0.03, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 or 3.0 and/or not more than 10.0, 7.5, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0 0.5, or 0.1.

[0176] Pre-hardened dispersion 150 is then discharged from unit 182 and hardened CE microbeads 112 recovered therefrom as described above.

[0177] Referring to FIG. 4, CE microbeads 112 are produced by separated dope and aqueous mixture formation, and combined emulsion/dispersion formation and particle hardening. In the example embodiment, particle formation begins as illustrated in FIG. 2, wherein CE dope 136 and aqueous mixture 138 are formed in separate units.

[0178] In FIG. 4, however, CE dope 136 and aqueous mixture 138 are fed to a common emulsion/dispersion formation and particle hardening unit 184. At unit 184, CE dope 136 and aqueous mixture 138 are combined and agitated to form the initial emulsion as described

herein. Once the initial emulsion is formed, extractant 154 is fed directly to unit 184 to perform de-solventization of the initial microparticles.

[0179] Referring to FIG. 5, CE microbeads 112 are produced by combined emulsion/dispersion formation. In the example embodiment, particle formation begins by combining all of CE 100, solvent 102, water 104, hydrocolloid 106, surfactant 108, and, optionally, recycled solvent 146 and recycled water 178 in a common unit 186. This mixture is agitated as described herein to produce pre-hardened dispersion 150 containing initial microparticles. Pre-hardened dispersion is received at unit 152 to de-solventize the initial microparticles as described herein.

[0180] Referring to FIG. 6, CE microbeads 112 are produced by combined emulsion/dispersion formation and particle hardening. In the example embodiment, particle formation begins by combining all of CE 100, solvent 102, water 104, hydrocolloid 106, surfactant 108, and, optionally, recycled solvent 146 and recycled water 178 in a common unit 188. At unit 188, these components are combined and agitated to form the initial emulsion as described herein. Once the initial emulsion is formed, extractant 154 is fed directly to unit 188 to perform de-solventization of the initial microparticles.

[0181] Referring to FIG. 7, CE microbeads 112 are produced by solvent flashing prior to particle hardening. In the example embodiment, pre-hardened dispersion 150 discharged from unit 144 is received at a flash unit 190, rather than at particle hardening unit 152. At unit 144, at least some of the solvent of pre-hardened dispersion 150 is removed from the liquid phase thereof, to thereby form a solvent-depleted dispersion 192 having a reduced solvent content. Solvent-depleted dispersion 192 is received at unit 152 to harden the pre-hardened microparticles contained therein, as described above. A flashed solvent stream 194 discharged from unit 190 may be channeled to unit 176 to perform liquids processing and recycle thereof.

[0182] In one embodiment or in combination with any embodiment mentioned herein, the removing at unit 144 is performed by pervaporation, crossflow membrane filtration (ultrafiltration or nanofiltration), flash pot, spray pot, or wiped film evaporation.

[0183] In one embodiment or in combination with any embodiment mentioned herein, the removing at unit 144 reduces the solvent in said dispersion by at least 30 percent, at least 50

percent, at least 75 percent, at least 90 percent, between 30 and 90 percent, or between 50 and 75 percent by weight.

[0184] In one embodiment or in combination with any embodiment mentioned herein, solvent-depleted dispersion 192 has a solids content of at least 3, 4, 5, or 6 and/or not more than 40, 30, 20, or 10 weight percent.

[0185] In one embodiment or in combination with any embodiment mentioned herein, a volume ratio of drowning liquid to the solvent-depleted dispersion used in unit 152 is less than 2.5:1, 2:1, 1.75:1, 1.5:1, 1.25:1, or 1:1.

HARDENED CE MICROBEADS

[0186] The hardened CE microbeads produced by the processes disclosed herein exhibit desirable tactile and/or optical qualities, for example, making them desirable for use in personal care products, cosmetics, and the like. As used herein, the terms "microparticles," "beads," and "microbeads" may be used interchangeably with the term "hardened CE microbeads."

[0187] In one embodiment or in combination with any embodiment mentioned herein, CE microbeads are produced at a rate of at least 50, 100, 250, 500, 1000, 2500, 5000, or 10000 kg/day and/or not more than 100000, 75000, or 50000 kg/day. To achieve these production rates, CE, solvent, and/or water is provided within the system at one or more of the following corresponding rates.

[0188] In one embodiment or in combination with any embodiment mentioned herein, CE is provided at unit 140 at a rate of at least 50, 100, 250, 500, 1000, 2500, 5000, or 10000 kg/day and/or not more than 100000, 75000, or 50000 kg/day.

[0189] In one embodiment or in combination with any embodiment mentioned herein, solvent is provided at unit 140 at a rate of at least at least 50, 100, 250, 500, 1000, 2500, 5000, or 10000 kg/day and/or not more than 100000, 75000, or 50000 kg/day.

[0190] In one embodiment or in combination with any embodiment mentioned herein, water is provided unit 152 at a rate of at least at least 500, 1000, 2500, 5000, 10000, 25000, 50000, or 100000 kg/day and/or not more than 1000000, 750000, or 500000 kg/day.

[0191] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a hardness at 20°C that is greater than the hardness at 20°C of the initial microparticles contained within pre-hardened dispersion 150 and/or formed in any of the processes described herein.

[0192] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a hardness of at least 1.1, 1.25, 1.5, 1.75, or 2 times greater than the hardness of the initial microparticles.

[0193] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a solvent content of less than 100, 50, 25, or 10 ppmw.

[0194] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a solvent content of less than the solvent content of the initial microparticles.

[0195] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a solvent content of less than 0.99, 0.95, 0.9, 0.8, 0.7, 0.6, or 0.5 of the solvent content of the initial microparticles.

[0196] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a solvent content that is at least 1, 2, 4, 8, 12, 16 or 20 weight percent less than the solvent content of the initial microparticles.

[0197] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D50 particle size that is within 50, 25, 15, 10, 5, or 2 percent of the D50 particle size of the initial microparticles.

[0198] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D50 particle size of less than the D50 particle size of the initial microparticles.

[0199] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D50 particle size of less than 0.99, 0.95, 0.9, 0.8, 0.7, 0.6, or 0.5 of the D50 particle size of the initial microparticles.

[0200] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D50 particle size in the range of 1 to 100, 1 to 80, 1 to 70, 1 to 60, 1 to 50, 1 to 40, 1 to 35, 1 to 30, 1 to 25, 1 to 20, 1 to 15, 1 to 10, 2 to 100, 2 to 80, 2 to 70, 2 to 60, 2 to 50, 2 to 40, 2 to 35, 2 to 30, 2 to 25, 2 to 20, 2 to 15, 2 to 10, 3 to 100, 3 to 80, 3 to 70, 3 to 60, 3 to 50, 3 to 40, 3 to 35, 3 to 30, 3 to 25, 3 to 20, 3 to 15, 3 to 10, 5 to 100, 5 to 80, 5 to 70, 5 to 60, 5 to 50, 5 to 40, 5 to 35, 5 to 30, 5 to 25, 5 to 20, 5 to 15, 5 to 10, 10 to 100, 10 to 80, 10 to 70, 10 to 60, 10 to 50, 10 to 40, 10 to 35, 10 to 30, 10 to 25, 10 to 20, 10 to 15, 15 to 100, 15 to 80, 15 to 70, 15 to 60, 15 to 50, 15 to 40, 15 to 35, 15 to 30, 15 to 25, 15 to 20, 20 to 100, 20 to 80, 20 to 70, 20 to 60, 20 to 50, 20 to 40, 20 to 35, 20 to 30, 25 to 100, 25 to 80, 25 to 70, 25 to 60, 25 to 50, 25 to 40, 25 to 35, 25 to 30, 30 to 100, 30 to 80, 30 to 70, 30 to 60, 30 to 50, 30 to 40, or 30 to 35 microns. For example, the hardened CE microbeads can have a D50 particle size of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 100 microns.

[0201] As used herein, the term "D50" means that 50% of the beads have a maximum dimension that is less than or equal to the noted value (e.g., 10 microns), based on a volume basis. The D50 value may also be treated as the median particle size. To ensure that a representative D50 value is obtained, the sample size of the beads should be at least 0.5 grams. The microbead sample size is then dispersed and mixed in 1.5 ounces of isopropanol. Testing for D50 is performed via laser diffraction and computer algorithms using the Mie theory to generate a particle size distribution. One suitable particle size analyzer for determining D50 values is the Malvern Mastersizer 3000 from Malvern Panalytical. When using the Malvern Mastersizer, the obscuration rate may be set between 2% and 5% and sample measurement time is set for three seconds for both red and blue light measurements. The dispersed sample is added until the desired obscuration rate (~4%) is attained and then the measurements are carried out. After the first measurement, the sample is sonicated at 50% power for 120 seconds. Subsequently, after sonication, the dispersed sample is measured again once the light energy stabilizes (usually less than one minute).

[0202] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D10 volume-based particle size of 0.5 to 20, 0.5 to 15, 0.5 to 12, 0.5 to 10, 0.5 to 5, 0.5 to 4, 0.5 to 3, 0.5 to 2, 0.5 to 1, 1 to 20, 1 to 15, 1 to 12, 1 to 5, 1 to 3, 2 to 20, 2 to 10, 2 to 5, 3 to 20, 3 to 15, 3 to 10, 4 to 20, 4 to 15, 4 to 10, 5 to 20, 5 to 15, 5

to 10, 10 to 20, or 10 to 15 microns. For example, the hardened CE microbeads can have a D10 volume-based particle size of 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 microns.

[0203] As used herein, the term "D10 volume-based" means that 10% of the beads have a maximum dimension that is less than or equal to the noted value (e.g., 10 microns), based on a volume basis. To ensure that a representative D10 value is obtained, the sample size of the beads should be at least 0.5 grams. The microbead sample size is then dispersed and mixed in 1.5 ounces of isopropanol. Testing for D10 is performed via laser diffraction and computer algorithms using the Mie theory to generate a particle size distribution. One suitable particle size analyzer for determining D10 values is the Malvern Mastersizer 3000 from Malvern Panalytical. When using the Malvern Mastersizer, the obscuration rate may be set between 2% and 5% and sample measurement time is set for three seconds for both red and blue light measurements. The dispersed sample is added until the desired obscuration rate (~4%) is attained and then the measurements are carried out. After the first measurement, the sample is sonicated at 50% power for 120 seconds. Subsequently, after sonication, the dispersed sample is measured again once the light energy stabilizes (usually less than one minute).

[0204] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D90 volume-based particle size in the range of 1 to 100, 1 to 80, 1 to 70, 1 to 60, 1 to 50, 1 to 40, 1 to 35, 1 to 30, 1 to 25, 1 to 20, 1 to 15, 1 to 10, 5 to 100, 5 to 80, 5 to 70, 5 to 60, 5 to 50, 5 to 40, 5 to 35, 5 to 30, 5 to 25, 5 to 20, 5 to 15, 5 to 10, 10 to 100, 10 to 80, 10 to 70, 10 to 60, 10 to 50, 10 to 40, 10 to 35, 10 to 30, 10 to 25, 10 to 20, 10 to 15, 15 to 100, 15 to 80, 15 to 70, 15 to 60, 15 to 50, 15 to 40, 15 to 35, 15 to 30, 15 to 25, 15 to 20, 20 to 100, 20 to 80, 20 to 70, 20 to 60, 20 to 50, 20 to 40, 20 to 35, 20 to 30, 25 to 100, 25 to 80, 25 to 70, 25 to 60, 25 to 50, 25 to 40, 25 to 35, 25 to 30, 30 to 100, 30 to 80, 30 to 70, 30 to 60, 30 to 50, 30 to 40, or 30 to 35 microns. For example, the hardened CE microbeads can have a D90 volume-based particle size of 100, 90, 80, 70, 60, 50, 49, 48, 47, 46, 45, 44, 43, 42, 41, 40, 39, 38, 37, 36, 35, 34, 33, 32, 31, 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, or 20 microns.

[0205] As used herein, the term "D90 volume-based" means that 90% of the beads have a maximum dimension that is less than or equal to the noted value (e.g., 10 microns), based on a volume basis. To ensure that a representative D90 value is obtained, the sample size of the

beads should be at least 0.5 grams. The microbead sample size is then dispersed and mixed in 1.5 ounces of isopropanol. Testing for D90 is performed via laser diffraction and computer algorithms using the Mie theory to generate a particle size distribution. One suitable particle size analyzer for determining D90 values is the Malvern Mastersizer 3000 from Malvern Panalytical. When using the Malvern Mastersizer, the obscuration rate may be set between 2% and 5% and sample measurement time is set for three seconds for both red and blue light measurements. The dispersed sample is added until the desired obscuration rate (~4%) is attained and then the measurements are carried out. After the first measurement, the sample is sonicated at 50% power for 120 seconds. Subsequently, after sonication, the dispersed sample is measured again once the light energy stabilizes (usually less than one minute).

[0206] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a D100 volume-based particle size in the range of 1 to 100, 1 to 80, 1 to 70, 1 to 60, 1 to 50, 1 to 40, 1 to 35, 1 to 30, 1 to 25, 1 to 20, 1 to 15, 1 to 10, 5 to 100, 5 to 80, 5 to 70, 5 to 60, 5 to 50, 5 to 40, 5 to 35, 5 to 30, 5 to 25, 5 to 20, 5 to 15, 5 to 10, 10 to 100, 10 to 80, 10 to 70, 10 to 60, 10 to 50, 10 to 40, 10 to 35, 10 to 30, 10 to 25, 10 to 20, 10 to 15, 15 to 100, 15 to 80, 15 to 70, 15 to 60, 15 to 50, 15 to 40, 15 to 35, 15 to 30, 15 to 25, 15 to 20, 20 to 100, 20 to 80, 20 to 70, 20 to 60, 20 to 50, 20 to 40, 20 to 35, 20 to 30, 25 to 100, 25 to 80, 25 to 70, 25 to 60, 25 to 50, 25 to 40, 25 to 35, 25 to 30, 30 to 100, 30 to 80, 30 to 70, 30 to 60, 30 to 50, 30 to 40, or 30 to 35 microns. For example, the hardened CE microbeads can have a D100 volume-based particle size of 100, 90, 80, 70, 60, 50, 49, 48, 47, 46, 45, 44, 43, 42, 41, 40, 39, 38, 37, 36, 35, 34, 33, 32, 31, 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, or 20 microns.

[0207] As used herein, the term "D100 volume-based" means that 100% of the beads have a maximum dimension that is less than or equal to the noted value (e.g., 10 microns), based on a volume basis. To ensure that a representative D100 value is obtained, the sample size of the beads should be at least 0.5 grams. The microbead sample size is then dispersed and mixed in 1.5 ounces of isopropanol. Testing for D100 is performed via laser diffraction and computer algorithms using the Mie theory to generate a particle size distribution. One suitable particle size analyzer for determining D100 values is the Malvern Mastersizer 3000 from Malvern Panalytical. When using the Malvern Mastersizer, the obscuration rate may be set between 2% and 5% and sample measurement time is set for three seconds for both red and blue light

measurements. The dispersed sample is added until the desired obscuration rate (~4%) is attained and then the measurements are carried out. After the first measurement, the sample is sonicated at 50% power for 120 seconds. Subsequently, after sonication, the dispersed sample is measured again once the light energy stabilizes (usually less than one minute).

[0208] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have an average sphericity of at least at least 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 95, 97, 98, or 99 percent and/or not more than 99, 95, 90, 80, 70, 60, 50, 40, or 30 percent.

[0209] Average sphericity is determined by: (1) obtaining a secondary emission/ETD detector scanning electron microscopy (SEM) image of a representative sample of at least 40 microbeads, (2) on the SEM image, selecting a square sample window centered at the center of the SEM that contains exactly 30 microbeads whose entire outer perimeters are clearly visible (i.e., not occluded), (3) measuring the maximum and minimum diameters (each extending through the particle's centroid and not necessarily perpendicular to one another) of the 30 clearly visible microbeads in the sample window, (4) for each of the 30 particles, dividing the minimum diameter by the maximum diameter and multiplying the result by 100% to obtain 30 individual particle sphericities, and (5) averaging the 30 individual particle sphericities to obtain the average sphericity.

[0210] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads exhibit a monomodal particle size distribution with a span of at least 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95, 1.0, 1.05, 1.1, 1.15, 1.2, 1.25, 1.3, or 1.4 and/or less than 3.0, 2.9, 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, or 1.5. In certain embodiments, the hardened CE microbeads exhibit a monomodal particle size distribution with a span of 1.0 to 3.0, 1.0 to 2.5, 1.0 to 2.0, 1.0 to 1.8, 1.0 to 1.6, 1.2 to 3.0, 1.2 to 2.5, 1.2 to 2.0, 1.2 to 1.8, 1.2 to 1.6, 1.3 to 3.0, 1.3 to 2.5, 1.3 to 2.0, 1.3 to 1.8, or 1.3 to 1.6. As used herein, "monomodal particle size distribution" refers to a particle size distribution for a material that only has a single notable peak of size distribution. This is in contrast to multi-modal particle size distributions, which will have two or more peaks of particle size

distributions. The "span" of the monomodal peak may be measured using the D10, D50, and D90 values of the particles using the following formula:

$(D_x(90) - D_x(10))/ D_x(50)$,

wherein "x" is the designated particle size.

[0211] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have an average smoothness of at least 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 95, 97, 98, or 99 percent and/or not more than 99, 95, 90, 80, 70, 60, 50, 40, or 30 percent.

[0212] Average smoothness is determined by: (1) obtaining a secondary emission/EDT detector scanning electron microscopy (SEM) image of a representative sample of at least 20 microbeads, (2) on the SEM, selecting a square sample window centered at the center of the SEM that contains exactly 10 microbeads whose entire outer perimeters are clearly visible (i.e., not occluded), (3) binarizing the sample window by manual binarization with upper and lower thresholds chosen to match the exact shape of the darker regions of the particles, (4) for each of the 10 microbeads, selecting a square window at or near the center of the particle having length and width that are approximately 1/3 of the particle diameter (before binarizing the particle), (5) dividing the dark region area in the square window by the total area of the square window and multiplying the result by 100% to obtain 10 individual particle smoothness, and (5) averaging the 10 individual particle smoothness to obtain the average smoothness.

[0213] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have an average BET surface area of at least 0.1, 0.5, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 5.0, 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 6.0, 6.1, 6.2, 6.3, 6.4. 6.5, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, or 8.0 m^2/g and/or not more than 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2.5, 2, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, or 1.3 m^2/g as measured according to ISO 9277 using a Micromeritics ASAP 2020 instrument and krypton gas.

[0214] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a BET average pore size of at least 25, 30, 35, 40, 45, 50, 55, 56, 57, 58, or 59 angstroms and/or less than 75, 70, 65, or 60 angstroms as measured according to ISO 9277 and ISO 15901-02 using a Micromeritics ASAP 2020 instrument and nitrogen gas.

[0215] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a BJH average pore size of at least 50, 60, 70, 80, 90, 100, 110, 120, 125, or 130 angstroms and/or less than 200, 190, 180, 170, 160, 150, 140, or 130 angstroms as measured according to ISO 15901-02 using a Micromeritics ASAP 2020 instrument and nitrogen gas.

[0216] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a BJH surface area of pores from 17 to 3,000 angstroms of at least 0.5, 1.0, 1.1, 1.2, 1.3, 1.4. or 1.5 and/or less than 2.5, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, or 1.3 m2/g as measured according to ISO 15901-02 using a Micromeritics ASAP 2020 instrument and nitrogen gas.

[0217] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a BJH volume of pores from 17 to 3,000 angstroms of at least 0.001, 0.002, 0.003, or 0.004 and/or less than 0.1, 0.05, or 0.01 mL/g as measured according to ISO 15901-02 using a Micromeritics ASAP 2020 instrument and nitrogen gas.

[0218] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a true specific gravity of at least 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, or 0.9 and/or not more than 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, or 0.6 as measured by JIS Z8807-1976.

[0219] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a bulk specific gravity of at least 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, or 0.8 and/or not more than 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, or 0.5 as measured by JIS 1201-1.

[0220] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a polydispersity index of less than 0.8, 0.7, 0.6, 0.5, 0.4, or 0.3.

[0221] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a surfactant content of less than 200, 150, 100, 50, 20, 10, 7.5, 5, 2.5, or 1 ppmw.

[0222] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a plasticizer content of less than 200, 150, 100, 50, 20, 10, 7.5, 5, 2.5, or 1 ppmw.

[0223] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a butyric acid content of less than 500, 400, 300, 200, 100, 50, 20, 10, 7.5, 5, 2.5, or 1 ppmw.

[0224] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have an acetic acid content of less than 500, 400, 300, 200, 100, 50, 20, 10, 7.5, 5, 2.5, or 1 ppmw.

[0225] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a propionic acid content of less than 500, 400, 300, 200, 100, 50, 20, 10, 7.5, 5, 2.5, or 1 ppmw.

[0226] The butyric acid, acetic acid, and propionic acid contents of the hardened CE microbeads may be measured via gas chromatography ("GC"). Under one GC methodology, the butyric acid, acetic acid, and propionic acid contents may be measured by adding about 100 mg of the hardened CE microbeads to a tared 4-dram vial, followed by the addition of an internal standard solution comprising nonane in a 90:10 mixture of dichloromethane/methanol. A magnetic stir bar is placed in the vial, and the sample is stirred for two hours. After stirring, 8.0 mL of n-heptane is added dropwise to precipitate the polymer, and then the sample is vortexed. Approximately 100 mg of the supernatant is transferred to a GC vial, along with 100 µL of pyridine and 450 µL of BSTFA. The samples are heated at 80°C for 30 minutes and then cooled to room temperature before injection. Samples are chromatographed simultaneously on 100% dimethylpolysiloxane and 14% cyanopropyl-phenyl-methylpolysiloxane columns using temperature programming and flame ionization detection. Alternatively, a second GC methodology involves preparing samples by adding approximately 30 mg of hardened CE microbeads to a tared GC vial, followed by 200 µL of an internal standard solution comprising

decane in pyridine, and 1.0 mL of BSTFA. The vials re heated at 80°C for 30 minutes and then cooled to room temperature before injection. Samples are then chromatographed simultaneously on 100% dimethylpolysiloxane and 6% cyanopropyl-phenyl-methylpolysiloxane columns using temperature programming and flame ionization detection.

[0227] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a sulfuric acid content of less than 500, 400, 300, 200, 100, 50, 20, 10, 7.5, 5, 2.5, or 1 ppmw. The sulfuric acid content of the hardened CE microbeads may be measured by the following methodology. First, the tested sample is added to a titration cell and dissolved in a solvent for a total volume of 70 mL. Solvent blanks are also prepared for comparison purposes. The samples and blanks are then titrated with 0.05 N potassium hydroxide in methanol using an automatic titrator equipped with a combination glass potentiometric electrode. Acid number is calculated based on the sample weight and the KOH consumed in the sample minus the KOH consumed in the blank.

[0228] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have a CE content of at least 50, 55, 60, 65, 70, 75, 80, 85, 90, 91, 92, 93, 94, 95, 96, 97, 98, or 99 weight percent of the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect, including any class or subclass of these aspects. Additionally, or in the alternative, the hardened CE microbeads may have a CE content of less than 99.9, 99.5, 99, 98, 97, 96, 95, 94, 93, 92, 91, 90, 89, 88, 87, 86, or 85 weight percent of the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect, including any class or subclass of these aspects. In certain embodiments, the hardened CE microbeads may consist essentially of the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect, including any class or subclass of these aspects.

[0229] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads may contain an additional biodegradable cellulose ester that is different from the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect. In such embodiments, this additional cellulose ester can be cellulose acetate, which exhibits at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 60 days according to at least

one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0230] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads may contain at least 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 weight percent the additional biodegradable cellulose ester that is different from the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect. Additionally, or in the alternative, the hardened CE microbeads may contain less than 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 weight percent of the additional biodegradable cellulose ester that is different from the mixed cellulose ester of the first aspect, the second aspect, and/or the third aspect.

[0231] In one embodiment or in combination with any embodiment mentioned herein, the hardened CE microbeads have moisture content in one or more of the following amounts: (1) greater than 0 weight percent; (2) not more than 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or 0.05 weight percent; and (3) in the range of 0-10, 0-5, 0-4, 0-3, or 1.3 weight percent.

[0232] In one embodiment or in combination with any other embodiment mentioned herein, the hardened CE microbeads exhibit at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 56 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0233] In one embodiment or in combination with any other embodiment mentioned herein, the hardened CE microbeads exhibit at least 40% biodegradability, at least 45% biodegradability, or at least 50% biodegradability, or at least 55% biodegradability, at least 60% biodegradability, or at least 65% biodegradability, or at least 70% biodegradability, or at least 75% biodegradability, or at least 80% biodegradability, or at least 85% biodegradability, at 60 days according to at least one of the OECD 301B, OECD 301C, OECD 301D, OECD 301F, OECD TG 310, OECD TG 306, ISO 14852, or ISO 14851 test methods.

[0234] In one embodiment or in combination with any other embodiment mentioned herein, the hardened CE microbeads exhibit an oil absorption of at least 30, 35, 40, 45, 50, 55,

60, 65, 70, 75, 80, 85, 90, 95, or 100 mL per 100 g as measured using test method ASTM D281, wherein mineral oil is used instead of castor oil.

[0235] In one embodiment or in combination with any other embodiment mentioned herein, the hardened CE microbeads exhibit a zeta potential of at least -95, at least -90, at least -85, at least -80, at least -75, at least -70, at least -65, at least -60, at least -55, at least -50, or at least -45 mV. Additionally, or in the alternative, the hardened CE microbeads may exhibit a zeta potential of less than -5, less than -10, less than -15, less than -20, less than -25, less than -30, less than -35, less than -40, less than -45, less than -50, less than -55, less than -60, or less than -65 mV.

[0236] Zeta potential was measured by dispersing the microbeads in water by vortex mixing for 30 seconds. The microbead concentration was controlled at 0.5 mg/ml. Zeta potential tests were done on a Zetasizer Nano series, model ZEN 3600 instrument from Malvern Panalytical with a sample cell DTS1070. A Smoluchowski model is then used for Zeta potential calculation.

[0237] In one embodiment or in combination with any other embodiment mentioned herein, the hardened CE microbeads exhibit a haze transmission of at least 10, at least 15, at least 20, at least 25, at least 30, at least 35, at least 40, or at least 45 percent. Additionally, or in the alternative, the hardened CE microbeads may exhibit a haze transmission of less than 90, less than 85, less than 80, less than 75, less than 70, less than 65, less than 60, less than 55, less than 50, less than 45, less than 40 percent. The haze transmission may be measured using a BYK Glossmeter and a BYK Haze Gard I by forming an aqueous emulsion comprising 5 weight percent of the biodegradable beads.

[0238] In one embodiment or in combination with any other embodiment mentioned herein, the hardened CE microbeads exhibit a total transmission of at least 50, at least 60, at least 70, at least 75, at least 80, at least 85, at least 86, at least 87, at least 88, or at least 89 percent as measured using a BYK Haze-Gard I unit.

COSMETIC FORMULATIONS

[0239] The hardened CE microbeads produced by the processes disclosed herein may be used to produce a variety of cosmetic compositions. The cosmetic compositions may be

produced by: (1) providing a plurality of the hardened CE microbeads; (2) combining the hardened CE beads with one or more cosmetic additives to thereby form a pre-cosmetic mixture; and (3) forming the cosmetic composition from the pre-cosmetic mixture.

[0240] In one embodiment or in combination with any other embodiment mentioned herein, the cosmetic composition can comprise at least 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 weight percent of the hardened CE microbeads. Additionally, or in the alternative, the cosmetic composition can comprise less than 99, 90, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, or 5 weight percent of the hardened CE microbeads. For example, the cosmetic composition can comprise 0.1 to 90, 0.1 to 50, 0.1 to 30, 0.1 to 20, 0.1 to 15, 0.1 to 10, 0.1 to 5, 1 to 90, 1 to 50, 1 to 30, 1 to 20, 1 to 15, 1 to 10, or 1 to 5 weight percent of the hardened CE microbeads.

[0241] In one embodiment or in combination with any other embodiment mentioned herein, the cosmetic composition can be a foundation, a sunscreen, a lipstick, a mascara, an eye shadow, a lotion, a dry shampoo, a liquid shampoo, a body wash, a lotion, a hair conditioner, a skin moisturizer, a face wash, a tablet, a foot powder, a baby powder, a shaving cream, or a shaving gel.

[0242] In one embodiment or in combination with any other embodiment mentioned herein, the cosmetic composition can be a loose powder, a compacted powder, a gel, an emulsion, a liquid, or an aerosol.

[0243] In one embodiment or in combination with any other embodiment mentioned herein, the cosmetic composition comprises at least 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 99 weight percent of at least one, two, three, four, or five cosmetic additives. Additionally, or in the alternative, the cosmetic composition can comprise less than 99, 95, 90, 85, 80, 75, 70, 65, 60, 55, or 50 weight percent of at least one, two, three, four, or five cosmetic additives. For example, the cosmetic composition can comprise 1 to 99, 1 to 95, 1 to 90, 1 to 85, 1 to 80, 5 to 99, 5 to 95, 5 to 90, 5 to 85, 10 to 99, 10 to 95, 10 to 85, 10 to 80, 15 to 99, 15 to 95, 15 to 90, 15 to 85, or 15 to 80 weight percent of at least one, two, three, four, or five cosmetic additives.

[0244] Generally, the cosmetic additives can include a solvent, a colorant, an oil, a wax, a fatty acid, an alcohol, an ester, a hydrocarbon, a silicone oil, a surfactant, a metal soap, a moisturizer, a thickener, a UV absorber, an antioxidant, an oil absorbent, an exfoliant, water, or a combination thereof.

[0245] In one embodiment or in combination with any other embodiment mentioned herein, the colorant comprises a pigment (e.g., an organic pigment and/or an inorganic pigment) and/or a dye.

[0246] In one embodiment or in combination with any other embodiment mentioned herein, the oil comprises triglycine, soybean oil, cocoa butter, palm oil, palm kernel oil, hardened oil, and/or hardened castor oil.

[0247] In one embodiment or in combination with any other embodiment mentioned herein, the wax comprises carnauba wax, candelilla wax, lanolin, lanolin, candelilla wax, cotton wax, Montan wax, Kapok wax, lanolin acetate, lanolin, and/or lanolin fatty acid isopropyl.

[0248] In one embodiment or in combination with any other embodiment mentioned herein, the fatty acid comprises lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, oleic acid, undecylenic acid, linoleic acid, eicosapentaenoic acid (EPA), and/or docosahexaenoic acid.

[0249] In one embodiment or in combination with any other embodiment mentioned herein, the alcohol comprises cetyl alcohol, stearyl alcohol, isostearyl alcohol, 2-octyldodecanol, lauryl alcohol, behenyl alcohol, myristyl alcohol, oleyl alcohol, and/or cetostearyl alcohol.

[0250] In one embodiment or in combination with any other embodiment mentioned herein, the ester comprises isopropyl myristate, 2-octyldodecyl myristate, cetyl 2-ethylhexanoate, diisostearyl malate, tripropylene glycol dineopentate, isononyl isononanoate, isotorideyl isononanoate, cetyl octanoate, isocetyl palmitate, butyl stearate, hexyl laurate, myristyl myristate, decyl oleate, hexyl decyl dimethyloctanate, cetyl lactate, myristyl lactate, lanolin acetate, isosetyl stearate, isosetyl isostearate, cholesteryl 12-hydroxystearate, di-2-ethylhexanoic acid ethylene glycol, dipentaerythritol fatty acid ester, monoisostearate N-

alkylglycol, dicaprate neopentyl glycol, di-2-heptylundecanoate glycerin, tri-2-ethylhexanoate trimethylpropane, Trimethylolpropane triisostearate, pentaerythritol tetra-2-ethylhexanoate, glycerin tri-2-ethylhexanoate, glycerin trioctanoate, glycerin triisopalmitate, trimethylolpropane triisostearate, ethylhexyl palmitate, glycerin trimyristate, tri-2-heptylundecanoic acid glyceride, castor oil fatty acid methyl ester, oleyl oleate, acetoglyceride, 2-heptylundecyl palmitate, diisobutyl adipate, N-lauroyl- L-Glutamic hexyldecyl palmitate, adipate hexyldecyl, diisopropyl sebacate, ethylhexyl succinate, and/or triethyl citrate.

[0251] In one embodiment or in combination with any other embodiment mentioned herein, the hydrocarbon comprises paraffin, petrolatum, and/or microcrystalline wax.

[0252] In one embodiment or in combination with any other embodiment mentioned herein, the surfactant comprises an anionic surfactant, a cationic surfactant, and/or a nonionic surfactant.

[0253] In one embodiment or in combination with any other embodiment mentioned herein, the thickener comprises guar gum, pectin, starch, gelatin, collagen, cellulosic derivatives, and/or mannan.

EXPERIMENTS

I. Experiment Set 1

[0254] CE dopes were prepared as shown in TABLE 1 below to determine the solubility of CE, such as cellulose acetate butyrate (CAB), Example 1, in a solvent system containing ethyl acetate (EA), n-propanol (nPrOH), and water. The preparation of Ex 1 is shown below.

[0255] Example 1: Cellulose Acetate Butyrate (DS_{Ac}=1.87, DS_{Bu}=1.2, DS_{OH}=0.91 M_w=90766)

[0256] Cellulose and acid mixture [cellulose (4.3 parts) and AcOH (11.8 parts)] was added to an agitated reactor and soaked unheated then, the mixture was heated to 55°C. Some amount of sulfuric acid was added and the reactor was cooled to 30°C. Following, a mixture of Ac_2O (8.9 parts) and Bu_2O (5.6 parts) was added and the mixture cooled to around 9°C with agitation. Additional sulfuric acid was added to a total of 0.6 parts and the resulting reaction mixture was warmed to 50°C. To this reaction mixture was added a mixture of BuOH (18 parts) and H_2O

(7.4 parts). The mixture was then stirred at 68°C for 1020 min, but with the addition of a mixture $Mg(OAc)_2$ (0.61 parts), BuOH (6.9 parts) and H_2O (2.7 parts) after 80 min. After the full length of time, the mixture was fully neutralized with a solution of $Mg(OAc)_2$ (0.86 parts), BuOH (1.5 parts) and H_2O (4.8 parts). The mixture was then precipitated in water, washed and dried by common methods.

Degree of Substitution

[0257] The degree of substitution for the substituents on the cellulose ester backbone is calculated using proton nuclear magnetic resonance spectroscopy. Gel permeation chromatography is performed on cellulose esters in stabilized tetrahydrofuran. The instrument is an Agilent 1260 which consists of a degasser, isocratic pump with a flow rate of 1.0 milliliters per minute, autosampler with an injection volume of 25 microliters, a column oven set at 28°C and a refractive index detector at 28°C. The column set consists of an Agilent PLgel 5 micron guard, Mixed-C and Oligopore in series. The system is calibrated with monodisperse polystyrene standard ranging from approximately 4 million to 162 molecular weight. The sample is prepared by weighing approximately 25 milligrams of sample in 10 milliliters of solvent with the addition of 10 microliters of toluene to be used as a flow rate marker, add a stir bar into an 8-dram screw cap vial and stir until dissolution.

Molecular Weight

[0258] The molecular weight is determined by gel permeation chromatography. Gel permeation chromatography is performed on cellulose esters in stabilized tetrahydrofuran. The instrument is an Agilent 1260 which consists of a degasser, isocratic pump with a flow rate of 1.0 milliliters per minute, autosampler with an injection volume of 25 microliters, a column oven set at 28°C and a refractive index detector at 28°C. The column set consists of an Agilent PLgel 5 micron guard, Mixed-C and Oligopore in series. The system is calibrated with monodisperse polystyrene standard ranging from approximately 4 million to 162 molecular weight. The sample is prepared by weighing approximately 25 milligrams of sample in 10 milliliters of solvent with the addition of 10 microliters of toluene to be used as a flow rate marker, add a stir bar into an 8-dram screw cap vial and stir until dissolution.

Preparation of CE Dopes

[0259] The CE dopes were prepared by charging a dry, 250 mL, 1-neck round-bottomed flask equipped with a magnetic stirrer with the respective amount of the solvent systems as shown in TABLE 1. The solvent systems were stirred, and the flask was then charged with the respective amount/type of CAB. The CAB was charged into the flask by slowly metering the solids at a rate such that the stirring vortex was able to move the solid particles into the solvent system without forming a large mass of powder at the top of the liquid phase. This mixture of solvent and CAB was stirred at room temperature for 45 minutes. If the mixture became homogeneous in this time period, the Dope was determined to be "soluble." If the solid particles remained undissolved in the solvent system at 60 minutes, the Dope was determined to be "insoluble."

[0260] In Dopes 1-1, 1-2, and 1-3, the solvent system contained ethyl acetate and n-propanol in varying amounts, but did not contain water. In Dopes 1-1a, 1-2a, and 1-3a, water was added to the solvent system. That is, the solvent systems of Dopes 1-1 and 1-1a, 1-2 and 1-2a, and 1-3 and 1-3a contained the same amount of ethyl acetate and n-propanol, and the only difference between the respective Dopes was the addition of water.

[0261] In Dope 1-4a, the amount of CAB contained in the CE dope was increased to match its % CAB by mass to the % CAB by mass of the Dopes that did not contain water (i.e., Dopes 1-1, 1-2, and 1-3).

TABLE 1

Dope	EA (g)	nPrOH (g)	Water (g)	CAB (g)	EtOAc (%)	nPrOH (%)	Water (%)	CAB (%)	Solubility
1-1	80.0	5.0	0	15.0	80.0	5.0	0	15.0	NO
1-1a	80.0	5.0	8.0	15.0	74.1	4.6	7.4	13.9	NO
1-2	75.0	10.0	0	15.0	75.0	10.0	0	15.0	NO
1-2a	75.0	10.0	8.0	15.0	69.4	9.3	7.4	13.9	YES
1-3	70.0	15.0	0	15.0	70.0	15.0	0	15.0	NO
1-3a	70.0	15.0	8.0	15.0	64.8	13.9	7.4	13.9	YES
1-4a	70.0	15.0	8.0	16.2	64.8	13.9	7.4	15.0	YES

[0262] Notably, CE dopes that did not contain water were unable to solubilize the CE contained therein. For example, Dope 1-1 provided a chunky and non-homogeneous mixture,

Dopes 1-2 and 1-3 initially provided stirrable slurries but became chunky and non-homogeneous after several minutes.

[0263] In comparison, Dope 1-1a provided a stirrable, rather than chunky, slurry. Dopes 1-2a and 1-3a provided homogeneous mixtures in which the CE was dissolved in the solvent system within 3 minutes.

[0264] As shown in Dope 1-4a, increasing the mass of the CE contained in the CE dope also provided a homogenous mixture in which the CE was dissolved in the solvent system within 3 minutes. That is, increasing the % CAB of the CE dope did not appear to negatively impact the solubility of the CE in the solvent system.

II. Experiment Set 2

Table 2 - Components

Material	Abbreviation	MW, g/mol	Den, g/cc
Aqueous Phase			
Ethyl Acetate	EtOAc	88.106	0.902
Methyl Cellulose	MC	--	0.25
DI Water	H2O	18.015	1.00
Tween-28 Surfactant	T-28		0.98
Organic Phase			
Ethyl Acetate	EtOAc	88.106	0.902
Cellulose Acetate Butryate	CAB		
Ethanol	EtOH	46.069	0.78945
DI Water	H2O	18.015	1.00
Drowning Bucket (5 Gallon)			
DI Water (in bucket)	H2O	18.015	1.00

Table 3 – Emulsion Formulation (180 g CAB basis):

Material	Mass, g	Mass fraction	Wt.% (based on drowned liquid)	n, mol	
Aqueous Phase		(based on emulsion)			
Ethyl Acetate	249	6.02%	1.65%	2.826	
Methyl Cellulose	13.5	0.33%	0.09%		
DI Water	2559	61.88%	17.00%	142.048	
Tween-28 Surfactant	27	0.65%	0.18%		
	2848.5				
Organic Phase					
Ethyl Acetate	885	21.40%	5.88%	10.045	CAB in dope = 14.0%
Cellulose Acetate Butyrate	180	4.35%	1.20%		CAB in total = 4.35%
Ethanol	144	3.48%	0.96%	3.126	
DI Water	78	1.89%	0.52%	4.330	
	1287.0	100%	27.47%		
Drowning Bucket (5 Gallon)					
DI Water (in bucket)	10917.72		72.53%	606.035	Water/(Aq. Phase + Org. Phase Mix)
Total Emulsion	4135.5		100%		2.64

Example 2

[0265] CE dope is prepared by adding EtOAc and EtOH to a stirred lab reactor with 2 pitched blade impellers and 2 baffles. Under agitation, slowly add the cellulose butyrate (CAB)

powder. Heat to 35-40 °C while mixing for 1-2 hours, then cool to room temperature and continue mixing until all the CAB is fully dissolved to form the CE Dope.

[0266] The aqueous phase and emulsion are prepared as follows: charge EtOAc to a stirred tank and stir at 300 RPM. Add the MC, then the DI water, and then T-28 under agitation until completely dissolved to form the aqueous phase. Add the CE Dope and the aqueous phase to a charge tank to form an emulsion. Circulate the emulsion through the IKA flow cell at 4000 RPM at an equivalent shear time of about 1.67 minutes in the IKA to form a sheared emulsion. The sheared emulsion is then transferred into a drowning bucket. Charge DI water to the drowning bucket and mix for 2 hours. Take a subset of the fully drowned material and centrifuge the contents @ 3000 RPM for 15 minutes to provide mother liquor and solids. Wash with DI water and centrifuge two more times to provide solids. Dry the solids in an oven at 95-100 °C under vacuum overnight. The resulting powder was analyzed for particle size and SEM analysis. The PS Light Scattering D(4,3) was ~6.3 microns, D50 was 5.8 microns, and about 1.3% of the particles were below 1 micron.

Example 3

[0267] Example 2 was repeated except the emulsion was circulated through the IKA flow cell at 4600 RPM and an equivalent shear time of about 1.5 minutes in the IKA, which resulted in a powder having a PS Light Scattering D(4,3) was 8.81 microns, D50 was 8.05 microns, and about 1.37% of the particles were below 1 micron.

Example 4

[0268] Example 2 was repeated a third time except the emulsion was circulated through the IKA flow cell at 4000 RPM and an equivalent shear time of about 1 minute in the IKA, which resulted in a powder having a PS Light Scattering D(4,3) was 10.4 microns, D50 was 9.65 microns, and about 2.0% of the particles were below 1 micron.

Example 5

[0269] Example 2 was repeated except that prior to drowning, the sheared emulsion is stripped by boiling out ethyl acetate-ethanol-water azeotrope (60:15:25) under vacuum pressure sufficient to keep the temperature below 50°C. The overall volume was held constant

such that water was added at the same volumetric rate that the azeotrope was removed to avoid agglomerating the particles. The stripped emulsion is then transferred into a drowning bucket. The composition of the condensate is shown below Shown below are the amounts of EtOAc in each condensate cut that is removed. Based on the amount of condensate collected and the levels of EtOAc in each cut, approximately 60-75% of the total EtOAc was removed when the condensate composition shifted toward mainly water.

Table 4 - Example 5 Stripping Data for Condensate Composition

Sample	Condensate removed	EtOAc	Ethanol	Water	Comments
	mL - approx	wt.%	wt.%	wt.%	
Cond. 1	125	90.23	2.96	6.81	Condensate Cut #1 - Mainly EtOAc
Cond. 2	300	90.01	3.00	6.99	Condensate Cut #2 - Mainly EtOAc
Cond. 3	450	1.94	6.68	91.38	Condensate Cut #3 - Mainly water, most EtOAc has been removed
Cond. 4	--	90.33	2.67	7.00	Top layer of total condensate sample
Cond. 5	--	6.55	6.04	87.41	Bottom layer of total condensate sample

[0270] Example 5 was repeated (Examples 6-11) except that the amount of EtOAc removed was varied for Examples 6-8, and the stripping speed was varied for Examples 9-11. Also, the reduction in the amount of drowning water compared to Example 2, which did not include a stripping step, is shown in Table 5.

Table 5 – Reduction in Drowning Water if Stripping Performed

	% EtOAc Removed	% of Example 2 Drowning Water Required	Comments
Example 5	60-75%	25-40%	
Example 6	60-75%	30%	15% level drowning water led to agglomeration
Example 7	~90%	--	Some agglomeration occurred in stripped emulsion at 90% removal
Example 8	75%	25%	Repeat Example 7, but limit drowning water to 25%, no agglomeration was observed.
Example 9	75%	25%	Slow stripping method was used to remove EtOAc. No agglomeration was observed.
Example 10	75%	25%	Repeat of Example 9. No agglomeration was observed.
Example 11	75%	25%	Fast stripping method was used to remove EtOAc quickly. No agglomeration was observed.

[0271] As show in Table 5, the data demonstrates that EtOAc could be reduced such that the amount of water used in drowning as compared to Example 2 where no stripping step was performed could be reduced to at least 25% of the original amount and still produce the target particle size with spherical particles.

[0272] 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."

[0273] Every document cited herein, if any, 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.

What is claimed is:

1. A method of making cellulose ester (CE) microbeads, the method comprising:

(a) combining a CE dope and an aqueous mixture to form an initial emulsion comprising a dispersed phase and a continuous phase, wherein the CE dope comprises a CE dissolved in a solvent;

(b) converting at least a portion of the initial emulsion into a dispersion comprising a solid phase and a liquid phase, wherein the solid phase comprises pre-hardened CE microparticles comprising at least a portion of the CE and at least a portion of the solvent, and the liquid phase comprises at least a portion of the solvent and at least a portion of the aqueous mixture;

(c) removing at least some of the solvent from the liquid phase to form a removed solvent and a solvent-depleted dispersion comprising the pre-hardened CE microparticles; and

(d) converting at least a portion of the pre-hardened CE microparticles in the solvent-depleted dispersion into hardened CE microbeads.

2. The method of Claim 1, wherein the converting of step (d) is performed by contacting the pre-hardened CE microparticles with a water-containing drowning liquid to form a hardened dispersion comprising the hardened CE microbeads and the drowning liquid.

3. The method of Claims 1 or 2, further comprising separating the solvent-depleted dispersion into a solid-enriched fraction and a separated mother liquor stream.

4. The method of Claim 3, further comprising distilling the separated mother liquor stream to produce a solvent-enriched stream and a water-enriched stream.

5. The method of Claim 4, further comprising recycling at least a portion of the solvent-enriched stream for use in forming the CE dope and/or for use as at least a portion of the aqueous mixture.

6. The method of Claims 4 or 5, further comprising recycling at least a portion of the water-enriched stream for use as at least a portion of the aqueous mixture and/or for use in the converting of step (d).

7. The method of Claims 4-6, wherein the solvent-enriched stream comprises one or more of the following components:

a C1-C4 alkyl acetate;

a C1-C4 alcohol; and

water.

8. The method of Claim 7, wherein the solvent-enriched stream comprises: (a) the C1-C4 alkyl acetate in an amount of at least 10, 25, 50, 60, or 70 weight percent and/or not more than 99, 95, 90, 85, or 80 weight percent; and/or (b) the C1-C4 alcohol in an amount of at least 1, 2, 4, 6, 8, or 10 weight percent and/or not more than 80, 60, 40, 30, 20, or 15 weight percent; and/or (c) water in an amount of at least 1, 2, 4, 6, or 8 weight percent and/or not more than 50, 40, 30, 20, or 10 weight percent.

9. The method of Claims 4-8, wherein the solvent-enriched stream comprises an azeotrope of water and at least one other solvent component.

10. The method of Claim 9, wherein the azeotrope is a water/alcohol azeotrope, a water/alkyl acetate azeotrope, or both a water/alcohol azeotrope and a water/alkyl acetate azeotrope.

11. The method of Claims 9 or 10, wherein the solvent-enriched stream comprises: (a) a plurality of binary azeotropes and/or (b) less than 10 weight percent, less than 1 weight percent, less than 0.1 weight percent, or 0.0 weight percent of a ternary azeotrope.

12. The method of Claims 9-11, wherein the solvent-enriched stream contains three total binary azeotropes, comprising a water/alcohol azeotrope, a water/alkyl acetate azeotrope, and an alcohol/alkyl acetate azeotrope.

13. The method of Claims 2-12, wherein a volume ratio of the drowning liquid to the solvent-depleted dispersion is less than 2.5:1.

14. The method of Claims 2-13, wherein the drowning liquid consists of, consists essentially of, or comprises water.

15. The method of Claims 2-14, wherein the drowning liquid is added to the solvent-depleted dispersion in an amount such that the weight ratio of the drowning liquid to the solvent-depleted dispersion is at least 0.1:1, 0.25:1, 0.5:1, 0.75:1, 1:1, 1:25:1, 1.5:1, or 1.75:1 and/or not more than 5:1, 4:1, 3:1, 2:1, 1.5:1, 1:1, or 0.5:1.

16. The method of Claims 1-15, wherein the removing of step (c) is performed by pervaporation, crossflow membrane filtration, flash pot, spray pot, or wiped film evaporation, and/or the removing of step (c) reduces the solvent in the dispersion by at least 30 percent, at least 50 percent, at least 75 percent, at least 90 percent, between 30 and 90 percent, or between 50 and 75 percent by weight.

17. The method of Claims 1-16, wherein the solvent-depleted dispersion has a solids content of at least 3, 4, 5, or 6 and/or not more than 40, 30, 20, or 10 weight percent.

18. The method of Claims 1-17, further comprising distilling at least a portion of the removed solvent of step (c) to produce a removed solvent-enriched stream.

19. The method of Claims 3-18, further comprising distilling the removed solvent of step (c) along with the separated mother liquor stream that has been separated from the solvent-depleted dispersion, which together forms a combined solvent-rich stream.

20. The method of Claim 19, further comprising recycling at least a portion of the combined solvent-enriched stream for use in the forming of the CE dope and/or for use in forming the aqueous mixture.

21. The method of Claims 1-20, wherein the CE has a hydroxyl degree of substitution of greater than about 0.7.

22. The method of Claims 1-21, wherein the CE comprises cellulose diacetate, cellulose acetate butyrate, or cellulose acetate propionate.

23. The method of Claims 1-22, wherein the hardened CE microbeads exhibit one or more of the following:

a. a D50 particle size of at least 0.5, 1, 2, 4, 6, or 8 microns and/or not more than 100, 75, 50, 25, 20, 15, or 10 microns;

b. an average sphericity of at least at least 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 95, 97, 98, or 99 percent and/or not more than 99, 95, 90, 80, 70, 60, 50, 40, or 30 percent; and

c. an average smoothness of at least 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 95, 97, 98, or 99 percent and/or not more than 99, 95, 90, 80, 70, 60, 50, 40, or 30 percent.

24. The method of Claims 1-23, wherein the hardened CE microbeads have a moisture content: (a) of greater than 0 weight percent and not more than 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or 0.05 weight percent; or (b) in the range of 0-10, 0-5, 0-4, 0-3, or 1-3 weight percent.

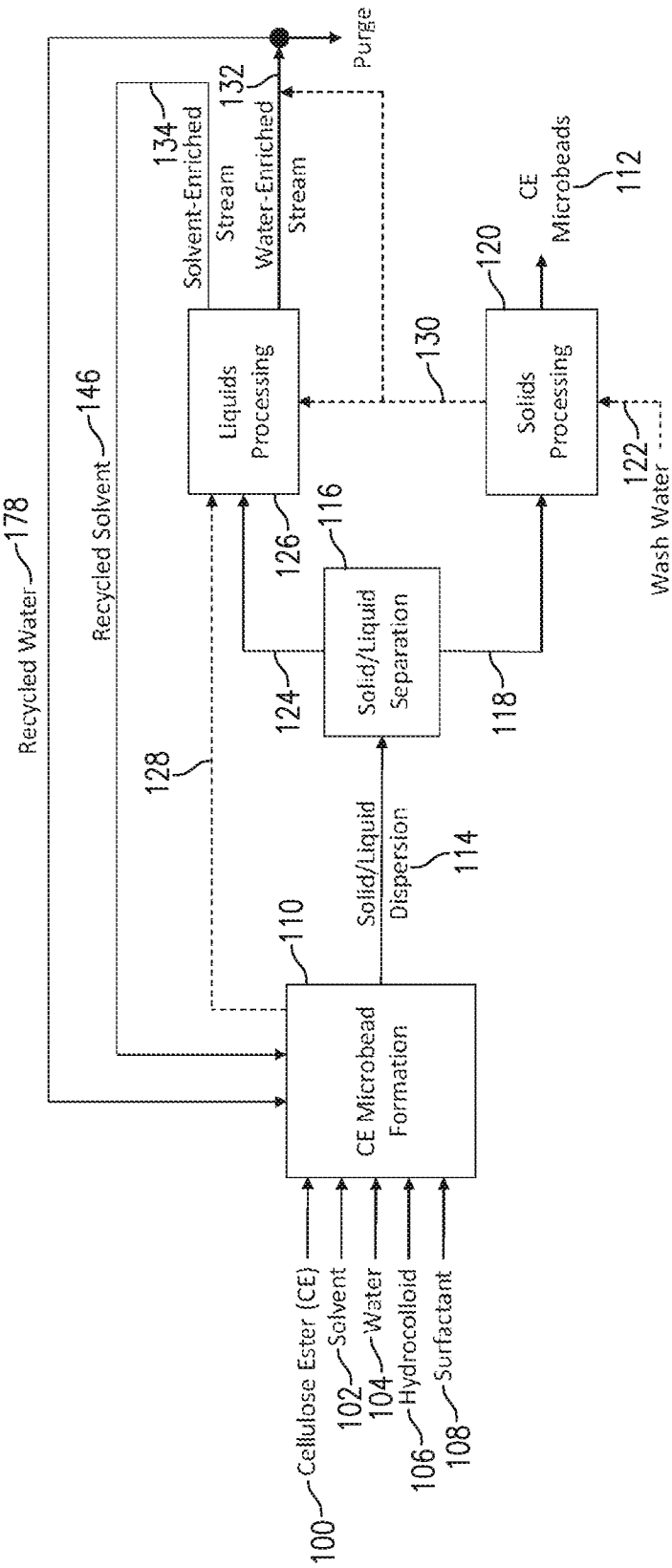
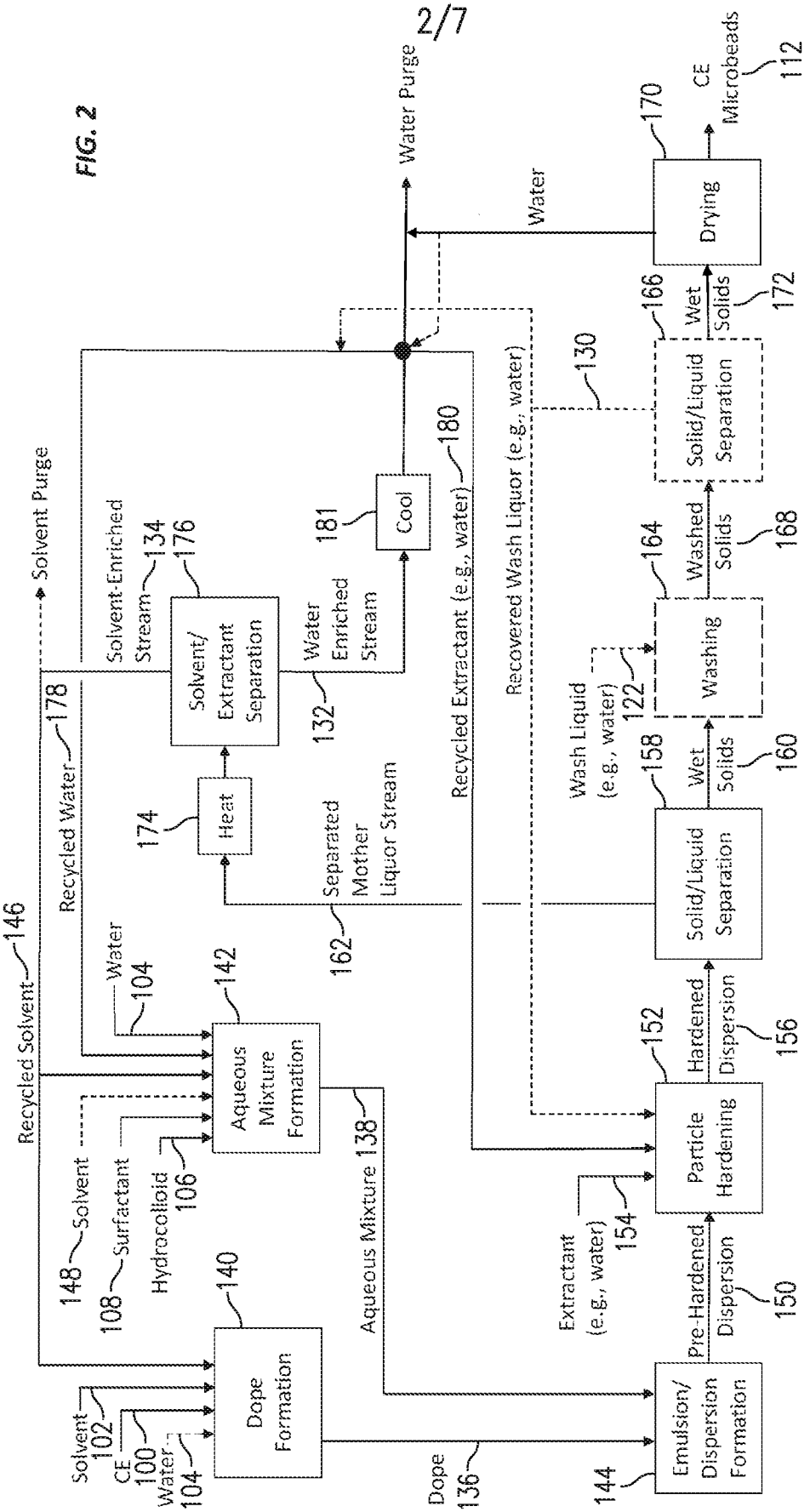

Cellulose Ester (CE)
Solvent
Water
Hydrocolloid
Surfactant
100
102
104
106
108
CE Microbead Formation
110
Solid/Liquid Dispersion
114
Solid/Liquid Separation
116
118
124
126
Liquids Processing
128
130
Solids Processing
120
CE Microbeads
112
122
Wash Water
Solvent-Enriched Stream
134
Water-Enriched Stream
132
Purge
Recycled Solvent
146
Recycled Water
178

FIG. 1

FIG. 2


Solvent 102
CE 100
Water 104
Dope Formation 140
Dope 136
Emulsion/ Dispersion Formation 144
Pre-Hardened Dispersion 150
Particle Hardening
Hardened Dispersion 156
Solid/Liquid Separation
Wet Solids 160
Washing
Washed Solids 168
Solid/Liquid Separation
Wet Solids 172
Drying
CE Microbeads 112
Water Purge
Water
Recycled Solvent 146
Solvent 148
Surfactant 108
Hydrocolloid 106
Aqueous Mixture Formation 142
Aqueous Mixture 138
Extractant (e.g., water) 154
Wash Liquid (e.g., water) 122
Recovered Wash Liquor (e.g., water) 130
Recycled Extractant (e.g., water) 180
Cool 181
Water Enriched Stream 132
Solvent/ Extractant Separation 176
Solvent-Enriched Stream 134
Heat 174
Separated Mother Liquor Stream 162
Recycled Water 178
Solvent Purge

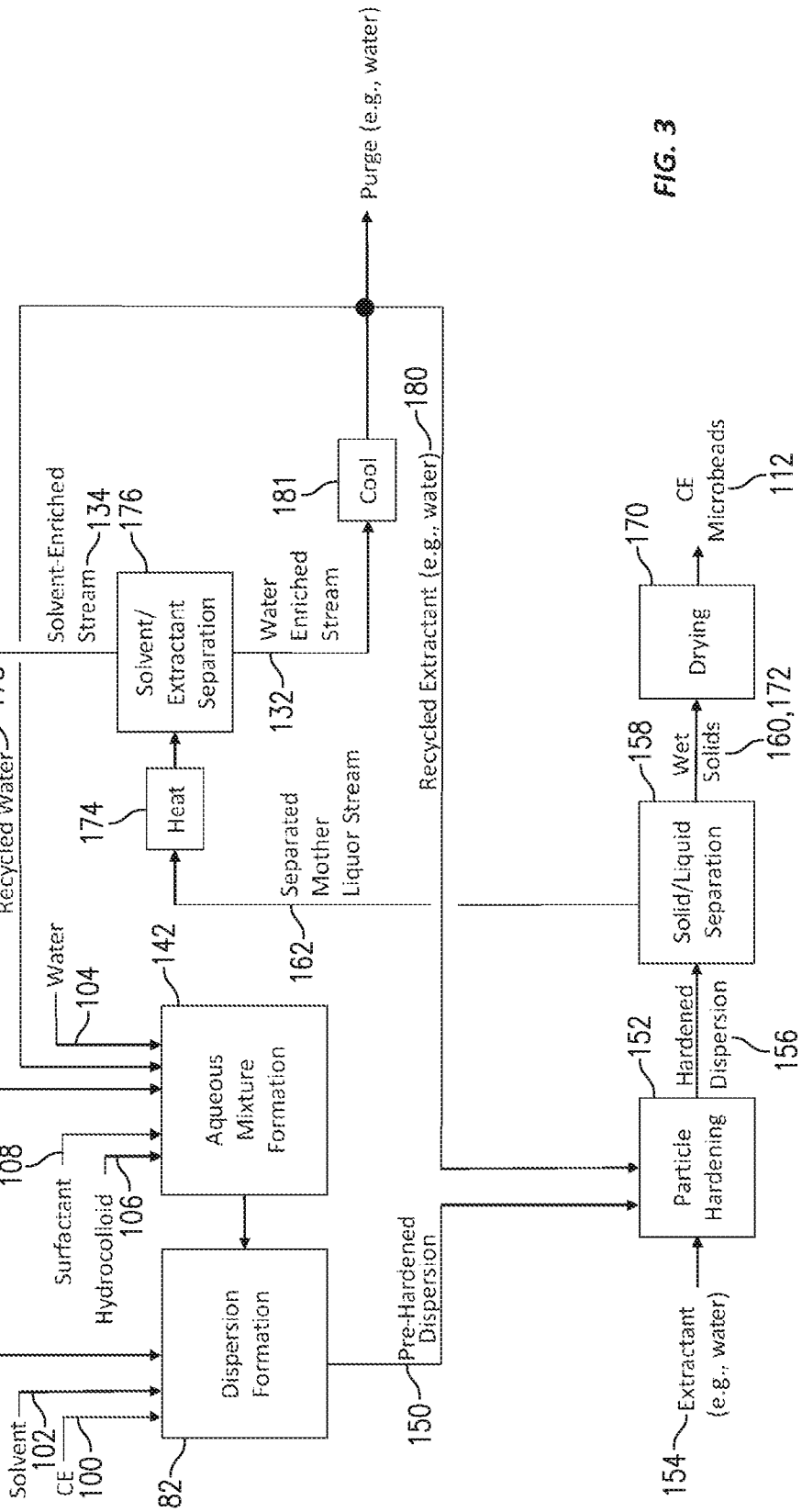

Purge (e.g., water)
Solvent-Enriched Stream
134
176
Solvent/ Extractant Separation
Water Enriched Stream
132
181
Cool
180
Recycled Extractant (e.g., water)
Recycled Water
178
Recycled Solvent
146
Water
104
142
Aqueous Mixture Formation
Separated Mother Liquor Stream
162
174
Heat
108
Surfactant
Hydrocolloid
106
Dispersion Formation
Solvent
102
CE
100
182
Pre-Hardened Dispersion
150
Solid/Liquid Separation
158
Wet Solids
160,172
Drying
170
CE Microbeads
112
Hardened Dispersion
156
152
Particle Hardening
Extractant (e.g., water)
154

FIG. 3

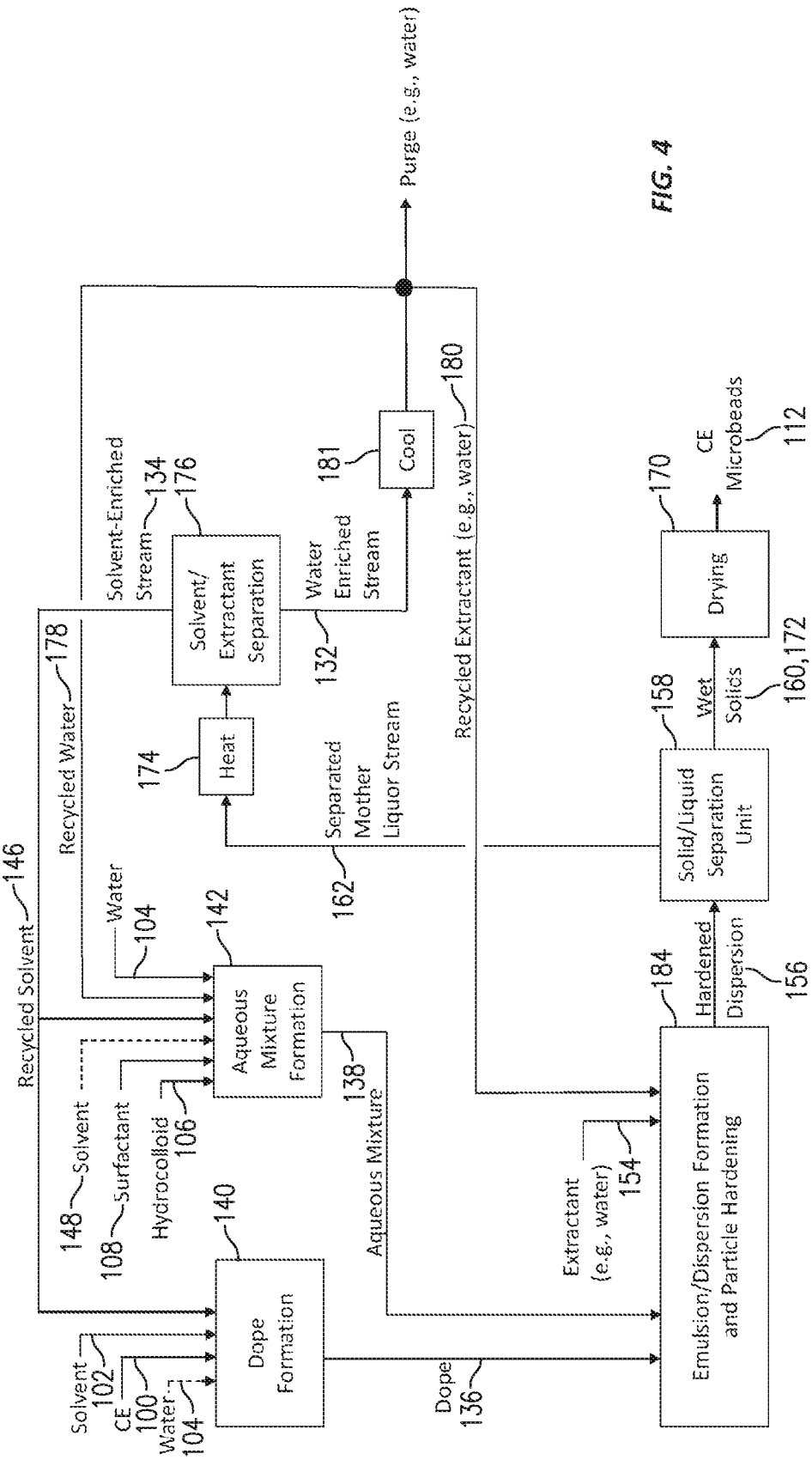

Purge (e.g., water)
Solvent-Enriched Stream 134
176
Solvent/ Extractant Separation
Water Enriched Stream 132
181
Cool
180
Recycled Extractant (e.g., water)
CE Microbeads 112
170
Drying
Recycled Water 178
Recycled Solvent 146
Water 104
142
Aqueous Mixture Formation
174
Heat
Separated Mother Liquor Stream 162
158
Wet Solids 160,172
Solid/Liquid Separation Unit
184
Hardened Dispersion 156
148 Solvent
108 Surfactant
Hydrocolloid 106
140
Dope Formation
Aqueous Mixture 138
Extractant (e.g., water) 154
Emulsion/Dispersion Formation and Particle Hardening
Solvent 102
CE 100
Water 104
Dope 136

FIG. 4

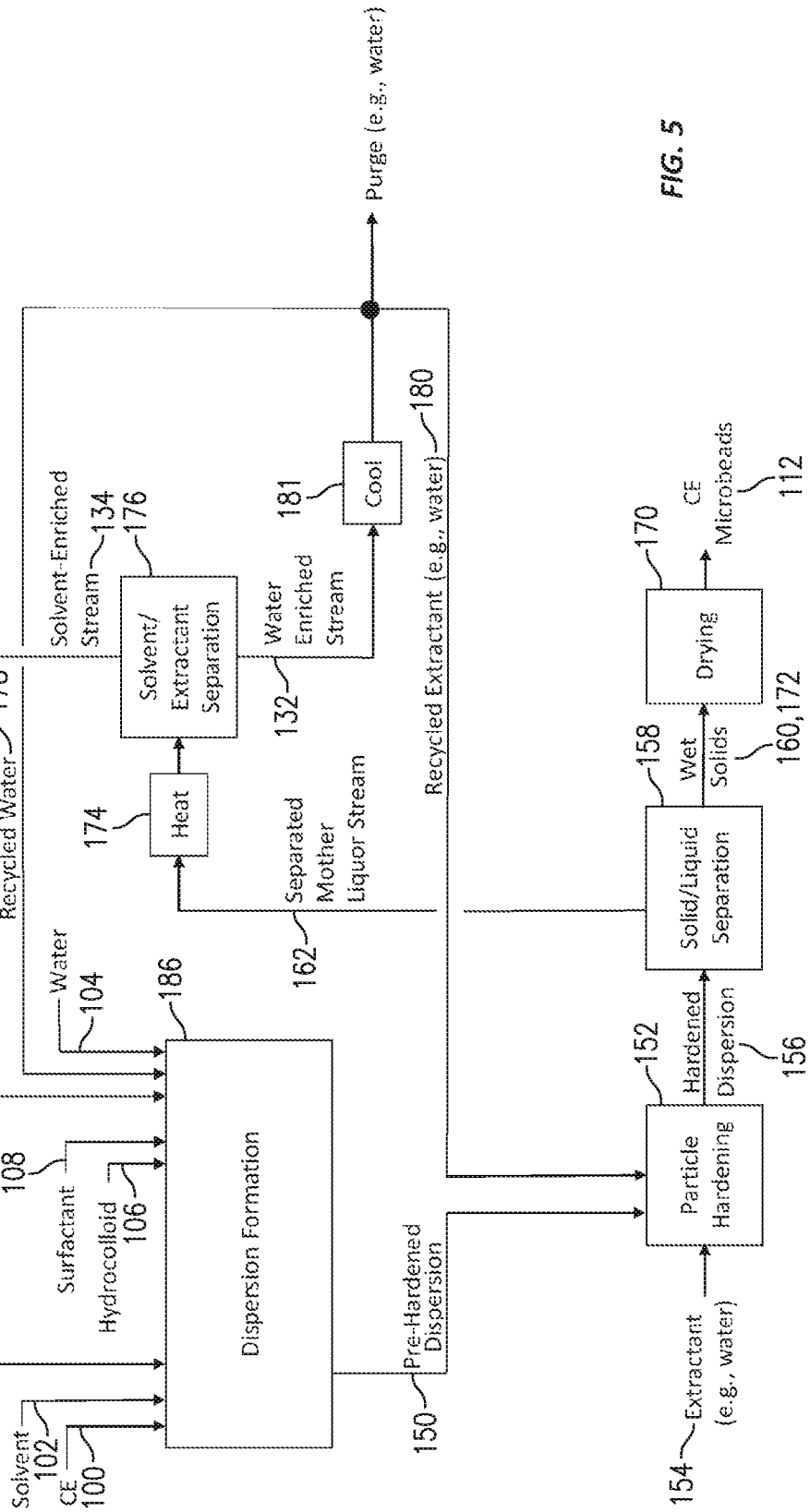

Purge (e.g., water)
Solvent-Enriched Stream
134
176
Solvent/ Extractant Separation
Water Enriched Stream
132
181
Cool
180
Recycled Extractant (e.g., water)
Recycled Water
178
Recycled Solvent
146
Water
104
186
Heat
174
Separated Mother Liquor Stream
162
Solid/Liquid Separation
158
Wet Solids
160,172
Drying
170
CE Microbeads
112
Surfactant
108
Hydrocolloid
106
Dispersion Formation
Pre-Hardened Dispersion
150
Particle Hardening
152
Hardened Dispersion
156
Solvent
102
CE
100
Extractant (e.g., water)
154

FIG. 5

FIG. 6

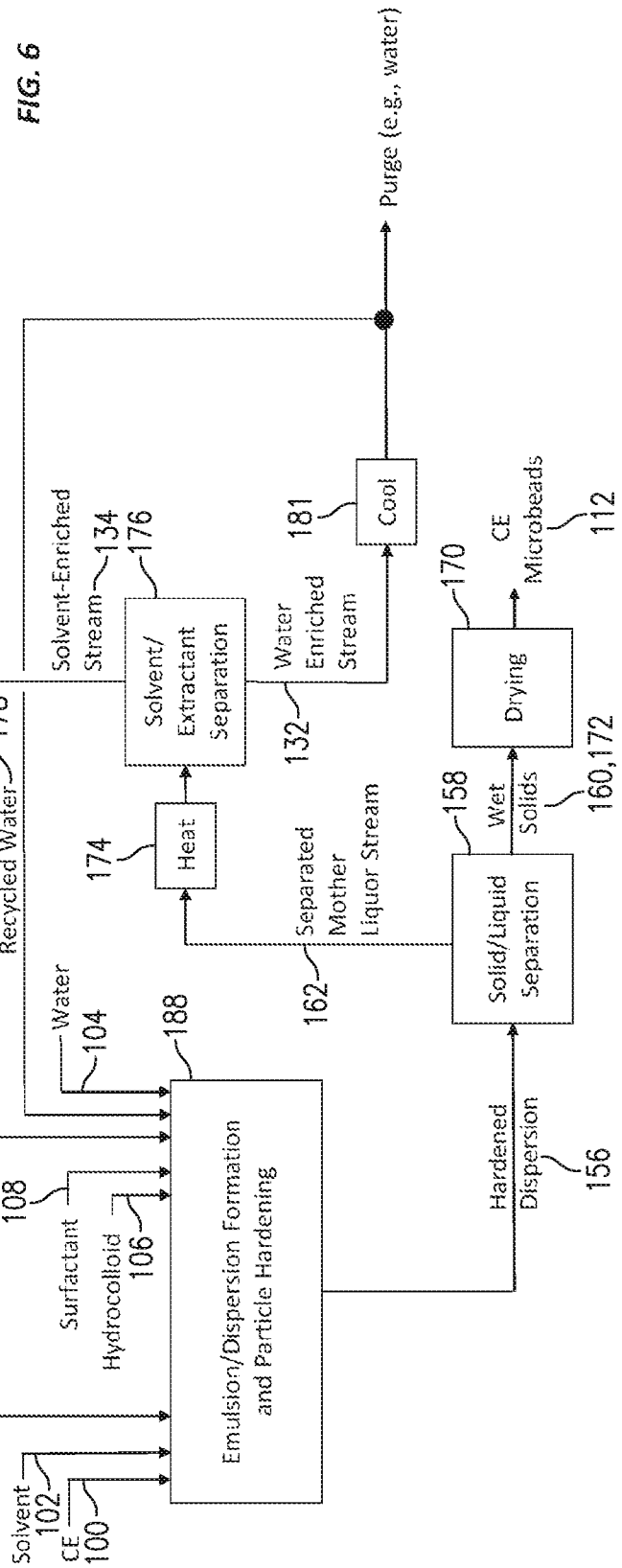
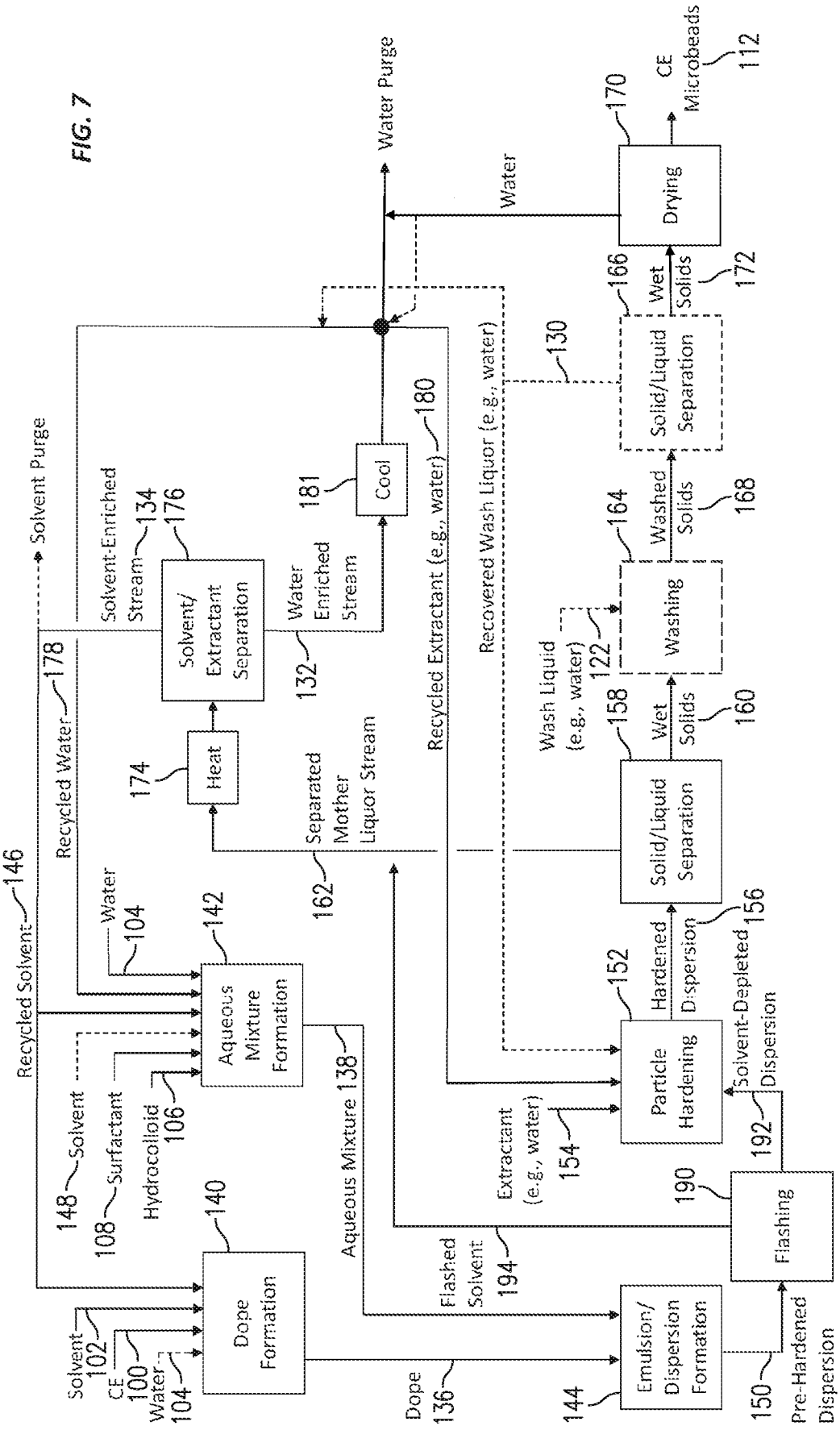

Solvent
102
CE
100
Surfactant
108
Hydrocolloid
106
Recycled Solvent
146
Water
104
Recycled Water
178
188
Emulsion/Dispersion Formation and Particle Hardening
Hardened Dispersion
156
Solid/Liquid Separation
158
Wet Solids
160,172
Drying
170
CE Microbeads
112
Separated Mother Liquor Stream
162
Heat
174
Solvent/ Extractant Separation
176
Solvent-Enriched Stream
134
Water Enriched Stream
132
Cool
181
Purge (e.g., water)

FIG. 7


Solvent 102
CE 100
Water 104
Dope Formation 140
Dope 136
Emulsion/ Dispersion Formation 144
Pre-Hardened Dispersion 150
Flashing
Flashed Solvent 194
Solvent-Depleted Dispersion 192
Particle Hardening
Hardened Dispersion 156
Extractant (e.g., water) 154
Aqueous Mixture 138
Aqueous Mixture Formation 142
Solvent 148
Surfactant 108
Hydrocolloid 106
Recycled Solvent 146
Recycled Water 178
Water 104
Solvent Purge
Solvent-Enriched Stream 134
Solvent/ Extractant Separation 176
Water Enriched Stream 132
Heat 174
Separated Mother Liquor Stream 162
Cool 181
Recycled Extractant (e.g., water) 180
Water Purge
Recovered Wash Liquor (e.g., water) 130
Wash Liquid (e.g., water) 122
Solid/Liquid Separation 158
Wet Solids 160
Washing
Washed Solids 168
Solid/Liquid Separation 166
Wet Solids 172
Drying 170
CE Microbeads 112

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/021412

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C08B 3/06; C08B 3/22; C08L 1/14 (2024.01)
ADD.

CPC - INV. C08B 3/06; C08B 3/22; C08L 1/14

ADD. C08J 2301/10

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)
See Search History document

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

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2022/0267573 A1 (DAINICHISEIKA COLOR & CHEM MFG CO LTD) 25 August 2022; Abstract; paragraphs [0013-0017], [0048-0054], [0057], [0059-0063], [0077], [0092-0093]	1-3 --- 4-5
Y	US 2009/0203899 A1 (EASTMAN CHEM CO et. al) 13 August 2009; Paragraphs [0014], [0152-0153], [0159-0164]: Figures 1 and 2.	4-5
A	US 5,047,180 A (HOECHST CELANESE CORP et. al) 10 September 1991; See entire document.	1-5
P,X	WO 2023/086529 A1 (EASTMAN CHEM CO et. al) 19 May 2023; See entire document.	1-3

☐ 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
"D" document cited by the applicant in the international application
"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	Date of mailing of the international search report
11 June 2024 (11.06.2024)	JUL 03 2024
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/021412

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-24
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.