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(54) SAC	Title: EMULSIFYING COMPOSITIONS		FATTY ACID OR FATTY ESTER REACTION PRODUCTS URFACTANTS
(57) be ol saccl surfa with	btained in an aqueous fluid in the presence haride polymer comprising a dextran, a dextra	of a hydroxide bain compound, or a ting compositions	duct of a saccharide polymer and a fatty acid or a fatty ester r ase and a neutral surfactant or a reaction product form thereof, any combination thereof. When further combined with a zwitteric may be obtained. The emulsifying compositions may be contact h may define an oil-in-water emulsion.

# EMULSIFYING COMPOSITIONS COMPRISING FATTY ACID OR FATTY ESTER REACTION PRODUCTS OF SACCHARIDE POLYMERS FORMULATED WITH MIXED SURFACTANTS

### BACKGROUND

[0001] Amphiphilic compounds having both hydrophobic and hydrophilic regions within their molecular structure are commonly referred to as "surfactants" or "surfactant compounds." By virtue of their molecular structure, surfactants tend to lower the surface tension at an interface between two components.
Surfactants may be found in a wide range of consumer and industrial products including, for example, soaps, detergents, cosmetics, pharmaceuticals, and dispersants. In addition, surfactants are also commonly used in the oil and gas industry. Among other functions in these applications and others, surfactants may promote solubility of an otherwise sparingly soluble substance, increase foaming, facilitate emulsification or de-emulsification, and/or lower viscosity in particular instances.

[0002] There are difficulties associated with various conventional surfactants. Poor biodegradation, including slow biodegradation in liquid environments, and/or poor biocompatibility of some common synthetic surfactants may negatively impact consumer and industrial products and processes incorporating such surfactants. In addition, some common surfactants may be expensive, have poor aqueous solubility, and/or be subject to environmental and/or other government regulations. Some surfactants may also promote high surface tension values at the critical micelle concentration, which may complicate fluid handling when formulating consumer and industrial products containing such surfactants. A further difficulty associated with conventional surfactants is that the hydrophilic-lipophilic balance (HLB) is fixed by virtue of the molecular structure of the particular amphiphilic compound employed, which may

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**[0003]** A versatile class of surfactants may be obtained in an aqueous phase by combining a reaction product of a fatty acid and a saccharide polymer

not be suitable for a specified application, even if the surfactant is otherwise

chemically compatible with anticipated use conditions.

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with a fatty acid amide neutral surfactant (co-surfactant), such as a fatty acid alkanolamide, as described in U.S. Patent Application Publication 2021/0340429. The fatty acid and the amount thereof relative to the saccharide polymer may be varied to tailor the hydrophilic-lipophilic balance of these types of surfactants.

5 Low surface tension values may arise as a consequence of a synergistic interaction between the reaction product and the neutral surfactant. The surfactants may promote short-term emulsification of oleaginous fluids, followed by spontaneous breaking over the course of several hours.

# BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Not applicable.

## **DETAILED DESCRIPTION**

- [0005] The present disclosure generally relates to surfactant technology 15 and, more specifically, emulsifying compositions comprising a surfactant formed from biologically sourced materials and that may promote emulsification of oleaginous substances to form an emulsion having extended stability, particularly an oil-in-water emulsion.
- [0006] As discussed above, conventional surfactants may present various issues such as high cost, poor biocompatibility, and/or poor solubility, which may limit their applicability in various applications. Moreover, there is no easy way to alter the hydrophobic-lipophilic balance (HLB) of conventional surfactants. Surface tension (interfacial tension) values are also frequently high for some types of surfactants as well, which may complicate their handling in various applications and/or preclude formulation thereof into various consumer and industrial products.

[0007] As described in U.S. Patent Application Publication
2021/0340429, incorporated herein by reference, aqueous surfactant compositions comprising a reaction product of a fatty acid and a saccharide
polymer, such as dextran or a dextrin compound, in combination with a neutral surfactant (co-surfactant), such as various alkanolamides based on fatty acids,

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are a versatile class of surfactant compounds. Not only is the hydrophilic-lipophilic balance readily altered by varying the identity and amount of the fatty acid, but surprisingly low surface tension values may be realized when the reaction product is present in combination with the neutral surfactant. Specifically, when the

- 5 reaction product of a fatty acid and the saccharide polymer is present in combination with a suitable neutral surfactant, the surface tension may be lower than that of the neutral surfactant by itself at substantially the same concentration in an aqueous fluid. That is, the reaction product of the fatty acid and the saccharide polymer may interact synergistically with the neutral surfactant to afford decreased surface tension values compared to the neutral surfactant alone at a substantially identical concentration. Fatty esters may be reacted to form
  - the reaction products under similar conditions with accompanying production of an alcohol, such as glycerol, originating from the fatty ester.
- **[0008]** As used herein, the term "fatty acid" refers to a linear, optionally 15 unsaturated, carboxylic acid containing 4 or more carbon atoms. As used herein, the term "fatty ester" refers to a compound containing one or more ester moieties, which comprises an alcohol component and a fatty acid component. The alcohol component may be a monohydric alcohol or a polyhydric alcohol, such as a diol or triol (e.g., glycerol). The fatty acid may be a straight chain, saturated or 20 unsaturated fatty acid, examples of which are provided hereinbelow. Accordingly, the reaction products, emulsifying compositions, and emulsified fluids described herein may be free or substantially free of branched fatty acids or products formed therefrom, according to various embodiments. That is, the reaction products, emulsifying compositions, and emulsified fluids described herein include reaction 25 products derived from one or more fatty acids that consist of straight-chain fatty acids.

**[0009]** The reaction products described above may be combined with a zwitterionic (amphoteric) surfactant to afford additional surprising results and beneficial advantages. Namely, the compositions described in brief above (*i.e.*, an aqueous surfactant composition comprising a reaction product of a saccharide polymer in combination with a neutral surfactant or a reaction product form

thereof, such as a fatty acid alkanolamide) may be combined with a zwitterionic surfactant to promote emulsification of an oleaginous substance, particularly as an oil-in-water emulsion. In other words, the saccharide polymer reaction products referenced above, when present in a composition with both a zwitterionic

- 5 surfactant and a neutral surfactant or a reaction product form thereof, such as a fatty acid alkanolamide, may promote emulsion formation, preferably wherein the emulsion exhibits stability over an extended period of time, such as a time period of about one day or more. Surprisingly, such emulsification performance may be realized even when neither the zwitterionic surfactant alone nor the combination
- 10 of a saccharide polymer reaction product and the neutral surfactant alone is effective to promote emulsification over an extended time period under similar conditions and concentrations. Thus, there is an unexpected synergistic enhancement of the emulsification performance when a zwitterionic surfactant is further combined with the reaction products described above in a sufficient 15 amount to promote stable emulsion formation over an extended time period. The terms "emulsion" and "emulsified fluid" are used equivalently and interchangeably herein.

[0010] Without being limited by theory, reaction products produced from a saccharide polymer and a fatty acid or a fatty ester may include at least one fatty ester saccharide polymer formed from a reaction between the saccharide polymer (*e.g.*, a dextran or a dextrin compound) and the fatty acid or the fatty acid component of the fatty ester, which may then interact synergistically with a neutral surfactant to afford low surface tension values. As described herein, the reaction products may exhibit further synergism in combination with a zwitterionic surfactant when promoting formation of an oil-in-water emulsion having extended stability lasting several days or more.

[0011] To form a fatty ester saccharide polymer, a fatty ester may undergo initial hydrolysis under alkaline conditions to generate a fatty acid component or a salt form thereof, which may then react with the saccharide 30 polymer to form at least one fatty ester reaction product. Alternately, a fatty ester may undergo direct transesterification with a saccharide polymer to form at

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least one fatty ester reaction product. Free fatty acids or a salt form thereof, in contrast, may react directly with a saccharide polymer to form the reaction products described herein. Any one or more than one of the primary or secondary alcohol functionalities upon the glucose monomer units of the saccharide polymer may undergo a reaction to form a fatty ester reaction product in the disclosure herein.

**[0012]** In the course of forming a fatty ester saccharide polymer reaction product from a fatty ester, such as an animal fat or vegetable oil, the alcohol component of the fatty ester may be released into an aqueous fluid in which the fatty ester saccharide polymer reaction product is being formed. The alcohol 10 component may persist with the fatty ester saccharide polymer reaction product in the aqueous fluid or undergo at least partial removal therefrom. Advantageously and surprisingly, the alcohol component released into the aqueous fluid does not significantly impact the low surface tension values 15 attainable when the fatty ester saccharide polymer reaction product and the neutral surfactant are present together. The alcohol component (*e.g.*, glycerol) released into the aqueous fluid may aid in solubilizing other components of the composition and/or other components blended with the compositions to make various consumer and industrial products. Optionally, additional glycerol or 20 another alcohol may be blended with the compositions, including compositions made from free fatty acids or compositions made from other types of fatty esters, without appreciably impacting the surface tension values and/or emulsification performance obtained.

[0013] Thus, the reaction products described herein may be advantageous due to their substantial biological origin, low cost and ability to afford low surface tension values when present in combination with a suitable neutral surfactant. Reaction products of maltodextrin, for example, represent a particularly useful class of dextrin-based reaction products due to the low cost and convenient molecular weight range of this saccharide polymer. Various fatty acids having a range of molecular weights may be used to produce reaction products having a span of HLB values. Moreover, a number of fats, oils and similar

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glycerol esters may serve as convenient and inexpensive sources for a fatty ester, or fatty acids obtained therefrom, used in forming the reaction products described herein. Likewise, fats, oils, similar glycerol esters, and other fatty esters, and amounts thereof may be selected to promote tailoring of the surfactant properties, such as altering HLB values and/or varying emulsification performance, for instance.

[0014] Maltodextrins may represent an advantageous saccharide polymer for use in the disclosure herein due to their low cost, environmentally benign nature, and the relative ease with which they may be chemically reacted with various free fatty acids or fatty acids originating from a fatty ester, such as 10 a glycerol ester. Depending on the fatty acid(s) reacted with a maltodextrin, the hydrophobic-lipophilic balance (HLB) of the reaction products may range from about 5 to about 20 or more, wherein known molecular contributions may be utilized to calculate the HLB value. In addition to property variation resulting from the fatty acid size and amount thereof, maltodextrins are available in a range of 15 oligomer sizes (e.g., 3-20 glucose monomers, or even up to about 25 glucose monomers), which may allow further property tailoring to be realized. Thus, maltodextrin reaction products may be adapted for use under a wide range of conditions anticipated to be present in a given application. Dextran reaction 20 products may offer similar advantages and features to those of maltodextrin

[0015] Maltodextrin and other dextrin compounds suitable for use in the present disclosure may comprise 2 to about 20 glucose monomers, or even up to about 25 glucose monomers, linked together with α(1,4) glycosidic bonds. At least a portion of the glucose monomers may form a reaction product upon being contacted under suitable conditions with a fatty acid or a fatty ester, including fatty acid salts obtained therefrom, such as a salt of a C<sub>4</sub>-C<sub>30</sub> fatty acid or a C<sub>4</sub>-C<sub>20</sub> fatty acid. The fatty acid or fatty ester may include one or more fatty acids or fatty acid components, which may be any combination of saturated or unsaturated fatty acids. Without being limited by theory, at least a portion of the glucose monomers in the dextrin compound may react to form a fatty ester dextrin

reaction products, including the ability to produce low surface tension values.

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compound, which may be optionally present in combination with unreacted fatty acid salt in the aqueous fluid. When formed, a fatty ester reaction product may form at any hydroxyl group of the dextrin compound, including any combination of primary and/or secondary hydroxyl groups. Hydroxyl groups upon the neutral surfactant may undergo a similar esterification reaction under the same reaction conditions.

**[0016]** Dextran is a saccharide polymer characterized by predominantly  $\alpha(1,6)$  glycosidic bonds between adjacent glucose monomers, with a limited number of glucose side chains linked to the main polymer backbone via  $\alpha(1,3)$  glycosidic bonds. The  $\alpha(1,3)$  glycosidic bonds may introduce crosslinks between adjacent saccharide polymer chains. Depending on the biological source, the extent of branching and the molecular weight of dextran may vary considerably, any of which may be utilized in the disclosure herein. At least a portion of the glucose monomers in dextran may form a reaction product upon being contacted under suitable conditions with a fatty acid or a fatty ester, including a fatty acid. Without being limited by theory, at least a portion of the glucose monomers may react to form a fatty ester dextran in some embodiments, which may be optionally

20 formed, a fatty ester reaction product may form at any hydroxyl group of the dextran.

present in combination with unreacted fatty acid salt in the aqueous fluid. When

[0017] In some embodiments, reaction products of the present disclosure may include a dextrin compound having 3 to about 20 glucose monomers, or even up to about 25 glucose monomers, that are covalently linked
25 by α(1,4) glycosidic bonds. Formula 1 below shows the generic structure of a dextrin compound having only α(1,4) glycosidic bonds between adjacent glucose monomers, wherein variable 'a' is a positive integer ranging from 1 to about 18, thereby providing a dextrin backbone with 3 to about 20 glucose monomers. In the case of a dextrin compound containing up to 25 glucose monomers, variable
30 'a' may range from 1 up to about 23. The terminal glucose unit is shown in its

closed form, but may also be present in the corresponding reducing sugar (open chain or acyclic) form as well.



#### Formula 1

5 Other dextrin compounds may contain only  $\alpha(1,6)$  glycosidic bonds or a mixture of  $\alpha(1,4)$  and  $\alpha(1,6)$  glycosidic bonds, and such dextrin compounds may also be suitable for use in forming the reaction products of the present disclosure. Particularly suitable dextrins may have a molecular weight (*e.g.*, M<sub>n</sub>) in the range of about 1200 to about 1400 or about 1100 to about 1500.

10 **[0018]** In some or other embodiments, the reaction products may include a dextran obtained from any suitable source. The structure of dextran is shown in Formula 2 below, in which the  $\alpha(1,3)$  glycosidic bonds are not shown in the interest of clarity. Where they occur, the  $\alpha(1,3)$  glycosidic bonds may append a terminal glucose monomer as a side chain to the  $\alpha(1,6)$ -linked saccharide polymer backbone, form crosslinks between adjacent  $\alpha(1,6)$ -linked saccharide polymer backbones, interrupt the  $\alpha(1,6)$ -linked saccharide polymer backbone with an  $\alpha(1,3)$  glycosidic bond, or any combination thereof. Depending on source, up to about 5% of the glucose monomers may be linked by  $\alpha(1,3)$  glycosidic bonds. Linkage by  $\alpha(1,3)$  glycosidic bonds may occur upon any of the glucose monomers.

20 The numbering of a single glucose monomer is shown in Formula 3 below.



### Formula 2

Suitable dextrans may have a molecular weight of about 1200, or about 1400, or about 5000 up to about 50,000,000, or about 100,000 up to about 20,000,000.

- 5 As such, variable 'b' may range from about 30 to about 300,000 depending on the particular dextran selected. Particularly suitable dextrans may have a molecular weight (*e.g.*, M<sub>n</sub>) ranging from about 1200 to about 1400, or about 1100 to about 1500, or about 1000 to about 100,000, or about 100,000 to about 1 million, or about 2 million to about 5 million, or about 5 million. Another
- 10 suitable dextran may have a molecular weight of about 500,000 and an activity level of about 9%.



Formula 3

[0019] The saccharide polymer may comprise a maltodextrin according 15 to some embodiments of the present disclosure. Maltodextrins may be characterized in terms of their dextrose equivalent (DE) value. Dextrose

equivalent is a measure of the amount of reducing sugars (*e.g.*, glucose monomers) that are present in a saccharide polymer, particularly a dextrin, expressed as a percentage relative to dextrose. Starch, which is functionally non-reducing, has a defined dextrose equivalent of 0, whereas dextrose itself has a

- 5 dextrose equivalent of 100. Dextrose equivalent may be calculated by dividing the molecular weight of glucose by M<sub>n</sub> and multiplying the result by 100. Higher dextrose equivalent values are characteristic of a lower number of covalently linked glucose monomers (shorter polymer backbone length, thereby providing a higher relative percentage of terminal reducing sugars). Maltodextrins suitable
- 10 for forming a reaction product with one or more fatty acids or one or more fatty esters according to the disclosure herein may exhibit dextrose equivalent values ranging from 3 to about 25 or from 3 to about 20. In more specific embodiments, dextrose equivalent values of the maltodextrins may range from about 4.5 to about 7.0, or from about 7.0 to about 10.0, or from about 9.0 to about 12.0.
- 15 [0020] Maltodextrins suitable for forming a reaction product may be obtained from hydrolysis or pyrolysis of starch, specifically the amylose component of starch, according to some embodiments. A maltodextrin having Formula 1 may be formed by hydrolysis or pyrolysis of amylose, for example. Alternative suitable dextrins may be obtained from hydrolysis or pyrolysis of the 20 amylopectin component of starch, in which case the dextrin may contain α(1,6) glycosidic bonds if the dextrin is obtained through hydrolysis of the amylopectin side chain. Starches from which the dextrins may be subsequently produced may be obtained from any starch source.
- [0021] Accordingly, reaction products suitable for use in the present disclosure may comprise an aqueous fluid, a neutral surfactant or a reaction product form thereof, and a reaction product of a saccharide polymer and a fatty acid or a fatty ester, in which the saccharide polymer comprises a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product of the neutral surfactant, if present, are formed in the presence of a hydroxide base in the aqueous fluid (*e.g.*, under aqueous alkaline conditions). A

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zwitterionic surfactant may be present in combination with the reaction products and the neutral surfactant in an amount sufficient to promote formation of an emulsion when combined with an oleaginous substance, thereby defining an emulsifying composition. The emulsifying composition may form an emulsified

5 fluid when contacted with an oleaginous substance under suitable conditions. The emulsified fluid may define an oil-in-water-emulsion and/or the emulsified fluid may maintain stability for at least about one day, as further discussed herein. Water-in-oil emulsions may also be possible through suitable modification of the disclosure herein.

10 **[0022]** Aqueous fluids that may be used to form the emulsifying compositions described herein may include, but are not limited to, water, salt water, sea water, brine, aqueous salt solutions, mixtures of water or an aqueous salt solution and a water-miscible organic solvent, or any combination thereof. Any of these aqueous fluids may be present in an emulsified fluid obtained upon contacting the emulsifying compositions with an oleaginous substance.

**[0023]** Oleaginous substances that may undergo emulsification according to the disclosure herein are not believed to be particularly limited. Illustrative oleaginous substances that may be suitably emulsified include, for example, petroleum, refined petroleum, diesel, plant oils, vegetable oils, or any combination thereof.

[0024] Accordingly, emulsified fluids of the present disclosure may comprise: an oleaginous substance emulsified with an emulsifying composition, the emulsifying composition comprising: an aqueous fluid; a neutral surfactant or a reaction product form thereof; a reaction product of a saccharide polymer 25 and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and a zwitterionic surfactant. The emulsified fluid may define an oil-in-water emulsion in particular embodiments.

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[0025] The emulsifying composition and the oleaginous substance may be present in any ratio at which an emulsion forms. In non-limiting examples, a ratio of the emulsifying composition to the oleaginous substance may range from about 1:99 to about 99:1, or about 1:1 to about 1:9, on a volume basis. In some examples, the emulsifying composition and the oleaginous substance may be present in a suitable ratio such that the combination of the emulsifying composition and the oleaginous substance collectively defines an oil-in-water emulsion.

[0026] In the emulsifying compositions and the emulsified fluids described herein, the reaction product of the saccharide polymer and the zwitterionic surfactant may be present in any ratio. In some examples, the zwitterionic surfactant may be present in an amount greater than an amount of the reaction product of the saccharide polymer, as measured on a mass basis. In non-limiting examples, a ratio of the zwitterionic surfactant to the reaction product of the saccharide polymer may be about 1.5:1 or greater, or about 2:1 or greater, or about 3:1 or greater, or about 4:1 or greater, or about 5:1 or greater, or about 6:1 or greater, or about 7:1 or greater, or about 8:1 or greater, or about 9:1 or greater, such as about 2:1 to about 8:1, or about 4:1 to about 8:1, or about 5:1

to about 7:1, or about 4:1 to about 6:1. By providing the zwitterionic surfactant
in a greater amount than the reaction product of the saccharide polymer,
emulsified fluids having extended stability may be realized.

[0027] The emulsified fluids may remain stable once emulsified for a specified period of time. An emulsified fluid may be classified as stable if the extent of breaking of the emulsion is about 10% or less over the specified period of time. Preferably, the extent of breaking may be about 50% or less over the specified time period. More preferably, the extent of breaking may be about 5% or less over at least 1 hour. In non-limiting examples, the emulsified fluids may remain emulsified (stable) for at least about 1 hour, or at least about 2 hours, or at least about 4 hours, or at least about 6 hours, or at least about 8 hours, or at

30 least about 12 hours, or at least about 24 hours (1 day), or at least about 2 days, or at least about 4 days, or at least about 1 week (7 days), or at least about 2

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weeks (14 days), or at least about 3 weeks (21 days), or at least about 1 month (30 days). Preferably, the emulsified fluids may remain stable (emulsified) for at least about 1 day, or at least about 2 days, or at least about 4 days, or at least about 7 days, or at least about 10 days, or at least about 15 days, or at least about 30 days, or at least about 60 days, such as about 1 day to about 60 days, or about 1 day to about 30 days, or about 30 days, or about 5 days to about 30 days, or about 10 days.

[0028] Illustrative fatty acids (or fatty acid components within fatty esters) that may be suitable for forming a reaction product included within the 10 emulsified fluids and emulsifying compositions of the present disclosure include, for example, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelabonic acid, capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, nonadecylic acid, arachidic acid, heneicosylic acid, behenic acid, trioscylic acid, lignoceric acid, 15 pentacosylic acid, cerotic acid, carboceric acid, montanic acid, nonacosylic acid, melissic acid, crotonic acid, cervonic acid, linoleic acid, linolelaidic acid, linolenic acid, arachidonic acid, docosatetraenoic acid, myristoleic acid, palmitoleic acid, sappenic acid, vaccenic acid, paullinic acid, oleic acid, pinolenic acid, stearidonic acid, eleostearic acid, elaidic acid, gondoic acid, gadoleic acid, erucic acid, 20 eicosenoic acid, eicosadiencoic acid, eicosatrienoic acid, eicosatetraenoic acid, docosadienoic acid, nervonic acid, mead acid, adrenic acid, the like, and any combination thereof.

[0029] Fatty esters have at least one alcohol component and at least one fatty acid component (one or more of the fatty acids mentioned above) that may be liberated under the alkaline conditions used to form a reaction product of the saccharide polymer. Suitable fatty esters for forming reaction products are not believed to be particularly limited, provided that the fatty esters undergo effective hydrolysis to release an alcohol component and one or more fatty acid components of the fatty ester. Fatty acids originating from the fatty esters and suitable for forming reaction products of the present disclosure may be chosen (through selection of a suitable fatty ester containing one or more desired fatty

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acids) to afford reaction products having a range of HLB values, such as HLB values of about 5 to about 20. Illustrative types of fatty esters are provided below. The fatty acids originating from the fatty esters may range in size from about  $C_4$  to about  $C_{30}$ , or about  $C_4$  to about  $C_{20}$ , or about  $C_6$  to about  $C_{18}$ , or about  $C_8$  to about  $C_{24}$ . Suitable fatty acids for forming a reaction product according to the disclosure herein may be saturated or unsaturated. When the reaction products are formed from a fatty ester sourced from plant oils, at least one unsaturated fatty acid, such as oleic, linoleic or linolenic acid, may be present in the reaction product.

**[0030]** In some embodiments, the fatty ester used to form the reaction 10 products may comprise a glycerol ester, which may also be present in the emulsifying compositions and emulsified fluids formed therefrom. A glycerol ester may undergo alkaline hydrolysis to liberate glycerol as an alcohol component, and up to three carboxylic acid components per glycerol alcohol component may be released for undergoing reaction with a saccharide polymer according to the 15 disclosure herein. The carboxylic acid components released from the glycerol ester may be the same or different, and/or at least one unsaturated fatty acid may be among the carboxylic acid components, according to some embodiments of the present disclosure. Accordingly, the reaction products, emulsifying 20 compositions, and emulsified fluids described herein may further contain glycerol, particularly when the compositions contain a reaction product formed from a glycerol fatty ester.

[0031] Glycerol esters suitable for forming a reaction product, emulsifying composition, or emulsified fluid in accordance with the disclosure herein are not believed to be particularly limited and may comprise any plant oil, animal oil, plant fat, animal fat, or any combination thereof that contains one or more desired fatty acids. The glycerol ester may undergo hydrolysis or transesterification in the course of forming a reaction product with a saccharide polymer. Suitable glycerol esters may be found in plant or animal sources including, for example, soybean oil, grapeseed oil, olive oil, palm oil, rice bran oil, safflower oil, corn oil, coconut oil, sunflower seed oil, canola oil, rapeseed oil,

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peanut oil, cottonseed oil, hazelnut oil, tea seed oil, linseed oil, sesame oil, acai oil, almond oil, beech nut oil, brazil nut oil, cashew oil, macadamia nut oil, pecan oil, pine nut oil, pistachio oil, walnut oil, pumpkin seed oil, apricot oil, avocado oil, grapefruit oil, lemon oil, orange oil, mango oil, flax seed oil, fish oil, cocoa butter, hemp oil, castor oil, tall oil, fish oil, cattle fat, buffalo fat, sheep fat, goat fat, duck fat, pig fat, poultry fat, and any combination thereof.

[0032] Soybean oil, for example, contains a mixture of saturated and unsaturated fatty acids, predominantly palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid, with the monounsaturated and polyunsaturated fatty acids (oleic acid, linoleic and linolenic acids) comprising a majority of the fatty acids obtainable from the soybean oil. Palm oil contains about 50% saturated fatty acids (palmitic acid, stearic acid, and myristic acid) and 50% unsaturated fatty acids (oleic acid, linoleic acid, and linolenic acid). Coconut oil contains predominantly saturated fatty acids (caprylic acid, capric acid, lauric acid, 15 myristic acid, palmitic acid, and stearic acid) and less than 10% unsaturated fatty acids (oleic acid and linoleic acid). These mixtures of fatty acids represent particular examples of fatty acid mixtures that may be present in the reaction products, emulsifying compositions, and emulsified fluids described herein.

- **[0033]** When glycerol esters are used as a direct (*in situ*) source of fatty acids for formation of reaction products of the present disclosure, glycerol may be present in the emulsifying compositions and emulsified fluids resulting therefrom. Optionally, the glycerol may be at least partially removed from the aqueous fluid of the emulsifying compositions or emulsified fluids, if desired. Otherwise, the amount of glycerol present in the emulsifying compositions and emulsified fluids
- 25 may be dictated by the amount of glycerol ester that is present when forming the reaction product. For example, for glycerol esters containing C<sub>8</sub>-C<sub>24</sub> fatty acids, particularly unbranched fatty acids in this size range, the weight percentage of glycerol in the glycerol esters may range from about 7 wt. % to about 17 wt. %, based on total mass of the glycerol ester. Accordingly, the corresponding weight percentages of glycerol in emulsifying compositions and emulsified fluids containing the reaction product, as measured relative to the fatty acid(s)

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originating from the glycerol upon alkaline hydrolysis, may range from about 7.5 wt. % to about 20 wt. %. Alternately, the weight percentage of glycerol in the emulsifying compositions and emulsified fluids may be substantially equivalent on a mass basis, with respect to the entirety of the composition, to the weight percentage of glycerol ester present in the reaction mixture, since each glycerol ester may release one glycerol molecule upon undergoing complete hydrolysis. It is to be appreciated, however, that additional glycerol may be added to emulsifying compositions and emulsified fluids beyond that liberated upon converting a glycerol fatty ester into a reaction product formed from a saccharide polymer, or glycerol may be further added to emulsifying compositions containing a reaction product prepared directly from a fatty acid.

**[0034]** Suitable hydroxide bases for forming the reaction products may include, for example, alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide, or any combination thereof. A stoichiometric excess or a stoichiometric deficit of the hydroxide base relative to an amount of the fatty ester or fatty acid may be present.

[0035] A molar ratio of fatty acid or fatty acid originating from a fatty ester to glucose monomers in the reaction product of the saccharide polymer may be about 0.05 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose</sub>

- 20 monomers in saccharide polymer, or about 0.08 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.1 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.2 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.2 or above on a basis of moles<sub>fatty acid or fatty acid or fatty acid or fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.3 or above on a basis of moles<sub>fatty acid or fatty ac</sub></sub></sub>
- 25 in saccharide polymer, or about 0.4 or above on a basis of molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.5 or above on a basis of molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.6 or above on a basis of molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.6 or above on a basis of molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.6 or above on a basis of molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.7 or above on a basis of molesfatty acid or fatty acid or fatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide
- 30 polymer, or about 0.8 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.9 or above on a basis of moles<sub>fatty acid or fatty acid in</sub>

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fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer. A maximum ratio of fatty acid to dextrin or dextran in the reaction product of the saccharide polymer, based upon glucose monomers, may be about 1.0 in most cases, although molar ratios above 1.0 also reside within the scope of the present disclosure. Thus, in some embodiments, 5 the molar ratio of fatty acid to glucose monomers in the reaction product of the saccharide polymer may range from about 0.05 molesfatty acid or fatty acid in fatty ester: molesquecese monomers in saccharide polymer to about 1.0 molesfatty acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.05 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.9 moles<sub>fatty</sub> acid or fatty acid in fatty 10 ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.05 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.8 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.05 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.7 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.05 moles<sub>fatty</sub> acid or fatty acid in fatty 15 ester: molesglucose monomers in saccharide polymer to about 0.6 molesfatty acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.05 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.5 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.05 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.4 moles<sub>fatty</sub> acid or fatty acid in fatty 20 ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.1 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.9 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.1 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.8 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.1 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.7 moles<sub>fatty</sub> acid or fatty acid in fatty 25 ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.1 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.6 moles fatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.1 molesfatty acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.5 moles<sub>fatty</sub> acid or fatty acid in fatty 30 ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.1 moles<sub>fatty</sub> acid or fatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.4 moles fatty acid or fatty acid in fatty

ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.2 moles<sub>fatty</sub> acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer to about 0.9 molesfatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer, or about 0.2 moles fatty acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.8 moles<sub>fatty</sub> acid or fatty acid in fatty 5 ester: molesglucose monomers in saccharide polymer, or about 0.2 molesfatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.7 moles fatty acid or fatty acid in fatty ester: molesquecese monomers in saccharide polymer, or about 0.2 molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer to about 0.6 molesfatty acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.2 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.5 moles fatty acid or fatty acid in fatty 10 ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.2 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.4 moles<sub>fatty</sub> acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.3 molesfatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.9 moles fatty acid or fatty acid in fatty 15 ester: molesglucose monomers in saccharide polymer, or about 0.3 molesfatty acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.8 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.3 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.7 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.3 moles<sub>fatty</sub> acid or fatty acid in fatty 20 ester: moles glucose monomers in saccharide polymer to about 0.6 moles fatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.3 molesfatty acid or fatty acid in fatty ester: molesglucose monomers to about 0.5 molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, Or about 0.3 moles fatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.4 molesfatty acid or fatty acid in fatty ester: molesglucose monomers in 25 saccharide polymer, or about 0.4 moles fatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer to about 0.9 molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer, or about 0.4 molesfatty acid or fatty acid in fatty ester: molesglucose monomers in saccharide polymer to about 0.8 moles fatty acid or fatty acid in fatty ester: moles glucose monomers in saccharide polymer, or about 0.4 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer to about 0.7 30 moles<sub>fatty</sub> acid or fatty acid in fatty ester: moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.4 molesfatty acid or fatty acid in fatty ester:molesglucose monomers in saccharide polymer to about 0.6

moles<sub>fatty</sub> acid or fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer, or about 0.4 moles<sub>fatty</sub> acid or fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer to about 0.5 moles<sub>fatty</sub> acid or fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer. The foregoing ratios may represent a molar ratio of fatty acid reacted with the dextran or dextrin

- 5 compound. One or more hydroxyl groups per glucose monomer may undergo a reaction in some cases, particularly at a molar ratio of about 1.0 or above. At least a portion of the glucose monomers may remain unfunctionalized, particularly at lower molar ratios. Unreacted fatty acids, if any, may remain in the reaction product as a fatty acid salt of the hydroxide base.
- 10 **[0036]** As such, reaction products suitable for use in the present disclosure may comprise one or more fatty ester dextrins and/or one or more fatty ester dextrans, optionally in further combination with a fatty acid salt (*e.g.*, an alkali metal carboxylate), and/or a hydroxide base (*e.g.*, an alkali metal hydroxide base). When using a fatty ester to form the reaction products, the hydroxide base
- 15 may be present in at least a sufficient molar quantity to react with at least a portion of the fatty ester to promote hydrolysis thereof and to convert the fatty acid component of the fatty ester into a fatty acid salt (*e.g.*, an alkali metal carboxylate) for reaction with the saccharide polymer. Alternately, the hydroxide base may be present in a sufficient amount to form a fatty acid salt (*e.g.*, an alkali
- 20 metal carboxylate) when forming the reaction products directly from a free fatty acid. The alcohol component released from a fatty ester (*e.g.*, glycerol) following hydrolysis may be present in combination with any of the reaction products as well. The hydroxide base may be neutralized with an acid or be at least partially removed through washing, and emulsifying compositions comprising the reaction
- 25 products may retain a low surface tension following neutralization or washing. The alcohol component, if present, may be at least partially removed from the reaction products and emulsifying compositions as well, if desired, such as through distillation or solvent extraction, for example.

[0037] Alternately, other saccharide polymers may be utilized to form 30 the reaction products in the emulsifying compositions and emulsified fluids described herein. Other saccharide polymers that may be used in this regard

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include, but are not limited to, glycogen, guar, xanthan, welan, scleroglucan, chitosan, schizophyllan, levan, pectins, inulin, arabinoxylans, pullulan, gellan, carrageenan, chitosan, chitin, cellulose, starch, or a combination thereof. Saccharide polymer fragments obtained from the foregoing and containing about 3 to about 25 monomers per fragment may also be utilized for forming the reaction products, emulsifying compositions, and emulsified fluids described herein.

**[0038]** In some embodiments and preferably, the reaction products of the present disclosure may promote lowering of the surface tension of the neutral surfactant, preferably a fatty acid alkanolamide neutral surfactant in an aqueous fluid. That is, the reaction products may be present in an effective concentration in the emulsifying composition or emulsified fluid to lower the surface tension of the neutral surfactant compared to that of the neutral surfactant alone at a substantially similar concentration in the aqueous fluid.

15 [0039] At the same time, the neutral surfactant or a reaction product form thereof may be present in the aqueous fluid in a sufficient concentration to solubilize the saccharide polymer prior to forming the reaction product and the reaction product of the saccharide polymer and the fatty acid or fatty ester after a reaction has taken place. In the emulsifying compositions and emulsified fluids of the present disclosure, the neutral surfactant may be present at a concentration of about 20 wt. % or less, or about 10 wt. % or less, or about 5 wt. % or less, such as about 1 wt. % to about 10 wt. %, or about 3 wt. % to about 8 wt. %, each based on total mass of the emulsifying composition.

[0040] Suitable neutral surfactants may comprise one or more fatty acid alkanolamide surfactants. Fatty acid alkanolamide surfactants that may have their surface tension lowered in combination with a reaction product of the present disclosure include cocamide-based surfactants, such as cocamide diethanolamine, cocamide monoethanolamine, cocamide monoisopropanolamine, cocamide diisopropanolamine, and the like. Cocamide diethanolamine (CocoDEA) or cocamide diisopropanolamine (CocoDIPA) may be particularly suitable neutral surfactants for use in the disclosure herein. Other fatty acid amide alkanolamines

(alkanolamides), such as palmitic acid amide diethanolamine, palmitic acid monoethanolamine, or palmitic acid diisopropanolamine may also be suitable for use in the disclosure herein.

**[0041]** Zwitterionic surfactants (also known as amphoteric surfactants) 5 suitable for use in the disclosure herein are not believed to be particularly limited in structure and may be selected from betaines and sultaines. Particular examples of suitable zwitterionic surfactants may include, for example, cocamidopropylbetaine, alkanoyl hydroxysultaines (*e.g.*, lauryl hydroxysultaine), cocamidopropyl hydroxysultaine, alkanamidopropyl hydroxysultaines (e.g., lauramidopropyl hydroxysultaine), sodium cocoamphohydroxypropylsulfonate, 10 and the like.

[0042] A zwitterionic surfactant may be present in a sufficient concentration in the aqueous fluid of the emulsifying compositions described herein to promote formation of an emulsified fluid, such as an oil-in-water 15 emulsion, when combined with an oleaginous substance. In the emulsified fluids and emulsifying compositions of the present disclosure, one or more zwitterionic surfactants may be present at a concentration of about 15 vol. % or less, or about 10 vol. % or less, or about 5 vol. % or less, or about 2.5 vol. % or less, or about 1 vol. % or less, or about 0.5 vol. % or less, or about 0.4 vol. % or less, or about 20 0.3 vol. % or less, or about 0.2 vol. % or less, or about 0.1 vol. % or less, or about 0.09 vol. % or less, or about 0.08 vol. % or less, or about 0.07 vol. % or less, or about 0.06 vol. % or less, or about 0.05 vol. % or less, or about 0.04 vol. % or less, or about 0.03 vol. % or less, or about 0.02 vol. % or less, or about 0.01 vol. % or less, each based on total volume of the emulsified fluid or emulsifying composition.

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[0043] Once formed, the pH of emulsifying compositions and emulsified fluids containing the reaction products disclosed herein may reside within a range of about 1 to about 14, such as a range of about 1 to about 5, or about 5 to about 7, or about 7 to about 9, or about 9 to about 14. The pH may be raised or lowered, if needed, after forming the reaction products in accordance with the disclosure herein. Lower surface tension values may be realized as the pH decreases in

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some instances. Decreased surface tension may also be realized in the presence of dissolved salt, such as potassium chloride.

[0044] Reaction products of the present disclosure, which may include those formed through a reaction of one or more fatty acids or one or more fatty esters with a dextrin compound and/or a dextran, may be prepared by a process comprising: heating a saccharide polymer comprising a dextran, a dextrin compound (*e.g.*, comprising 3 to about 20 glucose monomers, or even up to about 25 glucose monomers, linked together with α(1,4) glycosidic bonds, such as maltodextrin), or any combination thereof, a fatty acid or a fatty ester, a neutral surfactant (*e.g.*, a fatty acid alkanolamide) and a hydroxide base in an aqueous

- fluid, and obtaining a reaction product of the saccharide polymer and the fatty acid or fatty ester in the aqueous fluid. The aqueous fluid may further contain glycerol, which may originate from a fatty ester used to form the reaction products and/or additional glycerol may be added separately to the reaction products. The
- 15 reaction product may be present in the aqueous fluid at a concentration effective to lower a surface tension of the neutral surfactant, as measured relative to the neutral surfactant alone at a like concentration in the aqueous phase. For example, a 5 wt. % solution of the neutral surfactant in water may have a higher surface tension than does a emulsifying composition containing 5 wt. % of the
- 20 neutral surfactant in combination with a reaction product of the present disclosure in a surface tension-lowering amount. Any of the reaction products of a dextran or a dextrin compound may constitute a suitable saccharide polymer for forming emulsifying compositions or emulsified fluids having a low surface tension and further comprising at least one zwitterionic surfactant. Heating may be conducted 25 at a temperature of about 100°C or less, such as at about 50°C to about 80°C, or
- about 60°C to about 70°C, or about 50°C to about 60°C.

**[0045]** In the presence of a neutral surfactant, surface tension values for reaction products of the present disclosure may be about 40 dynes/cm or less, or about 38 dynes/cm or less, or about 36 dynes/cm or less, or about 34 dynes/cm or less, or about 32 dynes/cm or less, or about 30 dynes/cm or less, or about 28 dynes/cm or less. Alternately, the surface tension values may be lowered up to

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about 40% relative to the surface tension of the neutral surfactant in the aqueous fluid alone at a like concentration, or lowered up to about 30%, or lowered up to about 20%, or lowered up to about 15%, or lowered up to about 10%. In a particular example, the surface tension values may be lowered in an amount of about 10% to about 25%, or about 10% to about 20%, or about 15% to about 25%, as measured relative to the surface tension of the neutral surfactant in the aqueous fluid alone at a substantially identical concentration to that in a composition containing the reaction product.

**[0046]** In forming the reaction products suitable for use in the disclosure herein, methods may comprise combining the fatty acid or the fatty ester, the hydroxide base, and the neutral surfactant in water to form a mixture, and heating the mixture until the fatty acid or the fatty ester dissolves (*e.g.*, by undergoing hydrolysis and/or forming a fatty acid salt) and a homogeneous mixture forms. The saccharide polymer may be combined with the fatty acid or the fatty ester

- 15 during this process, or the saccharide polymer may be combined with the homogeneous mixture after formation thereof. Once the saccharide polymer is present in the homogeneous mixture, heating may be continued until the reaction product has formed to a sufficient degree. The resulting aqueous phase may be utilized directly in further applications, optionally after concentration, neutralization, or dilution, or by being further combined with additional components targeted for a particular formulation, such as with a zwitterionic surfactant to form the emulsifying compositions disclosed herein. Formulations
- and products in which emulsifying compositions and emulsified fluids of the present disclosure may be utilized are discussed hereinbelow. In some instances,
- 25 the emulsifying compositions may at least partially replace another surfactant in a specific formulation, such as a charged surfactant. In other instances, the emulsifying compositions may at least partially replace an ethoxylated alcohol surfactant in a formulation.

### Subterranean Treatment Operations

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**[0047]** The recovery of hydrocarbon resources, such as oil and gas, from subterranean formations is often performed in conjunction with introducing one

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or more subterranean treatment chemicals downhole. As used herein, the terms "treat," "treatment," "treating," and grammatical equivalents thereof refer to any compound, fluid, or combination thereof that is introduced to a subterranean formation with the goal of achieving a desired function and/or for a desired purpose. A suitable treatment chemical or a treatment fluid may be selected based upon particular conditions present or anticipated to be present downhole.

**[0048]** Reaction products of the present disclosure, including those formed from maltodextrin, other dextrin compounds, or dextran may be formulated as a subterranean treatment fluid, or emulsifying compositions further comprising a zwitterionic surfactant or emulsified fluids formed therefrom may be formulated as a subterranean treatment fluid. Treatment fluids may be used in a variety of subterranean treatment operations to facilitate or promote a desired outcome within the subterranean formation. As used herein, the term "treatment fluid" refers to any fluid used in a subterranean treatment reatment operation in conjunction

- 15 with achieving a desired function and/or for a desired purpose. Unless otherwise specified, use of the term "treatment fluid" does not imply any particular action by the treatment fluid or a component thereof. Illustrative treatment operations that may be facilitated through use of the reaction products, emulsifying compositions, and emulsified fluids of the present disclosure include, without limitation, drilling operations, stimulation operations, and the like, which may include,
- for example, fracturing operations, gravel packing operations, acidizing operations, descaling operations, consolidation operations, workover operations, cleanup operations, diversion operations, and the like. Any of these treatment
   operations may feature emulsification, de-emulsification, a change in surface wetting characteristics downhole, or any combination thereof.

**[0049]** As used herein, the term "drilling operation" refers to the process of forming a wellbore in a subterranean formation. As used herein, the term "drilling fluid" refers to a fluid used in drilling a wellbore.

**[0050]** As used herein, the term "stimulation operation" refers to an activity conducted within a wellbore to increase production therefrom. As used

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herein, the term "stimulation fluid" refers to a fluid used downhole during a stimulation activity to increase production of a hydrocarbon resource from the subterranean formation. In some instances, stimulation fluids may include a fracturing fluid or an acidizing fluid.

5 **[0051]** As used herein, the terms "clean-up operation" or "damage control operation" refer to any operation for removing extraneous material from a wellbore to increase production. As used herein, the terms "clean-up fluid" or "damage control fluid" refer to a fluid used for removing an unwanted material from a wellbore that otherwise blocks flow of a desired fluid therethrough. In one example, a clean-up fluid can be an acidified fluid for removing material formed by one or more perforation treatments. In another example, a clean-up fluid can be used to remove a filter cake upon the wellbore walls. For example, a reaction

product, emulsifying composition, or emulsified fluid of the present disclosure may promote liberation of a hydrocarbon resource from a subterranean formation to

- 15 promote wellbore cleanup by changing surface wetting characteristics. In another embodiment, treatment fluids comprising a reaction product of the present disclosure may be introduced to a subterranean formation in emulsified form and undergo a subsequent break (de-emulsification) therein to promote a desired action within the subterranean formation.
- 20 [0052] As used herein, the term "fracturing operation" refers to a highpressure operation that creates or extends a plurality of flow channels within a subterranean formation. As used herein, the term "fracturing fluid" refers to a viscosified fluid used in conjunction with a fracturing operation. A plurality of proppant particulates may be present in a fracturing fluid to maintain the flow 25 channels created or extended in the fracturing operation in an open state.

**[0053]** As used herein, the term "remediation operation" refers to any operation designed to maintain, increase, or restore a specific rate of production from a wellbore, which may include stimulation operations or clean-up operations. As used herein, the term "remediation fluid" refers to any fluid used in conjunction with a remediation operation.

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**[0054]** As used herein, the term "acidizing operation" refers to any operation designed to remove an acid-soluble material from a wellbore, such as an acid-soluble material that comprises at least a portion of the subterranean formation. As used herein, the term "acidizing fluid" refers to a fluid used during an acidizing operation. Mineral acids, such as hydrochloric acid or hydrobromic acid, or organic acids may be present in compositions utilized for acidizing a carbonate formation, whereas hydrofluoric acid may be present in compositions utilized for acidizing utilized for acidizing a siliceous formation.

**[0055]** As used herein, the term "spotting fluid" refers to a fluid designed for localized treatment of a subterranean formation. In one example, a spotting fluid can include a lost circulation material for treatment of a specific section of the wellbore, such as to seal off fractures in the wellbore and prevent sag. In another example, a spotting fluid can include a water control material or material designed to free a stuck piece of drilling or extraction equipment.

15 **[0056]** As used herein, the term "completion fluid" refers to a fluid used during the completion phase of a wellbore, including cementing compositions and cementing fluids.

**[0057]** As used herein, the term "cementing fluid" refers to a fluid used during cementing operations within a wellbore of a well.

20 **[0058]** Reaction products, emulsifying compositions, and emulsified fluids of the present disclosure may also be used in conjunction with enhanced oil recovery (EOR) operations. When used in conjunction with EOR operations, the reaction products of the present disclosure may change surface wetting within a subterranean formation to promote recovery of a hydrocarbon resource 25 therefrom.

**[0059]** In any of the foregoing treatment operations, the treatment fluid may be foamed. Foamed fracturing fluids, for example, may be advantageous compared to viscosified treatment fluids for delivery of proppant particulates to a location in a wellbore. When foamed, treatment fluids may have a foam quality ranging from about 1% to about 99%. Incorporation of a zwitterionic surfactant

within an emulsifying composition or an emulsified fluid may further aid the foaming process.

[0060] Reaction products, emulsifying compositions, or emulsified fluids of the present disclosure may be present in any of the treatment fluids discussed above. Treatment fluids of the present disclosure may feature a concentration of the reaction product of about 0.1 gallons per thousand gallons (gpt) to about 10 gpt, or about 0.1 gpt to about 1 gpt, or about 0.2 gpt to about 0.5 gpt. These concentrations correspond to volume/volume percentages ranging from about 0.01% to about 1%, or from about 0.01% to about 0.1%, or from 0.02% to about 0.05%. The chosen concentration may vary depending upon the particular requirements for a given treatment operation and/or the specific subterranean conditions that are encountered downhole. In some examples, the reaction product may be present in a concentration effective to lower a surface tension for a neutral surfactant also present in the treatment fluid.

15 **[0061]** Treatment fluids containing the reaction products of the present disclosure may optionally further comprise any number of additives that may be used in the oilfield services industry. Illustrative additives that may be present in a treatment fluid in combination with the reaction products of the present disclosure include, for example, surfactants, viscosifiers, gelling agents, gel 20 stabilizers, anti-oxidants, polymer degradation prevention additives, relative permeability modifiers, scale inhibitors, corrosion inhibitors, chelating agents, foaming agents, defoaming agents, antifoaming agents, emulsifying agents, deemulsifying agents, iron control agents, proppants or other particulates, particulate diverters, salts, acids, fluid loss control additives, gas, catalysts, other clay control agents, dispersants, flocculants, scavengers (e.g., H<sub>2</sub>S scavengers, 25 CO<sub>2</sub> scavengers or O<sub>2</sub> scavengers), lubricants, breakers, friction reducers, bridging agents, weighting agents, solubilizers, pH control agents (*e.g.*, buffers), hydrate

inhibitors, consolidating agents, bactericides, catalysts, the like, and any combination thereof. Suitable examples of these additives will be familiar to one

30 having ordinary skill in the art.

### **Other Products**

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**[0062]** The compositions of the present disclosure comprising a reaction product of a dextrin compound, a dextran, or any combination thereof with a fatty acid or fatty ester may be formulated in a wide range of industrial or consumer products in which surfactants may be used. Personal care products may represent

a beneficial class of products in which the compositions of the present disclosure may be present, given the relatively benign nature of the biomolecules present in the reaction products, emulsifying compositions, and emulsified fluids disclosed herein. Illustrative industrial and consumer products in which the foregoing may be present are provided further below.

**[0063]** Adjuvants are compositions that are used in combination with an active substance to increase the efficacy or potency of the active substance. In non-limiting examples, the active substance may be a pharmaceutical compound, a personal care compound, or an agricultural compound.

15 [0064] The emulsifying compositions or emulsified fluids of the present disclosure may be present in adjuvant compositions in which surfactants of various types may be used. The foregoing may replace a surfactant used in an adjuvant composition or be used in combination with a surfactant already present in an adjuvant composition. Within an adjuvant composition, the emulsifying 20 compositions or emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the adjuvant composition as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

[0065] An active compound may be present in the adjuvant compositions, or an adjuvant composition may be administered separately from an active compound. When administered separately, the adjuvant compositions may be administered before or after the active compound.

[0066] Examples of suitable additional components that may be present in adjuvant compositions containing a reaction product of the present disclosure
include, but are not limited to, other surfactants, anti-foam compounds, particulates, metal oxides (*e.g.*, silica, alumina, titania, zirconia, and the like),

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electrolytes, salts, organic solvents, wetting agents, dispersants, emulsifying agents, de-emulsifying agents, penetrants, preservatives, colorants, acids, bases, buffers, chelating agents, viscosifiers, thixotropic agents, stabilizers, film-forming agents, plasticizers, preservatives, antioxidants, and the like, including any combination thereof. Other surfactants that may be present in the adjuvant compositions are not particularly limited and may include any one or a combination of cationic, anionic, neutral or zwitterionic surfactants.

[0067] Foaming agents are compositions that are a stabilized dispersion of a large volume of gas in the form of bubbles of varying sizes in a relatively
10 small volume of liquid, or compositions that may form a foam upon suitable introduction of gas thereto (foamable formulations).

[0068] The emulsifying compositions and emulsified fluids of the present disclosure may be present in foaming agents in which surfactants of various types may be used. The foregoing may replace a surfactant used in a foaming agent or be used in combination with a surfactant already present in a foaming agent. Within a foaming agent, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the foaming agent as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

[0069] Foaming agents may contain any combination of cationic surfactants, anionic surfactants, zwitterionic surfactants, or neutral surfactants. The emulsifying compositions disclosed herein may be present in a foaming agent in combination with any of cationic surfactants, anionic surfactants, zwitterionic surfactants, neutral surfactants or any two or more of these surfactants.
 Alternately, the emulsifying compositions disclosed herein may replace all or a portion of any one or more of these surfactants in a foaming agent. The compositions may replace a sulfosuccinate surfactant or be used in combination with a sulfosuccinate surfactant in some foaming agent embodiments, for example.

30 **[0070]** Examples of suitable additional components that may be present in foaming agents containing a reaction product of the present disclosure include,

but are not limited to, other surfactants, amines (any one or a combination of primary amines, secondary amines, tertiary amines, diethanolamine, triethanolamine, ethoxylated amines and amidoamines), foam boosters such as amine oxides, solvents, water, salts, skin conditioners (e.g., ethylhexylglycerin,

hydroxyethylurea, urea, panthenol, glycerin, isopropyl myristate, propylene 5 glycol, tocopheryl acetate, and polyguaternium-11), moisturizers, liguefied gases, supercritical gases, acids, bases, salts, buffers, chelating agents, and the like, including any combination thereof. Suitable examples of these additional components will be familiar to one having ordinary skill in the art. Other 10 surfactants that may be present in the foaming agents are not particularly limited and may include any one or a combination of cationic, anionic, neutral or zwitterionic surfactants.

**[0071]** Hard surface cleaners are compositions that may be used to remove various substances from surfaces like glass, metals, plastics, stone, concrete, and the like. Hard surfaces that may be cleaned with hard surface 15 cleaners include, for example, windows, countertops, appliances, floors, driveways, toilets, showers and bathtubs, sinks, and the like. Substances removable from these types of hard surfaces and others span a wide range and include, but are not limited to, dirt, grease, soap scum, limescale and similar hard 20 water deposits, and the like.

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**[0072]** The emulsifying compositions and emulsified fluids of the present disclosure may be present in hard surface cleaners in which surfactants of various types may be used. The foregoing may replace a surfactant used in a hard surface cleaner or be used in combination with a surfactant already present in a hard surface cleaner. Within a hard surface cleaner, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the hard surface cleaner as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

**[0073]** Examples of suitable additional components that may be present 30 in hard surface cleaners containing a reaction product of the present disclosure include, but are not limited to, other surfactants, foaming compounds, anti-foam

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compounds, salts such as alkali metal carbonates, organic solvents such as glycols or glycol ethers, wetting agents, dispersants, emulsifying agents, de-emulsifying agents, colorants, acids, bases, buffers, chelating agents, anti-streaking agents, alkanolamines, and the like, including any combination thereof. Other surfactants that may be present in the hard surface cleaners are not particularly limited and may be any one or a combination of cationic, anionic, neutral or zwitterionic

surfactants.

[0074] Skin creams and lotions are compositions that may moisturize or otherwise improve the appearance of skin. Skin creams and lotions are inclusive
of gels formulated for application to the skin, which may have a higher viscosity than creams or lotions.

**[0075]** The emulsifying compositions and emulsified fluids of the present disclosure may be present in skin creams and lotions in which surfactants may be used. The foregoing may replace a surfactant used in a skin cream or lotion or be used in combination with a surfactant already present in a skin cream or lotion. Within a skin cream or lotion, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the skin cream or lotion as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt.

% to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

[0076] Examples of suitable additional components that may be present in skin creams or lotions disclosed herein include, but are not limited to, other surfactants, emulsifiers, essential oils, waxes, fats, solvents, viscosifying agents, mono-alcohols, diols, polyols, diol and polyol ethers, milk proteins, emollients, humectants, skin conditioners, preservatives, acids, bases, buffers, chelating agents, thickeners, vitamins, lubricants, wrinkle reducers, moisturizers, radical inhibitors and other antioxidants, Vitamin A, Vitamin E, ceramides, fatty acids, fatty esters, fatty alcohols, hyaluronic acid, sodium pyroglutamic acid, glycerin, aloe vera, fragrances, colorants, preservatives, sunscreens, and the like, including any combination thereof. Other surfactants that may be present in the skin
creams and lotions are not particularly limited and may be any one or a combination of cationic, anionic, neutral or zwitterionic surfactants. The reaction

products may replace at least a portion of one or more existing surfactants in a skin cream or lotion or supplement a quantity of one or more existing surfactants in a skin cream or lotion.

[0077] Body washes and shampoos are cleansing compositions 5 formulated for application to the skin or hair. Liquid soaps for more generalized personal cleansing are similar in composition to some body washes and shampoos and may be formulated with many of the same components.

[0078] The emulsifying compositions and emulsified fluids of the present disclosure may be present in body washes, shampoos, and liquid soaps in which surfactants may be used. The foregoing may replace a surfactant used in a body wash, shampoo, or liquid soap, or be used in combination with a surfactant already present in a body wash, shampoo or liquid soap. Within a body wash, shampoo, or liquid soap, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the body wash, shampoo, or liquid soap as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

[0079] Examples of suitable additional components that may be present in body washes, shampoos, or liquid soaps disclosed herein include, but are not limited to, other surfactants, conditioners, amidoamines, fragrances, colorants, essential oils, foaming agents, humectants, fatty acids, fatty esters, fatty alcohols, waxes, biocides, soaps, preservatives, acids, bases, buffers, chelating agents, thickeners, vitamins, pearlizing agents, viscosifying agents, moisturizers, antioxidants, sunscreens, and the like, including any combination thereof. Illustrative examples of body washes, shampoos, and liquid soaps may comprise water, an effective amount of the compositions, optionally in further combination with another surfactant, 0-4% pearlizing agent, 0-1% suspension aids, 0-2% fragrance, 0-0.25% chelating agent, 0-1% preservatives, 0-2% colorant and 0-25% conditioner. Other surfactants that may be present in the body washes, shampoos, and liquid soaps are not particularly limited and may be any one or a

30 combination of cationic, anionic, neutral or zwitterionic surfactants.

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**[0080]** Sunscreens are substances that may be applied to the skin to afford protection from the sun. Sunscreens may be formulated as creams or with a suitable wax base in "stick" format for application to the skin.

- [0081] The emulsifying compositions and emulsified fluids of the present
  disclosure (*e.g.*, a reaction product of a dextrin or dextran and a fatty ester, as specified above, in combination with a neutral surfactant or a zwitterionic surfactant) may be present in sunscreens in which surfactants may be used. The foregoing may replace a surfactant used in a sunscreen or be used in combination with a surfactant already present in a sunscreen. Within a sunscreen, the
  emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the sunscreen as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.
- [0082] Examples of suitable additional components that may be present in sunscreens include, but are not limited to, other surfactants, conditioners, titanium dioxide, zinc oxide, organic UV absorbers, film forming agents, solvents, aerosol propellants, waxes, fats, oils, moisturizers, fragrances, colorants, essential oils, fatty acids, fatty esters, fatty alcohols, preservatives, acids, bases, buffers, chelating agents, thickeners, insect repellents, skin conditioners, and the like, including any combination thereof. Other surfactants that may be present in the sunscreens are not particularly limited and may be any one or a combination of cationic, anionic, neutral or zwitterionic surfactants.

[0083] Organic UV absorbers that may be present in a sunscreen in combination with the compositions include, but are not limited to, para-25 aminobenzoic acid, avobenzone, cinoxate, dioxybenzone, homosalate, menthyl anthranilate, octyl salicylate, oxybenzone, padimate O, phenylbenzimidazole sulfonic acid, sulisobenzone, trolamine salicylate, diethanolamine methoxycinnamate, digalloy trioleate, ethyl dihydroxypropyl PABA, glyceryl aminobenzoate, lawsone with dihydroxyacetone, red petrolatum, ethylhexyl triazone, dioctyl butamido triazone, benzylidene malonate polysiloxane, 30 terephthalylidene dicamphor sulfonic acid, disodium phenyl dibenzimidazole

tetrasulfonate, diethylamino hydroxybenzoyl hexyl benzoate, bis diethylamino hydroxybenzoyl benzoate, bis benzoxazoylphenyl ethylhexylimino triazine, drometrizole trisiloxane, methylene bis-benzotriazolyl tetramethylbutylphenol, and bis-ethylhexyloxyphenol methoxyphenyltriazine, 4-

- 5 methylbenzylidenecamphor, isopentyl 4-methoxycinnamate, phenylbenzimidazole sulfonate, 2-hydroxy-4-methoxy benzophenone-5sulfonate, 4-(2-beta-glucopyrano-siloxy)propoxy-2-hydroxybenzophenone, and bis-sodium phenylene-1,4-bis(2-benzimidazyl)-3,3'-5,5'-tetrasulfonate, 2ethylhexyl-p-methoxycinnamate, 4-tert-4'-methoxydibenzoylmethane, 2,4-bis-[{4-(2-ethythexyloxy)-2-hydroxy}-phenyl]-6-(4-10 octocrylene,
- methoxyphenyl)-1,3,5-triazine, methylene bis-benzotriazolyl tetrarnethyl butylphenol, 2,4,6-tris-[4-(2-ethylhexyloxycarbonyl)anilino]-1,3,5-triazine, diethylamino hydroxybenzoyl hexyl benzoate, oxybenzone, and dihydroxy dimethoxy benzophenone, and mixtures thereof.
- [0084] Still other organic UV absorbers that may be suitable for inclusion in a sunscreen include, but are not limited to, bis-resorcinyl triazines; benzimidazole derivatives; 4-methylbenzylidene camphor; benzoyl piperazine derivatives; benzoxazole derivatives; diarylbutadiene derivatives; phenyl benzotriazole derivatives; benzylidene malonates; TEA-salicylate; imidazoline
   derivatives; naphthalates; merocyanine derivatives; aminobenzophenone derivatives; dibenzoylmethane derivatives; β,β-diphenylacrylate derivatives; and benzalmalonate derivatives.

**[0085]** In addition to formulations that are sunscreens alone, the emulsifying compositions and emulsified fluids of the present disclosure may be present in sunscreens that are incorporated into other products such as lotions, cologne, cosmetics, body washes and shampoos, and the like.

[0086] Hair gels and hair sprays are formulations that may be used for holding one's hair in place, or optionally to provide detangling of one's hair. Hair
30 sprays are aerosolized formations, whereas gels are high-viscosity fluids and may be applied by hand.

[0087] The emulsifying compositions and emulsified fluids of the present disclosure may be present in hair sprays and hair gels in which surfactants may be used. The foregoing may replace a surfactant used in a hair spray or hair gel or be used in combination with a surfactant already present in a hair spray or hair gel. Within a hair spray or hair gel, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the hair gel or hair spray as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

**[0088]** Examples of suitable additional components that may be present 10 in hair sprays or hair gels include, but are not limited to, other surfactants, cellulose-based biopolymers, water-soluble polymers, polyalkylene glycols, polyalkylene glycol esters, conditioning agents, emollients, humectants, emulsifiers, opacifying agents, thickening agents, foam stabilizers, viscosity builders, sequestrates, antioxidants, antidandruff agents, suspending agents, proteins, fragrances, sunscreens, botanical extracts, essential oils, fatty acids, 15 fatty esters, fatty alcohols, preservatives, acids, bases, buffers, chelating agents, thickeners, vitamins, waxes, oils, aerosol propellants, polyvinylpyrrolidone, polyvinyl acetate, vinyl acetate-crotonic acid copolymers, acrylic acid copolymers, plasticizers, alcohols, and the like, including any combination thereof. Other 20 surfactants that may be present in the hair sprays and hair gels are not particularly limited and may be any one or a combination of cationic, anionic, neutral or zwitterionic surfactants.

[0089] One or more examples of a hair spray or hair gel may comprise an emulsifying composition or emulsified fluid of the present disclosure and one or more of cetearyl alcohol, behentrimonium chloride, cyclopentasiloxane, dimethicone, ethylhexyl isononanoate, behenyl alcohol, meadowfoam seed oil, cyclohexasiloxane, olive fruit oil, prunus amygdalus dulcis, stearamidopropyl dimethylamine, behentrimonium methosulfate, amodimethicone, panthenol, glycol stearate, ceteth-2, hydroxyethylcellulose, phenoxyethanol, methylparaben, or propylparaben, citric acid, mica, titanium dioxide, iron oxide, fragrance, or any combination thereof.
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**[0090]** One or more examples of a hair spray or hair gel may comprise an emulsifying composition or emulsified fluid of the present disclosure and one or more of cyclomethicone, jojoba ester, dimethicone copolyol, nonfat dry milk, soy protein, stearic acid, capric/caprylic stearic triglyceride, jojoba oil, hybrid sunflower oil, cetearyl alcohol, glyceryl stearate, PEG-40 stearate, aloe vera gel, acrylates/C<sub>10-30</sub> alkyl acrylate crosspolymer, propylene glycol, tocopheryl acetate, methylparaben, propylparaben, fragrance, or any combination thereof.

[0091] Cosmetics are formulations that may be used for altering or improving one's physical appearance. Illustrative cosmetics include, but are not limited to, lipstick, blush, mascara, foundation, eyeliner, and the like. Forms of cosmetics may include, for example, emulsions, creams, gels, dispersions, sticks, and the like. Suitable emulsions within cosmetics may include oil-in-water or water-in-oil emulsions.

[0092] The emulsifying compositions and emulsified fluids of the present
disclosure may be present in various types of cosmetics in which surfactants may be used. The foregoing may replace a surfactant used in a cosmetic or be used in combination with a surfactant already present in a cosmetic. Within a cosmetic, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the cosmetic as a whole, or about 0.1
wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

[0093] Examples of suitable additional components that may be present in cosmetics include, but are not limited to, other surfactants, perfumes, preservatives, coloring materials, UV absorbers, moisture-retaining agents, emulsifiers, gelling agents, oils, thickening agents, foam stabilizers, viscosity builders, preservatives, sequestrates, antioxidants, suspending agents, proteins, fragrances, sunscreens, botanical extracts, essential oils, fats (*e.g.*, shea butter, mango seed butter, and cacao seed butter), fatty acids, fatty esters, fatty alcohols, biocides, soaps, preservatives, acids, bases, buffers, chelating agents, thickeners, vitamins, waxes (*e.g.*, myristyl myristate, camellia sinensis leaf extract, jojoba, sunflower seed, carnauba wax, candelilla wax, and beeswax), and

the like, including any combination thereof. Some examples of components that may be present in cosmetics may include, for example, higher fatty alcohols such as cetyl alcohol, stearyl alcohol and behenyl alcohol; higher fatty acids, including caprylic/capric triglyceride, lauric acid, myristic acid, palmitic acid and stearic

- 5 acid; hydrocarbons including ceresin; natural oils including meadowfoam seed oil, sunflower seed oil, macadamia seed oil, green tea seed oil, ginger oil, ginseng oil, coconut oil, olive oil and camellia oil; esters including phytosteryl/octyldodecyl lauroyl glutamate, isostearyl isostearate, methylheptyl isostearate, dicaprylyl carbonate and isopropyl palmitate; ethers including dicaprylyl ether; silicone oils
- 10 including dimethicone, cyclopentasiloxane, cyclohexasiloxane, phenyltrimethicone, trisiloxane and methyltrimethicone; and hydrocarbons including squalane. Other surfactants that may be present in the cosmetics are not particularly limited and may be any one or a combination of cationic, anionic, neutral or zwitterionic surfactants. Cosmetics of the present disclosure may be
- 15 formulated in any suitable form including, sticks, creams, powders, gels, and the like.

**[0094]** Deodorants and antiperspirants are formulations that may be utilized for controlling body odor. Deodorants and antiperspirants of the present disclosure may be formulated in stick form, gel form, powder form or aerosolizable form

20 form.

[0095] The emulsifying compositions and emulsified fluids of the present disclosure may be present in deodorants and antiperspirants in which surfactants may be used. The foregoing may replace a surfactant used in a deodorant or antiperspirant or be used in combination with a surfactant already present in a deodorant or antiperspirant. Within a deodorant or antiperspirant, the emulsifying compositions and emulsified fluids may be present in an amount of about 0.01 wt. % to about 20 wt. % of the deodorant or antiperspirant as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.

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**[0096]** Examples of suitable additional components that may be present in deodorants or antiperspirants disclosed herein include, but are not limited to,

other surfactants, aluminum salts (*e.g.*, alum, aluminum chloride, aluminum chlorohydrate, aluminum-zirconium compounds, aluminum-zirconium tetrachlorohydrex gly, and aluminum-zirconium tetrachlorohydrex gly), anti-bacterial agents, parabens, alcohols, propylene glycol, hexamethylenetetramine,

- 5 acids, bases, buffers, chelating agents, perfumes, preservatives, coloring materials, moisture-absorbing agents (desiccants), emulsifiers, gelling agents, oils, thickening agents, foam stabilizers, viscosity builders, sequestrates, antioxidants, suspending agents, fragrances, essential oils, fats, fatty acids, fatty esters, fatty alcohols, waxes, and the like, including any combination thereof.
- 10 Other surfactants that may be present in the deodorants and antiperspirants are not particularly limited and may be any one or a combination of cationic, anionic, neutral or zwitterionic surfactants. Deodorants and antiperspirants of the present disclosure may be formulated in any suitable form including, sticks, creams, powders, gels, and the like.
- 15 [0097] The emulsifying compositions and emulsified fluids of the present disclosure may also find exemplary uses and formulations outside the personal care space as well. In addition to the oilfield applications described above, the emulsifying compositions and emulsified fluids of the present disclosure may be incorporated in applications in which metal sequestration from a fluid is needed, such as within froth floatation processes. Froth floatation processes may be conducted in various instances, such as mining runoff or wastewater treatment. In such applications, the emulsifying compositions of the present disclosure may replace a surfactant used in froth floatation or be used in combination with a surfactant already present in froth floatation process. Within a given froth floatation process, the emulsifying compositions may be present in an amount of
- about 0.01 wt. % to about 20 wt. % of a froth floatation fluid as a whole, or about 0.1 wt. % to about 10 wt. %, or about 1 wt. % to about 15 wt. %, or about 5 wt. % to about 20 wt. %.
- [0098] In some examples, the emulsifying compositions and emulsified
   fluids of the present disclosure may be utilized in roughers and cleaner circuits to promote clay dispersion, water conditioning, additive enhancement and/or

emulsification of metal suppressants such as Mn and Fe. Any conventional frothing agent may be utilized in combination with the emulsifying compositions and emulsified fluids disclosed herein. Suitable frothing agents and details concerning frothing agents will be familiar to one having ordinary skill in the art.

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[0099] Embodiments disclosed herein include:

**[0100]** A. Emulsified fluids. The emulsified fluids comprise: an oleaginous substance emulsified with an emulsifying composition, the emulsifying composition comprising: an aqueous fluid; a neutral surfactant or a reaction product form thereof; a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and a zwitterionic surfactant.

15 **[0101]** A1. Subterranean treatment fluids comprising the emulsified fluid of A.

**[0102]** A2. Personal care products comprising the emulsified fluid of A.

[0103] B. Methods for forming an oil-in-water emulsion. The methods comprise: providing a zwitterionic surfactant; providing an aqueous surfactant composition comprising a reaction product of a saccharide polymer and a fatty acid or a fatty ester in an aqueous fluid, the aqueous surfactant composition also comprising a neutral surfactant or a reaction product form thereof; combining the zwitterionic surfactant with the aqueous surfactant composition to form an emulsifying composition; and contacting the emulsifying composition with an oleaginous substance to form an oil-in-water emulsion.

**[0104]** Embodiments A, A1, A2, and B may comprise one or more of the following additional elements in any combination.

**[0105]** Element 1: wherein the emulsifying composition further comprises glycerol.

**[0106]** Element 2: wherein the reaction product is formed from a fatty ester, and at least a portion of the glycerol originates from the fatty ester.

**[0107]** Element 3: wherein the fatty ester comprises a glycerol ester comprising up to three types of carboxylic acids each having about 4 to about 30 carbon atoms.

**[0108]** Element 4: wherein the reaction product of the saccharide 5 polymer and the fatty acid or the fatty ester is present in the emulsifying composition at a concentration effective to lower a surface tension of the neutral surfactant.

[0109] Element 5: wherein the neutral surfactant or the reaction product form thereof is present in a sufficient concentration in the emulsifying composition
to solubilize the reaction product of the saccharide polymer and the fatty acid or the fatty ester in the aqueous fluid.

**[0110]** Element 6: wherein the oleaginous substance and the emulsifying composition collectively define an oil-in-water emulsion.

[0111] Element 7: wherein the zwitterionic surfactant is present in asufficient concentration in the emulsifying composition to promote formation of the oil-in-water emulsion.

**[0112]** Element 8: wherein the saccharide polymer comprises a dextrin compound, and the dextrin compound comprises a maltodextrin.

[0113] Element 9: wherein the maltodextrin has a dextrose equivalentvalue of about 3 to about 25.

**[0114]** Element 10: wherein a molar ratio of fatty acid to saccharide polymer in the reaction product is about 0.2 or above on a basis of moles<sub>fatty acid or</sub> fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer.

[0115] Element 11: wherein the reaction product of the saccharide polymer comprises a fatty ester saccharide polymer reaction product.

**[0116]** Element 12: wherein the neutral surfactant comprises a fatty acid alkanolamide.

[0117] Element 13: wherein the fatty acid alkanolamide comprises a compound selected from the group consisting of cocamide diethanolamine,
 30 cocamide monoethanolamine, cocamide diisopropanolamine, palmitic amide

diethanolamine, palmitic amide monoethanolamine, palmitic amide diisopropanolamine, and any combination thereof.

**[0118]** Element 14A: wherein the oil-in-water emulsion is stable for at least about 1 day.

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**[0119]** Element 14B: wherein the emulsified fluid is stable for at least about 1 day.

[0120] By way of non-limiting example, exemplary combinations applicable to A, A1, A2, and B include, but are not limited, to: 1, 2, and/or 3, and 4; 1, 2, and/or 3, and 5; 1, 2, and/or 3, and 6; 1, 2, and/or 3, and 7; 1, 2, and
10 /or 3, and 8; 1, 2, and/or 3, and 8 and 9; 1, 2, and/or 3, and 10; 1, 2, and/or 3, and 11; 1, 2, and/or 3, and 12; 1, 2, and/or 3, and 12 and 13; 4 and 5; 4-6; 4 and 6; 4 and 7; 4, 5, and 7; 4 and 8; 4, 8, and 9; 4 and 10; 4 and 11; 4 and 12; 4, 12, and 13; 5 and 6; 5 and 7; 5-7; 5 and 8; 5, 8, and 9; 5 and 10; 5 and 11; 6 and 12; 6, 12, and 13; 7 and 8; 7-9; 7 and 10; 7 and 11; 7 and 12; 7, 12, and 13; 8 and 9; 8 and 10; 8 and 11; 8 and 12; 8, 12, and 13; 10 and 11; 10 and 12; 10, 12, and 13; 11 and 12; 11-13; and 12 and 13. Any of 1-13 may be in further combination with 14A or 14B, or 14A or 14B may be in further combination with any of the foregoing combinations.

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**[0121]** Additional embodiments disclosed herein include:

[0122] A'. Emulsified Fluids. The emulsified fluids comprise: an oleaginous substance emulsified with an emulsifying composition, the emulsifying composition comprising: an aqueous fluid; a neutral surfactant or a reaction product form thereof; a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and a zwitterionic surfactant.

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**[0123]** B': Emulsifying compositions. The emulsifying compositions comprise: an aqueous fluid; a neutral surfactant or a reaction product form

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thereof; a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant,

5 if present, being formed in the presence of a hydroxide base in the aqueous fluid; and a zwitterionic surfactant; wherein the zwitterionic surfactant is present in an amount greater than an amount of the reaction product of the saccharide polymer, as measured on a mass basis.

[0124] C'. Methods for emulsifying an aqueous fluid. The methods comprise: providing an emulsifying composition comprising: an aqueous fluid; a neutral surfactant or a reaction product form thereof; a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester 15 and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and a zwitterionic surfactant; and contacting the emulsifying composition with an oleaginous substance to form an emulsion.

[0125] A1': Personal care products comprising the emulsified fluid of A'20 or the emulsifying composition of B'.

**[0126]** A2': Subterranean treatment fluids comprising the emulsified fluid of A' or the emulsifying composition of B'.

**[0127]** Embodiments A', A1', A2', B', and C' may comprise one or more of the following additional elements in any combination.

**[0128]** Element 1': wherein the emulsifying composition further comprises glycerol.

**[0129]** Element 2': wherein the reaction product of the saccharide polymer is formed from a fatty ester, and at least a portion of the glycerol originates from the fatty ester.

**[0130]** Element 3': wherein the fatty ester comprises a glycerol ester comprising up to three types of fatty acids, each fatty acid having about 4 to about 30 carbon atoms.

[0131] Element 4': wherein the oleaginous substance and the 5 emulsifying composition collectively define an oil-in-water emulsion.

**[0132]** Element 5': wherein the zwitterionic surfactant is present in an amount greater than an amount of the reaction product of the saccharide polymer, as measured on a mass basis.

[0133] Element 6': wherein the zwitterionic surfactant is present in an amount of about 2:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.

**[0134]** Element 7': wherein the zwitterionic surfactant is present in an amount of about 4:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.

15 **[0135]** Element 8': wherein the saccharide polymer comprises a dextrin compound, and the dextrin compound comprises a maltodextrin.

**[0136]** Element 9': wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose monomers in saccharide polymer</sub>.

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**[0137]** Element 10': wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 to about 0.9 on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose monomers in saccharide polymer</sub>.

**[0138]** Element 11': wherein the reaction product of the saccharide polymer comprises a fatty ester saccharide polymer reaction product.

**[0139]** Element 12': wherein the neutral surfactant comprises a fatty acid alkanolamide.

**[0140]** Element 13': wherein the emulsified fluid is stable for at least about 1 day.

**[0141]** By way of non-limiting example, exemplary combinations applicable to A', A1', A2', B', and C' include, but are not limited, to: 1' and 5'; 1', and 6' or 7'; 1' and 8'; 1', and 9' or 10'; 1' and 12'; 1' and 13'; 4' and 5'; 4', and

6' or 7'; 4' and 8'; 4', and 9' or 10'; 4' and 12'; 4' and 13'; 5', 6', or 7', and 8; 5', 6', or 7', and 9' or 10'; 5', 6', or 7', and 12'; 8', and 9' or 10'; 8' and 11'; 8' and 12'; 8' and 13'; and 9' or 10', and 12.

**[0142]** To facilitate a better understanding of the disclosure herein, the 5 following examples of various representative embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

## EXAMPLES

[0143] Example 1: Representative Procedure for Preparation of Maltodextrin Reaction Products Using a Glycerol Ester. 25.00 g fatty acid 10 alkanolamide surfactant and 10.00 g KOH (45% active solution) were combined in water. The reaction mixture was mechanically stirred and heated to 65°C. Thereafter, soybean oil and 150.0 g maltodextrin (MALTRIN M100, Grain Processing Corporation, Muscatine, Iowa; DE=9.0-12.0) as a 30% active solution were added to the reaction mixture. The amount of soybean oil was selected to 15 provide a HLB of either 12 or 16 upon formation of a reaction product. The amount of water was selected to provide an alkanolamide surfactant concentration of 5 wt. %, a fatty ester (oil) concentration of 2.5 wt. %, and a maltodextrin concentration of 10 wt. %, based on all reaction components. Once the 20 maltodextrin dissolved, heating was discontinued and stirring was conducted until

the reaction mixture reached room temperature. The resulting aqueous phase containing the reaction products was used without further processing for the additional testing below. Dextran reaction products may be formed using a similar Other fatty esters and alkanolamide surfactants may be used procedure. 25 similarly.

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[0144] Example 2: Representative Procedure for Preparation of Maltodextrin Reaction Products Using Free Fatty Acids. 25.00 g fatty acid alkanolamide surfactant and 10.00 g KOH (45% active solution) were combined in water. The reaction mixture was mechanically stirred and heated to 65°C. Thereafter, a fatty acid mixture containing saturated fatty acids, including lauric acid and myristic acid as main components, and 150.0 g maltodextrin (MALTRIN

M100, Grain Processing Corporation, Muscatine, Iowa; DE=9.0-12.0) as a 30% active solution were added to the reaction mixture. The amount of the fatty acid mixture was selected to provide a HLB of either 12 or 16. The amount of water was selected to provide an alkanolamide surfactant concentration of 5 wt. %, a

5 fatty acid concentration of 2.5 wt. %, and a maltodextrin concentration of 10 wt. %, based on all reaction components. Once the maltodextrin dissolved, heating was discontinued and stirring was conducted until the reaction mixture reached room temperature. The resulting aqueous phase containing the reaction products was used without further processing for the additional testing below. Dextran 10 reaction products may be formed using a similar procedure. Other fatty esters and alkanolamide surfactants may be used similarly.

[0145] Preparation of Emulsifying Compositions. The as-made reaction products prepared as above were tested for emulsifying performance or further combined with a zwitterionic surfactant to form an emulsifying composition. The samples were diluted with 4% KCl or water after adding the zwitterionic surfactant. Emulsion performance was determined by combining the reaction products or an emulsifying composition formed therefrom, followed by shaking with a specified volume of oleaginous substance. After emulsifying the oleaginous substance, the emulsion stability was monitored over time, usually at

- 20 least overnight and in many instances over a period of days or weeks. For emulsions remaining stable over the observation period, a few drops of the emulsion were added to either water or the oleaginous substance itself to determine the nature of the emulsion. Oil-in-water emulsions remained dispersed when added to water and did not undergo phase separation, whereas phase
- 25 separation did occur when these types of emulsions were added to the oleaginous substance. Table 1 below summarizes the samples tested and outcomes obtained.

Emulsifying Composition [Vol. % Added]			Emulsified Fluid Composition [Vol. Added]					
2 Rxn.	Surfactant		Comp		Subs.			
Product								
	SOPALTERIC	Water	1.25	4% KCl	off-road	stable		
22%	CBS <sup>a</sup>	[45%]	mL	[3 mL]	diesel	emulsion		
	[33%]				[12 mL]	for 3		
						weeks		
	SOPALTERIC	Water	1.25	4% KCl	on-road	emulsion		
22%	CBS <sup>a</sup>	[45%]	mL	[3 mL]	diesel	broke		
	[33%]				[12 mL]	within 6		
						hours		
22%	SOPALTERIC	Water	0.1	water	avocado oil	stable		
	CBS <sup>a</sup>	[45%]	mL	[4 mL]	[16 mL]	emulsion,		
	[33%]					oil-in-		
						water		
22%	SOPALTERIC	Water	0.1	water	60% C <sub>8</sub>	stable		
	CBSª	[45%]	mL	[4 mL]	triglyceride,	emulsion,		
	[33%]				40% C <sub>10</sub>	oil-in-		
					triglyceride	water		
					[16 mL]			
22%	SOPALTERIC	Water	0.1	water	corn oil	stable		
	CBS <sup>a</sup>	[45%]	mL	[4 mL]	[16 mL]	emulsion,		
	[33%]					oil-in-		
						water		
100%			0.1	water	soybean oil	unstable		
			mL	[4 mL]	[16 mL]	emulsion		
	SOPALTERIC		0.1	water	soybean oil	unstable		
	CHS-50G <sup>♭</sup>		mL	[4 mL]	[16 mL]	emulsion		
	[100%]							
25%	SOPALTERIC	50%	0.1	water	soybean oil	stable		
	CHS-50G <sup>♭</sup>		mL	[4 mL]	[16 mL]	emulsion,		
	[25%]					oil-in-		
						water		
36%	SOPALEX		0.2	water	unrefined	stable		
	C-37 <sup>c</sup>		mL	[3.8 mL]	soybean oil	emulsion		
	[64%]				[16 mL]			

Table 1

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Emulsifying Composition [Vol. % Added]			Emulsified Fluid Composition [Vol. Added]				
Example 2 Rxn. Product	Zwitterionic Surfactant	Diluent	Emul. Comp	Diluent	Oleag. Subs.	Result	
36%	SOPALEX C-37 <sup>c</sup> [64%]		0.2 mL	120K brine [3.8 mL]	unrefined soybean oil [16 mL]	unstable emulsion	
35%	SOPALTERIC CHS <sup>d</sup> [65%]		0.4 mL	120K brine [3.8 mL]	unrefined soybean oil [16 mL]	stable emulsion	

<sup>a</sup>cocamidopropyl hydroxysultaine, 50% active solution, glycerin free (Southern Chemical)

<sup>b</sup>cocamidopropyl hydroxysultaine, 50% active solution (Southern Chemical) <sup>c</sup>cocamidopropyl betaine, 35-40% active solution (Southern Chemical)

5 <sup>d</sup>cocamidopropyl hydroxysultaine, 50% active solution (Southern Chemical)

The 120K brine had the following composition (g/L of each component): CaCl<sub>2</sub> (16.540), NaCl (103.730), MgCl<sub>2</sub> (4.230), NaHCO<sub>3</sub> (0.830), BaCl<sub>2</sub> (0.180), Na<sub>2</sub>SO<sub>4</sub> (0.740), SrCl<sub>2</sub> (0.180), and FeCl<sub>3</sub> (0.030).

10 [0146] The Brookfield viscosity of selected soybean oil emulsions were measured at room temperature (25°C). Soybean oil itself exhibited a Brookfield viscosity of 15 cP (63 spindle, 20 rpm). Unstable emulsions separating within a few hours tended to exhibit Brookfield viscosity values ranging from approximately 20-100 cP. Stable emulsions, in contrast, exhibited Brookfield 15 viscosity values in the 3000-6000 cP range.

**[0147]** In addition to the foregoing tests, 3 anionic surfactants, 3 neutral surfactants, and 1 cationic surfactant were tested for their emulsification performance for soybean oil in water and 120K brine. The following compositions were tested: a) 1 vol. % of the surfactant, 1 vol. % of the reaction product of Example 2, 18 vol. % of 120 K brine, and 80 vol. % soybean oil, and b) 0.5 vol. % of the surfactant, 0.5 vol. % of the reaction product of Example 2, 19 vol. % of the reaction product of Example 2, 19 vol. % of the surfactant, 0.5 vol. % of the reaction product of Example 2, 19 vol. %

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afforded a stable emulsion in 120 K brine, and only the cationic surfactant showed evidence of successful emulsification in deionized water.

[0148] Unless otherwise indicated, all numbers expressing quantities and the like in the present specification and associated claims are to be understood as 5 being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the embodiments of the present invention. At the very least, and not as an attempt to limit the application of the 10 doctrine of equivalents to the scope of the claim, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0149] One or more illustrative embodiments incorporating various features are presented herein. Not all features of a physical implementation are described or shown in this application for the sake of clarity. It is understood that in the development of a physical embodiment incorporating the embodiments of the present invention, numerous implementation-specific decisions must be made to achieve the developer's goals, such as compliance with system-related, business-related, government-related and other constraints, which vary by implementation and from time to time. While a developer's efforts might be time-consuming, such efforts would be, nevertheless, a routine undertaking for those of ordinary skill in the art and having benefit of this disclosure.

[0150] While various systems, compositions, tools and methods are described herein in terms of "comprising" various components or steps, the
25 systems, compositions, tools and methods can also "consist essentially of" or "consist of" the various components and steps.

**[0151]** As used herein, the phrase "at least one of" preceding a series of items, with the terms "and" or "or" to separate any of the items, modifies the list as a whole, rather than each member of the list (i.e., each item). The phrase "at least one of" allows a meaning that includes at least one of any one of the items, and/or at least one of any combination of the items, and/or at least one of each

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of the items. By way of example, the phrases "at least one of A, B, and C" or "at least one of A, B, or C" each refer to only A, only B, or only C; any combination of A, B, and C; and/or at least one of each of A, B, and C.

- [0152] Therefore, the disclosed systems, compositions, tools and 5 methods are well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the teachings of the present disclosure may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are
- 10 intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope of the present disclosure. The systems, compositions, tools and methods illustratively disclosed herein may suitably be
- 15 practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While systems, compositions, tools and methods are described in terms of "comprising," "containing," or "including" various components or steps, the systems, tools and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and
- 20 ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed
- 25 herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the elements that it introduces. If there
- 30 is any conflict in the usages of a word or term in this specification and one or more

patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

## CLAIMS

What is claimed is the following:

1. An emulsified fluid comprising:

an oleaginous substance emulsified with an emulsifying composition, the emulsifying composition comprising:

an aqueous fluid;

a neutral surfactant or a reaction product form thereof;

a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and

a zwitterionic surfactant.

- 2. The emulsified fluid of claim 1, wherein the emulsifying composition further comprises glycerol.
- 3. The emulsified fluid of claim 2, wherein the reaction product of the saccharide polymer is formed from a fatty ester, and at least a portion of the glycerol originates from the fatty ester.
- The emulsified fluid of claim 3, wherein the fatty ester comprises a glycerol ester comprising up to three types of fatty acids, each fatty acid having about 4 to about 30 carbon atoms.
- 5. The emulsified fluid of claim 1, wherein the oleaginous substance and the emulsifying composition collectively define an oil-in-water emulsion.
- 6. The emulsified fluid of claim 1, wherein the zwitterionic surfactant is present in an amount greater than an amount of the reaction product of the saccharide polymer, as measured on a mass basis.

- 7. The emulsified fluid of claim 6, wherein the zwitterionic surfactant is present in an amount of about 2:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.
- 8. The emulsified fluid of claim 6, wherein the zwitterionic surfactant is present in an amount of about 4:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.
- 9. The emulsified fluid of claim 1, wherein the saccharide polymer comprises a dextrin compound, and the dextrin compound comprises a maltodextrin.
- 10. The emulsified fluid of claim 1, wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose</sub> monomers in saccharide polymer.
- 11. The emulsified fluid of claim 1, wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 to about 0.9 on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose monomers in saccharide polymer</sub>.
- 12. The emulsified fluid of claim 1, wherein the reaction product of the saccharide polymer comprises a fatty ester saccharide polymer reaction product.
- 13. The emulsified fluid of claim 1, wherein the neutral surfactant comprises a fatty acid alkanolamide.
- 14. The emulsified fluid of claim 1, wherein the emulsified fluid is stable for at least about 1 day.
- 15. A subterranean treatment fluid comprising the emulsified fluid of claim 1.
- 16. A personal care product comprising the emulsified fluid of claim 1.
- 17. An emulsifying composition comprising:

an aqueous fluid;

a neutral surfactant or a reaction product form thereof;

a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the

saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and

a zwitterionic surfactant;

wherein the zwitterionic surfactant is present in an amount greater than an amount of the reaction product of the saccharide polymer, as measured on a mass basis.

- 18. The emulsifying composition of claim 17, wherein the zwitterionic surfactant is present in an amount of about 2:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.
- 19. The emulsifying composition of claim 17, wherein the zwitterionic surfactant is present in an amount of about 4:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.
- 20. The emulsifying composition of claim 17, further comprising: glycerol.
- 21. The emulsifying composition of claim 20, wherein the reaction product of the saccharide polymer is formed from a fatty ester, and at least a portion of the glycerol originates from the fatty ester.
- 22. The emulsifying composition of claim 17, wherein the saccharide polymer comprises a dextrin compound, and the dextrin compound comprises a maltodextrin.
- 23. The emulsifying composition of claim 17, wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 or above on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose monomers in saccharide polymer</sub>.
- 24. The emulsifying composition of claim 17, wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 to about 0.9 on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose monomers in saccharide polymer</sub>.
- 25. The emulsifying composition of claim 17, wherein the neutral surfactant comprises a fatty acid alkanolamide.

- 26. A subterranean treatment fluid comprising the emulsifying composition of claim 17.
- 27. A personal care product comprising the emulsifying composition of claim17.
- 28. A method comprising:

providing an emulsifying composition comprising:

an aqueous fluid;

a neutral surfactant or a reaction product form thereof;

a reaction product of a saccharide polymer and a fatty acid or a fatty ester, the saccharide polymer comprising a dextran, a dextrin compound, or any combination thereof, and the reaction product of the saccharide polymer and the fatty acid or the fatty ester and the reaction product form of the neutral surfactant, if present, being formed in the presence of a hydroxide base in the aqueous fluid; and

a zwitterionic surfactant; and

contacting the emulsifying composition with an oleaginous substance to form an emulsion.

- 29. The method of claim 28, wherein the oleaginous substance and the emulsifying composition collectively define an oil-in-water emulsion.
- 30. The method of claim 28, wherein the emulsifying composition further comprises glycerol.
- 31. The method of claim 30, wherein the reaction product of the saccharide polymer is formed from a fatty ester, and at least a portion of the glycerol originates from the fatty ester.
- 32. The method of claim 31, wherein the fatty ester comprises a glycerol ester comprising up to three types of fatty acids each having about 4 to about 30 carbon atoms.
- 33. The method of claim 28, wherein the saccharide polymer comprises a dextrin compound, and the dextrin compound comprises a maltodextrin.
- 34. The method of claim 28, wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 or

above on a basis of moles<sub>fatty acid</sub> or fatty acid in fatty ester:moles<sub>glucose</sub> monomers in saccharide polymer.

- 35. The method of claim 28, wherein a molar ratio of fatty acid to saccharide polymer in the reaction product of the saccharide polymer is about 0.2 to about 0.9 on a basis of moles<sub>fatty acid or fatty acid in fatty ester</sub>:moles<sub>glucose monomers in saccharide polymer</sub>.
- 36. The method of claim 28, wherein the neutral surfactant comprises a fatty acid alkanolamide.
- 37. The method of claim 28, wherein the zwitterionic surfactant is present in an amount greater than an amount of the reaction product of the saccharide polymer, as measured on a mass basis.
- 38. The method of claim 37, wherein the zwitterionic surfactant is present in an amount of about 2:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.
- 39. The method of claim 37, wherein the zwitterionic surfactant is present in an amount of about 4:1 or greater relative to the reaction product of the saccharide polymer, as measured on a mass basis.

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A. CLASS	IFICATION OF SUBJECT MATTER				
	60(2006.01)i; C11D 1/825(2006.01)i; C11D 1/66(2 //00(2006.01)i; C11D 17/08(2006.01)i	006.01)i; <b>C11D 1/94</b> (	2006.01)i; <b>C11D 1/83</b>	<b>35</b> (2006.01)i;	
According to In	nternational Patent Classification (IPC) or to both na	tional classification an	d IPC		
B. FIELDS	S SEARCHED				
Minimum docu	mentation searched (classification system followed	by classification symb	pols)		
	50(2006.01); A61K 8/46(2006.01); A61K 8/73(200 66(2006.01); C11D 3/20(2006.01)	6.01); C08B 30/18(20	06.01); C08B 37/00(2	2006.01);	
	searched other than minimum documentation to the	e extent that such docu	ments are included in	the fields searched	
	tility models and applications for utility models utility models and applications for utility models				
	base consulted during the international search (nam		-		
eKOMPA	ASS(KIPO internal) & Keywords: surfactant, saccha	aride polymer, dextran	, dextrin, fatty acid, fa	atty ester, emulsion	
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where a	appropriate, of the rele	vant passages	Relevant to claim No.	
X	WO 2021-222520 A1 (INTEGRITY BIO-CHEMICALS, L paragraphs [0028], [0029], [0044], [0058], [0096 1A			1,5-19,22-29,33-39	
Y				2-4,20,21,30-32	
Y U	JS 2004-0055678 A1 (HALES, R. H. et al.) 25 March 200 paragraph [0020]; claim 4	4 (2004-03-25)		2-4,20,21,30-32	
A	P 2017-071588 A (KOSE CORP.) 13 April 2017 (2017-0- paragraphs [0018]-[0070]; claims 1-9	4-13)		1-39	
A U	JS 2012-0316332 A1 (KOIKE, H. et al.) 13 December 20. the whole document	12 (2012-12-13)		1-39	
A	JS 2018-0085299 A1 (CHIBA FLOUR MILLING CO., L the whole document	TD.) 29 March 2018 (20	18-03-29)	1-39	
Further doc	cuments are listed in the continuation of Box C.	See patent famil	y annex.		
"A" document de	gories of cited documents: efining the general state of the art which is not considered ticular relevance	date and not in co		tional filing date or priority n but cited to understand the on	
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Date of the actua	l completion of the international search	Date of mailing of the	e international search	report	
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INTERNATIONAL SEARCH REPORT Information on patent family members International application No.

Patent document cited in search report		Publication date (day/month/year)	P	Patent family member(s)		Publication date (day/month/year)	
WO	2021-222520	A1	04 November 2021	AU	2021-26390	4 A1	04 November 2021
				EP	404562	2 A1	24 August 2022
				KR	10-2023-000287	'1 A	05 January 2023
				US	2021-034042	9 A1	04 November 2021
US	2004-0055678	A1	25 March 2004	AR	04110	0 A1	04 May 2005
				AU	2003-24455	5 A1	08 April 2004
				AU	2003-24455	5 B2	21 January 2010
				AU	2003-24455	5 C1	25 February 2010
				AU	2003-24455	5 C8	17 June 2010
				BR	030413	5 A	08 September 2004
				BR	030413	5 B1	08 April 2014
				CA	243765	4 A1	23 March 2004
				CA	243765	4 C	24 November 2009
				CO	550001	9 A1	31 March 2005
				MX	PA0300794	-1 A	25 March 2004
				NO	2003415	57 L	24 March 2004
				NO	32810	07 B1	07 December 2009
				PE	2004035	7 A1	25 June 2004
				RU	200312841	1 A	20 March 2005
				RU	232672	5 C2	20 June 2008
				SE	030249	7 L	24 March 2004
				SE	52714	-2 C2	10 January 2006
				TR	20030154	-1 A1	21 October 2005
				US	680857	3 B2	26 October 2004
				ZA	20030691	6 B	15 June 2004
JP	2017-071588	А	13 April 2017	JP	657781	8 B2	18 September 2019
US	2012-0316332	A1	13 December 2012	CN	10275358	3 A	24 October 2012
				CN	10275358	3 B	11 March 2015
				EP	253786	5 A1	26 December 2012
				EP	253786	5 B1	08 February 2017
				HK	117464	9 A1	14 June 2013
				JP	588219	2 B2	09 March 2016
				KR	10-169816		19 January 2017
					10-2012-013823		24 December 2012
				TW	20113885		16 November 2011
				TW	I49000		01 July 2015
				US	919380		24 November 2015
				wo	2011-10212		25 August 2011
US	2018-0085299	A1	29 March 2018	CN	10742879		01 December 2017
55	_010 00002//		2, maion 2010	CN	10742879		23 October 2020
				EP	329630		21 March 2018
				EP	329630		29 March 2023
				JP	2016-19969		01 December 2016
				JP	618169		16 August 2017
					10-2017-013220		01 December 2017
				US	2020-017091		04 June 2020
				wo	2016-16725		20 October 2016