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(54) Title: OIL-IN-WATER EMULSIONS THAT EXHIBIT STABILITY OVER TIME

(57) Abstract: An oil-in-water emulsion exhibits stability over time and includes (I) an oil phase present in the emulsion as droplets, (II) an aqueous phase, and (III) a polymer component. The polymer component includes (A) a starch component which includes a particular hydrophobically modified starch, (B) a non-starch polysaccharide, and (C) a cross-linked starch. The emulsion exhibits a stability of at least 4 weeks at room temperature.

OIL-IN-WATER EMULSIONS THAT EXHIBIT STABILITY OVER TIME

TECHNICAL FIELD

[0001] The present disclosure generally relates to oil-in-water emulsions that exhibit stability over time. This disclosure more particularly relates to an oil-in-water emulsion that includes a hydrophobically modified starch.

BACKGROUND

[0002] Oil-in-water (O/W) dispersions are widely used in lotions, creams, and moisturizers to provide moisturization, emollience, and other benefits to the skin. However, these dispersions can suffer from long-term stability issues, which can result in texture and appearance changing over time, leading to consumer dissatisfaction.

[0003] The following are some common problems with long-term stability of oil-in-water dispersions. Creaming occurs when oil droplets rise to the top of the dispersion, resulting in a cream or thick layer forming at the surface. This is typically caused by the difference in density between oil and water phases, and can be exacerbated by temperature changes, agitation, or aging. Phase separation occurs when oil and water phases separate, resulting in a clear layer of oil floating on top of a layer of water. This can occur due to various factors, including insufficient emulsification, temperature changes, and aging. Flocculation occurs when oil droplets in the dispersion aggregate, forming larger clusters that can settle or float to the top of the product. This can be caused by various factors, including changes in pH, ionic strength, and the presence of certain ingredients. Coalescence occurs when oil droplets in the dispersion fuse together, resulting in larger droplets that can settle or float to the top of the product.

[0004] These stability issues can lead to a variety of problems, including changes in the product's texture, appearance, and performance, as well as reduced shelf life and consumer dissatisfaction. Addressing these issues requires careful formulation and selection of ingredients, as well as appropriate manufacturing and storage conditions to ensure long-term stability.

[0005] Traditionally, synthetic materials including small molecules have typically been used as emulsifiers. However, certain small molecule emulsifiers may lead to irritation on skin and negative interactions with cosmetic functional materials in the formulations. In addition, certain small molecule emulsifiers also may not provide desired long-term emulsion stability.

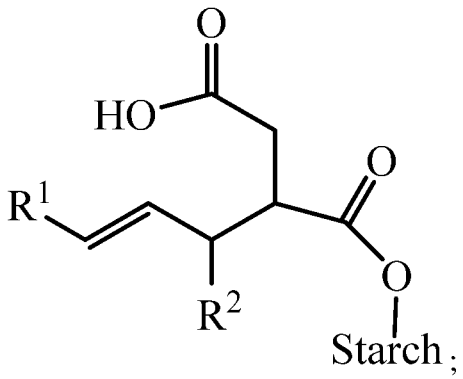
[0006] Hydrophobically modified cross-linked acrylate polymers, such as Carbopol and Pemulen

have been used to stabilize emulsions to overcome van der Waals forces and gravity. Van der Waals forces contribute to flocculation and coalescence while gravity contributes to creaming or sedimentation of dispersed phases of the emulsions. However, the known solutions to these problems include synthetic non-natural polymers.

[0007] Accordingly, there remains an opportunity for improvement. Furthermore, desirable features and characteristics of the present disclosure will become apparent from the subsequent detailed description of the disclosure and the appended claims, taken in conjunction with the accompanying drawings and this background of the disclosure.

SUMMARY

[0008] This disclosure provides an oil-in-water emulsion that exhibits stability over time and includes an oil phase present in an amount of from about 5 to about 60 weight percent actives based on a total weight of the emulsion wherein the oil phase is present in the emulsion as droplets, an aqueous phase present in an amount of from about 30 to about 94.5 weight percent actives based on a total weight of the emulsion, and a polymer component present in an amount of from about 0.5 to about 10 weight percent actives based on a total weight of the emulsion. The polymer component includes a starch component present in an amount of from about 15 to about 45 weight percent actives based on a total weight of the polymer component and including at least one hydrophobically modified starch having the following structure:



wherein R^1 is a C_3 to C_{19} branched or linear alkyl or alkenyl group and R^2 is H or an alkyl group having 1 to 10 carbons. The Starch represents an amylose and/or amylopectin moiety or a modified amylose and/or amylopectin moiety. The polymer component also includes a non-starch polysaccharide present in an amount of from about 0 to about 40 weight percent actives based on a total weight of the polymer component and a cross-linked starch present in an amount of from

about 3 to about 75 weight percent actives based on a total weight of the polymer component. The emulsion exhibits a stability of at least 4 weeks at room temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present disclosure will hereinafter be described in conjunction with the following drawing figures, wherein:

[0010] FIG. 1A is a diagram illustrating the differences between flocculation, coalescence, and creaming of an emulsion; and

[0011] FIG. 1B is a graph of system energy versus inter-droplet distance of droplets of an oil-in-water emulsion showing a first and a second energy barrier to coalescence, and energy trough to flocculation.

DETAILED DESCRIPTION

[0012] The following detailed description is merely exemplary in nature and is not intended to limit the current compositions. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0013] Embodiments of the present disclosure are generally directed to emulsions, compositions including the same, and methods for forming the same. For the sake of brevity, conventional techniques related to making emulsions and such compositions may not be described in detail herein. Moreover, the various tasks and process steps described herein may be incorporated into a more comprehensive procedure or process having additional steps or functionality not described in detail herein. In particular, various steps in the manufacture of emulsions and associated compositions are well-known and so, in the interest of brevity, many conventional steps will only be described briefly herein or will be omitted entirely without providing the well-known process details.

[0014] In this disclosure, the terminology “about” can describe values ± 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10%, in various embodiments. Moreover, it is contemplated that, in various non-limiting embodiments, it is to be appreciated that all numerical values as provided herein, save for the actual examples, are approximate values with endpoints or particular values intended to be read as “about” or “approximately” the value as recited. It is also contemplated that all isomers and chiral options for each compound described herein are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0015] Throughout this disclosure, the terminology percent "actives" is well recognized in the

art and means the percent amount of active or actual compound or molecule present as compared to, for example, a total weight of a diluted solution of a solvent and such a compound. Some compounds, such as a solvent, are not described relative to a percent actives because it is well known to be approximately 100% actives. Any one or more of the values described herein may be alternatively described as percent actives as would be understood by the skilled person.

[0016] In various embodiments, the terminology "free of" describes embodiments that include less than about 5, 4, 3, 2, 1, 0.5, or 0.1, weight percent (or weight percent actives) of the compound or element at issue using an appropriate weight basis as would be understood by one of skill in the art. In other embodiments, the terminology "free of" describes embodiments that have zero weight percent of the compound or element at issue.

[0017] The terminology "consists essentially of" may describe various non-limiting embodiments that are free of one or more optional compounds described herein and/or free of one or more polymers, surfactants, additives, solvents, etc.

[0018] It is to be understood that the subscripts of polymers are typically described as average values because the synthesis of polymers typically produces a distribution of various individual molecules.

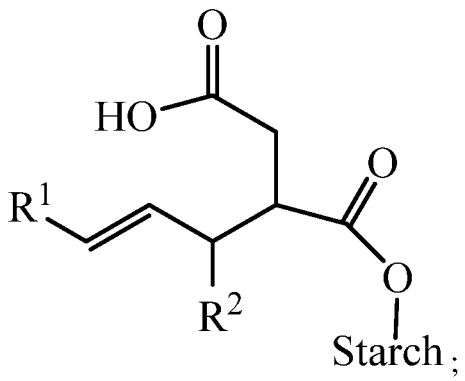
[0019] The emulsions, polymers, and compositions disclosed herein may suitably comprise, consist of, or consist essentially of the components, elements, and process delineations described herein. The embodiments illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein.

[0020] In various embodiments, the terminology "modified" as applied to starch refers to starch molecules that have been reacted at one or more of their hydroxyl groups. In other embodiments, the terminology "hydrophobically-modified" describes a starch molecule that has been substituted with one or more aliphatic or aromatic, saturated or unsaturated, linear, branched or cyclic C_8-C_{30} hydrocarbon-based chain(s). Typically, the "weight" of any starch or cellulose material is reported on a dry weight basis. In various embodiments, the terminology "stability" or "long term stability" can describe the stability of an emulsion over a period of at least 28 days, both at 22°C and 45° C, measured using a TURBISCAN® LAB stability analyzer as described in greater detail below.

[0021] This disclosure provides an oil-in-water (O/W) emulsion that exhibits stability over time, which is described in greater detail below.

[0022] More specifically, the emulsion includes (I) an oil phase present in an amount of from about 5 to about 60 weight percent actives based on a total weight of the emulsion wherein the oil phase is present in the emulsion as droplets, which may have a D_v50 of from about 0.2 to about 50 microns. The emulsion also includes (II) an aqueous phase present in an amount of from about 30 to about 94.5 weight percent actives based on a total weight of the emulsion. The emulsion further provides (III) a polymer component present in an amount of from about 0.5 to about 10 weight percent actives based on a total weight of the emulsion. The polymer component itself includes (A) a starch component present in an amount of from about 15 to about 45 weight percent actives based on a total weight of the polymer component The starch component includes a hydrophobically modified starch.

[0023] In one embodiment, the hydrophobically modified starch has the following structure:



wherein R^1 is a C_3 to C_{19} branched or linear alkyl or alkenyl group and R^2 is H or an alkyl group having 1 to 10 carbons. Moreover, the terminology "Starch" represents an amylose and/or amylopectin moiety or a modified amylose and/or amylopectin moiety. Alternatively, this terminology may be described as representing an amylose and/or amylopectin or modified amylose and/or amylopectin moiety wherein hydrogen atoms of hydroxyl groups of anhydroglucose units of the amylose and/or amylopectin or modified amylose and/or amylopectin moiety are replaced. The polymer component also includes (B) a non-starch polysaccharide present in an amount of from about 0 to about 40 weight percent actives based on a total weight of the polymer component. The polymer component further includes (C) a cross-linked starch present in an amount of from about 3 to about 75 weight percent actives based on a total weight of the polymer component. The emulsion exhibits a stability of at least 4 weeks at room temperature. Each is described in detail below.

Oil-In-Water Emulsion

[0024] As is known in the art, oil-in-water (O/W) emulsions are a type of mixture or dispersion in which small droplets of oil in the oil phase are suspended within a continuous phase, e.g. an aqueous or water phase. In an O/W emulsion, the oil droplets are typically dispersed in the continuous phase when interfacial tension between the oil and continuous phases is reduced, allowing them to mix and form a stable dispersion. Most typically, the continuous phase of the instant emulsion is an aqueous phase and is described as such below. However, the aqueous phase need not be entirely water and may include, or be free of, one or more of the components described below. The emulsion can be formed using any method known in the art.

[0025] In personal care products, O/W emulsions are commonly used as a means of delivering oil-based active ingredients or moisturizers to the skin in a form that is easily spreadable and non-greasy. The aqueous phase of the O/W emulsion serves as a carrier for the oil phase, helping to evenly distribute the oil-based ingredients throughout the product and ensuring their effective delivery to the skin.

[0026] In various embodiments, the emulsion exists at room temperature. For some oils with a solidification point at a temperature below about 100°C, the emulsion can also be a formulation wherein the oil was first dispersed in water, but upon cooling to room temperature the oil may have solidified to a certain extent. Typically, the aqueous phase forms the continuous phase, and the oil is not soluble in the aqueous phase. In an embodiment, the solubility in the aqueous phase is 0.1% by weight, typically 0.05% by weight, or lower.

[0027] In various embodiments, the emulsion is defined as a plurality of oil droplets substantially uniformly distributed or dispersed in a liquid medium. Usually, the emulsion is in this form at room temperature. For some oils with a solidification point at a temperature below about 100°C the emulsion can also be a formulation wherein the oil was first dispersed in water, but upon cooling to room temperature the oil may have solidified to a certain extent. The liquid medium forms the continuous phase, and the oil is not soluble in the liquid medium. In an embodiment, the solubility in the liquid medium is about 0.1% by weight, typically about 0.05% by weight, or lower. Some non-limiting examples of suitable liquid media include water, ethanol, methanol, isopropanol, glycerol, propylene glycol, or acetone or mixtures thereof. In an embodiment of the disclosure, the liquid medium is a mixture of water with one or more of ethanol, methanol,

isopropanol, glycerol, glycols, such as propylene glycol, or acetone. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

Stability Over Time

[0028] The oil-in-water emulsion exhibits stability over time. The terminology "stability over time" means that, for example, the emulsion may exhibit a stability of at least 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15+ weeks at any temperature from about 5 to about 45°C or any value or range of values therebetween, e.g. at room temperature, measured using a TURBISCAN® LAB stability analyzer. For example, emulsion "stability" can be quantitatively measured using a TURBISCAN® LAB stability analyzer that is used to obtain an initial backscattering signal for a sample of the emulsion. The samples can be stored at any temperature from about zero to about 45°C or 50°C or any value or range of values therebetween, e.g. at room temperature, and then scanned periodically over the course of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15+ weeks. In various embodiments, the emulsion may be stable for at least any number of weeks described above when stored at room temperature measured using a TURBISCAN® LAB stability analyzer. In other embodiments, the emulsion may be stable for at least any number of weeks described above when stored at 45°C measured using a TURBISCAN® LAB stability analyzer. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0029] To determine stability, the emulsions can be added to glass vials provided by Formulation. The diameter of the vial is about 1 inch and height about 2 inch. The emulsion sample is added into the vial to ensure that there are not any air bubbles or cavities in the fluid. The height of the filling is about 1 5/8 inch or 42mm. After filling, the TurbiScan samples can be conditioned at the desired aging condition for one day before the initial scan is taken. The reading of the TurbiScan is typically done when the sample is cooled down to about 22°C

[0030] Backscattering signals as measured over time can be compared with the signals of the initial samples. More specifically, if the maximum difference of a subsequent backscattering signal relative to the initial signal is larger than 20%, the days to reach this 20% difference in backscattering signal can be recorded as a measure of the stability, or "Turbiscan® Time." The longer this time is, the more stable the emulsion. This technique is able to detect potential instability of a sample well before such instability can be visually observed. The software supplied

with the TurbiScan is used for the purpose of data analysis, not only back scattering intensity, but also the oil droplet size variation over time.

Oil Phase

[0031] Typically, the emulsion includes an oil phase dispersed in water or a water-based medium, as the aqueous phase. In various embodiments, the oil phase is or includes a cosmetically acceptable oil that may provide a consumer with feel, protection, healing, UV protection, occlusion, slip, hydration, or radical scavenging. The cosmetically acceptable oil can be selected from hydrocarbon-based oils and natural oils. Non-limiting examples of cosmetically acceptable oils are palm oil, mineral oil, petroleum jelly, petrolatum, silicone, dimethicone, emu oils, castor oils, squalene, avocado oil, almond oil, coconut oil, cocoa butter, grapeseed oil, lanolin, peanut oil, sesame oil, jojoba oil, olive oil, silicone oil, sunflower oil, safflower oil, shea butter, and wheat germ oil. Other oils include argan oil, sweet almond oil, avocado oil, rosehip oil, tea tree oil, and lavender oil. In one embodiment, the cosmetically acceptable oil may be an aerosol propellant.

[0032] The oil phase may be present in the emulsion in any amount as chosen by the skilled person. In various embodiments, the oil phase is present in an amount of at least about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, or 80, weight percent of the emulsion. In other embodiments, the oil phase is present in an amount of less than about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, or 80, weight percent of the emulsion. In still other embodiments, the oil phase is present in an amount of about 5 to about 60, about 10 to about 55, about 15 to about 50, about 20 to about 45, about 25 to about 40, about 10 to about 40, or about 30 to about 35, weight percent of the emulsion. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0033] In various embodiments, the oil phase is present as droplets. The droplets are not particularly limited in size. In various embodiments, the droplets have a mean droplet size of from about 0.2 microns to about 100, about 0.2 to about 50, about 0.5 microns to about 35, about 1 to about 30, about 1 to about 25, or about 5 to about 30, microns. In other embodiments, the droplet size is from about 10 to about 25 or about 15 to about 20, microns. In other embodiments, the oil droplets in the emulsion have a mean average droplet size of from about 0.2 microns to about 100 microns. In another embodiment, the oil droplets have a mean average droplet size of from about 0.5 microns to 35 microns. In other embodiments, the mean average droplet size can have lower

limits of 0.2 microns, 0.5 microns and 1 micron, respectively, while the upper limits can be 100 microns, 35 microns and 25 microns, respectively, with embodiments having ranges being combinations of these lower and upper limits. Mean average droplet size can be measured, for example, by light scattering techniques such as are known to those skilled in the art and/or any described herein. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0034] This droplet size may be further defined as a Dn10, Dn50, Dn90, Dv10, Dv50, or Dv90. Alternatively, this droplet size may be further defined as any of Dn1-100 or Dv1-100, as is understood in the art. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0035] In various embodiments, droplet size can be determined with a particle size analyzer such as a Malvern MS2000, 3000, 3000E, etc.. However, any droplet size analyzer may be used. A volume distribution can be easily transformed by a particle size analyzer into many other types of distributions, such as surface area, length or number distributions. Accordingly, the volume and number distribution for the droplets can be determined by means of laser granulometry in the form of the sphere equivalent. A volume distribution provides information about the volume of particles within each droplet size subrange. The contribution of each particle in a volume distribution relates to the volume of that particle, hence the relative contribution per particle will be proportional to the cube of its size [i.e., (droplet size)]. Accordingly, particles with larger dimensions are disproportionately represented in a volume distribution (and vice versa; smaller particles are underrepresented in a volume distribution). A number distribution, however, provides information about the number of particles within each droplet size subrange. That is, in a number distribution each particle is given equal weighting, irrespective of its size; i.e., the relative contribution of each particle in the distribution is equal. A number distribution therefore provides information about the relative number of particles (% of total number) within each droplet size subrange, whereas a volume distribution provides information about the relative volume of particles (% of total volume) within each droplet size subrange. Throughout, the terminology "droplet" may be substituted for "particle" where appropriate, as would be understood by one of skill in the art.

[0036] Thus, a Dv_{10} value means the droplet size below which 10% of the sample volume exists, whereas the Dn_{10} value corresponds to the maximum droplet size for 10% of the total number of particles in the sample. These parameters therefore relate to distinct physical properties of any

given particulate material and have very different values. Analogous considerations apply to the other claimed parameters (e.g. D_{50}, D_{90}, etc.).

[0037] Any Dv or Dn parameters of the droplets are not absolute features of the droplets per se, rather they are constructs based on mathematical approximations of laser diffraction data ("equivalent spheres"). The values for each of these parameters can be influenced to a significant degree depending on the conditions used to measure them. Typically, the standard operating procedure used to measure the droplets is that which is pre-programmed into the droplet size analyzer itself. These parameters may be chosen as set forth in International Standard ISO 13320-1. In various embodiments, any one or more of these parameters may be as pre-programmed in the instrument itself.

[0038] In other embodiments, various oil droplet size measurement techniques can be used. The most frequently used method is dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS). It is commonly employed in the fields of colloid science, nanotechnology, and biophysics. The principle of DLS is based on the Brownian motion of particles suspended in a liquid medium. The intensity fluctuations detected by the photodetector in DLS are analyzed using autocorrelation techniques. Autocorrelation measures the correlation between the intensity fluctuations at different time intervals calculated by analyzing the rate at which the scattered light intensity fluctuates. The autocorrelation function provides information about the rate of movement (Brownian motion) of the particles in the sample. From this information, the diffusion coefficient of the particles can be determined. Further, using the Stokes-Einstein equation, which relates the diffusion coefficient to the droplet size, the droplet size distribution can be calculated. Static multiple light scattering (SMLS), also known as static light scattering (SLS), is another technique used for droplet size measurement. Unlike dynamic light scattering (DLS), which analyzes the intensity fluctuations of scattered light due to Brownian motion, SMLS relies on the measurement of the intensity of the scattered light at a fixed angle. SMLS operates in the Fraunhofer scattering regime, where the scattering angle is sufficiently large that the scattering pattern can be approximated by a simple scattering equation known as the Fraunhofer equation, which relates the scattered light intensity to the droplet size and concentration. From Backscattering intensity measurement, it is possible to calculate the Mean Particle Equivalent Diameter using the equation below:

$$I_{BS} = \left[\alpha^2 \frac{3\varphi(1-g)Q_e}{2D}\right]^{1/2} + \beta$$

whereas:

I_{BS}: backscattered light intensity;

g: asymmetry factor;

Q_e : extinction efficiency factor;

φ: volume fraction;

D: mean equivalent particle diameter; and

α and β: coefficients are linked to the geometry of optical set up in the instrument (angles, light bean size, glass cell, etc.) and embedded in the instrument software based on the setting of the instrument. In various embodiments, TurbiScan Lab and its software provided by Formulaction, 3-5 Rue Paule Raymondis, are utilized for the evaluation of stability of emulsion over time, and specifically the oil droplet size measurement for emulsion are made in accordance with ISO TS 21357:2022 "Nanotechnologies — Evaluation of the mean size of nano-objects in liquid dispersions by static multiple light scattering (SMLS)." Details can also be found in Mengual, O., Meunier, G., Cayré, I., Puech, K., and Snabre, P. (1999). "TURBISCAN MA 2000: multiple light scattering measurement for concentrated emulsion and suspension instability analysis", Talanta, 50(2), 445-456, which is expressly incorporated herein by reference in various non-limiting embodiments.

[0039] In various embodiments, the detailed experimental procedure is as follows:

1) The prepared emulsion containing all the key ingredients is added into the TurbiScan vial provided by the instrument company. Special care has to be taken to not leave any cavity or air-bubbles during the sample addition. Also no emulsion should leave any stain on the surface of the glass in the upper portion of vial where no sample is present. Over time, such stains could drip down into the bulk of the sample, therefore interfering with the integrity of the original emulsion condition.

2) Once prepared, the sample should be aged at the desired aging temperature for at least 12 hrs before the initial scanning. For samples aged at 45°C, the sample should be completely cooled down to 22°C before the scanning.

3) After the initial scan, the sample is sent back to the conditions where the targeted

temperatures are, namely 22°C or 45°C. Periodically the samples are taken out from the aging conditions, reconditioned to 22°C in the case of 45°C aging samples, and are scanned again by TurbiScan by adding the new trace into the original files to be compared to the original scan trace.

4) Due to the opaque nature of emulsions, back-scattering traces are used for the purpose of monitoring the stability nature of the emulsion system. Besides the oil-droplet size development over the time, the potential creaming or retrogradation development are also closely monitored. Typically, the criteria is that, given a specific time of duration, e.g. about 4 weeks, if any point of the back-scattering trace indicates no more than 20% relative variation over the original back-scattering trace, the sample would be viewed as stable for 4 weeks for a specific aging condition. Otherwise, the sample will be view unstable at the specified time of duration.

[0040] In various embodiment, the (I) oil phase includes an additive chosen from glycerol monostearate, fatty alcohols, and combinations thereof. The fatty alcohol is not particularly limited and may be any known in the art. For example, the fatty alcohol may be linear or branched and include from about 6 to about 20, about 8 to about 18, about 10 to about 16, or about 12 to about 14, carbon atoms. The fatty alcohol may be alkoxylated (e.g. ethoxylated) or non-alkoxylated. If alkoxylated, the number of moles of alkylene oxide used (e.g. ethylene oxide) is not limited and may be, for example, about 0.5 to about 20, about 0.5 to about 10, about 1 to about 10, about 1 to about 5, about 5 to about 10, etc. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments. In other embodiment, the oil phase, and optionally the emulsion as a whole, may be free of fatty acids and/or surfactants.

Aqueous Phase

[0041] The aqueous phase can be or include water. For example, the aqueous phase may be about 100% water or may include water and one or more co-solvents. Some non-limiting examples of suitable co-solvents are ethanol, methanol, isopropanol, glycerol, propylene glycol, or acetone or mixtures thereof. In an embodiment, the aqueous phase is a mixture of water with one or more of ethanol, methanol, isopropanol, glycerol, glycols, such as propylene glycol, or acetone. The particular weight percent of water and the one or more co-solvents may independently be any between 0.5 and 99.5, as is chosen by the skilled person. Typically, the aqueous phase is present in an amount of from about 30 to about 94.5, about 35 to about 90, about 40 to about 85, about 45 to about 80, about 50 to about 75, about 55 to about 70, or about 60 to about 65, weight precent

actives based on a total weight of the emulsion. As is known in the art, water is 100% actives. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

Polymer Component

[0042] The emulsion further provides (III) a polymer component present in an amount of from about 0.5 to about 10 weight percent actives based on a total weight of the emulsion. In various embodiments, the polymer component is present in an amount of from about 1 to about 9.5, about 1.5 to about 9, about 2 to about 8.5, about 2.5 to about 8, about 3 to about 7.5, about 3.5 to about 7, about 4 to about 6.5, about 4.5 to about 6, or about 5 to about 5.5, weight percent actives based on a total weight of the emulsion. In other embodiments, the polymer component is present in an amount of from about 1 to about 7, about 1.5 to about 6.5, about 2 to about 6, about 2.5 to about 5.5, about 3 to about 5, about 3.5 to about 4.5, or about 4 to about 4.5, weight percent actives based on a total weight of the emulsion. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

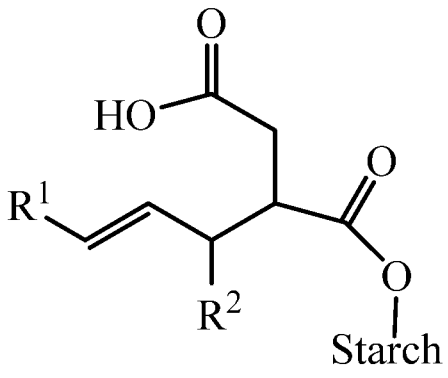
[0043] The (III) polymer component may be present in the (I) oil phase, in the (II) aqueous phase, in both the (I) oil and (II) aqueous phases, or between the (I) oil and (II) aqueous phases.

(A) Starch Component

[0044] The polymer component itself includes an (A) starch component present in an amount of from about 15 to about 45 weight percent actives based on a total weight of the polymer component. In various embodiments, the starch component is present in an amount of from about 20 to about 40, about 20 to about 35, about 25 to about 35, or about 30 to about 35, weight percent actives based on a total weight of the polymer component. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0045] The starch component includes a hydrophobically modified starch.

[0046] In one embodiment, the hydrophobically modified starch has the following structure:



wherein R^1 is a C_3 to C_{19} branched or linear alkyl or alkenyl group and R^2 is H or an alkyl group having 1 to 10 carbons.

[0047] In various embodiments, R^1 is branched or linear alkyl or alkenyl group that has 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, or 19 carbon atoms. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0048] In other embodiments, R^2 is H or an alkyl group having 1 to 10 carbons, e.g. 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, carbon atoms. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0049] Moreover, the terminology "Starch" represents an amylose and/or amylopectin moiety or a modified amylose and/or amylopectin moiety. Alternatively, this terminology may be described as representing an amylose and/or amylopectin or modified amylose and/or amylopectin moiety wherein hydrogen atoms of hydroxyl groups of anhydroglucose units of the amylose and/or amylopectin or modified amylose and/or amylopectin moiety are replaced.

[0050] In various embodiments, the starch can be hydrophobically modified with an alkenyl succinic anhydride which may be branched or unbranched. For example, the anhydride may be alternatively described as octenyl succinic anhydride (OSA). In the art, there are alternative structures provided for OSA such that the double bond shown above may be alternatively located. All versions of alkenyl succinic anhydride and OSA as would be recognized in the art are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0051] The starch can be rendered amphoteric via any reaction known in the art. For example, the starch may be rendered amphoteric via reaction with 2-chloroethylaminodipropionic acid (EDPA). The reaction between starch and EDPA typically proceeds via an etherification reaction, in which

the chloroethyl group of the EDPA reacts with the hydroxyl groups of the starch to form ether bonds.

[0052] The starch can be further hydrophobically modified via reaction with an alkenyl succinic anhydride (ASA) which introduces hydrophobic groups onto the surface of the starch. The reaction between starch and ASA typically proceeds via an esterification reaction, in which the anhydride group of the ASA reacts with the hydroxyl groups of the starch to form ester bonds. The reaction can be catalyzed by acids, such as sulfuric or hydrochloric acid, or by enzymes, such as lipases or proteases. During the reaction, the ASA molecule undergoes hydrolysis to form an acid, which acts as a catalyst for the esterification reaction. The reaction can also be catalyzed by base. In a typical base-catalyzed reaction, granular starch is treated in an aqueous slurry with ASA at a pH of 7 to 11, more preferably at a pH of about 7.5 to 9. Hydrophobic alkyl or alkenyl groups on the ASA molecule are thereby attached to the starch, which makes the modified starch more hydrophobic and less water-soluble than unmodified starch. The degree of modification, or the number of alkyl or alkenyl groups attached to the starch molecule, can be controlled by varying the reaction conditions, such as the amount of ASA used, the reaction time, and the temperature. In one embodiment, the starch is reacted with octenylsuccinic anhydride (OSA). In another embodiment, the starch is reacted with dodecenyl succinic anhydride (DDSA).

[0053] In alternative embodiments, the hydrophobically modified starch may be hydrophobically modified with one or more aliphatic or aromatic, saturated or unsaturated, linear, branched or cyclic C8-C30 hydrocarbon-based chain(s), in particular hydrophobic group(s) containing from 8 to 30 carbon atoms. In another embodiment, a hydrophobic substituent(s) used may include C8-C30. In another embodiment, C8-C22, alkyl, alkenyl, arylalkyl or alkylaryl groups and mixtures thereof can be utilized. In an embodiment, a hydrophobic substituent is C8-C22, such as C8-C12, alkenyl chains, such as octenyl (unsaturated C8) and linear or branched dodecenyl (unsaturated C12) groups. In an embodiment, hydrophobic groups are derived from natural sources, including without limitation tall oil, tallow, soy, coco, and palm-oil. The hydrophobic modifier can be attached to the starch substrate via an ether, ester or urethane linkage. Preferred is the ester linkage.

[0054] In one embodiment, the hydrophobically modified starch is present wherein R^1 is a C_5 linear alkyl group and R^2 is H. This may be described as an OSA-modified starch or an octenyl succinic anhydride modified starch.

[0055] In another embodiment, the hydrophobically modified starch is present wherein R^1 is a C_9

linear alkyl group and R^2 is H. In another embodiment, the hydrophobically modified starch is present wherein R^1 is a C_9 branched alkyl group and R^2 is H. These may be described as DDSA-modified amphoteric starches or dodecenyl succinic anhydride modified amphoteric starches since DDSA can be linear or branched.

[0056] The starch can be derived from a variety of sources, including plants, animals, and microorganisms. In various embodiments, the starch is derived from corn, wheat, rice, or combinations thereof. In other embodiments, the starch is derived from potatoes, cassava, tapioca, or combinations thereof. In other embodiments, the starch is derived from peas, beans such as soybeans, lentils, or combinations thereof. In other embodiments, the starch is derived from bone marrow and/or animal tissue. In other embodiments, the starch is derived from fermentation processes of microorganisms. Any combination of the above may be used.

[0057] The starch of this disclosure may be any type. Starch is a complex carbohydrate that is composed of two types of glucose polymers, amylose and amylopectin. Amylose is a linear polymer of glucose units that are linked by alpha-1,4-glycosidic bonds. This gives amylose a helical structure that is stabilized by intermolecular hydrogen bonds. The degree of polymerization of amylose can vary depending on the source, but typically ranges from several hundred to several thousand glucose units. Amylopectin is a branched polymer of glucose units that are linked by both alpha-1,4-glycosidic bonds and alpha-1,6-glycosidic bonds. This branching gives amylopectin a highly branched structure, with clusters of glucose units connected by alpha-1,6-glycosidic bonds. The degree of branching in amylopectin can vary depending on the source, but typically is from one branch point for every 20 to 30 glucose units. Both amylose and amylopectin are composed of glucose monomers that are connected by glycosidic bonds. The glycosidic bond is formed when the hydroxyl group of the first glucose unit undergoes a condensation reaction with the hydroxyl group of the second glucose unit, resulting in the formation of an oxygen bridge between the two units. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0058] While not intending to be bound by any particular theory, it is believed that the (A) starch component plays a role as a polymeric surfactant due to its amphoteric nature, whereas the hydrophobic functional group provides anchor points at oil-water interphase, on the side of the oil phase and on the aqueous side of the interphase, modified starch with high hydrodynamic volume due to the hydrophilicity from charges and hydroxyl functional group, as well as high molecular

weight, especially from amylopectin, function as energy barrier, as shown in the Figure 1B. Compared to a small molecular surfactant, the advantage of a polymeric surface active material is believed to give higher energy barrier at even longer inter-oil-droplet distance, results in even lower probability of oil droplet coalescence.

[0059] In various embodiments, the (A) starch component is gelatinized. The term "gelatinized starch" encompasses "pregelatinized starch," "prepasted starch" and "cold water swelling starch." The term "gelatinized" starch relates to swollen starch particles that have lost their birefringence crosses in polarized light. Gelatinized modified starches are soluble in cold water without cooking. In this context "soluble" does not necessarily mean the formation of a true molecular solution and instead also means that a colloidal dispersion is obtained. In one embodiment, the (A) starch component is completely gelatinized.

[0060] In one embodiment, the hydrophobically modified starch is hydrophobically modified amylopectin. In another embodiment, the hydrophobically modified starch is hydrophobically modified amylose. In yet another embodiment, the hydrophobically modified starch is a combination of hydrophobically modified amylose and hydrophobically modified amylopectin.

(B) Non-Starch Polysaccharide

[0061] The polymer component also includes the (B) non-starch polysaccharide present in an amount of from about 0 to about 40 weight percent actives based on a total weight of the polymer component. In various embodiments, this amount is from about 0 to about 35, about 0 to about 30, about 0 to about 25, about 0 to about 20, about 0 to about 15, about 0 to about 10, about 0 to about 5, about 5 to about 30, about 5 to about 25, about 5 to about 20, about 5 to about 15, about 5 to about 10, about 10 to about 30, about 10 to about 25, about 10 to about 20, about 10 to about 15, 15 to about 30 or about 20 to about 25, weight percent actives based on a total weight of the polymer component. In other embodiments, the (B) non-starch polysaccharide is present in an amount of from about 5 to about 40, about 10 to about 35, about 20 to about 35, or about 20 to about 30, weight percent actives based on a total weight of the polymer component. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0062] Starches and starch derivatives are known to impart desired tactile qualities to personal care formulations. Traditionally, starches that are used in such formulations can be used at concentrations above about 3%, otherwise the starches can undergo a phenomenon known as

retrogradation and precipitate from the formulation which is undesirable. However, in one embodiment wherein the (III) polymer component is present in an amount of from about 3.5 to about 10 weight percent actives based on a total weight of the emulsion, the (B) non-starch polysaccharide is optional, not present, or is present in an amount of less than about 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, or 0.01, weight percent actives based on a total weight of the polymer component. In another embodiment, wherein the (III) polymer component is present in an amount of from about 0.5 to less than about 3.5 weight percent actives based on a total weight of the emulsion and the (B) non-starch polysaccharide is present in an amount of greater than zero weight percent. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0063] As is known in the art, polysaccharides can form spiral, linear fibrous, or branched structures. Two general types of conformation for polysaccharides can be simply divided—ordered conformation and disordered conformation—which is decided by the regularity of the molecular structure. In aqueous solution, most non-starch polysaccharides with heterogeneous structure demonstrate disordered conformation, including random coil, rigid, and spherical conformation. High-performance size exclusion chromatography (HPSEC) can be used to study the conformational properties of polysaccharides in aqueous solution. Combined refractive index (RI) light scattering detectors (LALS and RALS) with an online viscometer, the relationship of Mw and the intrinsic viscosity [η], and Rg, Rh and Rg/Rh (ρ) can be obtained, wherein Rg is the Radius of Gyration and Rh is the Hydrodynamic Radius (Rh). Rg is a mathematically defined dimension describing the distribution of mass centers in the molecule, whereas Rh is a phenomenological property of the molecule.

[0064] In various embodiments, the (B) non-starch polysaccharide has a coil size (Rh) of at least 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, or 1600, nm. Alternatively, the coil size may be about 400 to about 1600, about 450 to about 1550, about 500 to about 1500, about 550 to about 1450, about 600 to about 1400, about 650 to about 1350, about 700 to about 1300, about 750 to about 1250, about 800 to about 1200, about 850 to about 1150, about 900 to about 1100, about 950 to about 1050, or about 950 to about 1000, nm. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments. Dynamic Light Scattering is most typically used to measure the hydrodynamic volume of the non-starch polysaccharides. The principle of polymer

hydrodynamic volume using dynamic light scattering (DLS) involves the measurement of the Brownian motion of polymer molecules in solution. In some non-limiting embodiments, the importance of the coil size of the non-starch polysaccharides is set forth in Figure 1B. When oil droplets and non-polysaccharides are co-dispersed in a water system, their interaction with water is completely opposite in nature, whereas the latter is compatible with water and forms a uniform solution. The former is incompatible with water, resulting in a phenomenon best known as Ostwald Ripening. On the microscopic level, when two oil droplets approach each other due to the van der waals forces, when the inter-oil droplet distance becomes slightly lower than the average size of hydrodynamic volume of non-starch polysaccharides, the polymer coil will be pushed away between this inter-oil droplet zone, resulting in the concentration of non-starch polysaccharide virtually to be zero. This demixing process when the two oil droplets approaching to each other generates an energy barrier, typically termed as depletion mechanism, which is thermodynamically unfavorable for two oil droplet to coalesce to each other, which is demonstrated in the right side of the energy vs. inter-droplet distance chart (Figure 1B). It is not difficult to conjecture from the simple geometric ,consideration, that the larger the hydrodynamic volume of the non-starch polysaccharide is, the further the inter oil droplets distance is for the energy barrier to occur, therefore reduce the probability of coalescence.

[0065] The non-starch polysaccharide is not particularly limited and may be any known in the art. In one embodiment, the non-starch polysaccharide is xanthan gum. In another embodiment, the (B) non-starch polysaccharide is chosen from xanthan gum, non-ionic cellulose, ionic cellulose, and combinations thereof. In other embodiments, the (B) non-starch polysaccharide is chosen from cellulose ethers such as methyl ethyl hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, and combinations thereof. In other embodiments, it is contemplated that the cellulose may be ionic as well.

[0066] In various embodiments, the non-starch polysaccharide is a cellulose ether. Cellulose is a polysaccharide built up from 1,4-anhydroglucose units. The cellulose molecules in native cellulose are insoluble in water. To make cellulose soluble, it typically has to be modified into a cellulose derivative, such as hydroxyethyl cellulose (HEC), ethyl hydroxyethyl cellulose (EHEC), hydroxypropyl cellulose (HPC), hydroxybutyl methylcellulose (HBMC), hydroxypropyl methylcellulose (HPMC), methyl ethyl hydroxyethyl cellulose (MEHEC), and hydrophobically modified ethyl hydroxyethyl cellulose (HMEHEC). Carboxymethyl cellulose may also be used.

[0067] To make the modified cellulose, the cellulose is typically subjected to an alkalization step, and then reacted with ethylene oxide and ethyl chloride to make EHEC, and also with methyl chloride to make MEHEC The anhydroglucose units of cellulose each have three hydroxyl groups available for reaction. The number of hydroxyl groups per anhydroglucose unit that have reacted is expressed as degree of substitution (DS) and ranges from 0 to 3. The molar substitution of ethylene oxide (MSEO) is the average total number of ethylene oxide groups per anhydroglucose unit.

[0068] The cellulose ether can be derived from any cellulose source, including, but not limited to, hardwood pulp, softwood pulp, cotton sources including cotton linters, bacterial cellulose, and regenerated cellulose.

[0069] In one embodiment, the cellulose ether is a non-ionic cellulose ether. In another embodiment, the cellulose ether is a hydroxy(C1-C4)alkylcellulose. Examples of non-ionic cellulose ethers are methyl cellulose, ethyl cellulose, propyl cellulose, butyl cellulose, hydroxyethyl cellulose, methylhydroxyethyl cellulose, ethylhydroxyethyl cellulose, methylethylhydroxyethyl cellulose, propylhydroxyethylcellulose, hydroxypropylmethyl cellulose, hydroxypropylethyl cellulose, hydroxypropylpropyl cellulose, hydroxypropylhydroxyethyl cellulose, methylhydroxypropylhydroxyethyl cellulose, hydroxypropyl cellulose, and mixtures thereof. In one embodiment, the cellulose ether may be chosen from methyl cellulose, ethyl cellulose, ethylhydroxyethyl cellulose, methylhydroxyethyl cellulose, methylethylhydroxyethyl cellulose, hydroxypropylmethyl cellulose and mixtures thereof.

[0070] In one embodiment, the cellulose ether is a methylethylhydroxyethyl cellulose, referred to herein as "MEHEC". In one embodiment, the cellulose ether is an ethylhydroxyethyl cellulose, referred to herein as "EHEC". Non-ionic cellulose ethers can be of particular utility for those applications in which good salt tolerance is desired.

[0071] In one embodiment, the cellulose ether is an anionic cellulose ether, particularly in formulations that do not require high tolerance of salt compounds. Examples of anionic cellulose ethers are carboxymethyl cellulose, hydroxyethylcarboxymethyl cellulose, hydroxypropylcarboxymethyl cellulose, sulfoethyl cellulose, hydroxyethylsulfoethyl cellulose, hydroxypropylsulfoethyl cellulose, and mixtures thereof.

[0072] The cellulose ether can be prepared according to conventional methods that are known to those of ordinary skill in the art. For example, alkali cellulose (activated cellulose) may be

prepared in one or several steps by first mercerizing cellulose with alkali and subsequently reacting the alkali cellulose in one or several steps with appropriate amounts of one or more etherifying agents selected from ethylene oxide, propylene oxide, butylene oxide, methyl chloride, ethyl chloride, monochloroacetic acid (MCA), and salts of MCA, in the presence of an organic reaction medium, for instance ethyl chloride, acetone, alkyl-blocked mono or poly(ethylene glycols), isopropanol, tert-butanol, ethers such as methyl tert-butylether, methyl sec-butylether, dimethoxyethane or mixtures thereof at a temperature of from about 50 to about 120°C.

[0073] The cellulose ethers can include one or more substituents on the cellulose chain.

[0074] In one embodiment, the cellulose ether is substituted with a hydroxyalkyl group such as ethylene oxide, known as MSEO. In various embodiments, the MSEO is at least 1.0, at least 1.5, at least 2.0, or at least 2.4. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0075] In other embodiments, the cellulose ether is methyl and/or ethyl substituted in which the sum of DS_{ethyl} and DS_{methyl} is at least 0.1, least 0.2, at least 0.4, at least 0.6, or at least 0.8. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0076] In one method of making alkyl-substituted cellulose ethers, the cellulose is mercerized in one or several steps with aqueous alkali in a total amount of about 0.8 to about 1.8 moles of alkali per mole of saccharide unit; and the mercerized cellulose is reacted with ethylene oxide in a total amount of about 2.6 to about 5.5 moles per mole of saccharide unit. The reaction product is then reacted with either ethyl chloride in a total amount of about 0.2 to about 1.5 moles per mole of saccharide unit, to make EHEC, or ethyl chloride and methyl chloride in a total amount of about 0.2 to about 1.5 moles per mole of saccharide unit to make MEHEC These components are added to and reacted with the mercerized cellulose in one or several steps in the presence of an organic reaction medium at a temperature from about 50 to about 120°C In an embodiment, the weight ratio between the reaction medium and the cellulose can be about 1:1 to about 10:1, and in another embodiment from about 4:3 to about 3:1. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0077] In one embodiment, methyl chloride or ethyl chloride can serve as both the etherifying agent and the reaction medium, in which case the desired amount of methyl or ethyl chloride is

already present in the reaction mixture and there is no need for further addition of methyl or ethyl chloride. The alkylation can be regulated by the source of cellulose, the amount of alkali used, the reaction temperature and reaction time. If desired, a part of the alkali may be added at a later stage during the reaction in order to further activate the cellulose. The total degree of substitution by methyl and ethyl can be controlled by the amount of alkali used in the mercerization process, since a corresponding equivalent amount of NaOH is consumed and forms sodium chloride. However, due to side reactions the yield of alkyl substitutions is about 40 to about 60%. U.S. Pat. No. 7,319,146, which is incorporated by reference in its entirety herein in various non-limiting embodiments, provides a general description of the methods used in making cellulose ether polymers. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0078] One method of making cellulose ethers suitable for use herein is disclosed in U.S. Publication No. 2009/0326217, incorporated herein by reference in its entirety in various non-limiting embodiments, wherein the cellulose ether is typically prepared in the presence of an ether-type solvent.

[0079] While not intending to be bound by any particular theory, it is believed that the (B) non-starch polysaccharide plays numerous roles. For example, the non-starch polysaccharide may suppress the retrogradation of the starch. It is well known that the two starch molecules will form the double-helix due to the intermolecular hydrogen bonding as well as the specific configuration of the starch molecules. The same can be said to the cellulose molecules as well whereas the intermolecular hydrogen bonding is the same, but due to the configuration difference, the ordered structures of cellulose will be very different in nature to that of starch. Nevertheless, the identical configuration of two adjacent polysaccharides molecules allows them to form intermolecular hydrogen bonding which will further developed into the order-structures. If two polysaccharides with different configurations approach each other, intermolecular hydrogen bonding will still be formed, but the likelihood of ordered structure with larger domain is low. The non-polysaccharides may enhance a thickening effect of the continuous phase of an emulsion. Non-starch polysaccharides with larger hydrodynamic volume can effectively thicken the system by the strong hydrophilicity, high molecular weight and relatively high glass transition temperatures.

(C) Cross-Linked Starch

[0080] The polymer component further includes (C) a cross-linked starch present in an amount of

from about 3 to about 75 weight percent actives based on a total weight of the polymer component. In various embodiments, this amount is from about 5 to about 75, about 10 to about 75, about 15 to about 75, about 20 to about 75, about 25 to about 70, about 30 to about 70, about 30 to about 65, about 35 to about 60, about 40 to about 55, or about 45 to about 50, weight percent actives based on a total weight of the polymer component. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0081] The cross-linked starch may be any known in the art or any described herein including a cross-linked version of the starches described above.

[0082] In various embodiments, the starch can be isolated from any plant source of starch, including, for example, corn, wheat, rice, sorghum, pea, potato, tapioca (cassava), sweet potato, and sago. In various embodiments, the starch comprises greater than about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, or 85 weight percent of amylopectin. In an embodiment, the starch comprises greater than about 90 weight percent of amylopectin. In another embodiment, the starch comprises greater than 95 weight percent of amylopectin. In yet another embodiment, the starch comprises greater than 97 weight percent of amylopectin. This high amylopectin starch is traditionally known in the art as waxy and there are many varieties of waxy starch commercially available. In an embodiment, a waxy starch is derived from corn, rice, potato, or tapioca. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0083] In various embodiments, the starch has a high molecular weight which is defined as the molecular weight of naturally occurring starches which have not been purposefully degraded to a lower molecular weight. That is, while some degradation may occur during the isolation of the starch and also during the chemical processing and drying of the starch, the high molecular weight starches are those that have their natural molecular weight maintained as much as possible. In another embodiment, the starch may be partially degraded in a controlled fashion by means known in the art including but not limited to acid catalyzed hydrolysis, enzyme catalyzed hydrolysis, and oxidative degradation. In the case where the starch is intentionally partially degraded, the Water Fluidity (WF) of the degraded starch will be less than 70, typically, less than 60 or, most typically, less than 45. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0084] Cross-linking of starch chains can be achieved by suitable cross-linking agents, such as bifunctional compounds. For example, cross-linking may be achieved by the reaction of a starch with epichlorohydrin. In one embodiment, the cross-linking method is phosphorylation, in which the starch is reacted with phosphorous oxychloride, phosphorous pentoxide, and/or sodium trimetaphosphate, such that two starch chains are cross-linked by an anionic P—O group. The anionic character of the cross-linking sites assists the emulsion-stabilizing action of the starch. In a further embodiment, the cross-linking method utilizes a C_4-C_{18} alkane or alkene dicarboxylic acid or a C_4-C_8 alkane dicarboxylic acids or adipic acid. The alkane or alkene dicarboxylic acid links two starch chains via ester bonds. It can be in straight or branched chain form. In a further embodiment, the cross-linked starches are obtained, e.g., by reacting starch with the mixed anhydrides of dicarboxylic acid and acetic acid. The starch may be cross-linked with from about 15 ppm to about 400 ppm of the cross-linking reagent, in another embodiment typically from about 50 to about 300 ppm, in yet another embodiment more typically from about 100 ppm to about 200 ppm. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0085] In a further aspect, the cross-linked starch is further modified by addition of a C2-C5 hydroxyalkyl moiety. Without wishing to be bound by theory, it is believed that the presence of a hydroxyl group, which is bound to the starch backbone via an alkyl group with 2 to 5 carbon atoms, leads to a suitable hydrophilic-lipophilic balance of the starch. The position of the hydroxyl group in the alkyl group is not critical and may be in the alpha to the omega positions. The degree of substitution is the average number of substituted OH groups of the starch molecule per anhydroglucose unit. In one embodiment, the degree of substitution of the hydroxyalkylation is approximately 0.08 to 0.3, and in another embodiment, the degree of substitution of the hydroxyalkylation is approximately 0.15 to 0.25. The hydroxyalkylation of a native starch can be brought about by reacting a native starch with alkylene oxides with the appropriate number of carbon atoms. In an embodiment, hydroxyethylated and/or hydroxypropylated starches obtained by reacting starches with ethylene oxide or propylene oxide are utilized. A starch can also include more than one hydroxyl group per alkyl group. In an embodiment, the starch is a cross-linked, hydroxypropyl di-starch phosphate or cross-linked acetylated di-starch adipate. All values and

ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0086] The cross-linked starch may be hydrophobically modified or not modified. For example, the cross-linked starch may be substituted with one or more aliphatic or aromatic, saturated or unsaturated, linear, branched or cyclic C_8-C_{30} hydrocarbon-based chain(s), in particular hydrophobic group(s) containing from 8 to 30 carbon atoms. In another embodiment, the hydrophobic substituent(s) used may include C_8-C_{30}, and in another embodiment typically C_8-C_{22}, alkyl, alkenyl, arylalkyl or alkylaryl groups and mixtures thereof. In an embodiment, the hydrophobic substituent is C_8-C_{22}, typically C_8-C_{12}, alkenyl chains, such as octenyl (unsaturated C_8) and linear or branched dodecenyl (unsaturated C_{12}) groups. In an embodiment, the hydrophobic groups are derived from natural sources, including without limitation tall oil, tallow, soy, coco, and palm-oil. In an embodiment, the hydrophobic substituent(s) according to the present disclosure are octenyl or dodecenyl groups. The hydrophobic modifier can be attached to the starch substrate via an ether, ester or urethane linkage. Preferred is the ester linkage. Exemplary modifying reagents include but are not limited to octenyl succinic anhydride and dodecenyl anhydride. The cross-linked starch may be alternatively modified using any method or compound described in this disclosure.

[0087] In an embodiment, the cross-linked, modified starch is gelatinized. The term "gelatinized starch" encompasses "pregelatinized starch," "prepasted starch" and "cold water swelling starch." The term "gelatinized" starch relates to swollen starch particles that have lost their birefringence crosses in polarized light. Gelatinized modified starches are soluble in cold water without cooking. In this context "soluble" does not necessarily mean the formation of a true molecular solution and instead also means that a colloidal dispersion is obtained. In one embodiment, the cross-linked starch is completely gelatinized.

[0088] The cross-linked starch may be gelatinized by cooking in water above the gelatinization temperature. Some non-limiting examples of gelatinization are bath cooking, steam injection cooking, jet cooking (at pressures of about 10 to about 150 PSI) and extrusion. The cross-linked starch can be cooked at a variety of temperatures and concentrations. In various embodiments, the cross-linked starch is cooked at about 90°C to about 200°C In another embodiment, the cross-linked starch is cooked at about 100°C to about 150°C Depending on the method of cooking, limitations on the concentration of starch in water will vary due to factors, for example, such as

viscosity, heat transfer and solution stability. In one embodiment, the cross-linked starch is cooked at concentrations from about 1 to about 40 percent by weight (wt %). In another embodiment, the cross-linked starch is cooked at concentrations from about 2 wt % to about 30 wt %. In yet another embodiment, the concentration is from about 3 wt % to about 15 wt %. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0089] Processes normally used for producing such gelatinized starches include drum drying, extrusion and spray drying. Drum drying includes the simultaneous cooking and drying of a very high viscosity, semi-solid starch paste on heated drums. The dried films are stripped from the drum with a metal blade and then ground. This process can be carried out up to a very high solids content. It is also possible to use extrusion for the simultaneous cooking and drying of starches. This process makes use of the physical processing of a starch/water mixture at elevated temperatures and pressures which brings about the gelatinization of the starch, followed by expansion after leaving the nozzle with sudden evaporation of the water. The use of a gelatinized cross-linked, modified starch allows the starch to be produced at ambient temperature or at a temperature which is considerably lower than the production conditions used for known starch-containing compositions. In an embodiment, typically the gelatinized cross-linked, modified starch is produced by spray drying.

[0090] In one embodiment, the cross-linked starch has a majority of intact starch granules. Aqueous dispersions of gelatinized cross-linked starches having a largely intact granular structure have a more uniform smooth texture than aqueous dispersions of starches without a granular structure, which are, e.g., obtained by drying starch solutions whose dispersions have a slightly gritty feel. In the case of gelatinized starches with an intact granular structure, the native internal structure of the hydrogen bonds is destroyed, but the external shape or form is maintained. A process for producing particularly suitable, spray dried, gelatinized starches is described in U.S. Pat. No. 4,280,851, which is incorporated by reference in its entirety herein in various non-limiting embodiments. An apparatus adapted for carrying out the process is described in U.S. Pat. No. 4,600,472, which is also incorporated by reference in its entirety herein in various non-limiting embodiments. In this process, a mixture of the granular starch or modified starch is cooked or gelatinized in the atomized state. The starch to be cooked is atomized through an atomizing opening into a nozzle arrangement in order to form a relatively finely divided sprayed material. In

addition, a heating medium is injected through an opening in the nozzle arrangement into the sprayed material so as to heat the starch to the temperature necessary for gelatinization. A closed chamber surrounds the injection openings for the atomizing and heating medium and defines a ventilation opening positioned in such a way that the heated starch spray material can leave the chamber. The arrangement is such that during the passage of the starch spray material through the chamber, i.e., from the atomizing opening to the ventilation opening, the time elapsed defines the starch's gelatinization time. The resulting spray dried, gelatinized starch includes uniformly gelatinized starch granules in the form of indented spheres, most of the granules being whole and unbroken and swollen after hydration. Nozzles usable for producing such starches are also described in U.S. Pat. No. 4,610,760, which is incorporated by reference in its entirety herein in various non-limiting embodiments.

[0091] For the production of suitable gelatinized starches or modified starches it is also possible to use the process of U.S. Pat. No. 5,149,799, which is incorporated by reference in its entirety herein in various non-limiting embodiments. In this process, starch is uniformly atomized and cooked by means of a single atomization stage in the presence of an aqueous medium. The atomization stage is performed in an apparatus having an internal mix two-fluid spray drying nozzle and it is coupled to a device for drying the cooked, atomized starch.

[0092] Spray dried, gelatinized starches or modified starches with suitable characteristics can also be produced by a continuous, coupled jet-cooking and spray-drying process. A starch suspension is gelatinized at 138°C to 160°C in a jet cooker with direct steam injection. The streams of starch suspension and steam are mixed in a cooking or boiling chamber. The outlet of the latter is connected to a pneumatic spray nozzle or a high pressure nozzle, which is located in a conventional spray dryer. The jet-cooked starch is directed at elevated temperature and pressure into the spray nozzle and can be atomized with cold air, hot air or typically steam. After atomizing, the hot, jet-cooked starch solution is handled in the same way as conventional spray dried starches. The drying process is adequately fast to prevent retrogradation of the starch molecules during the cooling and drying of the droplets. The spray dried starch is an amorphous material (i.e., it is substantially non-crystalline) which is easily soluble in water or colloidally dispersible.

[0093] In an embodiment, the cross-linked starch can be provided as a dry powdery composition which is reconstituted in an aqueous medium upon use.

[0094] In various embodiments, the cross-linked starches have use characteristics and tactile

qualities that are dermatologically desirable. They increase the water retention capacity of the skin, and help make the skin smooth and flexible.

[0095] In still other embodiments, the (C) cross-linked starch is a hydroxypropyl starch phosphate. In one embodiment, the (C) cross-linked starch is a hydroxypropyl starch phosphate derived from corn, potato, and/or tapioca. In another embodiment, the (C) cross-linked starch is a hydroxypropyl starch phosphate derived from corn.

[0096] While any emulsion is thermodynamically unstable, the effort in improving the emulsion stability is to address the dynamics of this unstable process. When the dispersion phase is small in size, e.g. at micron levels, the gravity force imposed on oil droplets is largely overshadowed by the much more significant intermolecular forces, which is largely the interfacial/surface force in nature. Given the gradually reduced surface to volume ratio, scaled by ~1/length scale of the dispersed phase, when coalescence occurs, the gravity force starts to become more important. This will result in the phenomena such as the creaming or sedimentation, depending on the density difference between the dispersed phase and the continuous phase of an emulsion system. One effective way to address the impact of gravity force is to thicken the continuous phase e.g. to prolong the molecular relaxation time of the molecules dispersed/dissolved in the continuous phase. It is believed that the cross-linked starch can significantly increase the molecular weight, therefore increase the viscosity of continuous phase to slow down the creaming/sedimentation process when the gravity force becomes more important with ever increasing size of dispersing phase, see Figure 1A.

Additives

[0097] The emulsion may include one or more additives, or be free of one or more additives, in one or more of the oil phase, the aqueous phase, and/or the polymer component. Such additives may include, but are not limited to, emollients, humectants, thickening agents, surfactants, UV light inhibitors, fixative polymers, pigments, dyes, colorants, alpha hydroxy acids, aesthetic enhancers such as starch, perfumes and fragrances, film formers (water proofing agents), antiseptics, antifungal, antimicrobial and other medicaments, preservatives, and solvents.

[0098] Surfactants which are useful include non-ionic and amphoteric surfactants. Non-ionic surfactants which may be used include polyoxyethyleneated, polyoxypropyleneated or polyglycerolated alcohols, alkylphenols and fatty acids with a linear fatty chain containing 8 to 22 carbon atoms and usually 2 to 30 mols of ethylene oxide, fatty acid amides, alkoxylated fatty

alcohol amines, fatty acid esters, glycerol esters, alkoxylated fatty acid esters, sorbitan esters, alkoxylated sorbitan esters, alkylphenol alkoxylates, aromatic alkoxylates and alcohol alkoxylates. Also useful are copolymers of ethylene oxide and propylene oxide, condensates of ethylene oxide and propylene oxide with fatty alcohols, polyoxyethyleneated fatty amides or amines, ethanolamides, fatty acid esters of glycol, oxyethyleneated or non-oxyethyleneated fatty acid esters of sorbitan, fatty acid esters of sucrose, fatty acid esters of polyethylene glycols, phosphoric acid triesters and fatty acid esters of glucose derivatives. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[0099] In other embodiments, the surfactant is bio-based. For example, the surfactant may be chosen from phospholipids, lecithin, palmitoyl oligopeptide, glycolipids, glycosphingolipids, sophorolipids, sphingolipids, and combinations thereof.

[00100] The additive may alternatively be or include a fatty alcohol. The fatty alcohol may be or include behenyl alcohol, C12-16 alcohols, cetearyl alcohol, cetyl alcohol, cinnamyl alcohol, citronellol, geraniol, linalool, octyl dodecanol, PEG-10 rapeseed sterol, phenoxyethanol, retinol, stearyl alcohol, tocopherol, or combinations thereof.

[00101] In various embodiments, one or more components, compounds, methods, or compositions as described in US Pat. No. 10,100,178 may be used herein, wherein this document is incorporated herein by reference in its entirety in various non-limiting embodiments.

Use of the Emulsion

[00102] The emulsion may be, or may be utilized to form, a cosmetic or personal care composition. In one embodiment, the emulsion is a personal care composition. Alternatively, the personal care composition is a skin care composition. In other embodiments, the personal care composition is a hair care or hair styling composition. The emulsion may be, or may be used to form, a hair styling composition selected from a gel, a mousse, a pomade, and a wax.

[00103] In another embodiment, the emulsion may be a personal care composition selected from the group consisting of a skin care composition, skin cleansing composition, make-up, facial lotion, cream moisturizer, body wash, body lotion, foot care products like foot cream, hand cream, lipstick, lip gloss, lip pencil, eyeshadow, gel eye color, eye liner, eye pencil, mascara, concealer, foundation, facial powder, liquid rouges, blush, deodorant, shaving cream composition, nail polish, gel polish removers, cuticle remover, cuticle cream, acne cream, acne cleansing scrub, toothpaste,

shaving lotion, cream depilatory, lotion depilatory, wax depilatory, facial mask made with clay materials, anti-aging product, shampoo, hair care products such as conditioners, hair treatment cream, styling gel, styling foam, hair mousse, hair spray, set lotion, blow-styling lotion, hair color lotion and dyes, hair bleaching cream hair relaxing composition, curl activator gel, fragrant hair gloss, sun care products like sun stick and sun screen, soap, handwash, hand sanitizer gels, antibacterial hand cleaner, body scrub, hand scrub, bubble bath, bath oils, instant hand sanitizer, baby lotion, diaper rash cream, wet wipe, baby bath, vitamin creams, and combinations thereof.

[00104] Alternatively, the emulsion may be the cosmetic composition itself. In other embodiments, the emulsion is present in the cosmetic composition in an amount of from about 1 to about 99.5, about 5 to about 90, about 10 to about 85, about 15 to about 80, about 20 to about 75, about 25 to about 70, about 30 to about 65, about 35 to about 60, about 40 to about 55, or about 45 to about 50, weight percent actives based on a total weight of the cosmetic or personal care composition. All values and ranges of values, including and between those set forth above, are hereby expressly contemplated for use herein in various non-limiting embodiments.

[00105] Preservatives are often used in personal care formulations to provide long term shelf stability, particularly microbiological shelf life stability. Suitable preservatives include, for example, methylparaben, propylparaben, butylparaben, DMDM hydantoin, imidazolidinyl urea, gluteraldehyde, phenoxyethanol, benzalkonium chloride, methane ammonium chloride, benzethonium chloride, benzyl alcohol, chlorobenzyl alcohol, methylchloroisothiazolinone, methylisothiazolinone, sodium benzoate, chloracetamide, triclosan, iodopropynyl butylcarbamate, sodium pyrithione, zinc pyrithione, and other cosmetically acceptable preservatives known to those skilled in the art.

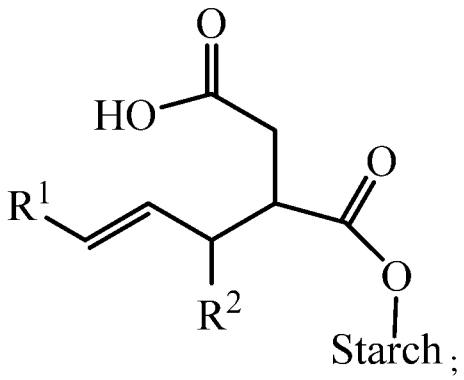
EXAMPLES

[00106] A first series of Compositions (Comp 1-5) was created as shown below. After formation, each of the Compositions was individually evaluated to determine Viscosity, Stability, and Droplet size, as also shown below.

	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5
Hydrophobically Modified Starch 1	0.75	1	0.75	1.5	0
Hydrophobically Modified Starch 2	0	0	0	0	2
Crosslinked Starch 1	3.25	3	3	2.5	2.5
Non-Starch	0	0	0	0	0

Polysaccharide					
Cetearyl Alcohol			1.5	1.5	1.5
Glyceryl Monostearate	16.7	16.7	16.7	16.7	16.7
Sun Flower Oil	0.5	0.5	0.75	0.75	0
Euxyl 9010	0	0	0	0	0.75
GLDA	0	0	0.25	0	
DI-Water	75.8	75.8	74.05	74.05	73.55
Total	100	100	100	100	100
Total Polymer Component	4	4	3.75	4	4.5
Viscosity at 6.31/sec shear rate (cps) Initial	36000	32000	30000	28000	22000
Viscosity at 6.31/sec shear rate (cps) at 22°C (After 12 weeks)	29648	31263	34434	40878	22227
Viscosity at 6.31/sec shear rate (cps) at 45°C (After 12 weeks)	29228	38822	46570	55039	36010
TurbiScan Stability at 22°C	>90days	>90days	>90days	>90days	>90days
TurbiScan Stability at 45°C	>90days	>90days	>90days	>90days	>90days
Droplet Size (µm) 45°C 0wks	22.98	13.55	20.81	33.53	13.48
Droplet Size (µm) 45°C 4wks	21.03	17.46	21.63	36.73	14.10
Droplet Size (µm) 22°C 0wks	16.87	14.77	14.54	21.67	11.11
Droplet Size (µm) 22°C 4wks	17.83	16.44	16.63	19.95	11.17
Stability - Visual Observation	Stable	Stable	Stable	Stable	Stable

[00107] Each of the first and second hydrophobically modified starches has the following structure:



wherein R^1 is a C_3 to C_{19} branched or linear alkyl or alkenyl group and R^2 is H or an alkyl group having 1 to 10 carbons.

[00108] The Crosslinked Starch 1 is a hydroxypropyl starch phosphate derived from corn.

[00109] The Non-Starch Polysaccharide is a xanthan gum commercially available under the tradename of Jungbunzlauer FNPC.

[00110] The Viscosity at 6.31/sec shear rate (cps) is determined using MCR 302 Rheometer, by Anton Parr, located at Anton Paar Strasse 20, 8054 GRAZ, Austria. For the samples which were aged at 45°C, they were cooled down to, and were conditioned at 22°C for 24 hours before the measurement. A parallel plate of 50mm in diameter is used for the measurement element, with the gap of 1mm. The measurement is conducted at the temperature of 22°C. The shear sweep testing protocol was used which scan from shear rate of 0.1/sec to 1000/sec, with 5 measurement points per decade.

[00111] The TurbiScan Stability is determined using the method described above using TurbiScan Lab.

[00112] The Droplet Size is also determined using the method described above using TurbiScan Lab.

[00113] The terminology "Stable" relative to the visual observation of stability refers to no clear sign of creaming on the top of the emulsion, due to density difference between oil and aqueous phase, no clear sign of serum development at the bottom of the vial or middle portion of the vial either due to the oil droplets floating up or the retrogradation developed in these regions. The data set forth above shows that the (A) hydrophobically modified starch and (C), the cross-linked starch can be used to unexpectedly achieve the long-term stability.

[00114] An additional composition (Comp 6) was also created as shown below and

evaluated to determine rheology (G' and tanδ) and Droplet size and Visual Stability as also shown below.

	Comp 6
Non-Starch Polysaccharide	0.625
Hydrophobically Modified Starch 1	0.625
Cross-Linked Starch 1	1.250
Total Polymer Component	12.00
Caprylic/Capric Triglycerides	1.50
Cetearyl Alcohol	3.00
Glyceryl Monostearate	1.00
Euxyl 9010	80.00
Water	100.00
Total	0.625
G' (0.1Hz) 0 week	27.049
G' (Pa at 0.1Hz) 4th week (22°C)	26.958
G' (Pa at 0.1Hz) 4th week (45°C)	39.094
tanδ at 0.1Hz (0wk) (22°C)	0.454
tanδ at 0.1Hz (4wk) (45°C)	0.456
tanδ at 0.1Hz (4wk) (22°C)	0.403
Droplet Size (µm) 45°C 0wks	11.15
Droplet Size (µm) 45°C 4wks	13.03
Droplet Size (µm) 22°C 0wks	10.08
Droplet Size (µm) 22°C 4wks	7.84
Stability - Visual Observation	Stable

[00115] Each of the Non-Starch Polysaccharide, the Hydrophobically Modified Starch 1, and the Cross-Linked Starch 1 are the same as described above.

[00116] The G' and tanδ values are determined using a MCR 302 Rheometer, manufactured by Anton Parr, located at Anton Paar Strasse 20, 8054 GRAZ, Austria. For the samples which were aged at 45° C, they were cooled down to, and were conditioned at 22 °C for 24 hours before the measurement. A parallel plate of 50mm in diameter is used for the measurement element, with

the gap of 1mm. The measurement is conducted at the temperature of 22° C. The oscillatory testing protocol was used which subject the emulsion sample with oscillatory frequency from 0.1Hz to 10Hz, with 5 measurement points per decade. 0.1Hz was chosen as the representative reading to evaluate the rheology at the slowest shear rate to understand the long-term flow behaviors which is crucial for emulsion to overcome the gravity force. G', in unit Pa, is the elastic modulus, which demonstrates how strong a viscoelastic material is for the suspending powder, and also indicates the capability to overcome the gravity force besides the viscosity. Tan δ is the ratio between viscous modulus and elastic modulus, and is unitless. The lower the value is, the stronger the suspending power is. The maximum value for the suspending power is 1.

[00117] The Droplet Size values are determined using the method described above.

[00118] The terminology "Stable" relative to the visual observation of stability is the same as described above.

[00119] While at least one exemplary embodiment has been presented in the foregoing detailed description, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope as set forth in the appended claims.

CLAIMS

What is claimed is:

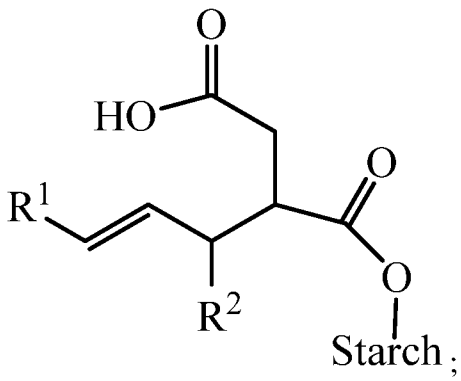
1. An oil-in-water emulsion that exhibits stability over time and comprises:

I. an oil phase present in an amount of from about 5 to about 60 weight percent actives based on a total weight of the emulsion wherein the oil phase is present in the emulsion as droplets;

II. an aqueous phase present in an amount of from about 30 to about 94.5 weight percent actives based on a total weight of the emulsion; and

III. a polymer component present in an amount of from about 0.5 to about 10 weight percent actives based on a total weight of the emulsion and comprising:

(A) a starch component present in an amount of from about 15 to about 45 weight percent actives based on a total weight of the (III) polymer component and comprising at least one hydrophobically modified starch having the following structure:



;

wherein R^1 is a C_3 to C_{19} branched or linear alkyl or alkenyl group and R^2 is H or an alkyl group having 1 to 10 carbons and Starch represents an amylose and/or amylopectin moiety;

(B) a non-starch polysaccharide present in an amount of from about 0 to about 40 weight percent actives based on a total weight of the (III) polymer component; and

(C) a cross-linked starch present in an amount of from about 3 to about 75 weight percent actives based on a total weight of the (III) polymer component;

wherein the emulsion exhibits a stability of at least 4 weeks at room temperature.

2. The oil-in-water emulsion of claim 1 wherein R^1 is a C_5 linear alkyl group and R^2 is H.

3. The oil-in-water emulsion of claim 2 wherein the hydrophobically modified starch is hydrophobically modified amylopectin.

4. The oil-in-water emulsion of claim 2 wherein the hydrophobically modified starch is hydrophobically modified amylose.

5. The oil-in-water emulsion of claim 2 wherein the hydrophobically modified starch is a combination of hydrophobically modified amylose and hydrophobically modified amylopectin.

6. The oil-in-water emulsion of claim 1 wherein R^1 is a C_9 linear or branched alkyl group and R^2 is H.

7. The oil-in-water emulsion of claim 6 wherein the hydrophobically modified starch is hydrophobically modified amylopectin.

8. The oil-in-water emulsion of claim 6 wherein the hydrophobically modified starch is hydrophobically modified amylose.

9. The oil-in-water emulsion of claim 6 wherein the hydrophobically modified starch is a combination of hydrophobically modified amylose and hydrophobically modified amylopectin.

10. The oil-in-water emulsion of any preceding claim wherein the (A) starch component is present in an amount of from about 20 to about 35 weight percent actives based on a total weight of the (III) polymer component.

11. The oil-in-water emulsion of any preceding claim wherein the (III) polymer component is present in an amount of from about 3.5 to about 10 weight percent actives based on a total weight of the emulsion and the (B) non-starch polysaccharide is optional.

12. The oil-in-water emulsion of any preceding claim wherein the (III) polymer component is present in an amount of from about 0.5 to less than about 3.5 weight percent actives based on a total weight of the emulsion and the (B) non-starch polysaccharide is present in an amount of greater than zero weight percent.

13. The oil-in-water emulsion of any preceding claim wherein the (B) non-starch polysaccharide is chosen from xanthan gum, non-ionic cellulose, and combinations thereof.

14. The oil-in-water emulsion of any preceding claim wherein the (B) non-starch polysaccharide is present in an amount of from about 5 to about 40 weight percent actives based on a total weight of the (III) polymer component.

15. The oil-in-water emulsion of any preceding claim wherein the (B) non-starch polysaccharide has a coil size of at least 400 nm.

16. The oil-in-water emulsion of any preceding claim wherein the (B) non-starch polysaccharide is chosen from methyl ethyl hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, and combinations thereof.

17. The oil-in-water emulsion of any preceding claim wherein the (C) cross-linked starch is a hydroxypropyl starch phosphate.

18. The oil-in-water emulsion of any preceding claim wherein the (C) cross-linked starch is a hydroxypropyl starch phosphate derived from corn, potato, and/or tapioca.

19. The oil-in-water emulsion of any preceding claim wherein the (C) cross-linked starch is a hydroxypropyl starch phosphate derived from corn.

20. The oil-in-water emulsion of any preceding claim wherein the (C) cross-linked starch is present in an amount of from about 30 to about 70 weight percent actives based on a total weight of the (III) polymer component.

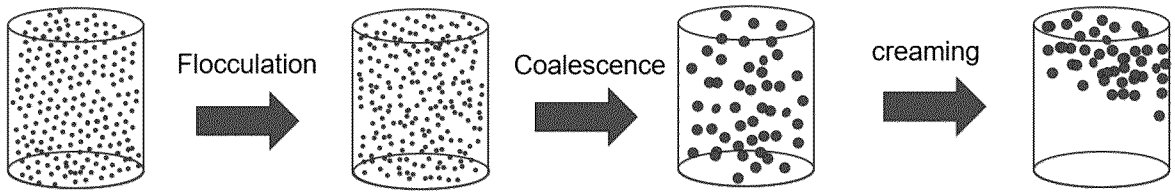

Flocculation
Coalescence
creaming

FIG. 1A

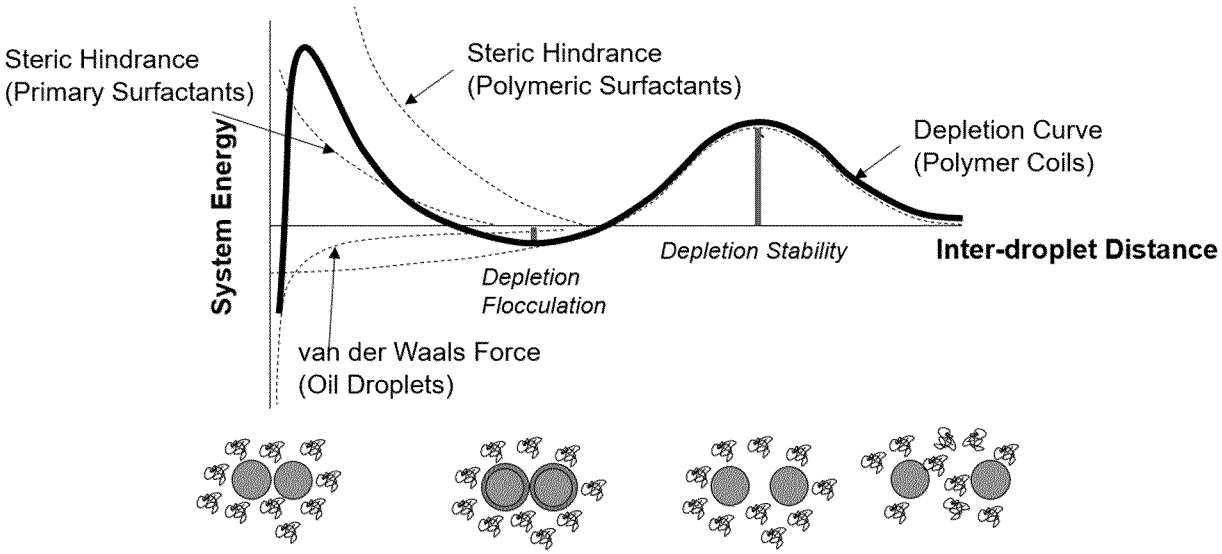

Steric Hindrance
(Primary Surfactants)
Steric Hindrance
(Polymeric Surfactants)
Depletion Curve
(Polymer Coils)
System Energy
Depletion Stability
Inter-droplet Distance
Depletion
Flocculation
van der Waals Force
(Oil Droplets)

FIG. 1B

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/071394

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08B31/16 C08L3/04 C08L3/06 C08L3/08 A61K8/06
A61K8/73 A61Q19/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K A61Q

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2022/192948 A1 (BELHAJ NABILA [FR] ET AL) 23 June 2022 (2022-06-23) paragraphs [0012] - [0023], [0026]; claims; example 1	1-20
X	WO 2007/017196 A2 (HENKEL KGAA [DE]; HLOUCHA MATTHIAS [DE] ET AL.) 15 February 2007 (2007-02-15) claim 1; examples	1-5,10, 12,17-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 October 2024	11/11/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Donovan-Beermann, T

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/071394

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2022192948 A1	23-06-2022	BR 112021018718 A2	23-11-2021
		CN 113645943 A	12-11-2021
		EP 3941420 A1	26-01-2022
		JP 2022526728 A	26-05-2022
		KR 20210141987 A	23-11-2021
		US 2022192948 A1	23-06-2022
		WO 2020190697 A1	24-09-2020
WO 2007017196 A2	15-02-2007	DE 102005038069 A1	08-03-2007
		EP 1913073 A2	23-04-2008
		WO 2007017196 A2	15-02-2007