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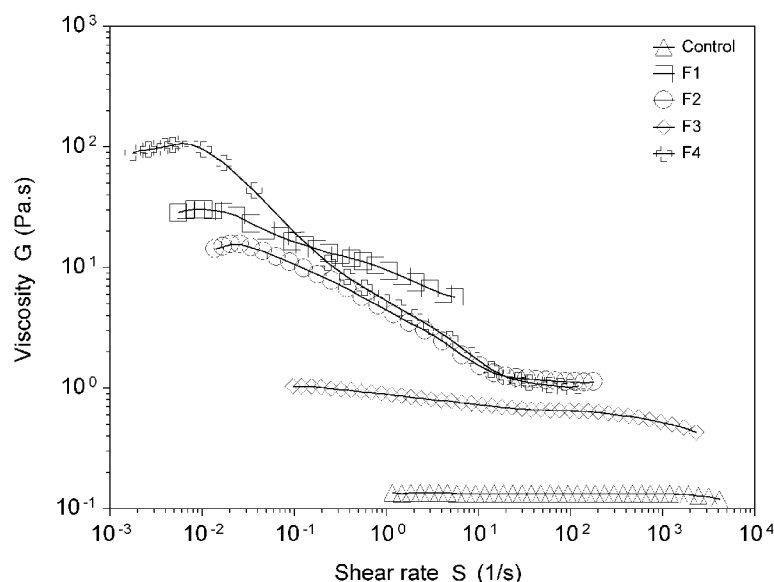


FIG. 1

(57) Abstract: Provided are personal care compositions including (a) hydrophobic ester oil, (b) at least one of a nonionic or anionic surfactant, and (c) one or more polymers containing polymerized units derived from (i) 84 to 95 weight % of C4-C8 (meth)acrylate monomers, (ii) 3 to 6 weight % of (meth)acrylic acid monomer, and (iii) 2 to 10 weight % of lipophilically modified (meth)acrylate monomer.



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OIL CLEANSER COMPOSITION COMPRISING A POLYMER DERIVED FROM  
C4-C8 (METH)ACRYLATE MONOMER

**FIELD OF THE INVENTION**

This invention relates generally to personal care compositions that are useful as oil  
5 cleansing formulations. The personal care compositions contain hydrophobic ester oil, a  
surfactant, and acrylic copolymers containing polymerized units derived from lipophilically  
modified (meth)acrylate monomer.

**BACKGROUND**

10 Personal care cleansing compositions contain a variety of additives that provide a wide  
array of benefits to the composition. One class of additives are oil thickeners that provide  
viscosity enhancements and impart good aesthetics, such as good sensory feel and clarity. Oil  
thickening agents that are known in the art include, for example, styrene-ethylene/butadiene-  
styrene copolymers, polyamide polymers, and cellulose-based polymers. These thickeners,  
15 however, come with certain drawbacks, including insufficient viscosity enhancement, high  
formulation temperature, and lack of consistency in viscosity control in consumer product  
formulations.

To this end, polyacrylate oil gels have been utilized in the art. For example, WO  
2014/204937 A1 discloses personal care compositions comprising a polyacrylate oil gel  
20 containing a cosmetically acceptable hydrophobic ester oil and a polymer including at least two  
polymerized units. The prior art does not, however, disclose a polyacrylate oil gel according to  
the present invention which achieves the significant viscosity performance at low formulation  
temperatures while also providing a clear formulation.

Accordingly, there is a need to develop thickeners that provide significant viscosity enhancements, while not suffering from the drawbacks of the prior art.

## STATEMENT OF INVENTION

5           One aspect of the invention provides a personal care composition comprising (a) at least one hydrophobic ester oil, (b) at least one surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, and mixtures thereof, and (c) one or more polymers comprising polymerized units derived from (i) 84 to 95 weight % of C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers, (ii) 3 to 6 weight % of (meth)acrylic acid monomer, and (iii) 2 to 10 weight % of  
10   lipophilically modified (meth)acrylate monomer.

          In another aspect, the invention provides a personal care composition comprising (a) 40 to 60 weight % of one or more aliphatic C<sub>8</sub>-C<sub>24</sub> alkyl triglycerides, (b) 40 to 60 weight % of a surfactant comprising a nonionic surfactant has a hydrophile-lipophile balance value of from 9 to 12, and an anionic surfactant selected from the group consisting of a triethanolamine salt, a  
15   monoisopropanolamine salt, and combinations thereof, and (c) 4 to 6 weight % of one or more polymers comprising polymerized units derived from (i) 84 to 95 weight % of i-butyl methacrylate and ethylhexyl methacrylate, (ii) 3 to 6 weight % of (meth)acrylic acid monomer, and (iii) 2 to 10 weight % of lipophilically modified (meth)acrylate monomer.

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## BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows the rheology profile (viscosity verses shear rate) of a personal care cleanser formulation in accordance with the present invention as compared against a non-inventive sample.

FIG. 2 shows the rheology profile (viscosity verses stress) of a personal care cleanser formulation in accordance with the present invention as compared against a non-inventive sample.

## DETAILED DESCRIPTION

The inventors have now surprisingly found that personal care compositions comprising hydrophobic ester oil, surfactant, and polymers having a high weight percent of polymerized units derived from C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomer, lipophilically modified (meth)acrylate monomer, and a small weight percent of (meth)acrylic acid monomer, provide significant viscosity enhancements while retaining clarity in personal care cleansing formulations.

Accordingly, the present invention provides in one aspect a personal care cleansing composition comprising (a) hydrophobic oil ester, and (b) at least one a nonionic or anionic surfactant, and (c) one or more polymers comprising polymerized units derived from (i) 84 to 95 weight % of C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers, (ii) 3 to 6 weight % of (meth)acrylic acid monomer, and (iii) 2 to 10 weight % of lipophilically modified (meth)acrylate monomer.

In the present invention, “personal care” is intended to refer to cosmetic and skin care compositions for application to the skin, including, for example, body washes and cleansers, as well as leave on application to the skin, such as lotions, creams, gels, gel creams, serums, toners, wipes, liquid foundations, make-ups, tinted moisturizer, oils, face/body sprays, and topical medicines. In the present invention, “personal care” is also intended to refer to hair care

compositions including, for example, shampoos, leave-on conditioners, rinse-off conditioners, styling gels, pomades, hair coloring products (e.g., two-part hair dyes), hairsprays, and mousses. Preferably, the personal care composition is cosmetically acceptable. “Cosmetically acceptable” refers to ingredients typically used in personal care compositions, and is intended to underscore that materials that are toxic when present in the amounts typically found in personal care compositions are not contemplated as part of the present disclosure. The compositions of the invention may be manufactured by processes well known in the art, for example, by means of conventional mixing, dissolving, granulating, emulsifying, encapsulating, entrapping or lyophilizing processes.

As used herein, the term “polymer” refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term “polymer” includes the terms “homopolymer,” “copolymer,” and “terpolymer.” As used herein, the term “polymerized units derived from” refers to polymer molecules that are synthesized according to polymerization techniques wherein a product polymer contains “polymerized units derived from” the constituent monomers which are the starting materials for the polymerization reactions. As used herein, the term “(meth)acrylate” refers to either acrylate or methacrylate, and the term “(meth)acrylic” refers to either acrylic or methacrylic. As used herein, the term “substituted” refers to having at least one attached chemical group, for example, alkyl group, alkenyl group, vinyl group, hydroxyl group, carboxylic acid group, other functional groups, and combinations thereof.

As used herein, the term “hydrophile-lipophile balance (HLB) value” refers to the value calculated from the mol fraction in a nonionic surfactant mixture starting from its concentration in a mixture in weight % followed by calculation of the concentration in mol by dividing the

concentration by molecular weight of the surfactants. The total nonionic surfactant concentration in mol is calculated and mol fraction of each surfactant in the mixture is calculated by dividing the mol concentration of a surfactant in the mixture with the total nonionic surfactant concentration in mol. In order to calculate the system HLB value, subsequently, the mol fraction of each non-ionic surfactant is multiplied by its HLB value and the sum of the resulting numbers is the system HLB value.

The inventive personal care compositions include one or more polymers comprising C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers, (meth)acrylic acid monomers, and lipophilically modified (meth)acrylate monomers. Suitable C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers include, for example, n-butyl (meth)acrylate, i-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-octyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, and 2-phenylethyl (meth)acrylate. Preferably, the C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers comprise one or more of i-butyl methacrylate, n-butyl methacrylate, and ethylhexyl methacrylate. In certain embodiments, the polymer comprises polymerized units of C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers in an amount of from 84 to 95 weight %, preferably from 85 to 94 weight %, and more preferably from 85.5 to 93.5 weight %, based on the total weight of the polymer. In certain embodiments, the C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers comprise i-butyl methacrylate and ethylhexyl methacrylate in a ratio of from 9:1 to 2:3, preferably from 3:2 to 2:3, and more preferably 1:1.

The polymers of the inventive personal care compositions also comprise (meth)acrylic acid monomer. In certain embodiments, the polymer comprises polymerized units of (meth)acrylic acid monomer in an amount of from 3 to 6 weight %, preferably from 3.5 to 5.5 weight %, and more preferably from 4 to 5 weight %, based on the total weight of the polymer.

The polymers of the inventive personal care composition also comprise lipophilically modified (meth)acrylate monomer, each of which may contain either one or a plurality of lipophilic groups. In certain embodiments, such groups are suitably in the same copolymer component as and attached to hydrophilic chains, such as for example polyoxyethylene chains.

5 According to another embodiment, the copolymer may contain a vinyl group which may be used to copolymerize the polymer to other vinyl-containing entities to alter or improve the properties of the polymer. Alternatively other copolymerization systems may be used. The polymerizable group may be attached to the lipophilic group directly, or indirectly for example via one or more, for example up to 60, preferably up to 40, water-soluble linker groups, for example,  
10 -CH[R]CH<sub>2</sub>O- or -CH[R]CH<sub>2</sub>NH- groups wherein R is hydrogen or methyl. Alternatively, the polymerizable group may be attached to the lipophilic group by reaction of the hydrophilic, for example polyoxyethylene, component with a urethane compound containing unsaturation. The molecular weight of the lipophilic-modifying group or groups is preferably selected together with the number of such groups to give the required minimum lipophilic content in the  
15 copolymer, and preferably, for satisfactory performance in a wide range of systems. In certain embodiments, the lipophilic-modifying groups themselves are straight chain saturated alkyl groups having at least 6, and up to 30 carbon atoms, although branched chain groups may be contemplated, as well as arylkyl or alkyl carbocyclic groups such as alkylphenyl groups. It is understood that the alkyl groups may be either of synthetic or of natural origin and, in the latter  
20 case particularly, may contain a range of chain lengths.

In certain preferred embodiments, the chain length of the lipophilic-modifying groups is minimized and the alkyl chain length, or predominant chain length, is a C<sub>8</sub>-C<sub>25</sub> alkyl group, preferably a C<sub>10</sub>-C<sub>20</sub> alkyl group, and more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl group. The hydrophilic



component of the lipophilically-modified copolymer may suitably be a polyoxyethylene component comprising of from 2 to 60 ethylene oxide units, preferably from 5 to 40 ethylene oxide units, and more preferably from 10 to 30 ethylene oxide units. In certain embodiments, such components are usually produced in a mixture of chain lengths. In certain embodiments, the polymer comprises polymerized units of lipophilically modified (meth)acrylate monomer in an amount of from 2 to 10 weight %, preferably from 3 to 9 weight %, and more preferably from 4 to 8 weight %, based on the total weight of the polymer.

In certain embodiments, the polymers have an average particle size of from 50 to 500 nm, preferably of from 75 to 250 nm, and more preferably of from 105 to 140 nm. Polymer molecular weights can be measured by standard methods such as, for example, size exclusion chromatography or intrinsic viscosity. In certain embodiments, the polymers of the present invention have a weight average molecular weight ( $M_w$ ) of 10,000,000 or less, preferably 8,500,000 or less, and more preferably 7,000,000 or less as measured by gel permeation chromatography. In certain embodiments, the copolymer particles have a  $M_w$  of 50,000 or more, preferably 100,000 or more, and more preferably 200,000 or more, as measured by gel permeation chromatography. In certain embodiments, the polymers are present in the personal care composition in an amount of from 0.1 to 20 weight %, preferably from 1 to 13 weight %, and more preferably from 4 to 6 weight %, based on the total weight of the personal care composition.

Suitable polymerization techniques for preparing the polymers contained in the inventive personal care compositions include, for example, emulsion polymerization and solution polymerization, preferably emulsion polymerization, as disclosed in U.S. Patent No. 6,710,161. Aqueous emulsion polymerization processes typically are conducted in an aqueous reaction

mixture, which contains at least one monomer and various synthesis adjuvants, such as the free radical sources, buffers, and reductants in an aqueous reaction medium. In certain embodiments, a chain transfer agent may be used to limit molecular weight. The aqueous reaction medium is the continuous fluid phase of the aqueous reaction mixture and contains more than 50 weight %  
5 water and optionally one or more water miscible solvents, based on the weight of the aqueous reaction medium. Suitable water miscible solvents include, for example, methanol, ethanol, propanol, acetone, ethylene glycol ethyl ethers, propylene glycol propyl ethers, and diacetone alcohol. In certain embodiments, the aqueous reaction medium contains more than 90 weight % water, preferably more than 95 weight % water, and more preferably more than 98 weight %  
10 water, based on the weight of the aqueous reaction medium.

The polymers of the present invention may be isolated by a spray drying process. While spray drying is one preferred embodiment of how to produce the dry powder, other suitable methods include, for example, freeze drying, a two-step process including the steps of (i) pan drying the emulsion and then (ii) grinding the pan dried material into a fine powder, coagulation  
15 of the acrylic emulsion and collection of the powder by filtration followed by washing and drying, fluid bed drying, roll drying, and freeze drying. Suitable techniques for spray drying the polymer beads of the present invention are known in the art, for example, as described in US 2014/0113992 A1. In certain embodiments, anti-caking agents are used when spray drying the polymer beads. Suitable anti-caking agents include, for example, mineral fillers (e.g., calcium  
20 carbonate, kaolin, titanium oxide, talc, hydrated alumina, bentonite, and silica), solid polymer particles with a  $T_g$  or  $T_m$  greater than 60°C (e.g., polymethylmethacrylate, polystyrene, and high density polyethylene), and water soluble polymers with a  $T_g$  greater than 60°C (e.g., polyvinyl alcohol and methylcellulose). The anti-caking agent can be mixed in the acrylic suspension prior

to spray drying or introduced as a dry powder in the spray drying process. In certain  
embodiments, the anti-caking agent coats the polymer beads to prevent the beads from sticking  
to each other inner wall of the dryer. In certain embodiments, the anti-caking agent is present in  
an amount of from 0 to 20 weight %, and more preferably from 0.01 to 10 weight %, based on  
5 the total weight of the polymer beads.

The personal care compositions of the present invention also contain a cosmetically  
acceptable hydrophobic ester oil. In general, any hydrophobic ester oil or mixtures thereof  
which are toxicologically safe for human or animal use may constitute the oil base of the present  
invention. In certain embodiments, the hydrophobic ester oil comprises aliphatic C<sub>8</sub>-C<sub>24</sub> alkyl  
10 triglycerides. Suitable hydrophobic ester oils include, for example, caprylic/capric triglycerides,  
saturated fatty esters and diesters (e.g., isopropyl palmitate, octyl palmitate, butyl stearate,  
isocetyl stearate, octadodecyl stearate, octadodecyl stearyl stearate, diisopropyl adipate, and  
dioctyl sebacate), and animal oils and vegetable oils (e.g., mink oil, coconut oil, soybean oil,  
palm oil, corn oil, cocoa butter, sesame oil, sunflower seed oil, jojoba oil, olive oil, and lanolin  
15 oil). In certain embodiments, the hydrophobic ester oil is diffused in an oil base. Suitable oil  
bases include any oil or mixture of oils which are conventionally used in personal care products  
including, for example, paraffin oils, paraffin waxes, and fatty alcohols (e.g., stearyl alcohol,  
isostearyl alcohol, and isocetyl alcohol). In certain preferred embodiments, the hydrophobic  
ester oil comprises one or more of caprylic/capric triglycerides and sunflower seed oil. In certain  
20 embodiments, the hydrophobic ester oils are present in the personal care composition in an  
amount of from 10 to 90 weight %, preferably from 30 to 70 weight %, and more preferably  
from 40 to 60 weight %, based on the total weight of the personal care composition.

The personal care compositions of the present invention also contain at least one of nonionic surfactants, anionic surfactants, and mixtures thereof. In certain embodiments, the total amount of surfactant is present in an amount of 10 to 90 weight %, preferably from 25 to 75 weight %, and more preferably from 40 to 60 weight %, based on the total weight of the personal care composition. In certain embodiments, the nonionic surfactant and anionic surfactant are present in a ratio of from 1:15 to 10:1, preferably from 1:2 to 5:1, more preferably from 1:3 to 2:1, and more preferably from 1:4 to 1:1.

In certain embodiments, the nonionic surfactant has an value of from 7 to 14, preferably from 8 to 13, and more preferably from 9 to 12, calculated from the mol fraction of individual nonionic surfactants in the nonionic surfactant mixture and the individual HLB values of nonionic surfactant. Suitable nonionic surfactants having such HLB values include, for example, those provided in Table 1.

**Table 1. HLB Values of Non-ionic Surfactants**

| Surfactant                     | HLB Value |
|--------------------------------|-----------|
| PEG-8 Dioleate                 | 8         |
| Sorbitan Laurate               | 8.6       |
| PEG-40 Sorbitan Peroleate      | 9         |
| Laureth-4                      | 9.7       |
| PEG-7 Glyceryl Cocoate         | 10        |
| PEG-20 Almond Glycerides       | 10        |
| PEG-25 Hydrogenated Castor Oil | 10.8      |
| Stearamide MEA                 | 11        |
| Polysorbate 85                 | 11        |

|                        |      |
|------------------------|------|
| PEG-7 Olivat           | 11   |
| Cetearyl Glucoside     | 11   |
| Sorbeth-30 Tetraoleate | 11.5 |
| PEG-8 Oleate           | 11.6 |
| Oleth-10               | 12.4 |
| Ceteth-10              | 12.9 |
| PEG-8 Laurate          | 13   |
| Cocamide MEA           | 13.5 |

In certain embodiments, suitable nonionic surfactants include, for example, sorbitan esters, (e.g., polyethylene glycol sorbitan stearic acid ester), fatty acid polyglycol esters or poly-condensates of ethyleneoxide and propyleneoxide.

- 5 Other suitable nonionic surfactants include, for example, long-chain fatty acid mono- and dialkanolamides, e.g., behenoyl monoethanolamide, coco monoethanolamide, isostearyl monoethanolamide, lauroyl monoethanolamide, myristoyl monoethanolamide, oleoyl monoethanolamide, ricinoleoyl monoethanolamide, stearyl monoethanolamide, behenoyl diethanolamide, caproyl diethanolamide, cocoyl diethanolamide, isostearyl diethanolamide, lauroyl diethanolamide, lineloyl monoethanolamide, myristoyl monoethanolamide, oleoyl monoethanolamide, palmitoyl diethanolamide, ricinoleoyl monoethanolamide, and stearyl monoethanolamide. Other suitable nonionic surfactants include, for example, C<sub>10</sub>-C<sub>22</sub> fatty alcohol ethoxylates, e.g., oleth-2, oleth-3, oleth-4, oleth-5, oleth-6, oleth-7, oleth-8, oleth-9, oleth-10, oleth-11, oleth-12, oleth-15, oleth-16, oleth-20, oleth-25, laureth-2, laureth-3, laureth-4, laureth-5, laureth-6, laureth-7, laureth-8, laureth-9, laureth-10, laureth-11, laureth-12, laureth-13, laureth-15, laureth-16, laureth-20, laureth-25, ceteth-10, ceteth-12, ceteth-14, ceteth-15, ceteth-

16, ceteth-17, ceteth-20, ceteth-25, cetoeth-10, cetoeth-12, cetoeth-14, cetoeth-15, cetoeth-16, cetoeth-17, cetoeth-20, cetoeth-25, cetareth-10, cetareth-12, cetareth-14, cetareth-15, cetareth-16, cetareth-18, cetareth-20, cetareth-22, cetareth-25, isostareth-10, isostareth-12, isostareth-15, isostareth-20, isostareth-22, isostareth-25, steareth-10, steareth-11, 5 steareth-14, steareth-15, steareth-16, steareth-20, and steareth-25. Other suitable nonionic surfactants include, for example, alkyl polyglucosides, e.g., decyl glucoside, carpylyl glucoside, cetearyl glucoside, cocoyl ethyl glucoside, lauryl glucoside, myristyl glucoside, and coco glucoside. Other suitable nonionic surfactants include, for example, polyalkylene glycol ethers of fatty acid glyceride or partial glyceride, e.g., PEG-30 hydrogenated castor oil, PEG-35 10 hydrogenated castor oil, PEG-40 hydrogenated castor oil, PEG-45 hydrogenated castor oil, PEG-50 hydrogenated castor oil, PEG-55 hydrogenated castor oil, PEG-60 hydrogenated castor oil, PEG-65 hydrogenated castor oil, PEG-80 hydrogenated castor oil, PEG-100 hydrogenated castor oil, PEG-200 hydrogenated castor oil, PEG-35 castor oil, PEG-50 castor oil, PEG-55 castor oil, PEG-60 castor oil, PEG-80 castor oil, and PEG-100 castor oil.

15           Suitable anionic surfactants of the present invention include, for example, anionic alkyl ether sulfate surfactants (e.g., triethanolamine (“TEA”) salts and monoisopropanolamine (“MIPA”) salts), alkyl ether sulfonate surfactants, and alkyl ether carboxylate surfactants. Suitable anionic alkyl ether sulfate surfactants include, for example, ammonium capryleth sulfate, ammonium C<sub>12</sub>-C<sub>15</sub> pareth sulfate, ammonium laureth sulfate, ammonium laureth-5 20 sulfate, ammonium myreth sulfate, DEA C<sub>12</sub>-C<sub>13</sub> pareth-3 sulfate, DEA laureth sulfate, DEA myreth sulfate, diethylamine laureth sulfate, magnesium coceth sulfate, magnesium laureth sulfate, magnesium laureth-5 sulfate, magnesium myreth sulfate, magnesium oleth sulfate, MEA laureth sulfate, MIPA C<sub>12</sub>-C<sub>15</sub> pareth sulfate, MIPA laureth sulfate, sodium coceth sulfate,

sodium C9-15 pareth-3 sulfate, sodium C<sub>10</sub>-C<sub>15</sub> pareth-3 sulfate, sodium C<sub>12</sub>C<sub>16</sub> pareth-2 sulfate, sodium C<sub>12</sub>-C<sub>13</sub> pareth sulfate, sodium C<sub>12</sub>-C<sub>14</sub> pareth-3 sulfate, sodium C<sub>12</sub>-C<sub>15</sub> pareth sulfate, sodium C<sub>12</sub>-C<sub>15</sub> pareth-3 sulfate, sodium C<sub>13</sub>-C<sub>15</sub> pareth-3 sulfate, sodium doceth sulfate, sodium laneth sulfate, sodium laureth sulfate, sodium laureth-5 sulfate, sodium myreth sulfate, sodium  
5 oleth sulfate, TEA laureth sulfate, TEA laneth sulfate, and TIPA laureth sulfate.

The personal care compositions according to the present invention may be formulated by conventional mixing processes known to those skilled in the art. In certain embodiments, the formulation temperature is from 20°C to 100°C, preferably from 25°C to 50°C.

The inventive personal care compositions also include a dermatologically acceptable  
10 carrier. Such material is typically characterized as a carrier or a diluent that does not cause significant irritation to the skin and does not negate the activity and properties of active agent(s) in the composition. Examples of dermatologically acceptable carriers that are useful in the invention include, without limitation, water, such as deionized or distilled water, emulsions, such as oil-in-water or water-in-oil emulsions, alcohols, such as ethanol, isopropanol or the like,  
15 glycols, such as propylene glycol, glycerin or the like, creams, aqueous solutions, oils, ointments, pastes, gels, lotions, milks, foams, suspensions, powders, or mixtures thereof. The aqueous solutions may contain cosolvents, e.g., water miscible cosolvents. Suitable water miscible cosolvents include, for example, ethanol, propanol, acetone, ethylene glycol ethyl ethers, propylene glycol propyl ethers, and diacetone alcohol. In some embodiments, the composition  
20 contains from about 99.99 to about 50 percent by weight of the dermatologically acceptable carrier, based on the total weight of the composition.

Other additives may be included in the compositions of the invention such as, but not limited to, abrasives, absorbents, aesthetic components such as fragrances, pigments,

colorings/colorants, essential oils, skin sensates, astringents (e.g., clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate), preservatives, anti-caking agents, a foam building agent, antifoaming agents, antimicrobial agents (e.g., iodopropyl butylcarbamate), antioxidants, binders, biological additives, buffering agents, bulking agents, 5 chelating agents, chemical additives, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film formers or materials, e.g., polymers, for aiding the film-forming properties and substantivity of the composition (e.g., copolymer of eicosene and vinyl pyrrolidone), opacifying agents, pH adjusters, propellants, reducing agents, sequestrants, skin bleaching and lightening agents (e.g., hydroquinone, kojic acid, ascorbic acid, magnesium 10 ascorbyl phosphate, ascorbyl glucosamine), skin-conditioning agents (e.g., humectants, including miscellaneous and occlusive), skin soothing and/or healing agents (e.g., panthenol and derivatives (e.g., ethyl panthenol), aloe vera, pantothenic acid and its derivatives, allantoin, bisabolol, and dipotassium glycyrrhizinate), skin treating agents, vitamins (e.g., Vitamin C) and derivatives thereof, silicones, and fatty alcohols. The amount of option ingredients effective for 15 achieving the desired property provided by such ingredients can be readily determined by one skilled in the art.

Some embodiments of the invention will now be described in detail in the following Examples.

20

## EXAMPLES

### Example 1



***Preparation of Exemplary Polymer and Comparative Polymers***

Exemplary polymers in accordance with the present invention and comparative polymers contain the components recited in Table 2.

**Table 2. Exemplary and Comparative Polymers Particles**

| Sample           | Monomer (wt %)                                  |
|------------------|-------------------------------------------------|
| P1               | 46.5 iBMA / 46.5 EHMA / 3.5 MAA / 3.5 Lipo1     |
| P2               | 44 iBMA / 44 EHMA / 5 MAA / 7 Lipo1             |
| P3               | 42.75 iBMA / 42.75 EHMA / 5.75 MAA / 8.75 Lipo1 |
| P4               | 44 iBMA / 44 EHMA / 5 MAA / 7 Lipo2             |
| C1*              | 48 iBMA / 48 EHMA / 2.6 MAA / 1.4 Lipo1         |
| C2* <sup>+</sup> | 41.5 iBMA / 41.5 EHMA / 6.5 MAA / 10.5 Lipo1    |
| C3* <sup>+</sup> | 41.5 iBMA / 41.5 EHMA / 8 MAA / 14 Lipo1        |

- 5 iBMA = isobutyl methacrylate  
 EHMA = ethylhexyl methacrylate  
 MAA = methacrylic acid  
 Lipo1 = lipophilically modified monomer having a linear saturated C<sub>12</sub> alkyl group contacted through 23 oxyethylene residues to a methacryloyl group  
 10 Lipo2 = lipophilically modified monomer having a linear saturated C<sub>18</sub> alkyl group contacted through 20 oxyethylene residues to a methacryloyl group  
 \*Comparative  
 \*Gelled in synthesis

Synthesis of exemplary polymer P2 was carried out as follows. A three liter round  
 15 bottom flask was equipped with a mechanical overhead stirrer, heating mantle, thermocouple, condenser, and inlets for the addition of monomer, initiator, and nitrogen. The kettle was charged with 900 grams deionized water and 7.46 grams of DS-4 (Polystep A-16-22: sodium dodecylbenzene sulfonate from Stepan). The kettle contents were set to stir with a nitrogen flow and heated to 87-89°C. To a plastic lined vessel, 17.68 grams of DS-4 and 256.65 grams

deionized water was added and mixed with overhead stirring. 39.59 grams of Lipo1, 248.56 grams of Isobutyl Methacrylate, 248.56 grams of 2-Ethylhexyl Methacrylate, and 28.28 grams of Methacrylic Acid was charged to the vessel and allowed to form a smooth, stable monomer emulsion. An initial catalyst charge of 0.28 grams of ammonium persulfate and 12.71 grams of deionized water was prepared and set aside. A kettle buffer solution of 1.92 grams of ammonium bicarbonate and 12.71 grams of deionized water was prepared and set aside. A preform seed of 22.38 grams was removed from the stable monomer emulsion and put into a small beaker. A rinse of 16.8 grams of deionized water was prepared. A co-feed catalyst charge of 0.28 grams of ammonium persulfate and 49.22 grams of deionized water was prepared and set aside.

When the kettle was at temperature, the kettle buffer solution and initial catalyst solution were added to the reactor, followed by the perform seed and rinse. The reaction was monitored for a small exotherm. After the exotherm, the temperature control was adjusted to 83-85°C. The monomer emulsion feed was added to the kettle, sub-surface, at a rate of 4.38 grams/minute for 15 minutes. After 15 minutes, the rate was increased to 8.77 grams/minutes for 75 minutes, giving a total feed time of 90 minutes. While the monomer emulsion feed was added to the kettle, the co-feed catalyst solution was also added over 90 minutes at a rate of 0.55 grams/minute. At the completion of the feeds, 16.8 grams of deionized water was added as a rinse. The reaction was then held for 20 minutes at 83-85°C.

During the hold, a chase promoter of 3.77 grams of a 0.15% iron sulfate heptahydrate solution was prepared. A chase activator solution of 1.12 grams of isoascorbic acid dissolved in 36.40 grams of deionized water was prepared. A chase catalyst solution of 2.14 grams of 70% tert-butyl hydroperoxide in 35.40 grams of deionized water was prepared.

At 80°C, the chase promoter solution was added as a shot to the kettle. The kettle contents were then cooled to 70°C, while adding the chase activator and chase catalyst solutions separately by syringe over 60 minutes at a feed rate of 0.7 grams/minute. The reaction was held for 10 minutes, and then cooled to room temperature. At room temperature, the emulsion was filtered through a 100 mesh bag.

Exemplary polymers P1, P3, and P4, and comparative polymers C1, C2, and C3 were prepared substantially as described above, with the appropriate changes in monomer and monomer amounts as recited in Table 2.

## Example 2

### *Particle Size Characterization of Exemplary Polymers*

Exemplary and comparative polymers as prepared in Example 1 were evaluated for particle size as shown in Table 3.

**Table 3. Particle Size Characterization**

| Sample | Particle Size (nm) |
|--------|--------------------|
| P1     | 111                |
| P2     | 118                |
| P3     | 178                |
| P4     | 110                |
| C1     | 119                |

The particle size distributions of exemplary polymers was determined by light diffraction using a Malvern Mastersizer 2000 Analyzer equipped with a 2000uP module. Approximately 0.5 g of polymer emulsion samples were pre-diluted into 5 mL of 0.2 weight % active Triton 405 in

degassed, DI water (diluent). The pre-diluted sample was added drop-wise to the diluent filled 2000uP module while the module was pumped at 1100 rpm. Red light obscurations were targeted to be between 4 and 8%. Samples were analyzed using a Mie scattering module (particle real refractive index of 1.48 and absorption of zero; Diluent real refractive index of 1.330 with absorption of zero). A general purpose (spherical) analysis model with “normal sensitivity” was used to analyze the diffraction patterns and convert them into particle size distributions.

### **Example 3**

#### ***Spray Drying of Exemplary and Comparative Polymers***

Exemplary and comparative polymers as prepared in Example 1 were spray dried according to the following procedure. A two-fluid nozzle atomizer was equipped on a Mobile Minor spray dryer (GEA Process Engineering Inc.). The spray drying experiments were performed under an inert atmosphere of nitrogen. The nitrogen supplied to the atomizer at ambient temperature was set at 1 bar and 50% flow, which is equivalent to 6.0 kg/hour of flow rate. The polymer emulsion was fed into the atomizer at about 30 mL/min using a peristaltic pump (Masterflex L/S). Heated nitrogen was used to evaporate the water. The inlet temperature was set at 140°C, and the outlet temperature was equilibrated at 40-50°C by fine tuning the emulsion feed rate. The resulting polymer powder was collected in a glass jar attached to the cyclone and subsequently vacuum dried at room temperature to removed residual moisture.

### **Example 4**

#### ***Preparation of Exemplary and Comparative Oil Cleansing Formulations***

Exemplary oil cleansing formulations in accordance with the present invention and comparative oil cleansing formulations contain the components recited in Table 4.

**Table 4. Exemplary and Comparative Oil Cleansing Formulations**

| Component                       | INCI Name                                     | Control<br>(wt %) | F1<br>(wt %) | F2<br>(wt %) | F3<br>(wt %) | F4<br>(wt %) | FC1<br>(wt %) |
|---------------------------------|-----------------------------------------------|-------------------|--------------|--------------|--------------|--------------|---------------|
| Sunflower Seed Oil <sup>+</sup> | Helianthus annuus                             | 50                | 47.5         | 47.5         | 47.5         | 47.5         | 47.5          |
| Lumolol K1000 <sup>++</sup>     | MIPA-laureth sulfate/Cocamide DEA / Laureth-4 | 40                | 38           | 38           | 38           | 38           | 38            |
| Rheodol 430V <sup>+++</sup>     | Sorbeth-30 Tetraloeate                        | 10                | 9.5          | 9.5          | 9.5          | 9.5          | 9.5           |
| P1                              | --                                            | --                | 5            | --           | --           | --           | --            |
| P2                              | --                                            | --                | --           | 5            | --           | --           | --            |
| P3                              | --                                            | --                | --           | --           | 5            | --           | --            |
| P4                              | --                                            | --                | --           | --           | --           | 5            | --            |
| C1*                             | --                                            | --                | --           | --           | --           | --           | 5             |

<sup>+</sup>Available from Spectrum Chemical

<sup>++</sup>Available from Zschimmer & Schwarz

<sup>+++</sup>Available from Kao Chemical

\*Comparative

Exemplary and comparative oil cleansing formulations were formulated by mixing the exemplary and comparative polymers as prepared in Example 3 together with the other components in the amounts specified in Table 4 under stirring at 500 rpm at room temperature for 1 hour.

## Example 5

### *Viscosity of Exemplary and Comparative Oil Cleansing Formulations*

The viscosities of exemplary and comparative oil cleansing formulations as prepared in Example 4 are shown in Table 5.

**Table 5. Viscosities of Exemplary and Comparative Oil Cleansing Formulations**

| Sample  | Viscosity (cP)                    | Clarity     |
|---------|-----------------------------------|-------------|
| Control | below detection limit             | hazy        |
| F1      | N/A                               | hazy        |
| F2      | 2,500                             | translucent |
| F3      | 1,250                             | clear       |
| F4      | 2,083                             | translucent |
| FC1     | polymer aggregated in formulation | N/A         |

5           The viscosity of each sample was measured with a Bookfield viscometer, Spindle S95 at 12 rpm. The results demonstrate that the inventive oil cleansing formulations exhibit superior viscosity enhancement and clarity, and that the polymer in the comparative oil cleansing formulation aggregated in formulation.

## 10   **Example 6**

### ***Rheology Characterization of Exemplary and Comparative Oil Cleansing Formulations***

Viscosities of oil cleansing formulations as prepared in Example 4 were measured using a DHR3 TA instrument rheometer with a 50 mm parallel plate geometry (Peltier plate Quartz, 1 mm gap). All measurements were performed at a strain of 2%, within the linear viscoelastic regime. All analyses were performed at 25°C, and isothermal flow sweep was conducted. A

logarithmic step ramp method was used ranging over the shear stress of 0.1-1000 Pa with 10 data points per decade after an initial 2 minute equilibration.

FIG. 1 shows the viscosity verses shear rate rheology profiles for exemplary oil cleansing formulations F1-F4 and the Control. FIG. 2 shows the viscosity verses shear stress rheology  
5 profiles for exemplary oil cleansing formulations F1-F4 and the Control. The exemplary oil cleansing formulations demonstrated an increase in viscosity and shear thinning behavior, which is highly desirable for oil cleansing formulations.

## WHAT IS CLAIMED IS:

## 1. A personal care composition comprising:

- (a) at least one cosmetically acceptable hydrophobic ester oil;
- (b) at least one surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, and mixtures thereof; and
- (c) one or more polymers comprising polymerized units derived from
  - (i) 84 to 95 weight % of C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers,
  - (ii) 3 to 6 weight % of (meth)acrylic acid monomer, and
  - (iii) 2 to 10 weight % of lipophilically modified (meth)acrylate monomer.

2. The personal care composition of claim 1, wherein the hydrophobic ester oil comprises one or more aliphatic C<sub>8</sub>-C<sub>24</sub> alkyl triglycerides.

## 3. The personal care composition of claim 1, wherein the at least one surfactant comprises a nonionic surfactant and an anionic alkyl ether sulfate surfactant, wherein the nonionic surfactant has a hydrophile-lipophile balance value of from 7 to 14.

## 4. The personal care composition of claim 3, wherein the nonionic surfactant has a hydrophile-lipophile balance value of from 9 to 12.

## 5. The personal care composition of claim 3, wherein the anionic surfactant comprises at least one of a triethanolamine salt and a monoisopropanolamine salt.



6. The personal care composition of claim 1, wherein the C<sub>4</sub>-C<sub>8</sub> (meth)acrylate monomers are selected from the group consisting of ethylhexyl (meth)acrylate, butyl (meth)acrylate, and combinations thereof.
7. The personal care composition of claim 1, wherein the lipophilically modified (meth)acrylate monomer comprises
  - (A) a polyoxyethylene component comprising of from 2 to 60 ethylene oxide units, and
  - (B) a lipophilic-modifying group comprising a C<sub>8</sub>-C<sub>25</sub> alkyl group.
8. The composition of 7, wherein (A) the polyoxyethylene component comprises of from 10 to 30 ethylene oxide units, and (B) the lipophilic-modifying group comprises a C<sub>10</sub>-C<sub>20</sub> alkyl group.
9. The composition of claim 1, wherein (a) the at least one cosmetically acceptable hydrophobic ester oil is present in an amount of from 10 to 90 weight %, based on the total weight of the personal care composition, (b) the at least one surfactant is present in an amount of from 10 to 90 weight %, based on the total weight of the of the personal care composition, and (c) the one or more polymers are present in an amount of from 0.1 to 20 weight %, based on the total weight of the personal care composition.
10. A personal care composition comprising:
  - (a) 40 to 60 weight % of one or more aliphatic C<sub>8</sub>-C<sub>24</sub> alkyl triglycerides;

(b) 40 to 60 weight % of a surfactant comprising a nonionic surfactant has a hydrophile-lipophile balance value of from 9 to 12, and an anionic surfactant selected from the group consisting of a triethanolamine salt, a monoisopropanolamine salt, and combinations thereof; and

(c) 4 to 6 weight % of one or more polymers comprising polymerized units derived from

(i) 84 to 95 weight % of i-butyl methacrylate and ethylhexyl methacrylate,

(ii) 3 to 6 weight % of (meth)acrylic acid monomer, and

(iii) 2 to 10 weight % of lipophilically modified (meth)acrylate monomer.

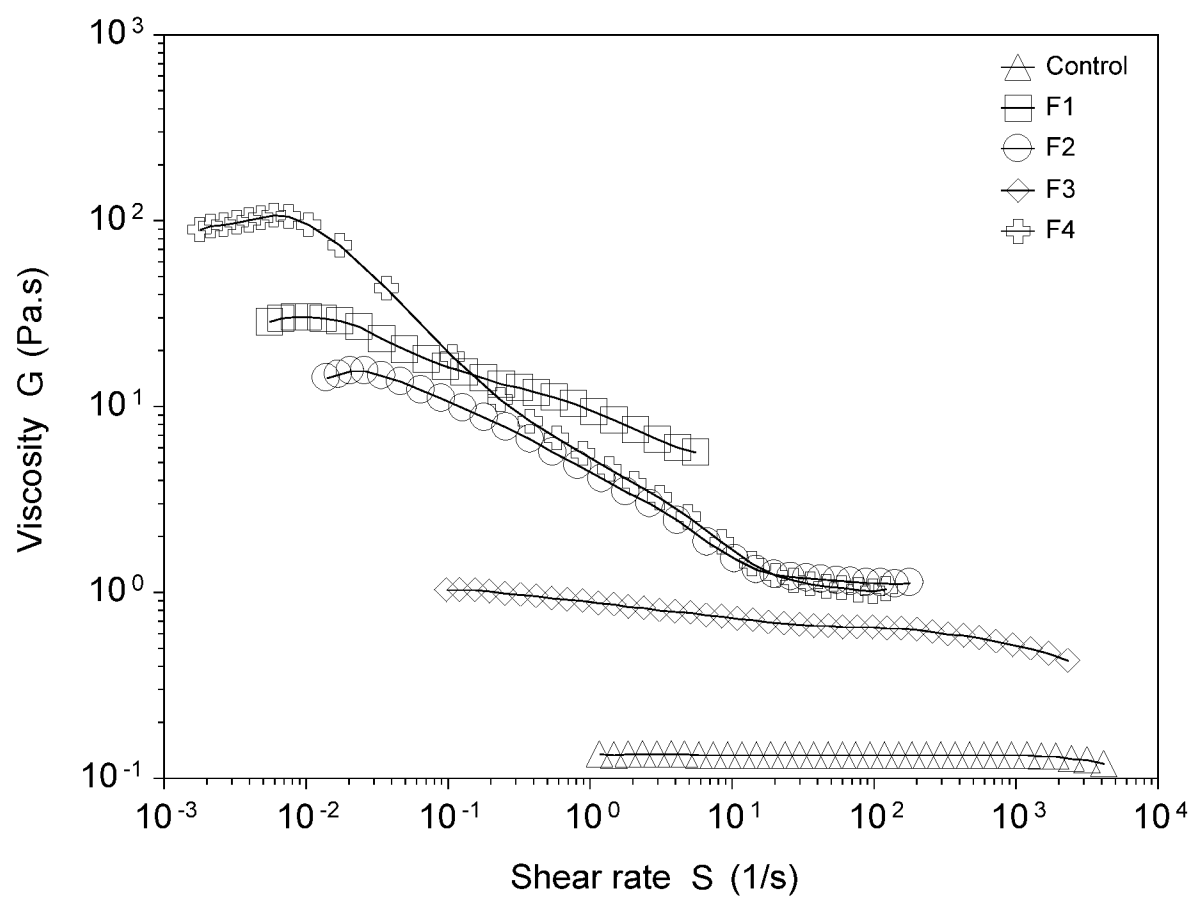


FIG. 1

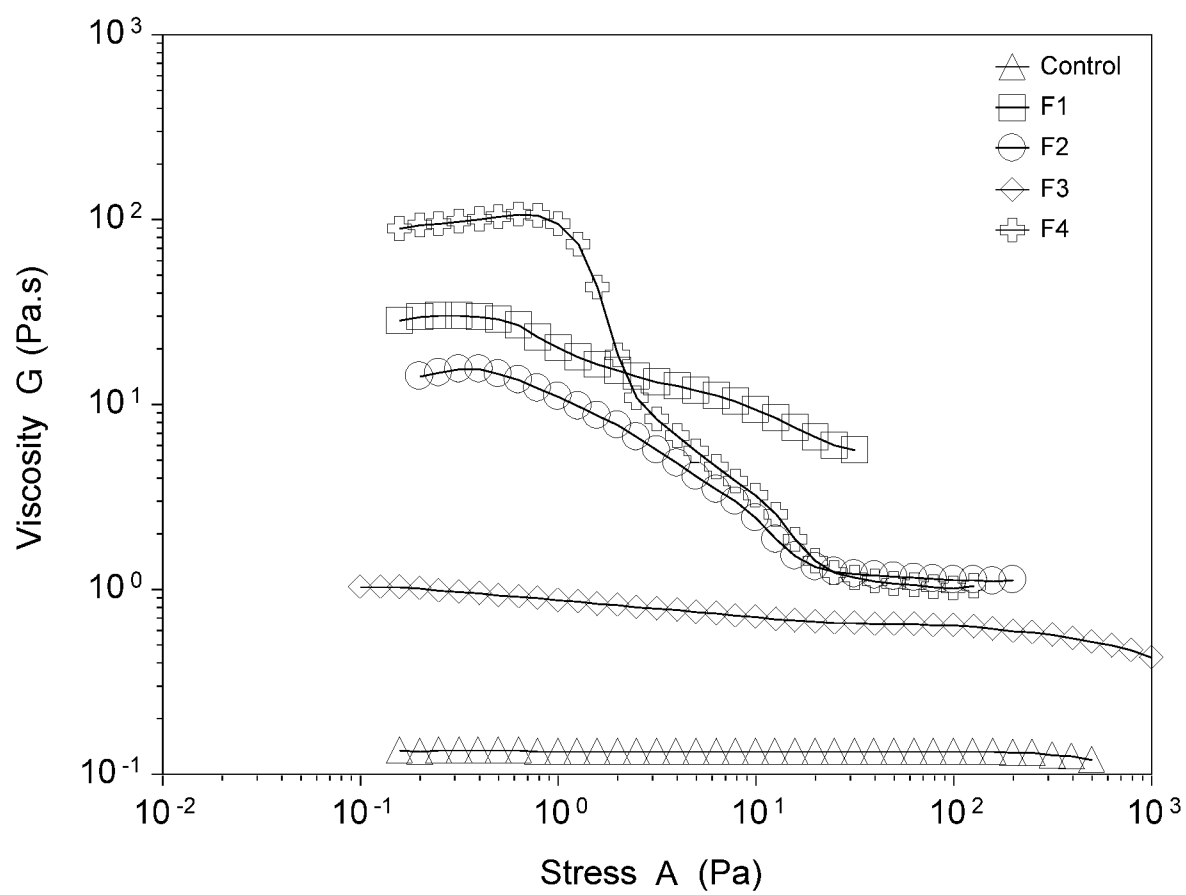


FIG. 2

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|                                                       |                                                                                                  |                                                                                     |
|-------------------------------------------------------|--------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Applicant's or agent's file reference<br>80118-WO-PCT | <b>FOR FURTHER ACTION</b><br>see Form PCT/ISA/220<br>as well as, where applicable, item 5 below. |                                                                                     |
| International application No.<br>PCT/US2017/062269    | International filing date ( <i>day/month/year</i> )<br>17 November 2017 (17-11-2017)             | (Earliest) Priority Date ( <i>day/month/year</i> )<br>22 November 2016 (22-11-2016) |
| Applicant<br><br>DOW GLOBAL TECHNOLOGIES LLC          |                                                                                                  |                                                                                     |

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒

It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of:

☒

the international application in the language in which it was filed

☐

a translation of the international application into \_\_\_\_\_, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐

This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6**bis**(a)).

c. ☐

With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐

**Certain claims were found unsearchable** (See Box No. II)

3. ☐

**Unity of invention is lacking** (see Box No III)

4. With regard to the **title**,

☐

the text is approved as submitted by the applicant

☒

the text has been established by this Authority to read as follows:

OIL CLEANSER COMPOSITION COMPRISING A POLYMER DERIVED FROM C4-C8 (METH)ACRYLATE MONOMER

5. With regard to the **abstract**,

☒

the text is approved as submitted by the applicant

☐

the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 1

☐

as suggested by the applicant

☒

as selected by this Authority, because the applicant failed to suggest a figure

☐

as selected by this Authority, because this figure better characterizes the invention

b. ☐

none of the figures is to be published with the abstract

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2017/062269

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                              |                                                                                                                               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>INV. A61K8/81 A61Q19/10 C08L33/06 C08F20/28 A61K8/92<br>ADD.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                              |                                                                                                                               |
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                              |                                                                                                                               |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>A61K A61Q C08L C08F                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                              |                                                                                                                               |
| 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)<br>EPO-Internal                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                              |                                                                                                                               |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                              |                                                                                                                               |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Citation of document, with indication, where appropriate, of the relevant passages                                                           | Relevant to claim No.                                                                                                         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 2016/243019 A1 (LI ZHANG [US] ET AL)<br>25 August 2016 (2016-08-25)<br>paragraphs [0004], [0020], [0022]; claim<br>1; tables 2,4<br>----- | 1-10                                                                                                                          |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | WO 2016/079003 A1 (BASF SE [DE]; HENKEL AG<br>& CO KGAA [DE]) 26 May 2016 (2016-05-26)<br>claim 13; example V1.2; table 2<br>-----           | 1-10                                                                                                                          |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 2012/070659 A1 (NAKAGAWA YOSHIO [JP] ET<br>AL) 22 March 2012 (2012-03-22)<br>paragraph [0103]<br>-----                                    | 1-10                                                                                                                          |
| <div style="display: flex; justify-content: space-between;"> <div> <input type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                              |                                                                                                                               |
| <div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p> </div> </div> |                                                                                                                                              |                                                                                                                               |
| Date of the actual completion of the international search<br><br><div style="text-align: center; font-size: 1.2em;">1 February 2018</div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                              | Date of mailing of the international search report<br><br><div style="text-align: center; font-size: 1.2em;">15/02/2018</div> |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                              | Authorized officer<br><br><div style="text-align: center; font-size: 1.2em;">Vayssié, Stéphane</div>                          |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/062269

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                       | Publication<br>date                                                                            |
|-------------------------------------------|---------------------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| US 2016243019 A1                          | 25-08-2016          | CN 104379123 A<br>EP 2814456 A2<br>JP 2015514089 A<br>US 2015079013 A1<br>US 2016243019 A1<br>WO 2013148614 A2                   | 25-02-2015<br>24-12-2014<br>18-05-2015<br>19-03-2015<br>25-08-2016<br>03-10-2013               |
| WO 2016079003 A1                          | 26-05-2016          | AU 2015348696 A1<br>CA 2968149 A1<br>CN 107001529 A<br>EP 3221372 A1<br>KR 20170084297 A<br>US 2017369602 A1<br>WO 2016079003 A1 | 13-07-2017<br>26-05-2016<br>01-08-2017<br>27-09-2017<br>19-07-2017<br>28-12-2017<br>26-05-2016 |
| US 2012070659 A1                          | 22-03-2012          | CN 102408844 A<br>EP 2431437 A1<br>JP 2012062454 A<br>US 2012070659 A1                                                           | 11-04-2012<br>21-03-2012<br>29-03-2012<br>22-03-2012                                           |