



(51) International Patent Classification:

A61K 8/04 (2006.01) A61Q 19/00 (2006.01)

A61K 8/81 (2006.01) A61K 8/31 (2006.01)

A61K 8/34 (2006.01) A61K 8/37 (2006.01)

(21) International Application Number:

PCT/US2018/043256

(22) International Filing Date:

23 July 2018 (23.07.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/536,078 24 July 2017 (24.07.2017) US

(71) Applicants: DOW GLOBAL TECHNOLOGIES LLC

[US/US]; 2040 Dow Center, Midland, Michigan 48674 (US). ROHM AND HAAS COMPANY [US/US]; 400 Arcola Road, Collegeville, PA 19426 (US).

(72) Inventors: CHEN, Liang; 1712 Bldg, Washington Street,

Midland, MI 48674 (US). CHEN, Yunshen; 400 Arcola Road, Collegeville, PA 19426 (US). GOLDEN, Shannon; 1714 Building, Midland, MI 48667 (US). KOENIG, Jennifer; 400 Arcola Road, Collegeville, PA 19426 (US). LEAL, Lyndsay M.; 400 Arcola Road, Collegeville, PA 19426 (US). NAKATANI, Alan Isamu; 400 Arcola Road, Collegeville, PA 19426 (US). SCHWARTZ, Curtis; 400 Arcola Road, Collegeville, PA 19426 (US). ZENG, Fanwen; 400 Arcola Road, Collegeville, PA 19426 (US).

(74) Agent: BRANT, Edward; The Dow Chemical Company,

Intellectual Property, P.O. Box 1967, Midland, Michigan 48641 (US).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH,

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PERSONAL CARE POLYACRYLATE OIL GEL COMPOSITION

(57) Abstract: Provided are personal care compositions comprising polyacrylate oil gel compositions comprising (a) at least one cosmetically acceptable hydrophobic ester oil, (b) one or more polymers comprising polymerized structural units of (i) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers, (ii) 0.1 to 2 weight % of (meth)acrylic acid monomer, and (iii) 0.01 to 2 weight % of at least one crosslinker, wherein the polymers are formed by (1) providing a first monomer mixture comprising the C₄-C₈ (meth)acrylate monomers and (meth)acrylic acid monomer, (2) providing a second monomer mixture comprising the crosslinker, and (3) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture.



PERSONAL CARE POLYACRYLATE OIL GEL COMPOSITION

FIELD OF THE INVENTION

This invention relates generally to personal care compositions that are useful as oil gel
5 formulations. The personal care compositions containing polyacrylate oil gel compositions
comprising hydrophobic ester oil and acrylic copolymers.

BACKGROUND

Personal care compositions contain a variety of additives that provide a wide array of
10 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, however,
come with certain drawbacks, including insufficient viscosity enhancement, high formulation
15 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
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
20 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

One aspect of the invention provides a personal care composition comprising a polyacrylate oil gel comprising (a) at least one cosmetically acceptable hydrophobic ester oil, (b) one or more polymers comprising polymerized structural units of (i) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers, (ii) 0.1 to 2 weight % of (meth)acrylic acid monomer, and (iii) 0.01 to 2 weight % of at least one crosslinker, wherein the polymers are formed by (1) providing a first monomer mixture comprising the C₄-C₈ (meth)acrylate monomers and (meth)acrylic acid monomer, (2) providing a second monomer mixture comprising the crosslinker, and (3) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture.

In another aspect, the invention provides a method for preparing a personal care composition comprising a polyacrylate oil gel comprising a cosmetically acceptable hydrophobic ester oil and polymer particles comprising (a) preparing a polymer emulsion by the steps of (i) providing a first monomer mixture comprising (1) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers, based on the total weight of monomers in the polymer emulsion, and (2) 0.1 to 2 weight % of (meth)acrylic acid monomer, based on the total weight of monomers in the polymer emulsion, (ii) providing a second monomer mixture comprising 0.01 to 2 weight % of at least one crosslinker, based on the total weight of monomers in the polymer emulsion, and (iii) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture, (b) spray drying the polymer emulsion to obtain polymer particles, and (c) mixing the polymer particles and the cosmetically acceptable hydrophobic ester oil together at a temperature of from 20 to 150°C.

DETAILED DESCRIPTION

The inventors have now surprisingly found that personal care compositions comprising polyacrylate oil gels comprising hydrophobic ester oil and polymers having a high weight

5 percent of polymerized structural units of C₄-C₈ (meth)acrylate monomer, a small weight percent of (meth)acrylic acid monomer, and a small weight percent of crosslinker, in which the polymer is prepared by adding a first monomer mixture containing the C₄-C₈ (meth)acrylate monomer and (meth)acrylic acid monomer to a polymerization reactor while simultaneously adding a second monomer mixture containing the crosslinker to the first monomer mixture, provide
10 significant viscosity enhancements while retaining clarity in personal care formulations.

Accordingly, the present invention provides in one aspect a personal care composition comprising a polyacrylate oil gel comprising (a) hydrophobic oil ester, and (b) one or more polymers comprising polymerized structural units of (i) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers, (ii) 0.1 to 2 weight % of (meth)acrylic acid monomer, and (iii) 0.01 to
15 2 weight % of at least one crosslinker, wherein the polymers are formed by (1) providing a first monomer mixture comprising the C₄-C₈ (meth)acrylate monomers and (meth)acrylic acid monomer, (2) providing a second monomer mixture comprising the crosslinker, and (3) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture.

20 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 structural units” of a given monomer refers to the remnant of the monomer after polymerization. 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 “polyacrylate oil gel” refers to a composition containing an oil and a polyacrylate, wherein the polyacrylate is miscible in the oil phase.

The inventive personal care compositions include one or more polymers comprising structural units of C₄-C₈ (meth)acrylate monomers, (meth)acrylic acid monomers, and

crosslinkers. Suitable C₄-C₈ (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 C₄-C₈ (meth)acrylate monomers comprise one or more of i-butyl methacrylate, n-butyl methacrylate, and ethylhexyl methacrylate. In certain embodiments, the polymer comprises polymerized structural units of C₄-C₈ (meth)acrylate monomers in an amount of from 96 to 99.89 weight %, preferably from 97 to 99.49 weight %, and more preferably from 98 to 99 weight %, based on the total weight of the polymer. In certain embodiments, the C₄-C₈ (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 structural units of (meth)acrylic acid monomer. In certain embodiments, the polymer comprises polymerized structural units of (meth)acrylic acid monomer in an amount of from 0.1 to 2 weight %, preferably from 0.75 to 1.75 weight %, and more preferably from 0.5 to 1.5 weight %, based on the total weight of the polymer.

The polymers of the inventive personal care composition also comprise polymerized structural units of at least one crosslinker. Crosslinkers are monomers having two or more non-conjugated ethylenically unsaturated groups. Suitable crosslinkers include, for example, di- or tri-allyl ethers and di- or tri-(meth)acrylyl esters of diols or polyols (e.g., trimethylolpropane diallyl ether (TMPDE), trimethylol propane trimethacrylate (TMPTMA), and ethylene glycol dimethacrylate (EGDMA)), di- or tri-allyl esters of di- or tri-acids (e.g., diallyl phthalate), allyl (meth)acrylate, divinyl sulfone, triallyl phosphate, and divinylaromatics (e.g., divinylbenzene). In certain embodiments, the polymer comprises polymerized structural units of crosslinker in an

amount of from 0.01 to 2 weight %, preferably from 0.03 to 1.1 weight %, and more preferably from 0.05 to 0.2 weight %, based on the total weight of the polymer.

In certain embodiments, the polymers have an average particle size of from 50 to 2,000 nm, preferably of from 75 to 1,100 nm, and more preferably of from 100 to 200 nm. Polymer
5 molecular weights can be measured by standard methods such as, for example, size exclusion chromatography or intrinsic viscosity. 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, more preferably from 2 to 6 weight %, and even more preferably from 3 to 5 weight %, based on the total weight of the personal care composition.

10 Suitable polymerization techniques for preparing the polymers contained in the inventive personal care compositions include, for example, emulsion polymerization. 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
15 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 % 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
20 embodiments, the aqueous reaction medium contains more than 90 weight % water, preferably more than 95 weight % water, and more preferably more than 98 weight % water, based on the weight of the aqueous reaction medium.

The polymer emulsions of the present invention are prepared using a “power feed” of monomers. Polymer emulsions made using power feed of monomers are known (see, e.g., US 9,587,057). In certain embodiments, the polymers are formed by providing a first monomer mixture comprising (1) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers (as described above), based on the total weight of monomers in the polymer emulsion, and (2) 0.1 to 2 weight % of (meth)acrylic acid monomer, based on the total weight of monomers in the polymer emulsion, (ii) providing a second monomer mixture comprising 0.01 to 2 weight % of at least one crosslinker, based on the total weight of monomers in the polymer emulsion, and (iii) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture. In certain embodiments, the C₄-C₈ (meth)acrylate monomers are selected from the group consisting of ethylhexyl (meth)acrylate, butyl (meth)acrylate, and combinations thereof. In certain embodiments, the crosslinker is selected from the group consisting of trimethylolpropane trimethacrylate, trimethylolpropane diallyl ether, ethylene glycol dimethylacrylate, and combinations thereof.

In certain embodiments, less than 10 weight % of the monomers is in the polymerization reactor prior to addition of the first monomer mixture, preferably less than 7 weight %, and more preferably less than 5 weight %. In certain embodiments, the monomers are added to the reactor over a period of time from 60 to 240 minutes, preferably from 70 to 170 minutes, and more preferably 80 to 100 minutes. In certain embodiments, the time of addition of the second monomer mixture to the first monomer mixture is from 50 to 120% of the time of addition of the first monomer mixture to the polymerization reactor, preferably from 70 to 100%, and more preferably from 85 to 100%. In certain embodiments, addition of the second monomer mixture

to the first monomer mixture begins no later than addition of the first monomer mixture to the polymerization reactor, preferably at the same time.

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 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 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 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 C₈-C₂₄ alkyl 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 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 embodiments, the hydrophobic ester oils are present in the personal care composition in an amount of from 80 to 99.9 weight %, preferably from 87 to 99 weight %, more preferably from 94 to 98 weight %, and even more preferably from 95 to 97 weight %, based on the total weight of the personal care composition.

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 to 150°C, preferably from 25 to 70°C.

In certain embodiments, the inventive personal care compositions also include a dermatologically acceptable 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, 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.

5 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 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
10 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,
15 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
20 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 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

5 Examples.

EXAMPLES

Example 1

Preparation of Exemplary Polymer and Comparative Polymers

10 Exemplary polymers in accordance with the present invention and comparative polymers contain the components recited in Table 1.

Table 1. Exemplary and Comparative Polymers Particles

Sample	Monomer (pbw)
P1 ⁺	99 iBMA / 1 MAA // 0.46 TMPTMA
P2 ⁺	79.5 iBMA / 19.5 EHMA / 1 MAA // 0.1 TMPDE
P3 ⁺	79.5 iBMA / 19.5 EHMA / 1 MAA // 0.3 EGDMA
P4 ⁺	59.4 iBMA / 39.6 EHMA / 1 MAA // 0.28 TMPTMA
C1 [*]	99 iBMA / 1 MAA // 0.46 TMPTMA
C2 [*]	79.5 iBMA / 19.5 EHMA / 1 MAA // 0.1 TMPDE
C3 [*]	79.5 iBMA / 19.5 EHMA / 1 MAA // 0.3 EGDMA
C4 [*]	59.4 iBMA / 39.6 EHMA / 1 MAA // 0.28 TMPTMA

iBMA = isobutyl methacrylate

EHMA = ethylhexyl methacrylate

15 MAA = methacrylic acid

TMPDE = trimethylolpropane diallyl ether

TMPTMA = trimethylol propane trimethacrylate

EGDMA = ethylene glycol dimethacrylate

*Inventive examples prepared using the power feed method in which the feed rate of crosslinker into the polymerization reactor increased with time.

- 5 *Comparative examples prepared using a method in which the feed rate of crosslinker into the polymerization reactor remained consistent throughout the reaction.

Synthesis of Exemplary Polymers Using Power Feed Method

Synthesis of exemplary polymer P2 was carried out as follows. A three liter round
10 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 sodium dodecylbenzene sulfonate. 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 sodium dodecylbenzene sulfonate and 256.65 grams deionized water was added
15 and mixed with overhead stirring. 410.22 grams of Isobutyl Methacrylate, 100.62 grams of 2-Ethylhexyl Methacrylate, and 5.16 grams of Methacrylic Acid was charged to the vessel and allowed to form a smooth, stable monomer emulsion (A). A Monomer emulsion additive (B) of 34.98 grams of Isobutyl Methacrylate, 8.58 grams of 2-Ethylhexyl Methacrylate, 0.44 grams of Methacrylic Acid, and 0.56 grams of Trimethylolpropane diallyl ether 90 was prepared and set
20 aside. An initiator solution C of 0.28 grams of ammonium persulfate and 12.71 grams of deionized water was prepared and set aside. A kettle solution D of 1.92 grams of ammonium bicarbonate and 12.71 grams of deionized water was prepared and set aside. A co-feed initiator solution E of 0.28 grams of ammonium persulfate and 49.22 grams of deionized water was prepared and set aside.

25 When the kettle was at temperature, the kettle solution D and initiator solution C were added to the reactor, followed by 22.38 grams of monomer emulsion (A) as the preform seed. After the exotherm, the temperature was adjusted to 83-85°C. Then the remaining monomer

emulsion (A) was charged into the kettle while Monomer emulsion additive (B) was charged simultaneously to monomer emulsion (A). The rate was controlled so that the monomer emulsion feeds finished in 90 min, while the Monomer emulsion additive (B) finished in 80 min. Separately, Initiator solution E was fed into the reactor in 90 min. 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, solution F of 1.12 grams of isoascorbic acid dissolved in 36.40 grams of deionized water was prepared. A solution (G) of 2.14 grams of 70% tert-butyl hydroperoxide in 35.40 grams of deionized water was prepared.

After the 20 minute hold, the reaction was gradually cooled to 70°C. During the cooling, 3.77 grams of a 0.15% iron sulfate heptahydrate solution was added to the kettle. Solutions F and G were charged simultaneously into the kettle over 60 minutes. 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 were prepared substantially as described above, with the appropriate changes in monomer and monomer amounts as recited in Table 2.

Synthesis of Comparative Polymers

Synthesis of comparative polymer C2 was carried out as follows. A three liter round 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 470 grams deionized water and 7.46 grams of sodium dodecylbenzene sulfonate. The kettle contents were set to stir with a nitrogen flow and heated to 87-89°C. To a plastic lined vessel, 7 grams of sodium dodecyl sulfonate and 181.65 grams deionized water was added and mixed with

overhead stirring. 445.20 grams of Isobutyl Methacrylate, 109.20 grams of 2-Ethylhexyl Methacrylate, 5.6 grams of Methacrylic Acid and 0.28 grams of Trimethylolpropane diallyl ether 90 was charged to the vessel and allowed to form a smooth, stable monomer emulsion (A). An initiator solution (B) of 0.28 grams of ammonium persulfate and 12.71 grams of deionized water was prepared and set aside. A kettle solution (C) 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 (D). A rinse of 16.8 grams of deionized water was prepared. An initiator solution (E) 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 solution (C) and initiator solution (B) were added to the reactor, followed by the preform seed (D) and rinse. The reaction was monitored for a small exotherm. After the exotherm, the temperature control was adjusted to 83-85°C. The remaining monomer emulsion (A) feed was added to the kettle, for 15 minutes at half speed. After 15 minutes, the rate was doubled so that monomer emulsion (A) had a total feed time of 90 minutes. Separately, initiator solution (E) was fed into the reactor in 90 minutes. 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, solution F of 3.77 grams of a 0.15% iron sulfate heptahydrate solution was prepared. A solution (G) of 1.12 grams of D-isoascorbic acid dissolved in 36.40 grams of deionized water was prepared. A solution H of 2.14 grams of 70% tert-butyl hydroperoxide in 35.40 grams of deionized water was prepared.

At 80°C, solution F was added to the kettle. The kettle contents were then cooled to 70°C, and solutions G and H were charged simultaneously to the kettle over 60 minutes. 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.

Comparative polymers C1, C3, and C4 were prepared substantially as described above, with the appropriate changes in monomer and monomer amounts as recited in Table 1.

5

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 2.

10 **Table 2. Particle Size Characterization**

Sample	Particle Size (nm)
P1	126
P2	120
P3	115
P4	129
C1	124
C2	121
C3	122
C4	130

The particle size distributions was determined by light scattering 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 (diluents). The pre-diluted sample was added drop-wise to the diluent filled 2000uP module

15

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 Gel Formulations

Exemplary oil gel formulations in accordance with the present invention and comparative oil gel formulations contain 96 weight % caprylic/capric triglyceride (available from Rita

Corporation) and 4 weight % of the respective exemplary polymer P1-P4 or comparative polymer C1-C4 as prepared in Example 3 to prepare exemplary oil gel formulations FP1-FP4 and FC1-FC4, respectively. The components were heated to 50°C under stirring at 500 rpm for 1 hour. The mixture was then cooled to room temperature.

5

Example 5

Clarity of Exemplary and Comparative Oil Cleansing Formulations

The clarity of exemplary and comparative oil cleansing formulations as prepared in Example 4 are shown in Table 3.

10 **Table 3. Clarity of Exemplary and Comparative Oil Gel Formulations**

Sample	Clarity (grayscale value) [0-255]
FP1	26
FP2	13
FP3	13
FP4	11
FC1	65
FC2	11
FC3	56
FC4	33

The clarity of each sample was evaluated using image analysis of oil gel solution pictures. The oil gel sample formulation was loaded into a 1 mL transparent glass vial and placed in front of a black background. Optical images were captured using side lighting and then analyzed with
 15 image recognition software based on grayscale values 0-255 (clear solution having a value of 0).

For good oil gel solutions, the grayscale value is typically less than 26. The results demonstrate that the inventive oil cleansing formulations exhibit superior clarity.

Example 6

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

Viscosity profiles of exemplary oil gel formulations in accordance with the present invention and comparative oil gel 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 1%, 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. Table 4 shows the viscosity versus shear stress rheology profile for exemplary and comparative oil gel formulations at 1 Pa, 10 Pa, and 100 Pa.

15 **Table 4. Viscosity of Exemplary Oil Cleansing Formulations**

Sample	Viscosity at 1 Pa (shear stress) [Pa·S]	Viscosity at 10 Pa (shear stress) [Pa·S]	Viscosity at 100 Pa (shear stress) [Pa·S]
FP1	0.589	0.481	0.366
FP2	7.375	6.536	1.763
FP3	1.900	1.446	0.648
FP4	1.434	1.051	0.643
FC1	0.162	0.147	0.135
FC2	0.597	0.515	0.404

FC3	0.333	0.280	0.193
FC4	0.586	0.455	0.325

The exemplary oil gel formulations demonstrated an increase in viscosity behavior when compared against their non-power feed comparative examples (e.g., FP1 vs FC1, FP2 vs FC2, FP3 vs FC3, and FP4 vs FC4), which is highly desirable for personal care oil gel formulations.

WHAT IS CLAIMED IS:

1. A personal care composition comprising a polyacrylate oil gel composition comprising:

- (a) at least one cosmetically acceptable hydrophobic ester oil;
- (b) one or more polymers comprising polymerized structural units of
 - (i) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers,
 - (ii) 0.1 to 2 weight % of (meth)acrylic acid monomer, and
 - (iii) 0.01 to 2 weight % of at least one crosslinker,

wherein the polymers are formed by (1) providing a first monomer mixture comprising the C₄-C₈ (meth)acrylate monomers and (meth)acrylic acid monomer, (2) providing a second monomer mixture comprising the crosslinker, and (3) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture.

2. The personal care composition of claim 1, wherein the hydrophobic ester oil comprises one or more aliphatic C₈-C₂₄ alkyl triglycerides.

3. The personal care composition of claim 1, wherein the C₄-C₈ (meth)acrylate monomers are selected from the group consisting of ethylhexyl (meth)acrylate, butyl (meth)acrylate, and combinations thereof.

4. The personal care composition of claim 1, wherein the crosslinker is selected from the group consisting of trimethylolpropane trimethacrylate, trimethylolpropane diallyl ether, ethylene glycol dimethylacrylate, and combinations thereof.

5. The composition of claim 1, wherein (a) the at least one cosmetically acceptable hydrophobic ester oil is present in an amount of from 80 to 99.9 weight %, based on the total weight of the personal care composition, and (b) 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.

6. A method for preparing a personal care composition comprising a polyacrylate oil gel comprising a cosmetically acceptable hydrophobic ester oil and polymer particles comprising:

(a) preparing a polymer emulsion by the steps of

(i) providing a first monomer mixture comprising (1) 96 to 99.89 weight % of C₄-C₈ (meth)acrylate monomers, based on the total weight of monomers in the polymer emulsion, and (2) 0.1 to 2 weight % of (meth)acrylic acid monomer, based on the total weight of monomers in the polymer emulsion,

(ii) providing a second monomer mixture comprising 0.01 to 2 weight % of at least one crosslinker, based on the total weight of monomers in the polymer emulsion, and

(iii) adding the first monomer mixture to a polymerization reactor while simultaneously adding the second monomer mixture to the first monomer mixture;

(b) spray drying the polymer emulsion to obtain polymer particles; and

(c) mixing the polymer particles and the cosmetically acceptable hydrophobic ester oil together at a temperature of from 20 to 150°C.

7. The method of claim 6, wherein the hydrophobic ester oil comprises one or more aliphatic C₈-C₂₄ alkyl triglycerides.
8. The method of claim 6, wherein the C₄-C₈ (meth)acrylate monomers are selected from the group consisting of ethylhexyl (meth)acrylate, butyl (meth)acrylate, and combinations thereof.
9. The method of claim 6, wherein the crosslinker is selected from the group consisting of trimethylolpropane trimethacrylate, trimethylolpropane diallyl ether, ethylene glycol dimethylacrylate, and combinations thereof.
10. The method of claim 6, wherein the at least one cosmetically acceptable hydrophobic ester oil is present in an amount of from 80 to 99.9 weight %, based on the total weight of the personal care composition, and 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.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/043256

A. CLASSIFICATION OF SUBJECT MATTER INV. A61K8/04 A61K8/81 A61K8/34 A61Q19/00 A61K8/31 A61K8/37 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, WPI Data, CHEM ABS Data																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>WO 2017/105957 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; ROHM & HAAS [US]) 22 June 2017 (2017-06-22)</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>page 1, line 4 - page 8, line 6; claims; example 4; tables 1-3</td> <td style="text-align: center; vertical-align: top;">6-10</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>----- WO 2014/165777 A1 (ROHM & HAAS [US]) 9 October 2014 (2014-10-09) page 11, line 5 - page 17, line 6; claims 6-11; tables 3,4 page 1, line 13 - line 24</td> <td style="text-align: center; vertical-align: top;">6-10</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>----- WO 2013/148614 A2 (ROHM & HAAS CHEMICALS LLC [US]) 3 October 2013 (2013-10-03) Polymer 1; page 1, line 12 - page 4, line 17; tables 1,4 page 9, line 1 - line 5 -----</td> <td style="text-align: center; vertical-align: top;">1-10</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	WO 2017/105957 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; ROHM & HAAS [US]) 22 June 2017 (2017-06-22)	1-5	Y	page 1, line 4 - page 8, line 6; claims; example 4; tables 1-3	6-10	Y	----- WO 2014/165777 A1 (ROHM & HAAS [US]) 9 October 2014 (2014-10-09) page 11, line 5 - page 17, line 6; claims 6-11; tables 3,4 page 1, line 13 - line 24	6-10	A	----- WO 2013/148614 A2 (ROHM & HAAS CHEMICALS LLC [US]) 3 October 2013 (2013-10-03) Polymer 1; page 1, line 12 - page 4, line 17; tables 1,4 page 9, line 1 - line 5 -----	1-10
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.															
X	WO 2017/105957 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; ROHM & HAAS [US]) 22 June 2017 (2017-06-22)	1-5															
Y	page 1, line 4 - page 8, line 6; claims; example 4; tables 1-3	6-10															
Y	----- WO 2014/165777 A1 (ROHM & HAAS [US]) 9 October 2014 (2014-10-09) page 11, line 5 - page 17, line 6; claims 6-11; tables 3,4 page 1, line 13 - line 24	6-10															
A	----- WO 2013/148614 A2 (ROHM & HAAS CHEMICALS LLC [US]) 3 October 2013 (2013-10-03) Polymer 1; page 1, line 12 - page 4, line 17; tables 1,4 page 9, line 1 - line 5 -----	1-10															
☐ 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 21 September 2018		Date of mailing of the international search report 05/10/2018															
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Loloiu, Teodora															

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/043256

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017105957	A1	22-06-2017	NONE

WO 2014165777	A1	09-10-2014	BR 112015025141 A2 18-07-2017
		CN 105143290 A	09-12-2015
		EP 2981562 A1	10-02-2016
		JP 2016525583 A	25-08-2016
		US 2016053103 A1	25-02-2016
		WO 2014165777 A1	09-10-2014

WO 2013148614	A2	03-10-2013	CN 104379123 A 25-02-2015
		EP 2814456 A2	24-12-2014
		JP 2015514089 A	18-05-2015
		JP 2018109047 A	12-07-2018
		US 2015079013 A1	19-03-2015
		US 2016243019 A1	25-08-2016
		WO 2013148614 A2	03-10-2013
