Abstract:
The present invention relates to aqueous surfactant containing compositions, particularly compositions containing an acrylic copolymer. The compositions provide desirable rheological, clarity, and aesthetic properties in aqueous surfactant containing compositions.
ACRYLATE COPOLYMER THICKENERS

TECHNICAL FIELD

[0001] In one aspect, the invention relates to an acrylic based thickener suitable for use in aqueous systems. A further aspect of the invention relates to the formation of stable, aqueous compositions containing an acrylic based rheology modifier, a surfactant, and optionally various components that are substantially insoluble materials requiring suspension or stabilization. A still further aspect of the invention relates to the formation of clear, ideologically and phase stable surfactant compositions formulated with an alkaline material and/or an acidic material without negatively impacting the rheology and clarity of the composition.

BACKGROUND OF THE INVENTION

[0002] Rheology modifiers, also referred to as thickeners or viscosifiers, are ubiquitous in surfactant containing personal care cleansing formulations. Rheological properties (e.g., viscosity and flow characteristics, foambiability, spreadability, and the like), aesthetic properties (e.g., clarity, sensory effects, and the like), mildness (dermal and ocular irritation mitigation), and the ability to suspend and stabilize soluble and insoluble components within a surfactant based formulation are often modified by the addition of a thickener.

[0003] Often, thickeners are introduced into surfactant formulations in solid form and mixed under conditions effective to dissolve the thickener into the liquid surfactant composition in order to effect a viscosity enhancement. Frequently, the mixing must be conducted at elevated temperatures (hot processing) in order to promote the dissolution of the solid thickener and obtain the desired viscosity improvement. Additionally, solid thickeners (e.g., carbomer powders) are known to resist "wet-out" upon contact with the surface of an aqueous based system. Consequently, carbomers are supplied as finely divided powders and/or must be sifted to reduce particle size which aids in dissolution by increasing the relative surface area of the particle. During processing, carbomer powders can become electrostatically charged as they are transferred in and out of containers and...
tend to adhere to oppositely charged surfaces including airborne dust, necessitating specialized dust extraction equipment. This means that preparation of aqueous dispersions is messy and time-consuming unless special precautions and expensive equipment is employed. Formulators of compositions containing thickened surfactant constituents desire the ability to formulate their products at ambient temperatures (cold processing). Accordingly, formulators desire thickeners which can be introduced to the liquid surfactant compositions in liquid form rather than as a solid. This provides the formulator with a greater degree of precision in introducing the thickener to the liquid surfactant composition, allows the ability to formulate products at ambient temperatures (cold processing), and better facilitates automated processing without the need for special safety and handling equipment.

[0004] One important class of liquid rheology modifier commonly employed to thicken aqueous based surfactant containing formulations is the alkali-swelling or alkali-soluble emulsion (ASE) polymers. ASE polymers are linear or crosslinked copolymers that are synthesized from (meth)acrylic acid and alkyl acrylates. The crosslinked polymers immediately thicken upon neutralization with an inorganic or an organic base. As liquid emulsions, ASE polymers are easily processed and formulated into liquid surfactant containing formulations by the product formulator. Examples of ASE polymer thickened surfactant based formulations are set forth in U.S. Patent No. 6,635,702; International Published Application No. WO 01/19946; and European Patent No. 1 690 878 B1, which disclose the use of a polymeric thickener for aqueous compositions containing surfactants.

[0005] As the industry desires new thickened surfactant based products that are formulated at a broad pH range, there is a developing need for a rheology modifier that, when used in combination with a surfactant, provides a high clarity composition when formulated in a broad pH range while maintaining a good viscosity/rheology profile, suspension (yield value), and enhanced aesthetics (clarity).
SUMMARY OF THE INVENTION

[0008] In one aspect, embodiments of the present invention relate to acrylic copolymers crosslinked with at least two different classes of crosslinking monomers that are suitable as thickening agents in surfactant containing compositions for use in personal care, home care, health care, and institutional and industrial care compositions.

[0007] In one aspect, an embodiment of the invention relates to a thickened aqueous composition comprising an acrylic based copolymer crosslinked with at least two different classes of crosslinking monomers and a surfactant selected from anionic, cationic, amphoteric and non-ionic surfactants, and mixtures thereof.

[0008] In one aspect of the invention, embodiments relate to aqueous compositions which have good rheological and clarity properties comprising an acrylic based copolymer crosslinked with at least two different classes of crosslinking monomers, an anionic surfactant, an amphoteric surfactant, a pH adjusting agent, and an optional surfactant selected from a cationic surfactant, a non-ionic surfactant, and mixtures thereof.

[0009] In one aspect, embodiments of the invention relate to stable personal care, home care, health care, and institutional and industrial care compositions having good rheological and clarity properties comprising an acrylic based copolymer crosslinked with at least two different classes of a crosslinking monomer, an anionic surfactant, an amphoteric surfactant, a pH adjusting agent, an insoluble component and/or a particulate material that is stabilized or suspended in the composition, an optional acid based preservative, and an optional surfactant selected from a cationic surfactant, a non-ionic surfactant, and mixtures thereof.

[0010] In still a further aspect, the invention relates to stable personal care, home care, health care, and industrial and institutional care compositions comprising an acrylic based copolymer crosslinked with at least two different classes of crosslinking monomers, at least one surfactant and a benefit agent.
These stable compositions maintain a smooth, acceptable rheology with good shear thinning properties without significant increases or decreases in viscosity, with no separation, settling, or creaming out, or loss of clarity over extended periods of time, such as for at least one month at 45°C.

In one embodiment, the compositions of the present invention comprise a crosslinked acrylic copolymer containing at least two crosslinkers each polymerized from a different class of crosslinking monomer, at least one surfactant, and a neutralizer to neutralize the acid groups on the crosslinked acrylic copolymer backbone.

In one embodiment, the crosslinked acrylic copolymer of the invention is polymerized from a monomer composition comprising:

a) from about 10% to about 80% by weight of a first monomeric component selected from one or more monoethylenically unsaturated monomers containing at least one carboxylic acid group;

b) from about 90% to about 15% by weight of a second monoethylenically unsaturated monomeric component selected from at least one linear or branched C₁ to C₅ alkyl ester of (meth)acrylic acid, at least one C₁ to C₅ hydroxyalkyl ester of (meth)acrylic acid, and mixtures thereof;

c) from about 0.01% to about 5% by weight of crosslinking component selected from a first polyunsaturated crosslinking monomer and a second polyunsaturated crosslinking monomer, wherein said first crosslinking monomer is selected from at least one (meth)acrylic acid ester of a polyol and said second crosslinking monomer is selected from at least one aliphatic ether of a polyol; and optionally

d) from about 1% to about 35% by weight of at least one other monoethylenically unsaturated monomer component different from monomeric components a), b), and c) wherein all monomer weight percentages are based on the weight of the total monomer composition.

The crosslinked acrylic copolymers and compositions thereof of the present invention may suitably comprise, consist of, or consist essentially of the components, elements, and process delineations described herein. The
invention illustratively disclosed herein suitably may be practiced in the absence of any element, which is not specifically disclosed herein.

[0015] Unless otherwise stated, all percentages, parts, and ratios expressed herein are based upon weight of the total compositions of the present invention, and all weights are expressed on the basis of 100 percent active ingredients.

[0016] As used herein, the term "(meth)acrylic" acid is meant to include both acrylic acid and methacrylic acid. Similarly, the term "alky! (meth)acrylate" as used herein is meant to include alky! acrylate and alky! methacrylate.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0017] Exemplary embodiments in accordance with the present invention will be described. Various modifications, adaptations or variations of the exemplary embodiments described herein may become apparent to those skilled in the art as such are disclosed. It will be understood that all such modifications, adaptations or variations that rely upon the teachings of the present invention, and through which these teachings have advanced the art, are considered to be within the scope and spirit of the present invention.

[0018] The term "personal care" as used herein includes, without being limited thereto, includes cosmetics, toiletries, cosmeceuticals, beauty aids, insect repellents, personal hygiene and cleansing products (e.g., shampoos, conditioning shampoos, anti-dandruff shampoos, body washes, facial scrubs, and the like) applied to the body, including the skin, hair, scalp, and nails of humans and animals.

[0019] The term "home care products" as used herein includes, without being limited thereto, products employed in a domestic household for surface cleaning or maintaining sanitary conditions, such as in the kitchen and bathroom (e.g., hard surface cleaners, hand and automatic dish care, toilet bowl cleaners and disinfectants), and laundry products for fabric care and cleaning (e.g., detergents, fabric conditioners, pre-treatment stain removers), and the like.

[0020] The term "health care products" as used herein includes, without being limited thereto, pharmaceuticals (controlled release pharmaceuticals),
pharmacosmetics, oral care (mouth and teeth) products, such as oral suspensions, mouthwashes, toothpastes, dentifrices, and the like, and over-the-counter products and appliances (topical and transdermal), such as patches, plasters and the like, externally applied to the body, including the skin, scalp, nails and mucous membranes of humans and animals, for ameliorating a health-related or medical condition, for generally maintaining hygiene or well-being, and the like.

[0021] The term "institutional and industrial care" ("i&i") as used herein includes, without being limited thereto, products employed for surface cleaning or maintaining sanitary conditions in institutional and industrial environments, textile treatments (e.g., textile conditioners, carpet and upholstery cleaners), automobile care (e.g., hand and automatic car wash detergents, tire shines, leather conditioners, liquid car polishes, plastic polishes and conditioners), paints and coatings, and the like.

[0022] As used herein, the term "rheological properties" and grammatical variations thereof, includes, without limitation such properties as Brookfield viscosity, increase or decrease in viscosity in response to shear stress, flow characteristics, gel properties such as stiffness, resilience, flowability, and the like, foam properties such as foam stability, foam density, ability to hold a peak, and the like, suspension properties such as yield value, and aerosol properties such as ability to form aerosol droplets when dispensed from propellant based or mechanical pump type aerosol dispensers.

[0023] The term "aesthetic property" and grammatical variations thereof as applied to compositions refers to visual and tactile psychosensory product properties, such as color, clarity, smoothness, tack, lubricity, texture, conditioning and feel, and the like.

[0024] Here, as well as elsewhere in the specification and claims, individual numerical values (including carbon atom numerical values), or limits, can be combined to form additional non-disclosed and/or non-stated ranges.

[0025] The headings provided herein serve to illustrate, but not to limit the invention in any way or manner.
Crosslinked Acrylic Copolymers

[0028] The crosslinked acrylic copolymers of the invention are polymerized from a monomer composition comprising a), b), c), and an optional fourth monomer component d). The first monomer component a) is selected from one or more monoethylenically unsaturated monomers containing at least one carboxylic acid group.

[0027] Exemplary monoethylenically unsaturated monomers containing at least one carboxylic acid group which are set forth under the first monomer component a) include (meth)acrylic acid, itaconic acid, citraconic acid, maleic acid, fumaric acid, crotonic acid, aconitic acid, and mixtures thereof.

[0028] In one aspect of the invention, the amount of the at least one carboxylic acid group containing monomer set forth under the first monomer component ranges from about 10% to 80% by weight in one aspect, from about 20% to about 70% by weight in another aspect, and from about 35% to about 65% by weight in a further aspect of the invention, based upon the total weight of the monomers in the polymerizable monomer composition.

[0029] The second monomer component b) is selected from one or more monoethylenically unsaturated monomers containing at least one linear or branched C₁ to C₅ alkyl ester of (meth)acrylic acid, at least one C₁ to C₅ hydroxyalkyl ester of (meth)acrylic acid, or mixtures thereof.

[0030] Exemplary linear or branched C₁ to C₅ alkyl (meth)acrylate and hydroxyalkyl (meth)acrylate monomers set forth under the second monomer component include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, n-amyl (meth)acrylate, iso-amyl (meth)acrylate, hydroxyethyi (meth)acrylate, hydroxypropyi (meth)acrylate, hydroxybutyl (meth)acrylate (butane dio mono(meth)acrylate), and mixtures thereof.

[0031] In one aspect of the invention, the alkyl and hydroxyalkyl (meth)acrylate monomers set forth under the second monomer component are utilized in an amount ranging from about 90% to about 15% by weight, from
about 80% to about 25% by weight in another aspect, and from about 65% to about 35% by weight in still another aspect of the invention, based upon the total weight of the monomers in the polymerizable monomer composition.

[0032] The third monomer component c) comprises a mixture of crosslinking monomers selected from at least two different polyunsaturated monomer types or classes. The first crosslinking monomer is selected from at least one polyfunctional acrylate having at least two polymerizable ethylenically unsaturated double bonds. The term "polyfunctional acrylate" refers to acrylate esters of organic polyols wherein the organic polyol is esterified by reacting it with (meth)acrylic acid. The polyfunctional acrylate can contain 2 to 6 polymerizable ethylenically unsaturated double bonds. Suitable polyols for the esterification reaction can contain 2 to 12 carbon atoms and have at least two hydroxyl groups. The polyol can be linear and branched or cyclic. Exemplary polyols suitable for esterification include, but are not limited to, alkenylene glycols containing 2 to 5 carbon atoms, poiyalkylene glycol dinners and trimers, trimethylolethane and dimers thereof, trimethylopropane and dimers thereof, triethylopropane and dimers thereof, tetramethylolethane (pentaerythritol), dipentaerythritol, and 1,4-cyclohexanediol.

[0033] Exemplary polyfunctional acrylates include, but are not limited to, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-butenylene glycol di(meth)acrylate, 1,4-butylenylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolethane tri(meth)acrylate, dtrimethylolpropylene tetra(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate; dipentaerythritol hexa(meth)acrylate, 1,4-cyclohexanediol dimethacrylate, and mixtures thereof.

[0034] The second crosslinking monomer is selected from at least one polyalkenyl poiyether having at least two polymerizable ethylenically unsaturated double bonds. The term "polyalkenyl poiyether" refers to alkenyl ethers of organic polyols wherein the organic poiyol is etherified by reacting it with alkenyl
halide, such as allyl chloride or allyl bromide. The polyalkenyl polyether (e.g., polyallyl polyether) can contain 2 to 8 polymerizable ethylenically unsaturated double bonds. Suitable polyols for the etherification reaction can contain 2 to 12 carbon atoms and have at least two hydroxyl groups. The polyol can be linear and branched or cyclic (e.g., monosaccharides and polysaccharides containing 1 to 4 saccharide units). Exemplary polyols suitable for etherification include, but are not limited to, glucose, galactose, fructose, sorbose, rhamnose, sucrose, arabinose, maltose, lactose, raffinose, pentaerythritol, dipentaerythritol, trimethylolpropane and dimers thereof, trimethylolpropane and dimers thereof, and triethylolpropane and dimers thereof. Additional polyols suitable for the etherification are disclosed in U.S. Patent No. 2,798,053, the disclosure of which is hereby incorporated by reference.

Exemplary polyalkenyl polyethers include, but are not limited to, polyallyl ethers of sucrose having from 2 to 8 allyl groups per molecule, pentaerythritol diallyl ether, pentaerythritol triallyl ether, and pentaerythritol tetraallyl ether; trimethylolpropane diallyl ether, trimethylolpropane triallyl ether, and mixtures thereof.

In one aspect of the invention, the mixture of crosslinking monomers (first and second crosslinking monomer components) set forth under the third monomer component is present in an amount ranging from about 0.01 % to about 5% by weight, from about 0.03 to about 3% by weight in another aspect, and from about 0.05 to about 1% by weight in a further aspect, based upon the total weight of the monomers in the polymerizable monomer composition. In one aspect of the invention, the weight ratio of the first crosslinking monomer to the second crosslinking monomer in the polymerizable monomer mixture ranges from about 1:99 to about 99:1; from about 1:9 to about 9:1 in another aspect, from about 2:8 to about 8:2 in a further aspect, from about 3:7 to about 7:3 in still another aspect, from about 4:6 to about 6:4 in another aspect, and from about 1:1 in still another aspect.

The optional fourth monomer component d) is a monoethylenically unsaturated monomer different from monomer components a), b), and c).
aspect of the invention, monomer component d) is selected from one or more monomers represented by the formulas:

\( \text{d1) CH}_2=\text{C(R)C(0)OR}^1 \),

wherein R is selected from hydrogen or methyl; and \( R^1 \) is selected from \( C_6 \text{-} C_{10} \) alkyl, \( C_6 \) to \( C_{10} \) hydroxyalkyl, \( -(\text{CH}_2)_2\text{OCH}_3 \), and \( -(\text{CH}_2)_2\text{C(0)GH} \)

\( \text{d2) CH}_2=\text{C(R)X} \),

wherein R is hydrogen or methyl; and X is selected from \(-\text{C}H_5, -\text{CN}, -\text{C(0)NH}_2, -\text{NC}_4\text{H}_6\text{O}, -\text{C(0)NHCH}_3\text{CH} \),

\( -\text{C(0)NHCH}_3\text{CH}_2\text{CH}_3 \), and \( -\text{C(0)NHCH}_3\text{CH}_2\text{S(0)}(0)\text{OH} \);

\( \text{d3) CH}_2=\text{CHOCH}(0)R^1 \),

wherein R is selected from hydrogen or methyl; and X is selected from \(-\text{C}H_5, -\text{CN}, -\text{C(0)NH}_2, -\text{NC}_4\text{H}_6\text{O}, -\text{C(0)NHCH}_3\text{CH} \),

\( -\text{C(0)NHCH}_3\text{CH}_2\text{CH}_3 \), and \( -\text{C(0)NHCH}_3\text{CH}_2\text{S(0)}(0)\text{OH} \);

\( \text{d4) CH}_2=\text{C(R)C(G)OAGR}^2 \),

wherein A is a divalent radical selected from \(-\text{CH}_2\text{CH(OH)CH}_2^\text{-} \) and \(-\text{CH}_2\text{CH(} \text{CH}_2\text{OH})_2 \), R is selected from hydrogen or methyl, and R2 is an acyl residue of a linear or branched, saturated or unsaturated \( C_6 \) to \( C_{22} \) fatty acid.

[0038] Exemplary ethylenically unsaturated monomers set forth under formulas d1) to d4) of optional fourth monomeric component d) include ethyl diglycol (meth)acrylate, 2-carboxyethyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, decyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, 10-hydroxydecyl (meth)acrylate, styrene, a-methyl styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, N,N'-dimethylaminoacrylamide, t-hutyiacrylamide, t-octylacrylamide, N-vinyl pyrrolidone, 2-acrylamido-2-methylpropane sulfonic acid, vinyl acetate, vinyl propionate, vinyl butanoate, vinyl valerate, vinyl hexanoate, vinyl octanoate, vinyl nonanoate, vinyl decanoate, vinyl neodecanoate, vinyl undecanoate, vinyl laurate, ACE™ and (M)ACE™ monomer available from Hexion Specialty Chemicals, Inc., Columbus, OH; and mixtures thereof. The foregoing monomers are commercially available and/or can be synthesized by procedures well known in the art, or as described herein.
[0039] The ACE monomer (CAS No. 94624-09-8) is the reaction product of glycidyl t-decanoate (CAS No. 71206-09-2) and acrylic acid. The (M)ACE Monomer is synthesized by reacting glycidyl t-decanoate and methacrylic acid. [0040] Monomers set forth under formula d4) of the optional fourth monomer component can be synthesized via esterification by reacting glycidol with a Cio to C12 fatty acid to obtain the glycidyl ester of the respective fatty acid(s). The so-formed glycidyl ester can in turn be reacted through its epoxy functionality with the carboxyl moiety of (meth)acrylic acid to obtain a preformed monomer. Alternatively, the glycidyl ester of the fatty acid can be added to the polymerization mixture comprising the previously described monomers and reacted in situ with a portion of the one or more ethylenically unsaturated monomers containing at least one carboxylic acid group described under monomer component a), subject to the proviso that the reactant stoichiometry is designed such that only a portion of the carboxyl groups are reacted. In other words, sufficient acid functionality must be retained to serve the purpose of the present invention.

[0041] In one aspect of the invention, suitable glycidyl esters for forming the preformed and in situ formed monomer components described under formula iv) are disclosed in U.S. Patent No. 5,179,157 (column 13). The relevant disclosure of which is herein incorporated by reference. A glycidyl ester of neodecanoic acid and isomers thereof is commercially available under the trade name Cardura™ E10P from Hexion Specialty Chemicals, Inc.

[0042] In one aspect of the invention, monomers set forth under formulas d1) to d4) of the optional fourth monomer component d) are utilized in an amount ranging from about 0% to about 35% by weight, from about 1% to about 30% by weight in another aspect, from about 2% to about 15% by weight in still another aspect, and from about 5% to about 10% by weight in a further aspect, based upon the total weight of the monomers in the polymerizable monomer composition.

[0043] As one of ordinary skill in the art will readily recognize the amounts of each of the first, second, third, and optional fourth monomer components set
forth herein will be selected from the disclosed ranges such that the sum of each of the monomer components in the polymerizable monomer compositions is equal to 100 wt.%.

Crosslinked Acrylic Copolymer Synthesis
[0044] The acrylic copolymers of the invention can be synthesized via emulsion polymerization techniques well known in the art. A mixture of the first, second, third, and optionally the fourth monomer components is emulsified in an aqueous phase. The emulsified monomers are polymerized in the presence of a suitable free radical forming initiator to provide an emulsion of acrylic copolymers useful as the fixative/film former and thickener component in the hair styling/personal care compositions of the invention.
[0045] If desired, the acrylic copolymers useful in the hair styling compositions and personal care compositions of the invention can be prepared from a monomer mixture comprising one or more chain transfer agents. The chain transfer agent can be any chain transfer agent which reduces the molecular weight of the polymers of the invention. Suitable chain transfer agents include, but are not limited to, thio and disulfide containing compounds, such as C₁₋₈ alkyl mercaptans, mercaptocarboxylic acids, mercaptocarboxylic esters, thioesters, C₁₋₁₈ alkyl disulfides, aryl disulfides, polyfunctional thiols such as trimethylo propane-fris-(3-mercaptopropionate), pentaerythritol-tetra-(3-mercaptopropionate), pentaerythritol-tetra-(thioglycolate), and pentaerythritol-tetra-(thiolactate), dipentaerythritol-hexa-(thioglycolate), and the like; phosphites and hypophosphites; halalkyl compounds, such as carbon tetrachloride, bromotrichloromethane, and the like; and catalytic chain transfer agents such as, for example, cobalt complexes (e.g., cobalt (II) chelates).
[0046] In one aspect of the invention, the chain transfer agent is selected from octyl mercaptan, n-dodecyl mercaptan, f-dodecyl mercaptan, hexadecyl mercaptan, octadecyl mercaptan (ODM), iso-octyl 3-mercaptopropionate (IMP), butyl 3-mercaptopropionate, 3-mercaptopropionic acid, butyl thioglycolate, iso-octyl thioglycolate, and dodecyl thioglycolate.
[0047] When utilized, the chain transfer agent can be present in an amount ranging from about 0.1% to 10% by weight, based on the total monomer mixture weight.

[0048] The emulsion polymerization can be carried out in a batch process, in a metered monomer addition process, or the polymerization can be initiated as a batch process and then the bulk of the monomers can be continuously metered into the reactor (seed process). Typically, the polymerization process is carried out at a reaction temperature in the range of about 20 to about 99°C; however, higher or lower temperatures can be used. To facilitate emulsification of the monomer mixture, the emulsion polymerization is carried out in the presence of at least one surfactant. In one embodiment, the emulsion polymerization is carried out in the presence of surfactant ranging in the amount of about 1% to about 10% by weight in one aspect, from about 3% to about 8% in another aspect, and from about 3.5% to about 7% by weight in a further aspect, based on a total emulsion weight basis. The emulsion polymerization reaction mixture also includes one or more free radical initiators which are present in an amount in the ranging from about 0.01% to about 3% by weight based on total monomer weight. The polymerization can be performed in an aqueous or aqueous alcohol medium. Surfactants for facilitating the emulsion polymerization include anionic, non-ionic, amphoteric, and cationic surfactants, as well as mixtures thereof. Most commonly, anionic and non-ionic surfactants can be utilized as well as mixtures thereof.

[0049] Suitable anionic surfactants for facilitating emulsion polymerizations are well known in the art and include, but are not limited to, sodium iauryl sulfate, sodium dodecyl benzene sulfonate, sodium (C₆-C₁₉) alkyl phenox benzene sulfonate, disodium (Ce-C₁ε) alkyl phenox benzene sulfonate, disodium (C₆-C₁ε) di-alkyl phenox benzene sulfonate, disodium iaueth-3 suifosuccinate, sodium dioctyl suifosuccinate, sodium di-sec-butyl napthalene sulfonate, disodium dodecyl diphenyi ether sulfonate, disodium n-octadecyl suifosuccinate, phosphate esters of branched alcohol ethoxylates, and the like.
Non-ionic surfactants suitable for facilitating emulsion polymerizations are well known in the polymer art, and include, without limitation, linear or branched C₈₋C₂₀ fatty alcohol ethoxylates, such as capryl alcohol ethoxyate, lauryl alcohol ethoxyate, myristyl alcohol ethoxyate, cetyl alcohol ethoxyate, stearyl alcohol ethoxyate, cetearyl alcohol ethoxyate, sterol ethoxyate, oleyl alcohol ethoxyate, and behenyl alcohol ethoxyate; alkylphenoi alkoxylates, such as octylphenol ethoxylates; and polyoxyethylene polyoxypropylene block copolymers, and the like. Additional fatty alcohol ethoxylates suitable as non-ionic surfactants are described below. Other useful non-ionic surfactants include C₆₋C₂₂ fatty acid esters of polyoxyethylene glycol, ethoxyiated mono- and diglycerides, sorbitan esters and ethoxyiated sorbitan esters, Ce-C-22 fatty acid glycol esters, block copolymers of ethylene oxide and propylene oxide, and combinations thereof. The number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 150 in another aspect.

Exemplary free radical initiators include, but are not limited to, watersoluble inorganic persulfate compounds, such as ammonium persulfate, potassium persulfate, and sodium persulfate; peroxides such as hydrogen peroxide, benzoyl peroxide, acetyl peroxide, and lauryl peroxide; organic hydroperoxides, such as cumene hydroperoxide and t-butyl hydroperoxide; organic peracids, such as peracetic acid; and oil soluble, free radical producing agents, such as 2,2'-azobisisobutyronitriile, and the like, and mixtures thereof. Peroxides and peracids can optionally be activated with reducing agents, such as sodium bisulfite, sodium formaldehyde, or ascorbic acid, transition metals, hydrazine, and the like. Particularly suitable free-radical polymerization initiators include water soluble azo polymerization initiators, such as 2,2'-azobis(tert-alkyl) compounds having a water solubilizing substituent on the alkyl group. Preferred azo polymerization catalysts include the Vazo™ free-radical polymerization initiators, available from DuPont, such as Vazo® 44 (2,2'-azobis(2-(4,5-dihydroimidazolyl)propane), Vazo® 56 (2,2'-azobis(2-methylpropionamidine) dihydrochloride), and Vazo® 68 (4,4'-azobis(4-cyanovaleric acid)).
Optionally, other emulsion polymerization additives and processing aids which are well known in the emulsion polymerization art, such as solvents, buffering agents, chelating agents, inorganic electrolytes, polymeric stabilizers, biocides, and pH adjusting agents can be included in the polymerization system. In a typical emulsion polymerization, a mixture of the monomers is added to a first reactor under inert atmosphere to a solution of emulsifying surfactant (e.g., anionic surfactant) in water. Optional processing aids can be added as desired. The contents of the reactor are agitated to prepare a monomer emulsion. To a second reactor equipped with an agitator, an inert gas inlet, and feed pumps are added under inert atmosphere a desired amount of water and additional anionic surfactant and optional processing aids. The contents of the second reactor are heated with mixing agitation. After the contents of the second reactor reaches a temperature in the range of about 55 to 98°C, a free radical initiator is injected into the so formed aqueous surfactant solution in the second reactor, and the monomer emulsion from the first reactor is gradually metered into the second reactor over a period typically ranging from about one half to about four hours. The reaction temperature is controlled in the range of about 45 to about 95°C. After completion of the monomer addition, an additional quantity of free radical initiator can optionally be added to the second reactor, and the resulting reaction mixture is typically held at a temperature of about 45 to 95°C for a time period sufficient to complete the polymerization reaction to obtain an emulsion of acrylic copolymer particles.

Surfactants

In one aspect, an embodiment of the present invention relates to stable, aqueous compositions comprising the crosslinked acrylic based rheology modifier and a surfactant(s). Suitable surfactants include anionic, cationic, amphoteric, and non-ionic surfactants, as well as mixtures thereof. Such compositions are useful in personal care cleansing compositions that contain various components such as substantially insoluble materials requiring suspension or stabilization (e.g., a silicone, an oily material, a pearlescent
material, aesthetic and cosmeceutical beads and particles, gaseous bubbles, exfoliants, and the like). The invention further relates to the incorporation of acidic materials before or after the addition of an alkaline material to reduce the pH of the composition without negatively impacting the viscosity, rheological and clarity properties of the composition.

[0055] The anionic surfactant can be any of the anionic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable anionic surfactants include but are not limited to alkyl sulfates, alkyl ether sulfates, alkyl sulphonates, alkaryl sulphonates, a-olefin-sulphonates, alkylamide sulphonates, alkarylpolyether sulphates, alkylamidoether sulphates, alkyl monoglyceride ether sulfates, alkyl monoamphipropyl ether sulfates, alkyl monoglyceride sulfonates, alkyl succinates, alkyl sulfo succinates, alkyl sulfo succinamates, alkyl ether sulphonates, alkyl amido ether sulphonates, alkyl amidosulphonic acids, alkyl suiphosacetates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, alkyl amido ether carboxylates, N-alkylamino acids, N-acyl amino acids, alkyl peptides, N-acyl taurates, alkyl isethionates, carboxylate salts wherein the acyl group is derived from fatty acids; and the alkali metal, alkaline earth metal, ammonium, amine, and triethanolamine salts thereof.

[0056] In one aspect, the cation moiety of the forgoing salts is selected from sodium, potassium, magnesium, ammonium, mono-, di- and triethanolamine salts, and mono-, di-, and tri-isopropylamine salts. The alkyl and acyl groups of the foregoing surfactants contain from about 6 to about 24 carbon atoms in one aspect, from 8 to 22 carbon atoms in another aspect and from about 12 to 18 carbon atoms in a further aspect and may be unsaturated. The aryl groups in the surfactants are selected from phenyl or benzyl. The ether containing surfactants set forth above can contain from 1 to 10 ethylene oxide and/or propylene oxide units per surfactant molecule in one aspect, and from 1 to 3 ethylene oxide units per surfactant molecule in another aspect.

[0057] Examples of suitable anionic surfactants include sodium, potassium, lithium, magnesium, and ammonium salts of laureth sulfate, trideceth sulfate, myreth sulfate, C12-C13 pareth sulfate, C12-C14 pareth sulfate, and C12-C15 pareth
sulfate, ethoxyiated with 1, 2, and 3 moles of ethylene oxide; sodium, potassium, lithium, magnesium, ammonium, and triethanolamine lauryl sulfate, coco sulfate, tridecyi sulfate, myristi sulfate, cetyl sulfate, celearyi sulfate, stearyi sulfate, oleyl sulfate, and tallow sulfate, disodium lauryl sulfosuccinate, disodium laueth sulfosuccinate, sodium cocoyl isethionate, sodium C12-C14 olefin sulfonate, sodium laureth-8 carboxylate, sodium methyl cocooyl taurate, sodium cocoyl giycinafe, sodium myristyl sarcocinate, sodium dodecyibenzene sulfonate, sodium cocooyl sarcosinate, sodium cocooyl glutamate, potassium myristoy! glutamate, triethanolamine monolauryi phosphate, and fatty acid soaps, including the sodium, potassium, ammonium, and triethanolamine salts of a saturated and unsaturated fatty acids containing from about 8 to about 22 carbon atoms.

[0058] The cationic surfactants can be any of the cationic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable classes of cationic surfactants include but are not limited to alky! amines, alky! imidazolines, ethoxyiated amines, quaternary compounds, and quaternized esters. In addition, alky! amine oxides can function as a cationic surfactant at a low pH.

[0059] Alkylamine surfactants can be salts of primary, secondary and tertiary-fatty C12-C22 alkyiamines, substituted or unsubstituted, and substances sometimes referred to as "amidoamines". Non-limiting examples of alkyiamines and salts thereof include dimethyl cocamine, dimethyl pa!mitamine, dioctylamine, dimethyl stearamine, dimethyl soyamine, soyamine, myristy! amine, tridecyi amine, ethyl stearyiamine, N-taliowpropane diamine, ethoxyiated steary!amine, dihydroxy ethyl stearyiamine, arachidylbehentlamine, dimethyl lauramine, stearyiamine hydrochloride, soyamine chloride, stearyiamine formate, N-taliowpropane diamine dichloride, and amodimethicone (INC! name for a silicone polymer and blocked with amino functional groups, such as aminoethylamino propylsiioxane).
Non-limiting examples of amidoamines and salts thereof include stearamido propyl dimethyl amine, stearamidopropyl dimethylamine citrate, palmitamidopropyl diethylamine, and cocamidopropyl dimethylamine lactate.

Non-limiting examples of alkyl imidazoline surfactants include alkyl hydroxyethyl imidazoline, such as stearyl hydroxyethyl imidazoline, coco hydroxyethyl imidazoline, ethyl hydroxymethyl oleyl oxazoinine, and the like.

Non-limiting examples of ethoxylated amines include PEG-cocopolyamine, PEG-15 tallow amine, quatemium-52, and the like.

Among the quaternary ammonium compounds useful as cationic surfactants, some correspond to the general formula: \((R^5R^6R^7R^8N^+)\) \(E^−\), wherein \(R^5\), \(R^6\), \(R^7\), and \(R^8\) are independently selected from an aliphatic group having from 1 to about 22 carbon atoms, or an aromatic, aikyox, polyoxyalkyene, aikyiamido, hydroxyaikyl, aikyl or aikylary group having 1 to about 22 carbon atoms in the aikyl chain; and \(E^−\) is a salt-forming anion such as those selected from halogen, (e.g., chloride, bromide), acetate, citrate, lactate, glycoiate, phosphate, nitrate, sulfate, and alkysulfate. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, ester linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. In one aspect, the aikyl groups are selected from phenyl and benzyl.

Exemplary quaternary ammonium surfactants include, but are not limited to cetyl trimethylammonium chloride, cetylpyridinium chloride, dicetyl dimethyl ammonium chloride, didecyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dioleosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, behenyl trimethyl ammonium chloride, benzalkonium chloride, benzethonium chloride, and di(coconutalkyl) dimethyl ammonium chloride, ditylndimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate,
dilaurodimethyl ammonium methyl sulfate, dilauro dipropyl ammonium phosphate, and dilauro dimethyl ammonium nitrate.


[0066] Amphoteric or zwitterionic surfactants are molecules that contain acidic and basic moieties and have the capacity of behaving either as an acid or a base. Suitable surfactants can be any of the amphoteric surfactants known or previously used in the art of aqueous surfactant compositions. Exemplary amphoteric surfactant classes include but are not limited to amino acids (e.g., N-alkyl amino acids and N-acyl amino acids), betaines, suitaines, and alkyl amphocarboxylates.

[0067] Amino acid based surfactants suitable in the practice of the present invention include surfactants represented by the formula:

\[ \text{Z} \begin{array}{c} R^+ \text{N} \end{array} \begin{array}{c} Y \text{C(O)} \end{array}^{-} \text{M}^{+} \]
wherein \( R^{10} \) represents a saturated or unsaturated hydrocarbon group having 10 to 22 carbon atoms or an acyl group containing a saturated or unsaturated hydrocarbon group having 9 to 22 carbon atoms, \( Y \) is hydrogen or methyl, \( Z \) is selected from hydrogen, \(-\text{CH}_3, -\text{CH}(\text{CH}_3)_2, -\text{CH}_2\text{CH(}\text{CH}_3)_2, -\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3, -\text{CH}_2\text{C}_6\text{H}_5, -\text{CH}_2\text{C}_6\text{H}_4\text{OH, -CH}_2\text{OH, -CH(OH)CH}_3, -(\text{CH}_2)_4\text{NH}_2, -(\text{CH}_2)_3\text{NHC(NH)NH}_2, -\text{CH}_2\text{C}(0)0^+\text{M}^+, -(\text{CH}_2)_2\text{C}(0)0^+\text{M}^+. M \) is a salt forming cation. In one aspect, \( R^{10} \) represents a radical selected from a linear or branched \( C_{10} \) to \( C_{22} \) alkyl group, a linear or branched \( C_{10} \) to \( C_{22} \) alkenyi group, an acyl group represented by \( R^{11}\text{C}(0)^- \), wherein \( R^{11} \) is selected from a linear or branched \( C_9 \) to \( C_{22} \) aikyl group, a linear or branched \( C_9 \) to \( C_{22} \) aikenyl group. In one aspect, \( M^+ \) is selected from sodium, potassium, ammonium, and triethanolamine (TEA).

[0068] The amino acid surfactants can be derived from the alkylation and acylation of a-amino acids such as, for example, alanine, arginine, asparic acid, glutamic acid, glycine, isoleucine, leucine, lysine, phenylalanine, serine, tyrosine, and valine. Representative N-acyl amino acid surfactants are, but not limited to the mono- and di- carboxyiate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated glutamic acid, for example, sodium cocoyl glutamate, sodium lauroyl glutamate, sodium myristoyl glutamate, sodium palmitoyl glutamate, sodium stearoyl glutamate, disodium cocoyl glutamate, disodium stearoyl glutamate, potassium cocoyl glutamate, potassium lauroyl glutamate, and potassium myristoyl glutamate; the carboxyiate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated alanine, for example, sodium cocoyl alaninate, and TEA lauroy alaninate; the carboxyiate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated glycine, for example, sodium cocoyl glycinate, and potassium cocoyl glycinate; the carboxyiate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated sarcosine, for example, sodium lauroy sarcosinate, sodium cocoyl sarcosinate, sodium myristoyl sarcosinate, sodium oleoyl sarcosinate, and ammonium lauroy sarcosinate; and mixtures of the foregoing surfactants.
The betaines and sultaines useful in the present invention are selected from alkyl betaines, alkylamino betaines, and alkylamido betaines, as well as the corresponding sulfobetaines (sultaines) represented by the formulas:

\[
\begin{align*}
R^{12}N^+ & \quad R^{14}^- \quad AM \\
R^{13} & \\
\end{align*}
\]

\[
\begin{align*}
R^{12}NH\left(CH_2\right)_nN^+ & \quad R^{14}^- \quad AM \\
R^{13} & \\
\end{align*}
\]

\[
\begin{align*}
R^{12}C-\quad NH-f\quad CHjjT\quad N-R\quad A^- \quad M^+ \\
R^{13} & \\
\end{align*}
\]

wherein \(R^{12}\) is a \(C7-C22\) alkyl or alkenyl group, each \(R^{13}\) independently is a \(C1-C4\) alkyl group, \(R^{14}\) is a \(C1-C5\) alkylene group or a hydroxy substituted \(C1-C5\) alkylene group, \(n\) is an integer from 2 to 6, \(A\) is a carboxylate or sulfonate group, and \(M\) is a salt forming cation. In one aspect, \(R^{12}\) is a \(C11-C18\) alkyl group or a \(C11-C18\) alkenyl group. In one aspect, \(R^{13}\) is methyl. In one aspect, \(R^{14}\) is methylene, ethylene or hydroxy propylene. In one aspect, \(n\) is 3. In a further aspect, \(M\) is selected from sodium, potassium, magnesium, ammonium, and mono-, di- and triethanolamine cations.

Examples of suitable betaines include, but are not limited to, lauryl betaine, coco betaine, oleyl betaine, cocohexadecyl dimethylbetaine, lauryl amidopropy! betaine, cocoamidopropy! betaine, and cocamidopropyl hydroxysuitaine.

The alkylamphocarboxyiates such as the alkylamphoacetates and alkylamphopropionates (mono- and disubstituted carboxyiates) can be represented by the formula:
wherein $R^2$ is a C7-C22 alkyl or aikeny! group, $R^5$ is $-\text{CH}_2\text{C(0)}0^+\ M^+$, $-\text{CH}_2\text{CH}_2\text{C(0)}0\ M^+$, or $-\text{CH}_2\text{CH(OH)}\text{CH}_2\text{SO}_3^-\ M^+$, $R^{16}$ is a hydrogen or ---$\text{CH}_2\text{C(0)}0\ M^+$, and M is a cation selected from sodium, potassium, magnesium, ammonium, and mono-, di- and triethanolamine.

[0072] Exemplary alkyamphocarboxyiates include, but are not limited to, sodium cocoamphoacetate, sodium lauroamphoacetate, sodium capryloamphoacetate, disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, and disodium capryloamphodipropionate.

[0073] The non-ionic surfactant can be any of the non-ionic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable non-ionic surfactants include, but are not limited to, aliphatic (C\textsubscript{6}–C\textsubscript{18}) primary or secondary linear or branched chain acids, alcohols or phenols; alkyl ethoxylates; alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/proxy moieties); block alkylene oxide condensates of alkyl phenols; alkylene oxide condensates of alkanols; and ethylene oxide/propiylene oxide block copolymers. Other suitable non-ionic surfactants include mono- or dialkyl aikanoiames; alkyl polyglucosides (APGs); sorbitan fatty acid esters; polyoxyethylene sorbitan fatty acid esters; poiyoxyethyene sorbitol esters; poiyoxyethyene acids, and poiyoxyethyene alcohols. Other examples of suitable non-ionic surfactants include coco mono- or diethanolamide, coco glucoside, decyl diglucoside, lauryl diglucoside, coco diglucoside, poisorbate 20, 40, 60, and 80, ethoxylated linear alcohols, ceteyral alcohol, lanolin alcohol, stearic acid, glyceryl stearate, PEG-100 stearate, laureth 7, and ol eth 20.

[0074] In another embodiment, non-ionic surfactants include, but are not limited to, alkoxylated methyl glucosides such as, for example, methyl gluceth-
10, methyl gluceth-20, PPG-10 methyl glucose ether, and PPG-20 methyl glucose ether, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucam® E10, Glucam® E20, Glucam® P10, and Glucam® P20, respectively; and hydrophobically modified alkoxylated methyl giucosides, such as PEG 120 methyl glucose dioleafe, PEG-120 methyl glucose trioleate, and PEG-20 methyl glucose sesquistearate, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucam® DOE-120, Glucamate™ LT, and Glucamate™ SSE-20, respectively, are also suitable. Other exemplary hydrophobically modified alkoxylated methyl giucosides are disclosed in United States Patent Nos. 8,573,375 and 6,727,357, the disclosures of which are hereby incorporated by reference in their entirety.


[0076] While the amounts of the surfactant utilized in a composition comprising the crosslinked acrylic polymer of the invention can vary widely depending on a desired application, the amounts which are often utilized generally range from about 1% to about 80% by weight in one aspect, from about 3% to about 65% weight in another aspect, from about 5% to about 30% by weight in a still another aspect, from about 6% to about 20% by weight in a further aspect, and from about 8% to about 16% by weight, based upon the total weight of the personal care, home care, heath care, and institutional and industrial care composition in which it is included.

[0077] In one aspect of the invention, the personal care, home care, health care and I&I care compositions of the invention comprise a crosslinked acrylic polymer in combination with at least one anionic surfactant. In another aspect of the invention, the compositions comprise a crosslinked acrylic polymer with at least one anionic surfactant and at least one amphoteric surfactant, in one
aspect, the anionic surfactant is selected from alkyl sulfates, alkyl ether sulfates, alkyl sulphonates, alkaryl sulfonates, alkarylpolyether sulphates, and mixtures thereof wherein the alkyl group contains 10 to 18 carbon atoms, the aryl group is a phenyl, and the ether group contains 1 to 10 moles of ethylene oxide.

Representative anionic surfactants include, but are not limited to, sodium and ammonium lauryl ether sulfate (ethoxylated with 1, 2, and 3 moles of ethylene oxide), sodium, ammonium, and triethanolamine lauryl sulfate.

In one aspect, the amphoteric surfactant is selected from an alkyl betaine, an alkylamino betaine, an alkylamido betaines, and mixtures thereof. Representative betaines include but are not limited to lauryl betaine, coco betaine, cocohexadecyl dimethylbetaine, cocoamidopropyl betaine, cocoamidopropyldimethyldihydroxy sulfaine, and mixtures thereof.

The personal care, home care, health care and I&I care compositions comprising the crosslinked acrylic polymer of the invention can be formulated at pH ranges from about 0.5 to about 12. The desired pH for the compositions of the present invention is obviously dependent upon the specific end product applications. Generally, personal care applications have a desired pH range of about 3 to about 7.5 in one aspect, and from about 3.5 to about 6 in another aspect. The crosslinked acrylic polymer/surfactant compositions of the invention form clear formulations while maintaining desirable rheology properties (e.g., viscosity and yield values).

Generally, home care applications have a desired pH range of about 1 to about 12 in one aspect, and from about 3 to about 10 in another aspect, depending on the desired end-use application.

The pH of the compositions of the present invention can be adjusted with any combination of acidic and/or basic pH adjusting agents known to the art. The polymeric rheology modifiers of the present invention are generally supplied in their acidic form. These polymers modify the rheology of a formulation through the neutralization of the carboxylic groups on the polymer with an alkaline material. Without wishing to be bound by theory, this causes ionic repulsion between like charged moieties along the backbone of the polymer and a three
dimensional expansion of the polymer network, resulting in an increase in viscosity and other rheological properties. This phenomenon is referred to in the literature as a "space filling" mechanism as compared to an associative thickening mechanism of the HASE polymers.

[0082] In one embodiment, compositions comprising the polymers of the invention can be acidified (pH reduction) without neutralizing the polymer. In another embodiment, compositions comprising the polymers can be neutralized with an alkaline material, in a further embodiment, compositions comprising the polymers of the invention can be neutralized subsequent to being acidified. In a still further embodiment, compositions comprising the polymers of the invention can be acidified subsequent to neutralization.

[0083] An alkaline material is incorporated to neutralize the polymer and can be referred to as a neutralizing agent or pH adjusting agent. Many types of neutralizing agents can be used in the present invention, including inorganic and organic bases, and combinations thereof. Examples of inorganic bases include but are not limited to the alkali metal hydroxides (especially sodium, potassium, and ammonium), and alkali metal salts of inorganic acids, such as sodium borate (borax), sodium phosphate, sodium pyrophosphate, and the like; and mixtures thereof. Examples of organic bases include, but are not limited to, triethanolamine (TEA), diisopropanolamine, triisopropanolamine, aminomethyl propanol, dodecylamine, cocamine, oleamine, morpholine, trimethylamine, triethyamine, tetrakis(hydroxypropyl)ethylenediamine, L-arginine, aminomethyl propanol, tromethamine (2-amino 2-hydroxymethyl-1,3-propanediol), and PEG-15 cocamine. Alternatively, other alkaline materials can be used alone or in combination with the above-mentioned inorganic and organic bases. Such materials include surfactants, surfactant mixtures, pre-neutralized surfactants or materials that when combined in a composition containing a polymer of the invention is capable of neutralizing or partially neutralizing the carboxyl groups on the polymer backbone. Any material capable of increasing the pH of the composition is suitable.
Various acidic materials can be utilized as a pH adjusting agent in the present invention. Such acidic materials include organic acids and inorganic acids, for example, acetic acid, citric acid, tartaric acid, alpha-hydroxy acids, beta-hydroxy acids, salicylic acid, lactic acid, glycolic acid, and natural fruit acids, or inorganic acids, for example, hydrochloric acid, nitric acid, sulfuric acid, sulfamic acid, phosphoric acid, and combinations thereof. As discussed above, the addition of the acidic pH adjusting agent can be incorporated before or after the addition of the basic pH adjusting agent in a desired composition. The addition of the acidic material after the addition of the alkaline neutralizing agents yields significantly improved rheological properties. This is discussed in greater detail under the "back acid" formulation technique below.

As with the alkaline pH adjusting agents, other acidic materials can be used alone or in combination with the above mentioned inorganic and organic acids. Such materials include materials which when combined in a composition containing the polymer of the invention is capable of reducing the pH of the composition. It will be recognized by the skilled artisan that various of the acidic pH adjusting agents can serve more than one function. For example, acidic preservative compounds and acid based cosmeceutical compounds (e.g., alpha- and beta-hydroxy acids) not only serve their primary preservative and cosmeceutical functions, respectively, they can also be utilized to reduce or maintain the pH of a desired formulation.

Buffering agents can be used in the compositions of the invention. Suitable buffering agents include, but are not limited to, alkali or alkali earth metal carbonates, phosphates, bicarbonates, citrates, borates, acetates, acid anhydrides, succinates, and the like, such as sodium phosphate, sodium citrate, sodium acetate, sodium bicarbonate, and sodium carbonate.

The pH adjusting agent and/or buffering agent is utilized in any amount necessary to obtain and/or maintain a desired pH value in the composition.
Back Acid Formulation

[0088] The polymeric rheology modifiers of the present invention do not start to build substantial viscosity until a pH of about 5 or 6 is achieved. There are some Home and Personal Care applications, however, that require a pH of less than 6 for optimal and desired performance. This has limited the use of such polymers in such compositions. Additionally, it is difficult to even formulate stable applications at this lower pH range.

[0089] It has been found that if these compositions are raised to a near neutral or even alkaline pH and then subsequently reduced in pH, the viscosity and yield value generally remain unchanged or often actually increase. This formulating technique is referred to herein as "Back Acid" thickening or "Back Acid Addition". This formulating technique broadens the scope of application of the present polymers and now allows for formulation in the acidic pH regime. Additionally, the process of "Back Acid" thickening can also be used to further increase the viscosity and stability of compositions formulated in the slightly acidic and in the alkaline pH regime.

[0090] The one or more polymers of the invention can be formulated into a desired composition in any order during the formulation procedure. An alkaline material is added and mixed to increase the pH of the composition to at least about 5 in one aspect, to at least about 6 in another aspect, and most to at least about 6.5 in a further aspect. The alkaline material can be any compound that can neutralize the polymer to a specified pH. In one aspect, the alkaline material is selected from any of the alkaline pH adjusting agents described above, such as, for example, sodium hydroxide, potassium hydroxide, triethanolamine, or another fatty acid amine neutralizing agent commonly used in said applications. Alternatively, other alkaline materials can be used, such as surfactants. In one aspect, the pH can be adjusted to at least about 0.5, 1, 1.5 or 2 pH units above the final target pH of the composition. In another aspect, the pH can be adjusted to at least 3, 4, or even 5 pH units above the final target pH of the composition. Subsequent to the pH adjustment with the alkaline material, an acidic material is added to reduce the pH of the composition to the desired target pH for the
composition. In one aspect of the invention, the target pH ranges from about 3.5 to about 8, from about 4 to about 5.5 in another aspect, and from about 4.5 to 5 in a further aspect.

[0091] The material used to decrease the pH of the composition can be any acidic material. In one aspect, the acidic material is selected from any of the acidic pH adjusting agents described above, such as, for example, an organic acid, such as citric acid, acetic acid, alpha-hydroxy acid, beta-hydroxy acid, salicylic acid, lactic acid, glycolic acid, natural fruit acids, or combinations thereof. In addition, inorganic acids, for example, hydrochloric acid, nitric acid, sulfuric acid, sulfamic acid, phosphoric acid, and combinations thereof can be utilized. Mixtures of organic acids and inorganic acids are also contemplated.

[0092] The polymers of the present invention can be formulated with or without at least one surfactant. Such compositions can comprise any combination of optional additives, adjuvants, and benefit agents suitable for a desired personal care, home care, health care, and institutional and industrial care product known in the art. The choice and amount of each optional component employed will vary with the purpose and character of the end product, and can be readily determined by one skilled in the formulation art and from the literature. It is recognized that various additive, adjuvant, and benefit agents and components set forth herein can serve more than one function in a composition, such as, for example, surfactants, emulsifiers, solubilizers, conditioners, emollients, humectants, lubricants, pH adjusting agents, and preservatives.

[0093] While overlapping weight ranges for the various components and ingredients that can be contained in the compositions of the invention have been expressed for selected embodiments and aspects of the invention, it should be readily apparent that the specific amount of each component in the disclosed personal care, home care, health care, and i&d care compositions will be selected from its disclosed range such that the amount of each component is adjusted such that the sum of all components in the composition will total 100 weight percent. The amounts employed will vary with the purpose and character
of the desired product and can be readily determined by one skilled in the formulation art and from the literature.

[0094] Optional additives and adjuvants include, but are not limited to insoluble materials, pharmaceutical and cosmeceutical actives, chelators, conditioners, diluents, solvents, fragrances, humectants, lubricants, solubiiizers, emollients, opacifiers, colorants, anti-dandruff agents, preservatives, spreading aids, emulsifiers, sunscreens, fixative polymers, botanicals, viscosity modifiers, propellants, and the like, as well as the numerous other optional components for enhancing and maintaining the properties of a desired personal care, home care, health care, and I&I care composition.

Insoluble Material
[0095] The materials or compounds which require stabilization and/or suspension can be soluble or insoluble in wafer. Such compounds include insoluble silicones, silicone gums and resins, volatile and nonvolatile silicone oils, natural and synthetic waxes and oils and fatty acids, pearlescent materials, particulates, and other types of compounds and/or components set forth hereinbelow.

Silicones
[0096] In one aspect, silicones are utilized as conditioning agents which are commonly used in rinse off hair conditioner products and in shampoo products, such as the so-called "two-in-one" combination cleansing/conditioning shampoos. In one aspect, the conditioning agent is an insoluble silicone conditioning agent. Typically, the conditioning agent will be mixed in the shampoo composition to form a separate, discontinuous phase of dispersed, insoluble particles (also referred to as droplets). The silicone hair conditioning agent phase can be a silicone fluid and can also comprise other ingredients, such as a silicone resin, to improve silicone fluid deposition efficiency or enhance the glossiness of the hair especially when high refractive index (e.g., above about 1.6) silicone conditioning agents are used. The optional silicone
hair conditioning agent phase may comprise volatile silicone, nonvolatile silicone, or combinations thereof. The silicone conditioning agent particles may comprise volatile silicone, non-volatile silicone, or combinations thereof. In one aspect, non-volatile silicone conditioning agents are utilized. If volatile silicones are present, they will typically be incidental to their use as a solvent or carrier for commercially available forms of non-volatile silicone materials ingredients, such as silicone gums and resins. The silicone hair conditioning agents for use in the present invention have a viscosity of from about 0.5 to about 50,000,000 centistokes (1 centistokes equals $1 \times 10^{-6} \text{ m}^2/\text{s}$) in one aspect, from about 10 to about 30,000,000 centistokes in another aspect, from about 100 to about 2,000,000 in a further aspect, and from about 1,000 to about 1,500,000 centistokes in a still further aspect, as measured at 25°C.

In one embodiment, the silicone conditioning agent particles can have a volume average particle diameter ranging from about 0.01 pm to about 500 μm. For small particle application to hair, the volume average particle diameters range from about 0.01 pm to about 4 pm in one aspect, from about 0.01 pm to about 2 pm in another aspect, and from about 0.01 pm to about 0.5 pm in still another aspect. For larger particle application to hair, the volume average particle diameters typically range from about 5 pm to about 125 pm in one aspect, from about 10 pm to about 90 pm in another aspect, from about 15 pm to about 70 pm in still another aspect, and from about 20 pm to about 50 pm in a further aspect.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, are found in Encyclopedia of Polymer Science and Engineering, vol. 15, 2d ed., pp 204-308, John Wiley & Sons, inc. (1989), incorporated herein by reference. Silicone fluids are generally described as aikyisioxane polymers. Non-limiting examples of suitable silicone conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584, U.S. Pat. No. 5,104,846, and U.S. Pat. No. 5,108,809, which descriptions are incorporated herein by reference.
Silicone oils include polyalkyl, polyaryl siloxanes, or polyalkyiaryl siloxanes which conform to the following formula:

\[
\begin{align*}
\text{R}^{20} & \quad \text{Si} - \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \\
\text{R}^{20} & \quad \text{Si} - \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \\
\end{align*}
\]

wherein \( R^{20} \) is an aliphatic group, independently selected from alkyl, alkenyl, and aryl, \( R^{20} \) can be substituted or unsubstituted, and \( w \) is an integer from 1 to about 8,000. Suitable unsubstituted \( R^{20} \) groups for use in the present invention include, but are not limited to alkoxy, aryloxy, aikaryl, aryalkyl, aryilaikenyl, aikamino, and ether-substituted, hydroxy-substituted, and halogen-substituted aliphatic and aryl groups. Suitable \( R^{20} \) groups also include amines, cationic ammonium groups.

In one aspect of the invention, exemplary \( R^{20} \) alkyl and alkenyl substituents include \( C_1-C_5 \) alkyl and \( C_1-C_5 \) alkenyl groups. In another aspect, \( R^{20} \) is methyl. The aliphatic portions of other alkyl- and alkenyl-containing groups (such as alkoxy, aikaryl, and aikamino) can be straight or branched chains, and contain from \( C_1-C_5 \) in one aspect, from \( C_1-C_4 \) in another aspect, and from \( C_1-C_2 \) in a further aspect. As discussed above, the \( R^{20} \) substituents can also contain amino functionalities (e.g., aikamino groups), which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri-alkylamino and alkoxyamino groups, wherein the aliphatic portion chain length is as described above. Exemplary aryl groups in the foregoing embodiments include phenyl and benzyl.

Exemplary siloxanes are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. These siloxanes are available, for example, from Momentive Performance Materials in their Viscasil R and SF 96 series, and from Dow Corning marketed under the Dow Corning 200 series. Exemplary polyalkyiaryl siloxane fluids that may be used, include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from
Momentive Performance Materials as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid, or from Wacker Chemical Corporation, Adrian, MI, under the trade name Wacker-Belsil \textsuperscript{©} PDM series of phenyl modified silicones (e.g., PDM 20, PDM 350 and PDM 1000).

[0102] Cationic silicone fluids are also suitable for use with the compositions of the invention. The cationic silicone fluids can be represented, but are not limited, to the general formula:

\[
(R^2) e G_3 r-Si^--(OSiG_2)_g--(OSiG_2 R_1)_{2-h}--0-SiG_3 e (R^2) f
\]

wherein \(G\) is hydrogen, phenyl, hydroxy, or \(C_1-C_8\) alkyl (e.g., methyl or phenyl);  \(e\) is 0 or an integer having of from 1 to 3;  \(f\) is 0 or 1;  \(g\) is a number from 0 to 1,999;  \(h\) is an integer from 1 to 2,000 in one aspect, and from 1 to 10 in another aspect;  the sum of \(g\) and \(h\) is a number from 1 to 2,000 in one aspect, and from 50 to 5(30 in another aspect of the invention;  \(R^2\) is a monovalent radical conforming to the general formula \(C_q H_{2q} L\), wherein \(q\) is an integer having a value from 2 to 8 and \(L\) is selected from the following groups:

a) \(-N(R^{22}) CH_2 CH_2 N(R^{22})_2\)

b) \(-N(R^{22})_2\)

c) \(-N^+(R^{22}) N^+ H_2 R^{22} CA^-\)

d) \(-N(R^{22}) CH_2 CH_2 N^+ H_2 R^{22} CA^-\)

wherein \(R^{22}\) is independently selected from hydrogen, \(C_1-C_20\) alkyl, phenyl, benzyl; and \(CA^-\) is a halide counter ion selected from chloride, bromide, fluoride, and iodide.

[0103] In another aspect, a cationic silicone useful in the compositions of the invention can be represented by the formula:

\[
(R^2) e G_3 r-Si^--(OSiG_2)_g--(OSiG_2 R_1)_{2-h}--0-SiG_3 e (R^2) f
\]
wherein $R$ represents a radical selected from a $C_1 - C_8$ alkyl and $C_1-C_{18}$ alkenyl group; $R_{24}$ independently represents a radical selected from a $C_1-C_{18}$ aikylene radical or a $C_1-C_{18}$ alkylenoxy radical; CA is a halide ion; $r$ represents an integer ranging from 2 to 20 in one aspect, and from 2 to 8 in another aspect; $s$ represents an integer ranging from 20 to 200 in one aspect, and from 20 to 50 in another aspect. In one aspect, $R^{23}$ is methyl. In another aspect, Q is a chloride ion. An example of a quaternary silicone polymer useful in the present invention is Abii® T Quat 60, available from Evonik Goidschmidt Corporation, Hopewell, VA.

[0104] Another class of suitable silicone fluids is the insoluble silicone gums. These gums are polysiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described in U.S. Pat. No. 4,152,418; Noll and Walter, Chemistry and Technology of Silicons, New York: Academic Press 1968; and in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54, and SE 76, all of which are incorporated herein by reference. The silicone gums typically have a mass molecule weight in excess of about 200,000 daltons, generally between about 200,000 to about 1,000,000 daltons, specific examples of which include polydimethylsiloxane, polydimethylsiloxane/methylvinylsiloxane copolymer, polydimethylsiloxane/diphenyl sioxane/methylvinylsioxane) copolymer, and mixtures thereof.

[0105] Another category of nonvolatile, insoluble silicone fluid conditioning agents are the high refractive index polysiloxanes, having a refractive index of at least about 1.46 in one aspect, at least about 1.48 in another aspect, at least about 1.52 in a further aspect, and at least about 1.55 in a still further aspect.
The refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. In this context, polysiloxane “fluid” includes oils, resins, and gums.

[0106] The high refractive index polysiloxane fluid includes those represented by the general formula set forth for the polyalkyl, polyaryi, and polyalkylaryl siloxanes described above, as well as cyclic polysiloxanes (cyciomethicones) represented by the formula:

\[
\begin{array}{c}
  \text{S} \\
  \text{R}_1 \quad \text{R}_2 \\
  \quad \text{O} \\
  \quad \text{R}_3 \quad \text{R}_4 \\
\end{array}
\]

wherein the substituent \( R^{20} \) is as defined above, and the number of repeat units, \( k \), ranges from about 3 to about 7 in one aspect, and from 3 to 5 in another aspect. The high refractive index polysiloxane fluids can contain an amount of aryl containing \( R^{20} \) substituents sufficient to increase the refractive index to a desired level, which is described above. Additionally, \( R^{20} \) and \( k \) must be selected so that the material is non-volatile. Aryl containing substituents include those which contain alicyclic and heterocyclic five and six member aryl rings and those which contain fused five or six member rings. The aryl rings can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include aikoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with C1-C5 alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g., phenyl C2-C4 alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

[0107] The high refractive index polysiloxane fluids can have a degree of aryl containing substituents of at least about 15% by weight in one aspect, at least
about 20% by weight in another aspect, at least about 25% by weight in a further aspect, at least about 35% by weight in still further aspect, and at least about 50% by weight in an additional aspect, based on the weight of the polysiloxane fluid. Typically, the degree of aryl substitution will be less than about 90% by weight, more typically less than about 85% by weight, and can generally range from about 55% to about 80% by weight of the polysiloxane fluid.

[0108] In another aspect, the high refractive index polysiloxane fluids have a combination of phenyl or substituted phenyl derivatives. The substituents can be selected from C₁-C₄ alkyl (e.g., methyl), hydroxy, and C₁-C₄ alkylamino.

[0109] When high refractive index silicones (silicone resins, silicone waxes, and phenyl modified silicones) are used in the compositions of the present invention, they optionally can be used in solution with a spreading agent, such as a silicone resin or a suitable surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby augment the glossiness (subsequent to drying) of hair treated with such compositions. Silicone fluids suitable for use in the compositions of the present invention are disclosed in U.S. Patent Nos. 2,826,551; 3,964,500; 4,364,837, and British Patent No. 849,433, all of which are incorporated herein by reference. High refractive index polysiloxanes and polyaryi siloxanes (trimethyi pentaphenyl trisioxane, available under the trade name DC PH-1555 HRI) are offered from Dow Corning Corporation (Midland, MI), Huis America (Piscataway, N.J.), and Momentive Performance Materials Inc. (Albany, N.Y.). Examples of silicone waxes include SF 1632 (INCI Name: Ceteryl Methicone) and SF1642 (INCI Name: C30-45 Alkyl Dimethicone), also available from Momentive Performance Materials, Inc.

[0110] Silicone resins and resin gels can be included as a silicone conditioning agent suitable for use in the compositions of the present invention. These resins are crosslinked polysiloxanes. The crosslinking is introduced through the incorporation of trifunctional and tetra-functional silanes with monofunctional and/or difunctional silanes during manufacture of the silicone resin.
As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetra-functional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they form a rigid or hard film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. In one aspect, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl diphenyl-, methyl/pbenzy monovinyl-, and methylvinyliclorosilanes, and terachlorosiliane, with the methyl-substituted silanes being most commonly utilized. In one aspect, suitable silicone resins are SS4230 (INC! Name: Cyclopetasiloxane (and) Trimethysiloxydsilicate) and SS4267 (INC! Name: Dimethicone (and) Trimethylsiloxydsilicate) available from Momentive Performance Materials, Inc. Suitable silicone resin gels include RG100 (INC! Name: Cyclopetasiloxane (and) Dimethicone/ vinyltrimethylsiloxydsilicate crosspolymer) from Wacker Chemical Corporation.

Silicone materials and silicone resins can be identified according to a shorthand nomenclature system known to those of ordinary skill in the art as "MDTQ" nomenclature. Under this naming system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit (CH$_3$)$_3$SiO; D denotes the difunctional unit (CH$_3$)$_2$SiO; T denotes the trifunctional unit (CH$_3$)$_3$SiO; and Q denotes the quadra- or tetra-functional unit SiO. Primes of the unit symbols (e.g. M', D', T', and Q') denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbol indicating the total number of each type of unit in the silicone (or an average
thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, G, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

[0113] Exemplary silicone resins for use in the compositions of the present invention include, but are not limited to MQ, MT, MTQ, MDT and MDTQ resins. In one aspect, methyl is the silicone resin substituent. In another aspect, the silicone resin is selected from a MQ resins, wherein the M:Q ratio is from about 0.5:1 to about 1.5:1 and the average molecular weight of the silicone resin is from about 1000 to about 10,000 daltons.

[0114] When employed with non-volatile silicone fluids having a refractive index below 1.46, the weight ratio of the non-volatile silicone fluid to the silicone resin component, ranges from about 4:1 to about 400:1 in one aspect, from about 9:1 to about 200:1 in another aspect, from about 19:1 to about 100:1 in a further aspect, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions thereof as the silicone fluid, i.e., the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

[0115] The volatile silicones described above include cyclic and linear polydimethylsiloxanes, and the like. As described previously in the formula for cyclic polysiloxanes (cyclomethicones), they typically contain about 3 to about 7 silicon atoms, alternating with oxygen atoms, in a cyclic ring structure. However, each R<sup>20</sup> substituent and repeating unit, k, in the formula is selected so that the compound is non-volatile. Typically, the R<sup>20</sup> substituent is substituted with two alkyl groups (e.g., methyl groups). The linear volatile silicones are silicone fluids, as described above, having viscosities of not more than about 25 mPa·s.

"Volatile" means that the silicone has a measurable vapor pressure, or a vapor
pressure of at least 2 mm of Hg at 20°C. Non-volatile silicones have a vapor pressure of less than 2 mm Hg at 20°C. A description of cyclic and linear volatile silicones is found in Todd and Byers, "Volatile Silicone Fluids for Cosmetics", Cosmetics and Toiletries, Vol. 91(1), pp. 27-32 (1976), and in Kasprzak, "Volatile Silicones", Soap/Cosmetics/Chemical Specialties, pp. 40-43 (December 1986), each incorporated herein by reference.

[0116] Exemplary volatile cyclomethicones are D4 cyclomethicone (octamethylcyclotetrasiloxane), D5 cyclomethicone (decamethylcyclopentasiloxane), D6 cyclomethicone (dodecamethylcyclohexasiloxane), and blends thereof (e.g., D4/D5 and D5/D6). Volatile cyclomethicones and cyclomethicone blends are commercially available from Momentive Performance Materials Inc as SF1202, SF 1214, SF1256, and SF1258, Dow Corning, Midland, MI under the Xiameter® cyclomethicone fluid product designations PMX-0244, PMX-245, PMX-246, PMX-345, and Dow Corning® 1401 fluid. Blends of volatile cyclomethicones and volatile linear dimethicones are also contemplated within the scope of the invention.

[0117] Exemplary volatile linear dimethicones include hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane and blends thereof. Volatile linear dimethicones and dimethicone blends are commercially available from Dow Corning as Xiameter® PMX-200 silicone fluids (e.g., product designations 0.65 CS, 1 CS, 1.5 CS, and 2 CS) and Xiameter® PMX 2-1 184 silicone fluid.

[0118] Emulsified silicones are also suitable for use in the compositions of the invention. In one aspect, suitable emulsified silicones are emulsions of dimethicone with at least one emulsifier selected from non-ionic, anionic, amphoteric, cationic surfactant, and/or cationic polymer and mixtures thereof. In one aspect, useful silicone emulsions have an average silicone particle size in the composition of less than 30 µm, less than 20 µm in another aspect, and less than 10 µm in a further aspect. In another aspect of the invention, the average silicone particle size of the emulsified silicone in the composition is less than 2 µm, and in another it ranges from 0.01 to 1 µm. Silicone emulsions having an
average silicone particle size of <0.15 μm are generally termed micro-emulsions. Particle size may be measured by means of a laser light scattering technique, using a 2600D Particle Sizer from Malvern Instruments. Suitable silicone emulsions for use in the invention are also commercially available in a pre-emulsified form. Examples of suitable pre-formed commercially available emulsions include Dow Corning® emulsions MEM-1 664, 2-1352, MEM-1764, MEM-1784, HMW 2220, 2-1865, MEM-1310, MEM-1491, and 5-7137. These are emulsions/microemulsions of dimethicone. Preformed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning (CE-8170, 5-71 13, 2-8194, 949, and CE 8401) and Momentive Performance Materials. Particularly suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant. Examples include Dow Corning® 939 cationic emulsion, 949 cationic emulsion, 2-8194 cationic microemulsion, and 2-8299 cationic emulsion, and 2-8177 non-ionic emulsion; as well as SM2115 and SME253, non-ionic microemulsions supplied by Momentive Performance Materials. Mixtures of any of the above types of silicone may also be used. Other examples of amino functional silicones are the aminosilicone oils. Suitable commercially available aminosilicone oils include Dow Corning® Q2-8166, Q2-8220, and 2-8566; and SF 1708, (Momentive Performance Materials).

[0119] Other suitable silicone oils include the dimethicone copolyols, which are linear or branched copolymers of dimethylsiloxane (dimethicone) modified with alkylene oxide units. The alkylene oxide units can be arranged as random or block copolymers. A generally useful class of dimethicone polyols are block copolymers having terminal and/or pendent blocks of polydimethylsiloxane and blocks of polyalkylene oxide, such as blocks of polyethylene oxide, polypropylene oxide, or both. Dimethicone copolyols can be water soluble or insoluble depending on the amount of polyalkylene oxide present in the dimethicone polymer and can be anionic, cationic, or non-ionic in character.

[0120] Wafer soluble or water dispersible silicones can also be used in the compositions of the invention. Such water soluble silicones contain suitable
anionic functionality, cationic functionality, and/or non-ionic functionality to render
the silicone water soluble or water dispersible. In one aspect, the water soluble
silicones contain a polysiloxane main chain to which is grafted at least one
anionic moiety. The anionic moiety can be grafted to a terminal end of the
polysiloxane backbone, or be grafted as a pendant side group, or both. By
anionic group is meant any hydrocarbon moiety that contains at least one
anionic group or at least one group that can be ionized to an anionic group
following neutralization by a base. As discussed previously, the quantity of the
hydrocarbon groups of anionic character which are grafted onto the silicone
chain are chosen so that the corresponding silicone derivative is water-soluble or
water-dispersible after neutralization of the ionizable groups with a base. The
anionic silicone derivatives can be selected from existing commercial products or
can be synthesized by any means known in the art. The non-ionic silicones
contain alkylene oxide terminal and/or pendant side chain units (e.g., the
dimethicone copolylols discussed above). Another example of non-ionic
silicones is the silicone polyglucosides from Wacker (e.g., Wacker-Belsil® SPG
128 VP, SPG 130 VP, and VSR 100 VP).

[0121] Silicons with anionic groups can be synthesized by reaction between
(i) a polysiloxane containing a siinic hydrogen and (ii) a compound containing
olefinic unsaturation that also contains an anionic functional group. Exemplary
of such a reaction is the hydrosilylation reaction between poly(dimethysiloxanes)
containing a Si-H group(s) and an olefin, $\text{CH}_2=\text{CHR}^2$, wherein $\text{R}^2$ represents a
moiety containing an anionic group. The olefin can be monomeric, oligomeric or
polymeric. Polysiloxane compounds that contain a pendant reactive thio (-SH)
group(s) are also suitable for grafting an unsaturated anionic group containing
compound to the poiy(siloxane) backbone.

[0122] According to one aspect of the present invention, the anionic
monomers containing ethylenic unsaturation are used alone or in combination
and are selected from linear or branched, unsaturated carboxyiic acids.
Exemplary unsaturated carboxyiic acids are acrylic acid, methacrylic acid, maleic
acid, maleic anhydride, itaconic acid, fumaric acid and crotonic acid. The
monomers can optionally be partially or completely neutralized by base to form an alkali, alkaline earth metal, and ammonium salt. Suitable bases include but are not limited to the alkali, alkaline earth (e.g., sodium, potassium, lithium, magnesium, calcium) and ammonium hydroxides. It will be noted that, similarly, the oligomeric and polymeric graft segments formed from the foregoing monomers can be post-neutralized with a base (sodium hydroxide, aqueous ammonia, etc.) to form a salt. Examples of such silicone derivatives which are suitable for use in the present invention are described in European Patent Application No. EP 0 582 152 and International Patent Application Publication No. WO 93/23009. An exemplary class of silicone polymers are the polysiloxanes containing repeat units represented by the following structure:

\[
\begin{array}{c}
\text{G}^1 \text{Si-O-} \ldots \text{Si-O-} \text{G}^3 \text{S-(G)}^2_j \\
\text{CH}_3 \text{CH}_3
\end{array}
\]

wherein \( G^1 \) represents hydrogen, C1-C10 alkyl and phenyl radical; \( G^2 \) represents C1-C10 alkylene; \( G^3 \) represents an anionic polymeric residue obtained from the polymerization of at least one anionic monomer containing ethylenic unsaturation; \( j \) is 0 or 1; \( t \) is an integer ranging from 1 to 50; and \( u \) is an integer from 10 to 350. In one embodiment of the invention, \( G^1 \) is methyl; \( j \) is 1; and \( G^2 \) is propylene radical; \( G^3 \) represents a polymeric radical obtained from the polymerization of at least one unsaturated monomer containing a carboxylic acid group (e.g., acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, maleic acid, or aconitic acid, and the like).

[0123] In one aspect, the carboxyiate group content in the final polymer ranges from 1 mole of carboxyiate per 200 g of polymer to 1 mole of carboxyiate per 5000 g of polymer. In one aspect, the number average molecular weight of the silicone polymer ranges from about 10,000 to about 1,000,000 daltons, and from 10,00(30 to 100,000 daltons in another aspect. Exemplary unsaturated
monomers containing carboxylic acid groups are acrylic acid and methacrylic acid. In addition, to the carboxylic acid group containing monomers, C1-C20 alkyl esters of acrylic acid and methacrylic acid can be copolymerized into the polymeric backbone. Exemplary esters include but are not limited to the ethyl and butyl esters of acrylic and methacrylic acid. A commercially available silicone-acrylate polymer is marketed by the 3M Company under the trademark Silcones "Plus" Polymer 9857C (VS80 Dry). These polymers contain a polydimethylsiloxane (PDMS) backbone onto which is grafted (through a thiopropylene group) random repeating units of poly(meth)acrylic acid and the butyl ester of poly(meth)acrylate. These products can be obtained conventionally by radical copolymerization between thiopropyi functionalized polydimethylsiloxane and a mixture of monomers comprising (meth)acrylic acid and of butyl(meth)acrylate.

[0124] In another aspect, the water soluble silicone copolyol useful in the practice of the present invention are silicone copolyol carboxylates represented by the formula:

\[
\begin{align*}
\text{R}^2\text{Si} & \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{R}^2 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{EO})_a(\text{PO})_b(\text{EO})_c & \quad \text{R}^{31} \\
\end{align*}
\]

wherein \(\text{R}^2\) and \(\text{R}^2\) are independently selected from C1-C30 alkyl, C6-C14 aryl, C7-C15 aralkyi, C1-C15 alkaryl or an alkenyi group of 1 to 40 carbons, hydroxyi,- R^3a-G^i or -(CH_2)_3O(EO)_a(PO)_b(EO)_c-G^i, with the proviso that both \(\text{R}^2\) and \(\text{R}^2\) are not methyl ; \(\text{R}^3\) is selected from C1-C5 alkyl or phenyl ; in this formula a, b, and c are integers independently ranging from 0 to 100; EO is ethylene oxide, -(CH2CH2O)_; PO is propylene oxide, -(CH_2CH(CH_3)O)_i; in this formula 0 is an integer ranging from 1 to 200, p is an integer ranging from 0 to 200, and q is an integer ranging from 0 to 1000; \(\text{R}^{31}\) is hydrogen, C1-C30 alkyl, aryl, C7-C15 aralkyi, C7-C15 alkaryl, or alkenyi group of 1 to 40 carbons or -C(0)-X wherein X is C-r
C₃₀alkyl, C₆₋C₁₄ aryl, C₇₋C₁₅ aralkyi, or an alkenyl group of 1 to 40 carbons, or a mixture thereof; R₃² is a divalent group selected from alkylene radical of 1 to 40 carbon atoms which may be interrupted with arylene group of 6 to 18 carbons or an alkylene group containing unsaturation of 2 to 8 carbons; and G’ is independently selected from a moiety represented by the formula:

\[
\begin{align*}
\text{O} & \quad \text{O} \quad \text{M}^+ \quad \text{O} \quad \text{O} \quad \text{M}^+ \\
\text{O} & \quad \text{O} \quad \text{M}^+ \quad \text{O} \quad \text{O} \quad \text{M}^+ \\
\text{O} & \quad \text{O} \quad \text{M}^+ \quad \text{O} \quad \text{O} \quad \text{M}^+ \\
\text{O} & \quad \text{O} \quad \text{M}^+ \quad \text{O} \quad \text{O} \quad \text{M}^+ \\
\end{align*}
\]

wherein R₃³ is a divalent group selected from alkylene of 1 to 40 carbons, an unsaturated group containing 2 to 5 carbon atoms, or an arylene group of 6 to 12 carbon atoms; where M is a cation selected from Na, K, Li, NH₄, or an amine containing at least one C₁-C₁₀ alkyl, C₆₋C₁₄ aryl (e.g., phenyl, naphthyl), C₂-C₁₀ alkenyl, C₁-C₁₀ hydroxyalkyl, C₇-C₂₄ arylalkyl or C₇₋C₂₄ alkaryl groups. Representative R₃³ radicals are: -CH₂CH₂⁻, -CH=CH⁻, -CH=CHCH₂⁻, and phenylene.

[0125] In another embodiment, the water soluble silicones useful in the practice of the present invention can be represented an anionic silicone copolyol represented by the formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{R}^{36} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{R}^{35} \quad \text{CH}_3 \\
\end{align*}
\]

wherein is R₃⁴ is methyl or hydroxyl; R₃⁵ is selected from C₁-C₇, alkyl or phenyl; R₃⁶ represents the radical \((\text{CH}_₂)₃\text{O}(\text{EO})_x(\text{PO})_y(\text{EO})_z\text{SG}_3\text{M}^+\); where M is a cation selected from Na, K, Li, or NH₄; in this formula x, y and z are integers.
independently ranging from 0 to 100; \( R^{37} \) represents the radical 
\(~(\text{CH}_2)_3\text{Q}(\text{EO})_x(\text{PO})y(\text{EO})_z-H\); in this formula \( a \) and \( c \) independently represent integers ranging from 0 to 50, and \( b \) is an integer ranging from 1 to 50; EO is ethylene oxide, e.g., \(-(\text{CH}_2\text{CH}_20)\); PO is propylene oxide, e.g., 
\(-(\text{CH}_2\text{CH}(\text{CH}_3)0)\).

[0126] In still another embodiment, the water soluble silicones useful in the practice of the present invention can be represented an anionic silicone copolyol represented by the formula:

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\]
\[
\text{Si} - \text{O} - \text{Si} \quad \text{O} - \text{Si} \quad \text{O} - \text{Si} - \text{R}^{38}
\]

wherein \( R^{38} \) and \( R^{39} \) independently are \(-\text{CH}_3\) or a radical represented by:
\(-(\text{CH}_2)_3\text{O}(\text{EO})_a(\text{PO})_b(\text{EO})_c\text{c-C}(0)\text{R}^{40} -\text{C}(0)\text{OH}, \) subject to the proviso that both \( R^{38} \) and \( R^{39} \) are not \(-\text{CH}_3\) at the same time; \( R^{41} \) is selected from the divalent radical \(-\text{CH}_2\text{CH}_2\), \(-\text{CH}=\text{CH}-\), and phenylene; \( R^{42} \) is selected from \( \text{C}1-\text{C}5 \) alkyl or phenyl; in this formula \( a, b \) and \( c \) are integers independently ranging from 0 to 20; EO is an ethylene oxide residue, e.g., \(-(\text{CH}_2\text{CH}_20)\); PO is a propylene oxide residue, e.g., 
\~-\text{H}2\text{C}2\text{CH}(\text{CH}_3)0\); in this formula \( 0 \) is an integer ranging from 1 to 200 and \( q \) is an integer ranging from 0 to 530.

[0127] Other water soluble silicones useful in the invention are quaternized silicone copolyol polymers. These polymers have a pendant quaternary nitrogen functional group present and are represented by the formula:

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\]
\[
\text{Si} - \text{O} - \text{Si} \quad \text{O} - \text{Si} \quad \text{O} - \text{Si} - \text{R}^{43}
\]

independently ranging from 0 to 100; \( R^{37} \) represents the radical 
\(~(\text{CH}_2)_3\text{Q}(\text{EO})_x(\text{PO})y(\text{EO})_z-H\); in this formula \( a \) and \( c \) independently represent integers ranging from 0 to 50, and \( b \) is an integer ranging from 1 to 50; EO is ethylene oxide, e.g., \(-(\text{CH}_2\text{CH}_20)\); PO is propylene oxide, e.g., 
\-(\text{CH}_2\text{CH}(\text{CH}_3)0)\).
wherein $R^{42}$ represents a quaternary substituent – $N^+R^{45}R^{46}R^{47} \text{CA}^-$, wherein $R^{45}$ and $R^{46}$, and $R^{47}$, independently, are selected from hydrogen and linear and branched C$_1$-C$_{24}$ alkyl, and CA$^-$ represents a counter anion suitable to balance the cationic charge on the nitrogen atom; $R^{43}$ is selected from C$_1$-C$_{10}$ alkyl and phenyl; $R^{44}$ is -$(\text{CH}_2)_n\text{O}(\text{EO})_x(\text{PO})_y(\text{EO})_z\text{H}$, where EO is an ethylene oxide residue, e.g., -(CH$_2$CH$_2$O)$_n$; PO is a propylene oxide residue, e.g., -(CH$_2$CH(CH$_3$)$_2$O)$_n$; in this formula $a$ is an integer from 0 to 200, $b$ is an integer from 0 to 200, and $c$ is an integer from 1 to 200; in this formula $x$, $y$ and $z$ are integers and are independently selected from 0 to 20. In one aspect, the counter anion CA$^-$ represents an anion selected from chloride, bromide, iodide, sulfate, methylsulfate, sulfonate, nitrate, phosphate, and acetate.

Other suitable water soluble silicones are amine substituted silicone copolymers represented by the formula:

![Formula Image]

wherein $R^{48}$ is selected from -NH(CH$_2$)$_n$NH$_2$ or -(CH$_2$)$_n$NH$_2$; in this formula $n$ is an integer from 2 to 6; and $x$, is $n$ integer from 0 to 20; where EO is an ethylene oxide residue, e.g., -(CH$_2$CH$_2$O)$_n$; PO is a propylene oxide residue, e.g., -(CH$_2$CH(CH$_3$)$_2$O)$_n$; in this formula $a$ is an integer from 0 to 200, $b$ is an integer from 0 to 200, and $c$ is an integer from 1 to 200; in this formula $x$, $y$ and $z$ are integers and are independently selected from 0 to 20.

Still other water soluble silicones can be selected from non-ionic silicone copolymers (dimethicone copolymers) represented by the formula:
wherein \( R^{49} \), independently, represents a radical selected from C1-C30 alkyl, C6-C14 aryl, and C2-C20 alkenyl; \( R^{50} \) represents a radical selected from C1-C30 alkyl, C6-C14 aryl, and C2-C20 alkenyl; EO is an ethylene oxide residue, e.g., -(CH2CH2O)-; PO is a propylene oxide residue, e.g., -(CH2CH(CH3)O)-; in this formula \( a \), \( b \), and \( c \) are, independently, 0 to 100; in this formula \( x \) is 0 to 200; and \( y \) is 1 to 200.

In another embodiment, water soluble silicones can be selected from non-ionic silicone copolymers represented by the formula:

\[
\text{HO-}(EO)_{a}(PO)_{b}(EO)_{c}(CH_{2})_{3}Si(OSiR^{51}R^{52})_{n}OSi(CH_{2})_{3}O(EO)_{a}(PO)_{b}(EO)_{c}-H
\]

wherein \( R^{51} \) and \( R^{52} \), independently, represent a radical selected from C1-C30 alkyl, C6-C14 aryl, and C2-C20 alkenyl; EO is an ethylene oxide residue, e.g., -(CH2CH2O)-; PO is a propylene oxide residue, e.g., -(CH2CH(CH3)O)-; in this formula \( a \), \( b \), and \( c \) are independently 0 to 100; and in this formula \( n \) is 0 to 200.

In the formulas set forth above, the EO and PO residues can be arranged in random, in nonrandom, or in blocky sequences.

Water soluble silicones are disclosed in U.S. Patent Nos. 5,136,063 and 5,180,843, the disclosures of which are incorporated herein by reference. Such silicones are commercially available under the Siisoft® and Siwet® trade names.
names from Momentive Performance Materials. Specific product designations include, but are not limited to, Silsoft product designations 430, 440, 475, 805, 810, 840, 870, 875, 880, 895, 900, and 910; Silwet product designation L-7604. Other commercially available products include Dow Corning® 5103 and 5329; Abil® product designations B 88183, B 8843, Evonik Goldschmidt, and Silsense™ dimethicone copolys, such as Silsense Copolyol-1 and Silsense Copolyol-7, available from Lubrizol Advanced Materials, Inc, Cleveland, OH.

[0133] The concentration of the silicone agents described above can range from about 0.01 % to about 10%, by weight of the composition in which it is included. In another aspect, the amount of silicone agent ranges from about 0.1 % to about 8%, from about 0.1 % to about 5% in still another aspect, and from about 0.2% to about 3% by weight in a further aspect, all based on the total weight of the composition.

Natural and Synthetic Waxes, Oils, Fatty Acids and Alcohols

[0134] In one aspect, the natural and synthetic waxes, oils, fatty acids, fatty alcohols, as well as their derivatives are useful in the compositions of the present invention as a benefit agent, and can be useful, for example, as conditioners, emollients, and humectants for the hair and skin.

[0135] The natural and synthetic wax agents that can suitably be employed in the compositions of the invention, include, but are not limited to, carnauba wax, hydrolyzed carnauba wax, carnauba acid wax, ethoxylated carnauba wax (e.g., PEG-12 carnauba wax), candelilla wax, hydrolyzed candelilla wax, hydrogenated castor wax, bayberry wax, alfa wax, paraffin wax, ozokerite wax, olive wax, ouricury wax, palm kernel wax, rice wax, hydrogenated jojoba wax, bees wax, modified bees wax, e.g., oxidized beeswax, ethoxylated beeswax (e.g., PEG-6 beeswax, PEG-8 beeswax, PEG-12 beeswax, PEG-20 beeswax), dimethicone copolyoic beeswax esters and dimethiconol beeswax ester (e.g. Bis-Hydroxyethoxypropyl Dimethicone Beeswax Esters, Dimethicone PEG-8 Beeswax, and Dimethiconol Beeswax available from Lubrizol Advanced Materials, inc. under the Ultrabee™ trademark), cerabelliina wax, marine waxes,
Lanolin and derivatives thereof, and polyolefin waxes, e.g., polyethylene wax; and mixtures thereof.

[0136] Lanolin and lanolin derivatives are selected from lanolin, lanolin wax, lanolin oil, lanolin alcohols, lanolin fatty acids, esters of lanolin fatty acids such as the isopropyl esters of lanolin fatty acid (e.g., isopropyl lanolates), aikoxyiated lanolin, acetylated lanolin alcohols, and combinations thereof. Lanolin and lanolin derivatives are commercially available from Lubrizol Advanced Materials, inc. under the trade names Lanolin LP 108 USP, Lanolin USP AAA, Acetulan™, Ceralan™, Lanocerin™, Lanogel™ (product designations 21 and 41), Lanogene™, Modulan™, Ohian™, Solulan™ (product designations 18, 75, L-575, 98, and C-24), and Vilvanolin™ (product designations C, CAB, L-101, and P).

[0137] Suitable oily agents for use in the compositions of the present invention include, but are not limited to, hydrocarbon oils having at least about 10 carbon atoms, such as cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated), including polymers and mixtures thereof. Straight chain hydrocarbon oils typically contain about 12 to 19 carbon atoms. Branched chain hydrocarbon oils, including hydrocarbon polymers, typically will contain more than 19 carbon atoms. Specific non-limiting examples of these hydrocarbon oils include paraffin oil, mineral oil, petrolatums, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, polybutene, polydecene, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used, examples of which include highly branched, saturated or unsaturated, alkanes such as the permethyl-substituted isomers, e.g., the permethyl-substituted isomers of hexadecane and eicosane, such as 2,2,4,4,6,6,8,8-dimethyl-1 0-methylundecane and 2,2,4,4,6,8-dimethyl-8-methylnonane, available from Permethyl Corporation. Hydrocarbon polymers include polybutene and polydecene.
Mining oils and petrolatums include cosmetic, USP and NF grades and are commercially available from Penreco under the Drakeol® and Penreco® trade names. Mineral oil includes hexadecane and paraffin oil.

Liquid polyolefin oils can be used in the compositions of the present invention. The liquid polyolefin agents are typically poly-a-olefins that have been hydrogenated. Polyolefins for use herein can be prepared by the polymerization of C_4 to about C_4 olefinic monomers. Non-limiting examples of olefinic monomers for use in preparing the polyolefin liquids herein include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, and 1-hexadecene, branched isomers such as isobutylene, 4-methyl-1-pentene, and mixtures thereof. In one aspect, a suitable hydrogenated polyolefin is the copolymer of isobutylene and butene. A commercially available material of this type is Panalane® L-14E (INC! Name: Hydrogenated Polyisobutene) marketed by Lipo Chemicals Inc, Patterson, N.J.

Fluorinated and perfluorinated oils are also contemplated within the scope of the present invention. Fluorinated oils include perfluoropolyethers described in European Patent No. EP 0 486 135 and the fluorohydrocarbon compounds described in International Patent Application Publication No. VVO 93/11103. The fluoridated oils may also be fluorocarbons such as fluoramines, e.g., perfluorotributylamine, fluoridated hydrocarbons, such as perfluorodecahydronaphthaene, fluoroesters, and fluoroethers.

Natural oils that are useful in the practice of this invention include, but are not limited to, peanut, sesame, avocado, coconut, cocoa butter, canola, babassu, almond, corn, grape seed, cottonseed, sesame seed, walnut, castor, olive, jojoba, palm, palm kernel, soybean, wheat germ, linseed, safflower, shea nut, sunflower seed, eucalyptus, lavender, vetiver, litsea, cubeba, lemon, sandalwood, rosemary, chamomile, savory, nutmeg, cinnamon, hyssop, caraway, orange, geranium, cade, and bergamot oils, fish oils, as well as glycerides (mono- di- and triglycerides) derived from plant oils, vegetable oils, and animal fats (e.g., tallow and lard); and mixtures thereof.
[0142] Oils as benefit agents can be in the form of organogel particles (oil and wax) as described in U.S. Patent No. 8,737,394.

[0143] Suitable glycerides (mono-, di-, and triglycerides) can be derived through the esterification of glycerol, a monoglyceride, or a diglyceride with a fatty acid(s) by techniques well known in the art, or by glycerolysis of animal fats and vegetable oils in the presence of a base at elevated temperature and under an inert atmosphere (See RSC Green Chemistry Book Series, The Royal Society of Chemistry, The Future of Glycerol: New Uses Of A Versitile Material!, Chapter 7, Mario Pagliaro and Michele Rossi, © 2008). Fatty acids suitable for use in the esterification reaction include saturated and unsaturated Cs-C30 fatty acids.

[0144] Also useful in the compositions of the present invention are the free fatty acids and their derivatives. Suitable fatty acids include saturated and unsaturated Cs to C30 fatty acids. Exemplary fatty acids include, but are not limited to, caprylic acid, capric acid, iauric acid, myristic acid, palmitoleic acid, stearic acid, oleic acid, ricinoleic acid, vaccenic acid, linoleic acid, α-linolenic acid, γ-linolenic acid, arachidic acid, gadoleic acid, arachidonic acid, EPA (5,8,11,14,17-eicosapentaenoic acid), behenic acid, erucic acid, DHA (4,7,10,13,16,19-docosahexaenoic acid), lignoceric acid, and mixtures thereof.

[0145] Aikoxylated fatty acids are also useful herein and can be formed by esterifying a fatty acid with an ethylene oxide and/or propylene oxide or with a pre-formed polymeric ether (e.g., polyethylene glycol or polypropylene glycol). The product is a polyethylene oxide ester, polypropylene oxide ester, or a polyethylene/polypropylene oxide ester of the respective fatty acid. In one aspect, an ethoxylated fatty acid can be represented by the formula:

\[ R'-C(0)(\text{CH}_2\text{O})_n\text{-H} \]

wherein \( R' \) represents the aliphatic residue of a fatty acid and \( n' \) represents the number of ethylene oxide units. In another aspect, \( n' \) is an integer ranging from about 2 to about 50, from about 3 to about 25 in another aspect, and from about 3 to about 10 in a further aspect. In still another aspect of the invention, \( R' \) is derived from a saturated or unsaturated fatty acid containing 8 to 30 carbon atoms, in another aspect, diesters can be formed by
reacting two moles of the fatty acid with one mole of polyethylene or polypropylene glycol. The diesters can be represented by the formula:

\[ R'-C(0)\left(\text{CH}_2\text{CH}_2\right)_n\text{OR} \]

where \( R' \) and \( n \) are as defined immediately above.

[0146] Exemplary alkoxylated fatty acids include, but are not limited to, capric acid ethoxylate, lauric acid ethoxylate, myristic acid ethoxylate, stearic acid ethoxylate, oleic acid ethoxylate, coconut fatty acid ethoxylate, and the like, wherein the number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 5/3 in another aspect. More specific examples of ethoxylated fatty acids are PEG-8 stearate (the 8 meaning the number of repeating ethylene oxide units), PEG-8 distearate, PEG-8 oleate, PEG-8 behenate, PEG-8 caprate, PEG-8 caprylate, PEG cocoates (PEG without a number designation meaning that the number of ethylene oxide units ranges from 2 to 50), PEG-15 dicocoate, PEG-2 diisononanoate, PEG-8 diisostearate, PEG-diaurates, PEG-dioleates, PEG-distearates, PEG-diailates, PEG-isostearates, PEG-jojoba acids, PEG-iaurates, PEG-inoles, PEG-myristates, PEG-oleates, PEG-palmitates, PEG-ricioleates, PEG-stearates, PEG-tailates, and the like.

[0147] Another fatty acid derivative that can be suitably employed in the compositions of the invention is a fatty acid ester. Fatty acids can be esterified by alcohols in the presence of a suitable acid catalyst to give a desired fatty acid ester. In one aspect, any of the saturated and unsaturated C\(_8\) to C\(_{30}\) fatty acids disclosed above can be esterified by a saturated or unsaturated C\(_1\) to C\(_{22}\) alcohol to give the respective fatty acid ester. In another aspect, longer chain fatty acid esters can be derived from the esterification of the above mentioned fatty acids by a saturated or unsaturated C\(_8\) to C\(_{30}\) fatty alcohol and can be represented by the formula: R''C(0)OR where R'' independently represents a saturated and unsaturated, linear and branched alkyi group containing 1 to 24 carbon atoms. Suitable fatty alcohols include the fatty alcohols that are disclosed below.

[0148] Exemplary fatty acid esters include, but are not limited to, methyl laurate, hexyl laurate, isohexyl laurate, decyl oleate, methyl cocoate, isopropyl stearate, isopropyl isostearate, butyl stearate, decyl stearate, octyl stearate, cetyl...
searate, stearyl stearate, oleyl stearate, myristyl myristate, octyldodecyl stearoyl searate, octyihydroxystearate, isopropyl myristate, oleyl myristate, isopropyl palmitate, ethyl hexyl palmitate, cetyl palmitate, decyl oleate, isodecyl oleate, oleyl oleate, isodecyl neopentanoate, diisopropyl sebacate, isostearyl lactate, lauryl lactate, cetearyl octanoate, and mixtures thereof.

Still other fatty esters suitable for use in the compositions of the present invention are mono-, di- and tri-alkyl and alkenyl esters of carboxylic acids, such as esters of C2 to C8, monocarboxylic acids, C4 to C10 dicarboxylic acids, C8 to C10 tricarboxylic acids (e.g., C1 to C22 esters of acetic acid, lactic acid, succinic acid, glutaric acid, adipic acid, citric acid, trimelietic acid, trimesic acid, and 1,3,5-pentane tricarboxylic acid). Specific non-limiting examples of mono-, di- and tri-alkyl and alkenyl esters of carboxylic acids include lauryl acetate, cetyl propionate, lauryl lactate, myristyl lactate, cetyl lactate, diisopropyl adipate, dihexyldecyi adipate, dioleyl adipate, and triestearyl citrate.

Other fatty esters suitable for use in the compositions of the present invention are those known as polyhydric alcohol esters. Such polyhydric alcohol esters include alkylene glycol esters, such as ethylene glycol mono- and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol mono- and di-fatty acid esters, and sorbitol mono- and di-fatty esters, wherein the acyl portion of the fatty acid ester is derived from a saturated or unsaturated C8 to C22 fatty acid. These esters can be optionally ethoxylated. Representative polyhydric alcohol fatty acid esters include, but are not limited to, polyethylene glycol monooioate, polypropylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glycercyld monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyl fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters.

Other polyhydric alcohol esters include the partial esters of polyglycerols. These esters contain 2 to 10 glycerol units and are esterified with 1 to 4 saturated or unsaturated, linear or branched, optionally hydroxylated C8 to
C₃₀ fatty acid residues. Representative partial esters of polyglycerols include, but are not limited to, diglycerol mono- and dicaprylate, diglycerol monolaurate, triglycerol monopropionate, triglycerol monostearate, tetraglycerol monostearate, pentaglycerol monopalmitate, pentaglycerol monostearate, hexaglycerol mono- and dicaprylate, hexaglycerol monolaurate, heptaglycerol monopalmitate, heptaglycerol monostearate, octaglycerol monopalmitate, octaglycerol monostearate, nonaglycerol monopalmitate, nonaglycerol monostearate, decaglycerol monopalmitate, decaglycerol monostearate, decaglycerol monopalmityl, decaglycerol monostearite, decaglycerol monolaurate, and mixtures thereof. The fatty alcohols suitable for use in the compositions of the invention include, but are not limited to, the saturated and unsaturated C₈-C₃₀ fatty alcohols. Exemplary fatty alcohols include caprylyl alcohol, pelargonic alcohol, capric alcohol, decyl alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, isostearic alcohol, stearyl alcohol, isostearyl alcohol, cetearyl alcohol, palmitoleyl alcohol, elauidyl alcohol, sterol, oleyl alcohol, linoleyl alcohol, elaidyl linoleyl alcohol, linolenyl alcohol, ricinoleyl alcohol, arachidyl alcohol, icosenyl alcohol, behenyl alcohol, erucyl alcohol, lignoceryl alcohol, ceryl alcohol, montanyl alcohol, myricyl alcohol, and mixtures thereof. Fatty alcohols are widely available and can be obtained through the hydrogenation of esterified vegetable and animal oils and fats. Aikoxiyated fatty alcohol compounds are ethers formed from the reaction of a fatty alcohol with an alkylene oxide, generally ethylene oxide or propylene oxide. Suitable ethoxylated fatty alcohols are adducts of fatty alcohols...
and polyethylene oxide. In one aspect of the invention, the ethoxylated fatty alcohols can be represented by the formula \( R''^\prime-(OCH_2CH_2)_n-OH \), wherein \( R''^\prime \) represents the aliphatic residue of the parent fatty alcohol and \( n'' \) represents the number of ethylene oxide units. In another aspect of the invention, \( R''^\prime \) is derived from a fatty alcohol containing 8 to 30 carbon atoms. In one aspect, \( n'' \) is an integer ranging from 2 to 50, 3 to 25 in another aspect, and 3 to 10 in a further aspect. In a still further aspect, \( R''^\prime \) is derived from a fatty alcohol set forth immediately in the paragraph above. Exemplary ethoxylated fatty alcohols are but are not limited to capryl alcohol ethoxylate, lauryl alcohol ethoxylate, myristyl alcohol ethoxylate, cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, cetearyl alcohol ethoxylate, sterol ethoxylate, oleyl alcohol ethoxylate, and behenyl alcohol ethoxylate, wherein the number of ethylene oxide units in each of the foregoing ethoxyiates can range from 2 and above in one aspect, and from 2 to about 150 in another aspect. It is to be recognized that the propoxyiated adducts of the foregoing fatty alcohols and mixed ethoxylated/propoxyiated adducts of the foregoing fatty alcohols are also contemplated within the scope of the invention. The ethylene oxide and propylene oxide units of the ethoxylated/propoxyiated fatty alcohols can be arranged in random or in blocky order.

[0154] Exemplary ethoxylated sterols include ethoxylated vegetable oil sterols such as, for example, soya sterols. The degree of ethoxyiation is greater than about 5 in one aspect, and at least about 10 in another aspect. Suitable ethoxylated sterols are PEG-10 Soy Sterol, PEG-16 Soy Sterol and PEG-25 Soy Sterol.

[0155] Additional examples of ethoxylated alcohols are but are not limited to Beheneth 5-30 (the 5-30 meaning the range of repeating ethylene oxide units), Ceteareth 2-100, Ceteth 1-45, Cetoleth 24-25, Chioeth 10-24, Coceth 3-10, C9-11 Pareth 3-8, C11-15 Pareth 5-40, C11-21 Pareth 3-10, C12-13 Pareth 3-15, Deceth 4-6, Dodoxynoi 5-12, Glycereth 7-26, Isoceteth 10-30, isodeceth 4-6, isoiaureth 3-6, isosteareth 3-50, Laneth 5-75, Laureth 1-40, Nonoxynoi 1-120,
Nonylnonoxynol 5-150, Octoxynol 3-70, Oleth 2-50, PEG 4-350, Steareth 2-100, and Trideceth 2-10.

Specific examples of propoxylated alcohols are but are not limited to PPG-10 Cetyl Ether, PPG-20 Cetyl Ether, PPG-28 Cetyl Ether, PPG-30 Cetyl Ether, PPG-50 Cetyl Ether, PPG-2 Lanolin Alcohol Ether, PPG-5 Lanolin Alcohol Ether, PPG-10 Lanolin Alcohol Ether, PPG-20 Lanolin Alcohol Ether, PPG-30 Lanolin Alcohol Ether, PPG-4 Lauryl Ether, PPG-7 Lauryl Ether, PPG-10 Oleyl Ether, PPG-20 Oleyl Ether, PPG-23 Oleyl Ether, PPG-30 Oleyl Ether, PPG-50 Oleyl Ether, PPG-11 Stearyl Ether, PPG-15 Stearyl Ether, PPG-2 Lanolin Ether, PPG-5 Lanolin Ether, PPG-10 Lanolin Ether, PPG-20 Lanolin Ether, PPG-30 Lanolin Ether, and PPG-1 Myristyl Ether.

Hydrogenated Lanolin, PPG-2-PEG-1, Hydrogenated Lauryl Alcohol Ether, PPG-12-PEG-50 Lanolin, PPG-12-PEG-65 Lanolin Oil, PPG-40-PEG-60 Lanolin Oil, PPG-1-PEG-9 Lauryl Glycol Ether, PPG-3-PEG-6 Oleyl Ether, PPG-23-Steareth-34, PPG-30 Steareth-4, PPG-34-Steareth-3, PPG-38 Steareth-6, PPG-1 Trideceth-6, PPG-4 Trideceth-6, and PPG-6 Thdeceth-8.


[0159] In addition to the foregoing benefit agents, other benefit agents for the hair and skin include, alantoin, urea, pyrrolidone carboxylic acid and its salts, hyaluronic acid and its salts, sorbic acid and its salts, amino acids (e.g., lysine, arginine, cystine, guanidine), C₃ to C₆ polyhydroxy alcohols such as glycerin, propylene glycol, hexylene glycol, hexanetriol, ethoxypolyglycol, and sorbitol, and the esters thereof, polyethylene glycols (e.g., Polyox WSR-25, Polyox WSR-N-60K, and Polyox WSR-N-750, available from Dow Chemical), sugars and starches, sugar and starch derivatives (e.g., alkoxyiated glucose), pantothenic such as dl-pantothenoi, lactarnide monoethanolamine, acetarnide monoethanolamine, and the like, and mixtures thereof.

[0160] The natural and synthetic waxes, oils, fatty acids and alcohols, as well as the other benefit agents described above can be utilized in an amount ranging from about 0.1% to about 30% by weight in one aspect, from about 0.5% to 25% by weight in another aspect, from about 3% to 20% by weight in a further aspect,
and from 5% to about 10% by weight in a still further aspect, based on the total weight of the composition in which it is included.

Pharmaceutical and Cosmeceutical Actives

[0161] The compositions of the present invention can be formulated with a pharmaceutical and/or a cosmeceutical active to deliver a desired effect. Examples of such active ingredients include, but are not limited to, caffeine, vitamin C, vitamin D, vitamin E, anti-stretch mark compounds, astringents (e.g., alum, oatmeal, yarrow, witch hazel, bayberry, and isopropyl alcohol), draining compounds, depilatories (e.g., calcium and sodium hydroxide, calcium or sodium thioglycolate, or mixtures thereof), hair growth promoting compounds (e.g., monoxidil), skin and hair nourishing compounds, skin and hair protecting compounds, self-tanning compounds (e.g., mono- or polycarbonyl compounds such as, for example, isatin, alloxan, ninyhydrin, glyceraldehyde, mesotartaric aldehyde, glutaraldehyde, erythriose, tyrosine, tyrosine esters, and dihydroxyacetone), UV absorbers (e.g., ethylhexyl methoxy cinnamate, octinoxate, octisalate, oxybenzone), skin lighteners (e.g., kojic acid, hydroquinone, arbutin, frutial, vegetal or plant extracts, such as lemon peel extract, chamomile, green tea, paper mulberry extract, and the like, ascorbyl acid derivatives, such as ascorbyl palmitate, ascorbyl stearate, magnesium ascorbyl phosphate, and the like), lip plumping compounds, anti-aging, anti-cellulite, and anti-acne compounds (e.g., acidic agents such as alpha-hydroxy acids (AHAs), beta-hydroxy acids (BHAs), alpha amino-acids, alpha-keto acids (AKAs), acetic acid, azeiaic acid, and mixtures thereof), anti-inflammatory compounds (e.g., aspirin, ibuprofen, and naproxen), analgesics (e.g., acetaminophen), antioxidant compounds, antiperspirant compounds (e.g., aluminum halides, aluminum hydroxyhalides, aluminum sulfate, zirconium (zirconyl) oxyhalides, zirconium (zirconyl) hydroxyhalides, and mixtures or complexes thereof), deodorant compounds (e.g., 2-amino-2-methyl-1-propano! (AMP), ammonium phenolsulfonate; benzalkonium chloride; benzethonium chloride, bromochlorophene, cetyltrimethylammonium bromide, cetyl pyridinium chloride,
chlorophyllin-copper complex, chlorothymol, chloroxylenol, cloflucarban, dequalinium chloride, dichlorophene, dichloro-m-xylenol, disodium dihydroxyethyl sulfosuccinylundecylenate, domiphen bromide, hexachlorophene, lauryl pyridinium chloride, methylbenzethonium chloride, phenol, sodium bicarbonate, sodium phenolsulfonate, triclocarban, triclosan, zinc phenolsulfonate, zinc ricinoleate, and mixtures thereof); and suitable mixtures of any of the above.

Opacifying/Pearlescent Materials

[0162] Some formulations are often opacified by deliberately incorporating pearlescent materials therein to achieve a cosmetically attractive pear-like appearance, known as pearlescence. An opacifier often is included in a composition to mask an undesirable aesthetic property, such as to improve the color of a composition that is darkened due to the presence of a particular ingredient, or to mask the presence of particulate matter in the composition. Opacifiers also are included in aqueous compositions to improve the aesthetics and consumer acceptance of an otherwise esthetically unpleasing composition. For example, an opacifier can impart a pearlescent appearance to a clear composition, thereby communicating an appearance of creaminess, mildness and body to the consumer. Persons skilled in the art are aware of problems faced by formulators in consistently preparing a stable pearlescent formulation. A detailed discussion is found in the article Opacifiers and pearling agents in shampoos" by Hunting, Cosmetic and Toiletries, Vol. 98, pages 65-78 (July 1981), incorporated herein by reference.

[0163] The opacifying or pearlescent material includes ethylene glycol monostearate, ethylene glycol distearate, polyethylene glycol distearate, stearic alcohol, bismuth oxychloride coated mica, mica coated metal oxides (e.g., titanium dioxide, chromium oxide, iron oxides), myristyi myristate, guanine, glitter (polyester or metallic), and mixtures thereof. Other pearlescent materials can be found in U.S. Patent No. 4,654,207, U.S. Patent No. 5,019,376, and U.S. Patent No. 5,384,14, which are herein incorporated by reference.
In one aspect, the amount of the pearlescent material can be used in amounts ranging from about 0.05% to about 10% by weight, and from about 0.1% to about 3% by weight in another aspect, based upon the total weight of the stabilized composition.

Opacifiers

An opacifier is an ingredient included in a composition to reduce or eliminate the clear or transparent appearance of the composition. In addition, an opacifier also can impart other advantageous properties to a composition, such as thickening, suspending and emulsifying properties.

An opacifier can be selected from a number of different chemical classes including inorganic compounds, e.g., various aluminum and magnesium salts, and organic compounds, like fatty alcohols, fatty esters and various polymers and copolymers. A representative listing of opacifiers is found in the CTFA Cosmetic Ingredient Handbook, J. Nikitakis, ed., The Cosmetic, Toiletry and Fragrance Association, Inc., Washington, D.C., 1988, at page 75.

Particulates

Numerous other substantially insoluble compounds and components which require stabilization and/or suspension can be utilized in the compositions of the invention. Examples of such other insoluble compounds include pigments, exfoliants, and anti-dandruff agents.

Exemplary pigments are metal compounds or semi-metallic compounds and may be used in ionic, non-ionic or oxidized form. The pigments can be in this form either individually or in admixture or as individual mixed oxides or mixtures thereof, including mixtures of mixed oxides and pure oxides. Examples are the titanium oxides (e.g., TiO2), zinc oxides (e.g., ZnO), aluminum oxides (for example, Al2O3), iron oxides (for example, Fe2O3), manganese oxides (e.g., MnO), silicon oxides (e.g., SiO2), silicates, cerium oxide, zirconium oxides (e.g., ZrO2), barium sulfate (BaSO4), and mixtures thereof.
Other examples of pigments include D&C Red No. 3\(3\), D&C Red No. 36, D&C Orange No. 17, Green 3 Lake, Ext. Yellow 7 Lake, Orange 4 Lake, Red 28 Lake, the calcium lakes of D&C Red Nos. 7, 11, 31 and 34, the barium lake of D&C Red No. 12, the strontium lake D&C Red No. 13, the aluminum lakes of FD&C Yellow No. 5 and No. 6, the aluminum lakes of FD&C No. 40, the aluminum lakes of D&C Red Nos. 21, 22, 27, and 28, the aluminum lakes of FD&C Blue No. 1, the aluminum lakes of D&C Orange No. 5, the aluminum lakes of D&C Yellow No. 10; the zirconium lake of D&C Red No. 33, iron oxides, thermochromic dyes that change color with temperature, calcium carbonate, aluminum hydroxide, calcium sulfate, kaolin, ferric ammonium ferrocyanide, magnesium carbonate, carmine, barium sulfate, mica, bismuth oxychloride, zinc stearate, manganese violet, chromium oxide, titanium dioxide nanoparticles, barium oxide, ultramarine blue, bismuth citrate, hydroxyapatite, zirconium silicate, carbon black particles and the like. Other suitable particulates include various optical modifiers as described in US 7,202,199.

Numerous cosmetically useful particulate exfoliating agents are known in the art, and the selection and amount is determined by the exfoliating effect desired from the use of the composition, as recognized by those skilled in the cosmetic arts. Useful exfoliating agents include, but are not limited to, natural abrasives, inorganic abrasives, synthetic polymers, and the like, and mixtures thereof. Representative exfoliants include, but are not limited to, ground or powdered pumice, stone, zeolites, nut shells (e.g., almond, pecan, walnut, coconut, and the like), nut meals (e.g., almond, and the like), fruit pits (e.g., apricot, avocado, olive, peach, and the like), hulls, seed and kernel (e.g., oat bran, corn meal, rice bran, grape seed, kiwi seed, wheat, jojoba seed, loofah seed, rose hip seed, and the like), plant matter (e.g., tea tree leaves, corn cob, fruit fibers, seaweed, loofah sponge, microcrystalline cellulose, and the like), bivalve shells (oyster shell, and the like), calcium carbonate, dicalcium pyrophosphate, chalk, silica, kaolin clay, silicic acid, aluminum oxide, stannic oxide, sea salt (e.g., Dead Sea salt), talc, sugars (e.g., table, brown, and the like), polyethylene, polystyrene, microcrystalline polyamides (nylons),
microcrystalline polyesters, polycarbonates, and stainless steel fibers. The foregoing exfoliants can be used in the form of granules, powders, flours, and fibers.

[0171] Other generally insoluble components suitable for use in the present compositions include clay, swellable clay, laponite, gas bubbles, liposomes, microsponges, cosmetic beads and flakes. Cosmetic beads, flakes and capsules can be included in a composition for aesthetic appearance or can function as micro- and macro-encapsulants for the delivery of benefit agents to the skin and hair. Exemplary bead components include, but are not limited to, agar beads, alginate beads, jojoba beads, gelatin beads, Styrofoam™ beads, polyacrylate, polymethylmethacrylate (PMMA), polyethylene beads, Unispheres™ and Unipearls™ cosmetic beads (Induchem USA, Inc., New York, NY), Lipocapsule™, Lipoosphere™, and Lipopearl™ microcapsules (Lipo Technologies Inc., Vandalia, OH), and Confetti II™ dermal delivery flakes (United-Guardian, Inc., Hauppauge, NY).

[0172] Any suitable anti-dandruff agent can be employed in the compositions of the present invention. Exemplary anti-dandruff agents include, but are not limited to, sulfur, zinc pyrithione, zinc omadine, miconazole nitrate, selenium sulfide, piroctone Diamine, N, N- bis(2- hydroxyethyl)undecenamide, cade oil, pine tar, Allium cepa extract Picea abies extract, and Undecyleneth-6, and the like, and mixtures thereof.

[0173] In one aspect of the invention, the amount of particulate component can range from about 0.1% to about 10% by weight based on the total weight of the composition.

Botanicals

[0174] Optionally, the compositions of the invention can contain botanical material extracts. Extracted botanical materials can include any water soluble or oil soluble material extracted from a particular plant, fruit, nut, or seed. In one aspect of the invention, the antiperspirant compositions the botanical actives are present in an amount ranging from about 0.1% to about 10% by weight, from
about 0.5% to about 8% by weight in another aspect, and from about 1% to
about 5% by weight in a further aspect, based of the total weight of the
composition.

[0175] Suitable botanical agents can include, for example, extracts from
Echinacea (e.g., sp. angustifolia, purpurea, pallida), yucca glauca, willow herb,
basil leaves, Turkish oregano, carrot root, grapefruit, fennel seed, flax seed (e.g.,
flax seed oil), rosemary, tumeric, thyme, blueberry, bell pepper, blackberry,
spirulina, black currant fruit, tea leaves, such as for, example, Chinese tea, black
tea (e.g., var. Flowery Orange Pekoe, Golden Flowery Orange Pekoe, Fine
Tippy Golden Flowery Orange Pekoe), green tea (e.g., var. Japanese, Green
Darjeeling), oolong tea, coffee seed, dandelion root, date palm fruit, gingko leaf,
green tea, hawthorn berry, licorice, sage, strawberry, sweet pea, tomato, vanilla
fruit, comfrey, arnica, centelia asiatica, cornflower, horse chestnut, ivy, magnolia,
oat, pansy, skullcap, seabuckthorn, white nettle, and witch hazel. Botanical
extracts include, for example, chlorogenic acid, glutathione, glycerrhizin,
neohesperidin, quercetin, rutin, morin, myricetin, absinthe, and chamomile.

Cationic Polymers and Compounds

[0176] Cationic polymers and compounds are useful in the compositions of
the invention. Those of ordinary skill in the art will recognize that many of these
cationic agents serve multiple functions. Typically, these agents are useful as
conditioners (e.g., hair and skin), antistatic agents, fabric softening, and as
antimicrobial agents. Cationic polymers can be synthetically derived or obtained
by modifying natural polymers such as the cationically modified polysaccharides
and polygalactomannans.

[0177] Representative cationic polymers include but are not limited to
homopolymers and copolymers derived from free radically polymerizable acrylic
or methacrylic ester or amide monomers. The copolymers can contain one or
more units derived from acrylamides, methacrylamides, diacetone acrylamides,
acrylic or methacrylic acids or their esters, vinylactams such as vinyl pyrroidone
or vinyl caprolactam, and vinyl esters. Exemplary polymers include copolymers
of acrylamide and dimethyl amino ethyl methacrylate quaternized with dimethyl sulfate or with an alkyl halide; copolymers of acrylamide and methacryloyloxyethyl trimethyl ammonium chloride; the copolymer of acrylamide and methacryloyloxyethyl trimethyl ammonium methosulfate; copolymers of vinyl pyrrolidone/dialkylaminoalkyl acrylate or methacrylate, optionally quaternized, such as the products sold under the name GAFQUAT™ by International Specialty Products Inc., Wayne, NJ; the dimethyl amino ethyl methacrylate/vinyl caprolactam/vinyl pyrrolidone terpolymers, such as the product sold under the trade name GAFFIX™ VC 713 by International Specialty Products Inc.; the vinyl pyrrolidone/methacrylamidopropyl dimethylamine copolymer, marketed under the trade name STYLEZE™ CC 10 available from International Specialty Products Inc.; and the vinyl pyrrolidone/quaternized dimethyl amino propyl methacrylamide copolymers such as the product sold under the trade name GAFQUAT™ HS 100 by international Specialty Products, Inc.

Cationic agents can also be selected from the quaternary polymers of vinyl pyrrolidone and vinyl imidazole such as the products sold under the trade name Luviquat® (product designation FC 370 and FC 550) by BASF. Other cationic polymer agents that can be used in the compositions of the invention include polyalkyleneimines such as polyethylenimines, polymers containing vinyl pyridine or vinyl pyridinium units, condensates of polyamines and epichlorhydrins, quaternary polysaccharides, quaternary polyurethanes, quaternary silicones, and quaternary derivatives of chitin.

Other non-limiting examples of quaternary ammonium compounds (monomeric and polymeric) useful as cationic agents in the present invention include acetamidopropyl trimonium chloride, behenamidopropyl dimethylamine, behenamidopropyl ethylidimonium ethosulfate, behentrionium chloride, ceteth-20 morphoiminium ethosulfate, cetrimonium chloride, cocoamidopropyl ethylidimonium ethosulfate, dicetyldimonium chloride, dimethicone hydroxypropyl trimonium chloride, hydroxyethyl behenamidopropyl dimonium chloride, Silicone Quaternium-8, Quafernium-22, Quaternium-26, Quafernium-27, Quaternium-52, Quaternium-53, Quaternium-63, Quaternium-70, Quaternium-72,

Other useful cationic polymers include the cationic polygalactomannans (e.g., quaternized derivatives of guar and cassia, such as, guar hydroxypropyl trimonion chloride, hydroxypropyl guar hydroxypropyl trimonion chloride, and cassia hydroxypropyl trimonion chloride).

Cationic agents useful in the invention also include, but are not limited to, proteins and protein derivatives, amines, protonated amine oxides, betaines, and the like. Protein derivatives include cocodimionium hydroxypropy hydrolyzed casein, cocodimionium hydroxypropy hydrolyzed collagen, cocodimionium hydroxypropy hydrolyzed hair keratin, cocodimionium hydroxypropy hydrolyzed rice protein, cocodimionium hydroxypropy hydrolyzed silk, cocodimionium hydroxypropy hydrolyzed soy protein, cocodimionium hydroxypropy hydrolyzed wheat protein, cocodimionium hydroxypropy hydrolyzed silk amino acids, hydroxypropy trimonion hydrolyzed collagen,
hydroxypropyl trimonium hydrolyzed keratin, hydroxypropyl trimonium hydrolyzed silk, hydroxypropyl trimonium hydrolyzed rice bran, hydroxypropyl trimonium hydrolyzed vegetable protein, hydroxypropyl trimonium hydrolyzed wheat protein, hydrolyzed wheat protein, hydrolyzed sweet almond protein, hydrolyzed rice protein, hydrolyzed soy protein, hydrolyzed milk protein, hydrolyzed vegetable protein, hydrolyzed keratin, hydrolyzed collagen, hydrolyzed wheat gluten, potassium cocoyi hydrolyzed collagen, hydroxypropyl trimonium hydrolyzed collagen, cocodimonium hydroxypropyl hydrolyzed milk protein, lauryldimonium hydroxypropyl hydrolyzed wheat protein, lauryldimonium hydroxypropyl hydrolyzed collagen, keratin amino acids, collagen amino acids, soyethydidimonium ethosulfate, soyethy morphoiinium ethosulfate, and the like.

[0182] The monomeric quaternary ammonium compounds include, for example, alkyibenzimidimethyl ammonium salts, betaines, heterocyclic ammonium salts, and tetraalkyiammonium salts. Long-chain (fatty) alkyibenzimidimethyl ammonium salts are utilized as conditioners, as antistatic agents, and as fabric softeners, discussed in more detail below.

[0183] Non-limiting examples of alkybenzyldimethyiammonium salts include, but are not limited to, stearalkonium chloride, benzalkonium chloride, Quaternium-63, olealkonium chloride, didecydimonium chloride, and the like. The betaine compounds include the alkylamidopropyl betaines and the alkylamidopropyl hydroxysultaines, as described in the formulas set forth previously above. Non-limiting examples of aikyl betaine compounds include oieyl betaine, coco-betaine, cocoamidopropyi betaine, coco-hydroxy sultaine, coco/oleamidopropyl betaine, coco-sultaine, cocoamidopropylhydroxy sultaine, and sodium lauramidopropyi hydroxyphostaine.

[0184] The heterocyclic ammonium salts include the alkyiethyi morphoiinium ethosulfates, isostearyl ethylimidionium ethosulfate, and the alkypyridinium chlorides. Non-limiting examples of heterocyclic ammonium salts include, but are not limited to, cetylpyridinium chloride, isostearylthelimidonium ethosulfate, and the like.
Non-limiting examples of tetraalkylammonium salts include cocamidopropyl ethyldimonium ethosulfate, hydroxyethyl cetyldimonium chloride, Quaternium-18, and cocodimonium hydroxypropyl hydrolyzed protein, such as hair keratin, and the like.

A number of quaternary ammonium compounds are used as antistatic agents for fabric conditioning and fabric care. They include long-chain alkylated quaternary ammonium compounds such as dialkyldimethyl quaternary ammonium compounds, imidazoline quaternary compounds, amidoamine quaternary compounds, diaikyi ester quat derivatives of dihydroxypropyl ammonium compounds; diaikyi ester quat derivatives of methytriethanol ammonium compounds, ester amide amine compounds, and diester quat derivatives of dimethydiethanol ammonium chloride, as described in the review article by Whailey, "Fabric Conditioning Agents", HAPPI, pp. 55-58 (February 1995), incorporated herein by reference.

Non-limiting examples of dialkyldimethyl quaternary ammonium compounds, include N,N-dioleyl-N,N-dimethyiammonium chloride, N,N-di(tallowy!)N,N-dimethylammonium ethosulfate, N,N-di(hydrogenated-tailowyl)~N,N-dimethylammonium chloride, and the like. Non-limiting examples of imidazoline quaternary compounds include 1-N-methyi-3-N-tallowamidoethylimidazoliium chloride, 3-methyi-1-tallowylamidoethyl!-2-tailowyiimidazolinium methyi!sulfate, and the like. Non-limiting examples of amidoamine quaternary compounds include N-alkyi-N-methyl-N,N-bis(2-tallowamidoethyl)ammonium salts where the alkyl group can be methyl, ethyl, hydroxyethyl, and the like. Non-limiting examples of diaikyi ester quat derivatives of dihydroxypropyl ammonium compounds include 1,2-ditallowoyloxy-3-N,N,N-trimethylammoniopropane chloride, 1,2-dicanoloyloxy-3-N,N,N-trimethylammoniopropane chloride, and the like.

In addition, other types of long chain (e.g., natural oil and fatty acid-derived) alkylated quaternary ammonium compounds are suitable fabric softening agents. In one aspect, the long-chain alkyl groups are derived from tallow, canola oil, or from palm oil, however, other alkyl groups derived from
soybean oil and coconut oil, for example, are also suitable, as are lauryl, oleyl, ricinoleyl, stearyl, and palmityl groups. Representative compounds include, but not limited, to N,N-di(alkyloxyethyl)-N,N-dimethylammonium salts such as N,N-di(tallowyloxyethyl)-N,N-dimethylammonium chloride, N,N-di(canolyloxyethyl)-N,N-dimethylammonium chloride, and the like; N,N-di(alkyloxyethyl)-N-methyl-N-(2-hydroxyethyl)ammonium salts such as N,N-di(tallowyloxyethyl)-N-methyl-N-(2-hydroxyethyl)ammonium chloride, N,N-di(canolyloxyethyl)-N-methyl-N-(2-hydroxyethyl)ammonium chloride, and the like; N,N-di(2-alkyloxy-2-oxoethyl)-N,N-dimethylammonium salts, such as N,N-di(tallowyloxy-2-oxoethyl)-N,N-dimethylammonium chloride, N,N-di(2-canolyloxy-2-oxoethyl)-N,N-dimethylammonium chloride, and the like; N,N-di(2-canolyloxy-2-oxoethyl)-N,N-dimethylammonium chloride, and the like; N,N-di(2-alkyloxyethylcarbonyloxyethyl)-N,N-dimethylammonium salts, such as N,N-di(tallowyloxyethylcarbonyloxyethyl)-N,N-dimethylammonium chloride, N,N-di(canolyloxyethylcarbonyloxyethyl)-N,N-dimethylammonium chloride, and the like; N-(2-alkanoyloxy-2-ethyl)-N-(2-alkyloxy-2-oxoethyl)-N,N-dimethyl ammonium salts, such as N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxoethyl)-N,N-dimethyl ammonium chloride, N-(2-canolyloxy-2-ethyl)-N-(2-canolyloxy-2-oxoethyl)-N,N-dimethyl ammonium chloride, and the like; N,N,N-tri(alkyloxyethyl)-N-methyl ammonium salts, such as N,N,N-tri(tallowyloxyethyl)-N-methylammonium chloride, N,N,N-tri(canolyloxyethyl)-N-methylammonium chloride, and the like; N-(2-alkyloxy-2-oxoethyl)-N-aikyl-N,N-dimethyl ammonium salts, such as N-(2-tallowyloxy-2-oxoethyl)-N-tallowyN,N-dimethyl ammonium chloride, N-(2-canolyloxy-2-oxoethyl)-N-canolyi-N,N-dimethyl ammonium chloride, and the like.

[0189] In another aspect, quaternary ammonium fabric softening compounds include N-methyl-N,N-bis(tallowamidoethyl)-N-(2-hydroxyethyl)ammonium methylsulfate and N-methyl-N,N-bis(hydrogenated-tallowamidoethyl)-N-(2-hydroxyethyl) ammonium methylsulfate, dialkyl esferquat derivatives of methytriethanol ammonium salts such as the bis(acyloxyethyl)hydroxyethyl)methylammonium methosulfate esterquats, and the
iike; and N,N-di(tallowoyloxyethyl)-N,N-dimethylammonium chloride, where the tallow chains are at least partially unsaturated.

[0190] In a further aspect, fabric softening agents include the well-known dialkyldimethyl ammonium salts such as N,N-ditallowyl-N,N-dimethyl ammonium methylsulfate, N,N-di(hydrogenated-tallowyl)-N,N-dimethyl ammonium chloride, N,N-distearyl-N,N-dimethyl ammonium chloride, N,N-dibehenyl-N,N-dimethylammonium chloride, N,N-di(hydrogenated tallow)-N,N-dimethyloammonium chloride, N,N-ditallowyl-N,N-dimethyl ammonium chloride, N,N-distearoyl-N,N-dimethyl ammonium chloride, N,N-dibehenyl-N,N-dimethyl ammonium chloride, and N,N-dimethyl-N-stearyl-N-benzyiammonium chloride.

[0191] The foregoing monomeric and polymeric quaternary ammonium salt compounds can have any anionic group as a counter-ion, for example, chloride, bromide, methosulfate (i.e., methylsulfate), acetate, formate, sulfate, nitrate, and the like.

[0192] For fabric softening applications, any suitable quaternary ammonium agent can be utilized in combination with the polymer surfactant compositions of the present invention. For ester-containing fabric softening agents, the pH of the compositions can influence the stability of the fabric softening agents, especially in prolonged storage conditions. The pH, as defined in the present context, is measured in the neat compositions at about 20°C. In one aspect, the pH of the composition is less than about 6. In another aspect, the pH is in the range of from about 2 to about 5, and from about 2.5 to about 3.5 in a further aspect.

[0193] In one aspect, the cationic agent(s) can be employed in amounts ranging from about 0.05% to 15% by weight, from about 0.1% to about 10% by weight in another aspect, and from about 0.5% to about 3% by weight in a further aspect, based on the weight of the final composition, but is not limited thereto.
Preservatives

[0194] In one aspect, any preservative suitable for use in personal care, home care, health care, and institutional and industrial care products, can be used in the compositions of the present invention. Suitable preservatives include polymethoxy bicyclic oxazolidine, methyl paraben, propyl paraben, ethyl paraben, butyl paraben, benzytriazole, DMDM hydantoin (also known as 1,3-dimethyl-5,5-dimethyl hydantoin), imidazolidinyi urea, phenoxyethanol, phenoxyethylparaben, methylisothiazolione, methychloroisothiazolinone, benzoisothiazolinone, triclosan, and suitable polyquaternium compounds disclosed above (e.g., Polyquaternium-1).

[0195] In another aspect, acid based preservatives are useful in the compositions of the present invention. The use of acid based preservatives facilitates the formulation of products in the low pH range. Lowering the pH of a formulation inherently provides an inhospitable environment for microbial growth. Moreover, formulating at low pH enhances the efficacy of acid based preservatives, and affords a personal care product which maintains an acidic pH balance on the skin as discussed by by Wiechers, 2008, supra. Surprisingly, it has been discovered that the polymers of the invention can be used to thicken surfactant compositions formulated at low pH while maintaining excellent clarity and rheological properties such as viscosity and yield value.

[0196] Any acid based preservative that is useful in personal care, home care, health care, and institutional and industrial care products can be used in the compositions of the present invention. In one aspect the acid preservative is a carboxylic acid compound represented by the formula: \( \text{R}^{53}\text{C}(0)\text{OH} \), wherein \( \text{R}^{53} \) represents hydrogen, a saturated and unsaturated hydrocarbyl group containing 1 to 8 carbon atoms or \( \text{C}_n \text{to C}_t \text{aryly} \). in another aspect, \( \text{R}^{53} \) is selected from a hydrogen, a \( \text{C}_t \) to \( \text{Cs} \) alkyl group, a \( \text{C}_2 \) to \( \text{C}_8 \) aikenyi group, or phenyl. Exemplary acids are, but are not limited to, formic acid, acetic acid, propionic acid, sorbic acid, caprylic acid, and benzoic acid, and mixtures thereof.

[0197] In another aspect, suitable acids include but are not limited to, oxalic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, maleic acid, fumaric
acid, lactic acid, glyceric acid, tartronic acid malic acid, tartaric acid, gluconic acid, citric acid, ascorbic acid, salicylic acid, phthalic acid, mandelic acid, benzilic acid, and mixtures thereof.

[0198] Salts of the foregoing acids are also useful as long as they retain efficacy at low pH values. Suitable salts include the alkali metal (e.g., sodium, potassium, calcium) and ammonium salts of the acids enumerated above.

[0199] The acid based preservatives and/or their salts can be used alone or in combination with non-acidic preservatives typically employed in personal care, home care, health care, and institutional and industrial care products.

[0200] The preservatives typically comprise from about 0.01% to about 3.0% by weight in one aspect, from about 0.1% to about 1% by weight in another aspect, and from about 0.3% to about 1% by weight in a further aspect, of the total weight of the personal care compositions of the present invention.

Auxiliary Rheology Modifier

[0201] In another aspect of the invention, the compositions of the invention can be formulated in combination with one or more auxiliary rheology modifiers and thickeners. Suitable rheology modifiers and thickeners include synthetic and semi-synthetic rheology modifiers. Exemplary synthetic rheology modifiers include acrylic based polymers and copolymers. One class of acrylic based rheology modifiers are the carboxyl functional alkali-swellable and alkali-soluble thickeners (ASTs) produced by the free-radical polymerization of acrylic acid alone or in combination with other ethylenically unsaturated monomers. The polymers can be synthesized by solvent/precipitation as well as emulsion polymerization techniques. Exemplary synthetic rheology modifiers of this class include homopolymers of acrylic acid or methacrylic acid and copolymers polymerized from one or more monomers of acrylic acid, substituted acrylic acid, and salts and alkyl esters of acrylic acid and substituted acrylic acid. As defined herein, the substituted acrylic acid contains a substituent positioned on the alpha and/or beta carbon atom of the molecule, wherein in one aspect the substituent is independently selected from C1-C30 alkyl, -CN, and -COGH.
Optionally, other ethylenically unsaturated monomers such as, for example, styrene, vinyl acetate, ethylene, butadiene, acrylonitrile, as well as mixtures thereof can be copolymerized into the backbone. The foregoing polymers are optionally crosslinked by a monomer that contains two or more moieties that contain ethylenic unsaturation. In one aspect, the crosslinker is selected from a polyalkenyi polyether of a polyhydric alcohol containing at least two alkenyl ether groups per molecule. Other Exemplary crosslinkers are selected from allyl ethers of sucrose and ayl ethers of pentaerythritoi, and mixtures thereof. These polymers are more fully described in U.S. Patent No. 5,087,445; U.S. Patent No. 4,509,949; and U.S. Pat. No. 2,798,053 herein incorporated by reference.

In one aspect, the AST rheology modifier or thickener is a crosslinked homopolymer polymerized from acrylic acid or methacrylic acid and is generally referred to under the INCI name of Carbomer. Commercially available Carbomers include Carbopol® polymers 934, 940, 941, 956, 980 and 996 available from Lubrizoi Advanced Materials, Inc. in a further aspect, the rheology modifier is selected from a crosslinked copolymer polymerized from a first monomer selected from one or more monomers of acrylic acid, substituted acrylic acid, salts of acrylic acid and salts of substituted acrylic acid and a second monomer selected from one or more C10-C30 alkyl acrylate esters of acrylic acid or methacrylic acid. In one aspect, the monomers can be polymerized in the presence of a steric stabilizer such as disclosed in U.S. Patent No. 5,288,814, which is herein incorporated by reference. Some of the foregoing polymers are designated under INCI nomenclature as Acrylates/C 10-30 Alkyl Acrylate Crosspolymer and are commercially available under the trade names Carbopol® 1342 and 1382, Carbopol® Uitrez 20 and 21, Carbopol® ETD 2020 and Pemulen® TR-1 and TR-2 from Lubrizoi Advanced Materials, inc.

In another aspect, the auxiliary rheology modifier can be a crosslinked, linear polyvinyl amide/acrylic acid) copolymer as disclosed in U.S. Patent No. 7,205,271 , the disclosure of which is herein incorporated by reference.

Another class of optional synthetic rheology modifiers and thickeners suitable for use in the present invention includes the hydrophobically modified
ASTs, commonly referred to as hydrophobically modified alkali-soluble and alkali-soluble emulsion (HASE) polymers. Typical HASE polymers are free radical addition polymers polymerized from pH sensitive or hydrophilic monomers (e.g., acrylic acid and/or methacrylic acid), hydrophobic monomers (e.g., C1-C30 alkyl esters of acrylic acid and/or methacrylic acid, acrylonitrile, styrene), an "associative monomer", and an optional crosslinking monomer. The associative monomer comprises an ethylenically unsaturated polymerizable end group, a non-ionic hydrophilic midsection that is terminated by a hydrophobic end group. The non-ionic hydrophilic midsection comprises a polyoxyalkylene group, e.g., polyethylene oxide, polypropylene oxide, or mixtures of polyethylene oxide/polypropylene oxide segments. The terminal hydrophobic end group is typically a C8-C40 aliphatic moiety. Exemplary aliphatic moieties are selected from linear and branched alkyl substituents, linear and branched akenyl substituents, carbocyclic substituents, aryl substituents, aralkyl substituents, arylalky substituents, and alkylaryl substituents. In one aspect, associative monomers can be prepared by the condensation (e.g., esterification or etherification) of a polyethoxylated and/or polypropoxyiaed aliphatic alcohol (typically containing a branched or unbranched C8-C40 aliphatic moiety) with an ethylenically unsaturated monomer containing a carboxylic acid group (e.g., acrylic acid, methacrylic acid), an unsaturated cyclic anhydride monomer (e.g., maleic anhydride, itaconic anhydride, citraconic anhydride), a monoethylenically unsaturated monoisocyanate (e.g., α,α-dimethyl-m-(isopropeny! benzyl isocyanate) or an ethylenically unsaturated monomer containing a hydroxy! group (e.g., vinyl alcohol, allyl alcohol). Polyethoxylated and/or polypropoxyiaed aliphatic alcohols are ethylene oxide and/or propylene oxide adducts of a monoalcohol containing the C8-C40 aliphatic moiety. Non-limiting examples of alcohols containing a C8-C40 aliphatic moiety are capryl alcohol, iso-octyl alcohol (2-ethyl hexanol), pelargonic alcohol (1-nonanol), decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, cetyl alcohol, cetearyl alcohol (mixture of C10-C18 monoalcohols), stearyl alcohol, isostearyl alcohol, elaidy! alcohol, oleyl alcohol, arachidyl alcohol, behenyi alcohol, lignoceryl alcohol, ceryl alcohol, montanyi
alcohol, meissyl, lacceryl alcohol, geddyl alcohol, and C2-C20 alkyl substituted phenols (e.g., nonyl phenol), and the like.


Commercially available HASE polymers are sold under the trade names, Aculyn® 22 (INCI Name: Acrylates/Steareth-20 Methacrylate Copolymer), Aculyn® 44 (INCI Name: PEG-150/Decyl Alcohol/SMIDI Copolymer), Aculyn 46® (INCI Name: PEG-150/Stearyl Alcohol/SMIDI Copolymer), and Aculyn® 88 (INCI Name: Acrylates/Steareth-20 Methacrylate Crosspolymer) from Rohm & Haas, and Novethix™ L-10 (INCI Name: Acrylates/Beheneth-25 Methacrylate Copolymer) from Lubrizol Advanced Materials, Inc.

[0206] In another embodiment, acid swellable associative polymers can be used with the hydrophobically modified, cationic polymers of the present invention. Such polymers generally have cationic and associative characteristics. These polymers are free radical addition polymers polymerized from a monomer mixture comprising an acid sensitive amino substituted hydrophilic monomer (e.g., dialkyiamino alkyl (meth)acrylates or (meth)acrylamides), an associative monomer (defined hereinabove), a lower alkyl (meth)acrylate or other free radically polymerizable comonomers selected from hydroxyalkyl esters of (meth)acrylic acid, vinyl and/or allyl ethers of polyethylene glycol, vinyl and/or allyl ethers of polypropylene glycol, vinyl and/or allyl ethers of polyethylene glycol/polypropylene glycol, polyethylene glycol esters of (meth)acrylic acid, polypropylene glycol esters of (meth)acrylic acid, polyethylene glycol/polypropylene glycol esters of (meth)acrylic acid, and combinations thereof. These polymers can optionally be crosslinked. By acid
sensitive is meant that the amino substituent becomes cationic at low pH values, typically ranging from about 0.5 to about 6.5. Exemplary acid swellable associative polymers are commercially available under the trade names Structure® Plus (INCI Name: Acrylates/Aminoacrylates/C10-C30 Alky l PEG-20 itaconate) from Akzo Nobel, and Carbopol® Aqua CC (INCI Name: Polyacrylates-1 Crosspolymer) from Lubrizol Advanced Materials, Inc. In one aspect, the acid swellable polymer is a copolymer of one or more C1-C5 alkyl esters of (meth)acrylic acid, C-1-C4 dialkylamino C1-C5 alky l methacrylate, PEG/PPG-30/5 alky l ether, PEG 20-25 C10-C30 alky l ether methacrylate, hydroxy C2-C6 alky l methacrylate crosslinked with ethylene glycol dimethacrylate. Other useful acid swellable associative polymers are disclosed in U.S. Patent No. 7,378,479, the disclosure of which is herein incorporated by reference.

[0207] Hydrophobically modified alkoxylated methyl glucoside, such as, for example, PEG-120 Methyl Glucose Dioleate, PEG-120 Methyl Glucose Trioleate, and PEG-20 Methyl Glucose Sesquistearate, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucamate® DOE-120, Glucamate™ LT, and Glucamate™ SSE-20, respectively, are also suitable as auxiliary rheology modifiers.

[0208] Polysaccharides obtained from tree and shrub exudates, such as gum Arabic, gum gahatti, and gum tragacanth, as well as pectin; seaweed extracts, such as alginates and carrageenans (e.g., lambda, kappa, iota, and salts thereof); algae extracts, such as agar; microbial polysaccharides, such as xanthan, gellan, and welian; cellulose ethers, such as ethylhexyiethylicelulose, hydroxybuty1methylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, and micro-fibrous cellulose such as disclosed in U.S. Patent No. 7,776,807; polygalactomannans, such as fenugreek gum, cassia gum, locust bean gum, tara gum, and guar gum; starches, such as corn starch, tapioca starch, rice starch, wheat starch, potato starch and sorghum starch can also be employed in the compositions herein as suitable auxiliary thickeners, suspending agents, and rheology modifiers.
[0209] The auxiliary rheology modifiers, when employed, can be used alone or in combination and typically are used in an amount ranging from about 0.1 wt. % to about 8 wt. % in one aspect, from about 0.3 wt. % to about 3 wt. % in another aspect, and from about 0.5 wt. % to about 2 wt. % in further aspect, based on the total weight of the personal care compositions of the present invention.

Emulsifier

[0210] Emulsifiers when employed in the compositions of the present invention include, but are not limited to, the C_{12-22} fatty alcohols, C_{12-22} alkoxyated alcohols, C_{12-22} fatty acids, C_{12-22} alkoxylated fatty acids (the alkoxylates each having 10 to 80 units of ethylene oxide, propylene oxide, and combinations of ethylene oxide/propylene oxide present in the molecule), C_{8-22} APGs, ethoxiated sterols (wherein the number of ethylene oxide units ranges from 2 to about 150), partial esters of polyglycerols, esters and partial esters of polyols having 2 to 6 carbon atoms, partial esters of polyglycerols, and organosiloxanes, and combinations thereof.

[0211] The C_{8-22} alkyi APG emulsifiers are prepared by reacting glucose or an oligosaccharide with primary fatty alcohols having 8 to 22 carbon atoms, and comprise a glucosidically bonded C_{9-18} alky group on an oligoglucoside residue whose average degree of oligomerization is 1 to 2. In addition to the APGs described as surfactants above, APGs are available under the trademark Plantacare® (Cognis Corporation, Cincinnati, OH). Exemplary alkyi glucosides and oligoglycosides are selected from octyl glucoside, decyl glucoside, lauryl glucoside, paimityl glucoside, isostearyl glucoside, stearyl glucoside, arachidy glucoside and behenyl glucoside, and mixtures thereof.

[0212] Emulsifiers based on the esters and partial esters of polyols having 2 to 6 carbon atoms are condensed with linear saturated and unsaturated fatty acids having 12 to 33 carbon atoms are, for example, the monoesters and diesters of glycerol or ethylene glycol or the monoesters of propylene glycol with saturated and unsaturated C_{12-30} fatty acids.
Exemplary fatty alcohols and fatty acids, as well as their alkoxylates, the partial esters of polyglycerols, as well as the organosiloxanes are described above.

**Chelating Agents**

Chelating agents can be employed to stabilize the personal care, home care, health care, and institutional care compositions of the invention against the deleterious effects of metal ions. When utilized, suitable chelating agents include EDTA (ethylene diamine tetraacetic acid) and salts thereof such as disodium EDTA, citric acid and salts thereof, cyclodextrins, and the like, and mixtures thereof. Such suitable chelators typically comprise about 0.001 wt. % to about 3 wt. %, preferably about 0.01 wt. % to about 2 wt. %, and more preferably about 0.01 wt. % to about 1 wt. % of the total weight of the personal care compositions of the present invention.

**Auxiliary Solvents and Diluents**

The personal care, home care, health care, and institutional care compositions containing the thickened surfactant compositions of the present invention in combination with one or more of the foregoing active ingredients and/or with the one or more additives and/or adjuvants, conventionally or popularly included in personal care, health care, home care, and institutional care products discussed above can be prepared as water-free or water-based formulations, and formulations containing water-miscible auxiliary solvents and/or diluents, but are not limited thereto. Useful solvents commonly employed are typically liquids, such as water (deionized, distilled or purified), alcohols, fatty alcohols, polyols, and the like, and mixtures thereof. Non-aqueous or hydrophobic auxiliary solvents are commonly employed in substantially water-free products, such as nail lacquers, aerosol propellant sprays, or for specific functions, such as removal of oily soils, sebum, make-up, or for dissolving dyes, fragrances, and the like, or are incorporated in the oily phase of an emulsion. Non-limiting examples of auxiliary solvents, other than water, include linear and
branched alcohols, such as ethanol, propanol, isopropanol, hexanol, and the like; aromatic alcohols, such as benzyl alcohol, cyclohexanol, and the like; saturated C₈ to C₃₀ fatty alcohol, such as lauril alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, and the like. Non-limiting examples of polyols include polyhydroxy alcohols, such as glycerin, propylene glycol, butylene glycol, hexylene glycol, C₂ to C₄ alkoxylated alcohols and C₂ to C₄ alkoxylated polyols, such as ethoxylated, propoxylated, and butoxylated ethers of alcohols, diols, and polyols having about 2 to about 30 carbon atoms and 1 to about 40 alkoxy units, polypropylene glycol, polybutylene glycol, and the like. Non-limiting examples of non-aqueous auxiliary solvents or diluents include silicons, and silicone derivatives, such as cyclomethicone, and the like, ketones such as acetone and methyethyl ketone; natural and synthetic oils and waxes, such as vegetable oils, plant oils, animal oils, essential oils, mineral oils, C₇ to C₁₀ isoparaffins, alkyl carboxylic esters, such as ethyl acetate, amyl acetate, ethyl lactate, and the like, jojoba oil, shark liver oil, and the like. Some of the foregoing non-aqueous auxiliary solvents or diluents may also be conditioners and emulsifiers.

Propellants

Where desired, any known aerosol propellant can be utilized to deliver the personal care, home care, health care, and institutional care compositions containing the polymers of the present invention in combination with one or more of the foregoing active ingredients and/or with the one or more additives and/or adjuvants, conventionally or popularly included in such products. Exemplary propellants include, but are not limited to, lower boiling hydrocarbons such as C₃-C₆ straight and branched chain hydrocarbons. Exemplary hydrocarbon propellants include propane, butane, isobutene, and mixtures thereof. Other-suitable propellants include ethers, such as, dimethyl ether, hydrofluorocarbons, such as, 1,1-difluoroethane, and compressed gasses, such as air and carbon dioxide.
In one aspect, these compositions can contain from about 0.1 % to about 60% by weight of a propellant, and from about 0.5 to about 35% by weight in another aspect, based on the total weight of the composition.

The polymers of the invention can be utilized in any personal care, home care, health care, and institutional and industrial care composition requiring rheology and/or aesthetic property modification. In a given composition or application, the polymers of this invention can, but need not, serve more than one function, such as a thickener, stabilizer, emulsifier, film former, carrier a deposition aid, and the like. The amount of polymer that can be employed depends upon the purpose for which they are included in a formulation and can be determined by person skilled in the formulation arts. Thus, as long as the physicochemical and functional properties of a desired product are achieved, a useful amount of polymer on a total composition weight basis, typically can vary in the range of from about 0.01 % to about 25% by weight in one aspect, from about 0.1 % to about 15% by weight in another aspect, from about 0.5% to about 10% by weight in a further aspect, and from about 1% to about 5% by weight in a still further aspect, but is not limited thereto.

The personal care, home care, health care, and institutional and industrial care compositions comprising the polymers of the invention can be packaged and dispensed from containers such as bottles, pump containers, jars, tubes, sprays, wipes, roll-ons, sticks and the like, without limitation. There is no limitation as to the form of the product in which these polymers can be incorporated, so long as the purpose for which the product is used is achieved. For example, personal and health care products containing the polymers can be applied to the skin, hair, scalp, and nails, without limitation in the form of gels, sprays (liquid or foams), emulsions (creams, lotions, pastes), liquids (rinses, shampoos), bars, ointments, suppositories, and the like.

In one personal care aspect, the polymers of this invention are suitable for preparation of personal care (cosmetics, toiletries, cosmeceuticals), including, without limitation, hair care products (shampoos, combination shampoos, such as "two-in-one" conditioning shampoos), post-shampoo rinses, setting and style
maintenance agents (including setting aids, such as geis and sprays, grooming aids such as pomades, conditioners, perms, relaxers, hair smoothing products, and the like), skin care products (facial, body, hands, scalp and feet), such as creams, lotions and cleansing products, antiacne products, antiaging products (exfoliant, keratolytic, anticellulite, antiwrinkle, and the like), skin protectants (sun care products, such as sunscreens, sunblock, barrier creams, oils, silicones and the like), skin color products (whiteners, lighteners, sunless tanning accelerators and the like), hair colorants (hair dyes, hair color rinses, highlighters, bleaches and the like), pigmented skin colorants (face and body make-ups, foundation creams, mascara, rouge, lip products, and the like) bath and shower products (body cleansers, body wash, shower gel, liquid soap, soap bars, syndet bars, conditioning liquid bath oil, bubble bath, bath powders, and the like), nail care products (polishes, polish removers, strengtheners, lengtheners, hardeners, cuticle removers, softness, and the like).

Toiletries and beauty aids containing the polymers of the invention can include, without limitation, hair-removal products (shaving creams and lotions, epilators, after-shaving skin conditioner, and the like), hair growth promoting products, deodorants and antiperspirants, oral care products (mouth, teeth, gums), such as mouth wash, dentifrice, such as toothpaste, tooth powder, tooth polishes, tooth whiteners, breath fresheners, denture adhesives, and the like; facial and body hair bleach and the like. Other beauty aids that can contain the polymers of the invention include, without limitation, sunless tanning applications containing artificial tanning accelerators, such as dihydroxyacetone (DHA), tyrosine, tyrosine esters and the like: skin depigmenting, whitening and lightening, formulations containing such active ingredients as kojic acid, hydroquinone, arbutin, fruital, vegetable or plant extracts, (lemon peel extract, chamomile, green tea, paper mulberry extract, and the like), ascorbyl acid derivatives ascorbyl palmitate, ascorbyl stearate, magnesium ascorbyl phosphate and the like).

The polymers of the invention are useful as suspending agents for particulates making them suitable for dermal cleansing products containing
particulates, insoluble benefit agents, microabrasives, and abrasives and combinations thereof. Dermal cleansing products include shampoos, body washes, shower gels, bath gels, masks and skin cleansers.

Body Wash

[0223] In one aspect, a personal care composition in which the polymer of this invention is useful is a body wash. Typical components of a body wash, in addition to the polymer thickener and water are: at least one surfactant; a sufficient pH adjusting agent (base and/or acid) to attain a pH of from about 3.5 to about 7.5 in one aspect, from about 4.0 to about 6.5 in another aspect, and from about 5.0 to about 6.0 in a further aspect; and optional ingredients selected from the adjuvants, additives and benefit agents discussed above, and mixtures thereof, including benefit agents selected from silicones, pearlizing agents, vitamins, oils, fragrances, dyes, preservatives including acids, botanicals, exfoliating agents, insoluble gas bubbles, liposomes, microsponges, cosmetic beads and flakes. In one aspect, the surfactant is an anionic surfactant. In another aspect, the surfactant is a mixture of an anionic surfactant and an amphoteric surfactant, in optional combination with a non-ionic surfactant. In another aspect, the surfactant is a mixture of an anionic surfactant and an amphoteric surfactant, in optional combination with a cationic and/or a non-ionic surfactant. In one aspect, the anionic surfactant can be present in an amount ranging from about 5% to about 40% by weight, from about 6% to about 33% by weight in another aspect, and from 8% to about 25% by weight in a further aspect, based on the total weight of the body wash composition. When mixtures of anionic and amphoteric surfactants are used, the ratio of anionic surfactant:amphoteric surfactant can range from about 1:1 to about 15:1 in one aspect, from about 1.5:1 to about 10:1 in another aspect, from about 2.25:1 to about 9:1 in a further aspect, and from about 4.5:1 to about 7:1 in a still further aspect. The amount of the acrylic polymer blend(s) can range from about 0.5% to about 5% by weight in one aspect, from about 1% to about 3% by weight in
another aspect, and from about 1.5% to about 2.5% by weight in a further aspect, based on the total weight of the body wash composition.

[0224] Body wash embodiments of the invention can be formulated as moisturizing body washes, antibacterial body washes, bath gels, shower gels, liquid hand soaps, body scrubs; bubble baths, facial scrubs, foot scrubs, and the like.

Shampoo Compositions
[0225] In one aspect, a personal care composition in which the polymer of this invention is useful is a shampoo. Typical components of a shampoo, in addition to the polymer thickener and water are: at least one surfactant; a sufficient pH adjusting agent (base and/or acid) to attain a pH of from about 3.0 to about 7.5 in one aspect, from about 3.5 to about 6.0 in another aspect, and from about 4.0 to about 5.5 in a further aspect; and optional ingredients selected from the adjuvants, additives and benefit agents discussed above, and mixtures thereof, including benefit agents selected from conditioning agents (e.g., silicones and/or cationic conditioning agents; small and/or large particle sized silicones), pearlizing agents, vitamins, oils, fragrances, dyes, preservatives including acids, botanicals, and insoluble gas bubbles, liposomes, and cosmetic beads and flakes, and anti-dandruff agents, and mixtures thereof. In one aspect, the surfactant is an anionic surfactant. In another aspect, the surfactant is a mixture of an anionic surfactant and an amphoteric surfactant, in optional combination with a cationic and/or a non-ionic surfactant. In one aspect, the anionic surfactant can be present in an amount ranging from about 5% to about 40% by weight, from about 6% to about 30% by weight in another aspect, and from 8% to about 25% by weight in a further aspect, based on the total weight of the shampoo composition. When mixtures of anionic and amphoteric surfactants are used, the ratio of anionic surfactant to amphoteric surfactant can range from about 1:1 to about 10:1 in one aspect, from about 2.25:1 to about 9:1 in another aspect, and from about 4.5:1 to about 7:1 in a further aspect. The amount of polymer can range from about 0.5% to about 5% by weight in one aspect, from
about 1% to about 3% by weight in another aspect, and from about 1.5% to about 2.5% by weight in a further aspect, based on the total weight of the shampoo composition.

Shampoo embodiments of the invention can be formulated as 2-in-1 shampoos, baby shampoos, conditioning shampoos, bodifying shampoos, moisturizing shampoos, temporary hair color shampoos, 3-in-1 shampoos, antidandruff shampoos, hair color maintenance shampoos, acid (neutralizing) shampoos, medicated shampoos, and salicylic acid shampoos, and the like.

**Liquid Fatty Acid Soap Based Cleansers**

In one aspect, a personal care composition in which the polymer of this invention is useful is a fatty acid soap based cleanser. Typical components of a fatty acid based soap cleanser, in addition to the polymer thickener are: at least one fatty acid salt; an optional surfactant or mixture of surfactants; a sufficient pH adjusting agent (base and/or acid) to attain a pH of above 7 in one aspect, from about 7.5 to about 14 in another aspect, from about 8 to about 12 in still another aspect, and from about 8.5 to about 10 in a further aspect; and optional ingredients selected from the adjuvants, additives and benefit agents discussed above, and mixtures thereof, including benefit agents selected from silicones, humectants, pearlizing agents, vitamins, oils, fragrances, dyes, preservatives, botanicals, anti-dandruff agents, exfoliating agents, insoluble gas bubbles, liposomes, microsponges, cosmetic beads and flakes.

In one aspect, the fatty acid soaps are selected from at least one the fatty acid salt (e.g., sodium, potassium, ammonium) containing from about 8 to about 22 carbon atoms. In another aspect of the invention the liquid soap composition contains at least one fatty acid salt containing from about 12 to about 18 carbon atoms. The fatty acids utilized in the soaps can be saturated and unsaturated and can be derived from synthetic sources, as well as from the saponification of fats and natural oils by a suitable base (e.g., sodium, potassium and ammonium hydroxides). Exemplary saturated fatty acids include but are not limited to octanoic, decanoic, lauric, myristic, pentadecanoic, palmitic, margaric,
steric, isostearic, nonadecanoic, arachidic, behenic, and the like, and mixtures thereof. Exemplary unsaturated fatty acids include but are not limited to the salts (e.g., sodium, potassium, ammonium) of myristoleic, palmitoleic, oleic, linoleic, linolenic, and the like, and mixtures thereof. The fatty acids can be derived from animal fat such as tallow or from vegetable oil such as coconut oil, red oil, palm kernel oil, palm oil, cottonseed oil, olive oil, soybean oil, peanut oil, corn oil, and mixtures thereof. The amount of fatty acid soap that can be employed in the liquid cleansing compositions of this embodiment ranges from about 1% to about 50% by weight in one aspect, from about 10% to about 35% by weight in another aspect, and from about 12% to 25% by weight in a further aspect of the invention, based on the weight of the total composition.

[0229] An optional anionic surfactant can be present in the soap composition in an amount ranging from about 1% to about 25% by weight in one aspect, from about 5% to about 20% by weight in another aspect, and from 8% to about 15% by weight in a further aspect, based on the weight of the total weight of the soap composition. Mixtures of anionic and amphoteric surfactants can be used. The ratio of anionic surfactant to amphoteric surfactant can range from about 1:1 to about 10:1 in one aspect, from about 2.25:1 to about 9:1 in another aspect, and from about 4.5:1 to about 7:1 in a further aspect.

[0230] In the foregoing soap embodiments of the invention, the amount of polymer can range from about 0.5% to about 5% by weight in one aspect, from about 1% to about 3% by weight in another aspect, and from about 1.5% to about 2.5% by weight in a further aspect, based on the total weight of the soap composition.

[0231] The liquid fatty acid soap based cleanser embodiments of the invention can be formulated as body washes, bath gels, shower gels, liquid hand soaps, body scrubs; bubble baths, facial scrubs, and foot scrubs, 2-in-1 shampoos, baby shampoos, conditioning shampoos, bodifying shampoos, moisturizing shampoos, temporary hair color shampoos, 3-in-1 shampoos, anti-dandruff shampoos, hair color maintenance shampoos, acid (neutralizing)
shampoos, anti-dandruff shampoos, medicated shampoos, and salicylic acid
shampoos, and the like.

Cosmeceuticals
[0232] In one cosmeceutical aspect, the polymers of the invention can be
employed as a thickener for active skin treatment lotions and creams containing,
as active ingredients, acidic anti-aging, anti-cellulite, and anti-acne agents,
hydroxy carboxyiic acids, such as alpha-hydroxy acid (AHA), beta-hydroxy acid
(BHA), alpha-amino acid, alpha-keto acids (AKAs), and mixtures thereof. In one
aspect, AHAs can include, but are not limited to, lactic acid, glycolic acid, fruit
acids, such as malic acid, citric acid, tartaric acid, extracts of natural compounds
containing AHA, such as apple extract, apricot extract, and the like, honey
extract, 2-hydroxyoctanoic acid, glyceric acid (dihydroxypropionic acid), tartronic
acid (hydroxypropanedioic acid), gluconic acid, mandelic acid, benzilic acid,
azeiaic acid, alpha-lipoic acid, salicylic acid, AHA salts and derivatives, such as
arginine glycoiate, ammonium glycoiate, sodium glycolate, arginine lactate,
ammonium lactate, sodium lactate, alpha-hydroxybutyric acid, alpha-
hydroxyisobutyric acid, alpha-hydroxyisocaproic acid, alpha-hydroxyisovaleric
acid, atrolactic acid, and the like. BHAs can include, but are not limited to, 3-
hydroxy propanoic acid, beta-hydroxybutyric acid, beta-phenyl lactic acid, beta-
phenyipyruvic acid, and the like. Alpha-amino acids include, without being
limited thereto, alpha-amino dicarboxylic acids, such as aspartic acid, glutamic
acid, and mixtures thereof, sometimes employed in combination with fruit acid.
AKAs include pyruvic acid. In some antiaging compositions, the acidic active
agent may be retinoic acid, a haicarboxylic acid, such as trichloroacetic acid, an
acidic antioxidant, such as ascorbic acid (vitamin C), a mineral acid, phytic acid,
lysophosphatidic acid, and the like. Some acidic anti-acne actives, for example,
can include salicylic acid, derivatives of salicylic acid, such as 5-octanoylsalicylic
acid, retinoic acid, and its derivatives, and benzoic acid.
[0233] A discussion of the use and formulation of active skin treatment
compositions is in COSMETICS & TOILETRIES, C&T ingredient Resource
Series, "AHAs & Celulite Products How They Work", published 1995, and "Cosmeceuticals", published 1998, both available from Allured Publishing Corporation, incorporated herein by reference. Compositions containing alpha-amino acids acidified with ascorbic acid are described in U.S. No. 6,197,317 B1, and a commercial cosmeceutical preparation utilizing these acids in an anti-aging, skin care regimen is sold under the tradename, AFAs, by exCel Cosmeceuticals (Bioomfield Hills, MI). The term "AFA", as described in the supplier's trade literature, was coined by the developer to describe the amino acid/vitamin C combination as Amino Fruit Acids and as the acronym for "Amino Acid Flaggrin based Antioxidants."

Health Care

[0234] Health care embodiments in which the instant polymers can be included are medical products, such as topical and non-topical pharmaceuticals, and devices. In the formulation of pharmaceuticals, a polymer embodiment of the invention can be employed as a thickener and/or lubricant in such products as syrups, creams, pomades, gels, pastes, ointments, tablets, gel capsules, purgative fluids (enemas, emetics, colonics, and the like), suppositories, antifungal foams, eye products (ophthalmic products, such as eye drops, artificial tears, glaucoma drug delivery drops, contact lens cleaner, and the like), ear products (wax softeners, wax removers, otitis drug delivery drops, and the like), nasal products (drops, ointments, sprays, and the like), and wound care (liquid bandages, wound dressings, antibiotic creams, ointments, and the like), without limitation thereto.

[0235] Other health care embodiments relate to foot care products, such as keratolytic corn and callous removers, foot soaks, medicated foot products such as antifungal athlete's foot ointments, gels, sprays, and the like, as well as antifungal, anti-yeast, and antibacterial creams, gels, sprays, and ointments.

[0236] In addition, the instant polymers can be included in topical, transdermal, and non-topical pharmaceutical applications, and devices as thickeners, spreading aids, suspending agents, and film formers in skin
protective sprays, creams, lotions, gels, and sticks for in the formulation of insect repellants, itch relief agents, antiseptic agents, disinfectants, sun blocks, sun screens, skin tightening and toning agents, and in wart removal compositions, and the like.

[0237] In another pharmaceutical aspect, the polymers of the invention can be employed in the manufacture of pharmaceutical dosage forms (e.g. tablets, caplets, capsules, and the like) for the controlled release and targeted delivery of active pharmacologically active ingredients and medicaments to the stomach and gut. They can be employed as pharmaceutical excipients such as binders, enteric coatings, film formers and controlled release agents. They can be used alone or in combination with other controlled release and/or enteric polymers known in the pharmaceutical arts.

[0238] If desired, the clarity and/or appearance of the personal care, home care, health care, and institutional and industrial care compositions of the invention can be adjusted. The clarity of the compositions may vary from substantially transparent with little visual haze where insoluble component additives such as beads, air bubbles, pearlizing agents, are clearly visible to visually opaque. Visually distinct, multiple phase compositions where one phase is clear and another phase is opaque are also envisioned. In one embodiment of the invention, a pattern comprising phases that are visually distinct from each other may be formed by mixing clear and opaque components. The visual distinction between each phase can be in color, texture, density, and the type of insoluble component or benefit agent contained therein. The specific pattern can be chosen from a wide variety of patterns, including, but not limited to striping, marbling, geometries, spirals, and combinations thereof. Compositions of this invention demonstrate excellent stability with time in suspending insoluble components and/or benefit agents and stabilizing the visually distinct phases. Multiple-phase compositions are disclosed in U.S. Published Patent Application Nos. 2006/0079417, 2006/0079418, 2006/0079419, 2006/0079420, 2006/0079421, 2006/0079422, 2007/0009463, 2007/0072781, 2007/0280976, and 2008/0317698 to the Proctor and Gamble Company, which are herein
incorporated by reference. The acrylic copolymers of the invention are suitable to provide phase stability to the multi-phase compositions disclosed therein.

[0239] This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Methods
Viscosity

[0240] Brookfield rotating spindle method (all viscosity measurements reported herein are conducted by the Brookfield method whether mentioned or not): The viscosity measurements are calculated in mPa-s, employing a Brookfield rotating spindle viscometer, Model RVT (Brookfield Engineering Laboratories, Inc.), at about 20 revolutions per minute (rpm), at ambient room temperature of about 20 to 25°C (hereafter referred to as viscosity). Spindle sizes are selected in accordance with the standard operating recommendations from the manufacturer. Generally, spindle sizes are selected as follows:

<table>
<thead>
<tr>
<th>Spindle Size No.</th>
<th>Viscosity Range (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 - 50</td>
</tr>
<tr>
<td>2</td>
<td>500 - 1,000</td>
</tr>
<tr>
<td>3</td>
<td>1,000 - 5,000</td>
</tr>
<tr>
<td>4</td>
<td>5,000 - 10,000</td>
</tr>
<tr>
<td>5</td>
<td>10,000 - 20,000</td>
</tr>
<tr>
<td>6</td>
<td>20,000 - 50,000</td>
</tr>
<tr>
<td>7</td>
<td>&gt;50,000</td>
</tr>
</tbody>
</table>

[0241] The spindle size recommendations are for illustrative purposes only. The artisan of ordinary skill in the art will select a spindle size appropriate for the system to be measured.

Yield Value

[0242] Yield Value, also referred to as Yield Stress, is defined as the initial resistance to flow under stress. It is measured by the Brookfield Yield Value
(BYV) Extrapolation Method using a Brookfield viscometer (Model RVT) at ambient room temperature of about 20 to 25°C. The Brookfield viscometer is used to measure the torque necessary to rotate a spindle through a liquid sample at speeds of 0.5 to 100 rpm. Multiplying the torque reading by the appropriate constant for the spindle and speed gives the apparent viscosity. Yield Value is an extrapolation of measured values to a shear rate of zero. The BYV is calculated by the following equation:

\[ \text{BYV, dyn/cm}^2 = \frac{\eta_1 - \eta_2}{100} \]

where \( \eta_1 \) and \( \eta_2 \) are apparent viscosities obtained at two different spindle speeds (0.5 rpm and 1.0 rpm, respectively). These techniques and the usefulness of the Yield Value measurement are explained in Technical Data Sheet Number 244 (Revision: 5/98) from Noveon Consumer Specialties of Lubrizol Advanced Materials, inc., herein incorporated by reference.

Clarity

The clarity (turbidity) of a composition is determined in Nephelometric Turbidity Units (NTU) employing a nephelometric turbidity meter (Mircro 130 Turbidimeter, HF Scientific, inc.) at ambient room temperature of about 20 to 25°C. Distilled water (NTU = 0) is utilized as a standard. Six dram screw cap vials (70 mm x 25 mm) are filled almost to the top with test sample and centrifuged at 100 rpm until all bubbles are removed. Upon centhfugation, each sample vial is wiped with tissue paper to remove any smudges before placement in the turbidity meter. The sample is placed in the turbidity meter and a reading is taken. Once the reading stabilizes the NTU value is recorded. The vial is given one-quarter turn and another reading is taken and recorded. This is repeated until four readings are taken. The lowest of the four readings is reported as the turbidity value. Compositions having an NTU value of about 50 or greater were judged hazy or turbid.
Suspension Stability Test

Suspension Testing Procedure: The ability of a polymer system to suspend active and/or aesthetically pleasing insoluble oily and particulate materials is important from the standpoint of product efficacy and appeal. A six dram vial (approximately 70 mm high x 25 mm in diameter) is filled to the 50 mm point with a bath gel test formulation. Each sample vial is centrifuged to remove any trapped air bubbles contained in the formulation. Cosmetic beads (e.g., Lipopearl™ gelatin capsules; average diameter 500-3000 microns) are weighed into the centrifuged sample (1.0 wt.% based on the weight of the total composition) and stirred gently with a wooden stick until they are uniformly dispersed throughout the bath gel sample. The position of approximately 10 of the beads within each sample vial is noted by drawing a circle around the bead with black marker pen on the outer glass surface of the vial and photographed to establish the initial position of the beads within the gel. The vials are placed in a 45°C oven to age for a 12 week period. The bead suspension properties of each sample is monitored on a daily basis. The suspension results are visually ranked using a scale of 3 to 0 where: 3 indicates no noticeable settling/rise relative to the initial bead position in the gel; 2 indicates slight settling/rise or less than approximately ¼ drop/rise in distance relative to the initial bead position in the gel; 1 indicates greater than ¼ drop/rise to ½ drop/rise in distance relative to the initial position in the bath gel; and 0 indicates greater than ½ drop/rise in distance relative to the initial position of the bead in the bath gel. A rating of 0 or 1 designates that a sample failed, and a rating of 2 or 3 indicates that the sample passed.

Abbreviation and Trade Name ingredient List

The following ingredients are utilized in the examples of the present invention:
### Monomers

<table>
<thead>
<tr>
<th>AA</th>
<th>Acrylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACE</td>
<td>ACE™ Hydroxy! acry!ate monomer is the reaction product of acrylic acid with Cardura™ . Cardura is the glycidyl ester of VERSAT!C™ acid 10, a highly branched saturated carboxylic acid containing 10 carbon atoms.</td>
</tr>
<tr>
<td>nBA</td>
<td>n-Butyl Acrylate</td>
</tr>
<tr>
<td>tBAM</td>
<td>t-butyl acrylamide</td>
</tr>
<tr>
<td>EA</td>
<td>Ethyl Acrylate</td>
</tr>
<tr>
<td>2-EHA</td>
<td>2-Ethylhexyl Acrylate</td>
</tr>
<tr>
<td>HEMA</td>
<td>Hydroxyethyl Methacrylate</td>
</tr>
<tr>
<td>MA</td>
<td>Methyl Acrylate</td>
</tr>
<tr>
<td>MAA</td>
<td>Methacrylic Acid</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl Methacrylate</td>
</tr>
<tr>
<td>NVP</td>
<td>N-vinyl pyrrolidone</td>
</tr>
<tr>
<td>STY</td>
<td>Styrene</td>
</tr>
<tr>
<td>TMPDAE</td>
<td>Trimethylolpropane Diallyl ether (crosslinker)</td>
</tr>
<tr>
<td>TMPTA</td>
<td>Trimethylolpropane Triacrylate (crosslinker)</td>
</tr>
<tr>
<td>VND</td>
<td>Vinly neodecanoate</td>
</tr>
</tbody>
</table>

### Components

<table>
<thead>
<tr>
<th>Chembetaine™ CAD</th>
<th>Cocamidopropyl Betaine (amphoteric surfactant), Lubrizo Advanced Materials, Inc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chembetaine™ CGF</td>
<td>Cocamidopropyl Betaine (amphoteric surfactant - glycerin free), Lubrizo Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Chembetaine™ LEG</td>
<td>INCI Name: Lauramidopropyl Betaine (amphoteric surfactant), Lubrizo Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Chemonic™ SI-7</td>
<td>PEG-7 Glyceril Soyate (non-ionic surfactant), Lubrizo Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Chemoxy™ SFB-10SK</td>
<td>INCI Name: Disodium Laureth Sulfosuccinate (and) Sodium Cocoyl Isethionate (and) Cocamidopropyl Betaine (sulfate and amide free surfactant blend), Lubrizo Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Chemoxide™ CAW</td>
<td>INCI Name: Cocamidopropylamine Oxide (amine oxide surfactant), Lubrizo Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Dow Corning® 2-8194 Silicone</td>
<td>INCI Name: Amodimethicone and Trideceth-2 and Cetrimonium Chloride (microemulsion of amine functional silicone polymers), Dow Corning</td>
</tr>
<tr>
<td>Florabeads™ Gypsy Rose</td>
<td>INCI Name: Jojoba Esters (exfoliating agent pigmented with Red 30 (and) Talc), International Flora Technologies, Ltd.</td>
</tr>
<tr>
<td>Florabeads™ Sonora Sand</td>
<td>INCI Name: Jojoba Esters (exfoliating agent pigmented with Iron oxides, Red 30 (and) Talc, TiO₂, Yellow 5 Lake), International Flora Technologies, Ltd.</td>
</tr>
<tr>
<td>Florasun® 90</td>
<td>INCI Name: Helianthus Annuus (sunflower oil), International Flora Technologies, Ltd.</td>
</tr>
<tr>
<td>Geogard® Ultra</td>
<td>INCI Name: Gluconoisoitone (and) Sodium Benzoate, (preservative), Lanza Inc</td>
</tr>
<tr>
<td>Glydant® Pius</td>
<td>Blend of 1,3-dimethyl-5,5-dimethyl hydantoin and iodopropynyl butylcarbamate, (preservative), Lonza Inc</td>
</tr>
<tr>
<td>Glueam™ E-10</td>
<td>INCI Name: Methyl Gluceth-10 (non-ionic surfactant/humectant), Lubrizo Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Jaguar Excel</td>
<td>INCI Name: Guar Hydroxypropyltrimonium Chloride (quaternized guar gum), Rhodia Inc.</td>
</tr>
<tr>
<td>Lebermuth No. 50-8001 -30</td>
<td>Fragrance Oil (apple fresh green), The Lebermuth Company, Inc.</td>
</tr>
<tr>
<td>Name</td>
<td>Description</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Lebermuth No. 90-3000-62</td>
<td>Fragrance Oil (tangerine grapefruit), The Lebermuth Company, Inc.</td>
</tr>
<tr>
<td>Lipopearl™ 0091 Beads</td>
<td>Pigmented Cosmetic Beads of Gelatin and Cellulose Gum containing Tridecyl Stearate, Tridecyl Trimellitate, Chromium Hydroxide Green, Mica, Titanium Dioxide, Tocopheryl Acetate, and Vitamin E, Lipo Technologies Inc.</td>
</tr>
<tr>
<td>Lipopearl™ 0293 Beads</td>
<td>Pigmented Cosmetic Beads of Gelatin and Cellulose Gum containing Tridecyl Stearate, Tridecyl Trimellitate, Neopentyl Glycol, Mica, Titanium Dioxide, Tocopheryl Acetate, and Vitamin E, Lipo Technologies Inc.</td>
</tr>
<tr>
<td>Liposphere™ 0031</td>
<td>Pigmented Cosmetic Beads containing personal care benefit agents (Dimethicone, Neopentyl Glycol), Lipo Technologies Inc.</td>
</tr>
<tr>
<td>Merquat® Plus</td>
<td>Polyquaternium-39 (cationic conditioning polymer, a terpolymer of acrylic acid, diethyl dimethyl ammonium chloride and acrylamide), Naico Company</td>
</tr>
<tr>
<td>Neoione® 950</td>
<td>Methylisothiazolone (preservative), Rohm and Haas Company</td>
</tr>
<tr>
<td>N-Hance® 3000</td>
<td>INCI Name: Guar Hydroxypropyltrimonium Chloride (quaternized guar gum), Ashland Inc. (Ashland Aquafine Functional Ingredients)</td>
</tr>
<tr>
<td>Phenonip™</td>
<td>Blend of phenoxyethanol, methylparaben, ethylparaben, propylparaben, butylparaben and isobutylparaben, (antibacterial), Clariant Corporation-Nipa Laboratories</td>
</tr>
<tr>
<td>Sulfocem™ ALS</td>
<td>Ammonium Lauryle Sulfate (anionic surfactant), Lubrizol Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Sulfocem™ AOS</td>
<td>Sodium C14-15 Olefin Sulfonate (anionic surfactant), Lubrizol Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Sulfocem™ ALS-K</td>
<td>Ammonium Lauryle Sulfate (anionic surfactant preserved with Kathon® CG preservative from Rohm and Haas Company), Lubrizol Advanced Materials, Inc.</td>
</tr>
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<td>Sulfocem™ EA-3</td>
<td>Ammonium Lauryle Ether Sulfate - 3 moles of ethoxylation (anionic surfactant), Lubrizol Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Sulfocem™ ES-2 CVVK</td>
<td>Sodium Lauryle Ether Sulfate - 2 moles of ethoxylation (anionic surfactant preserved with Kathon® CG preservative from Rohm and Haas Company), Lubrizol Advanced Materials, Inc.</td>
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<td>Sulfocem™ ES-2K</td>
<td>Sodium Lauryle Ether Sulfate - 2 moles of ethoxylation (anionic surfactant preserved with Kathon® CG preservative from Rohm and Haas Company), Lubrizol Advanced Materials, Inc.</td>
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<td>Sulfocem™ ES-70</td>
<td>Sodium Lauryle Ether Sulfate - 2 moles of ethoxylation (anionic surfactant), Lubrizol Advanced Materials, Inc.</td>
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<td>Sulfocem™ SLS</td>
<td>Sodium Lauryle Sulfate (anionic surfactant), Lubrizol Advanced Materials, Inc.</td>
</tr>
<tr>
<td>Tween® 20</td>
<td>Polysorbate 20 (solubilizer), Croda Inc</td>
</tr>
<tr>
<td>Unispheres NTL-2312</td>
<td>INCI Name: Mannitol (and) Cellulose (and) Hydroxypropyl Methylcellulose (pigmented with chromium hydroxide green and loaded with vitamin E), Induchem AG</td>
</tr>
<tr>
<td>Versene™ 220</td>
<td>Tetrasodium Ethylenediaminetetraacetate Tetrahydrate (chelating agent), Dow Chemical</td>
</tr>
<tr>
<td>Zema™ Propanediol</td>
<td>Bio-based 1,3-propanediol, DuPont, Tate &amp; Lyle</td>
</tr>
</tbody>
</table>

**Example 1**

[0246] Into an agitator equipped first reactor containing 112.0 grams of deionized water (D.L) and 13.33 grams of sodium lauryl sulfate (30% active in
water wt./wt.), 260.8 grams of ethyl acrylate, 138 grams of methacrylic acid, 0.6 grams of trimethylolpropane triacrylate, and 0.2 grams of trimethylolpropane diallyl ether are added under nitrogen atmosphere and mixed at 900 rpm to form a monomer emulsion. To an agitator equipped second reactor are added 620 grams of deionized water and 1.27 grams of sodium lauryl sulfate (30% active in water wt./wt.). The contents of the second reactor are heated with mixing agitation (300 rpm) under a nitrogen atmosphere. When the contents of the second reactor reaches a temperature of approximately 90°C, 10.0 grams of an ammonium persulfate solution (2.0% aqueous solution wt./wt.) is injected into the heated surfactant solution. The monomer emulsion from the first reactor is gradually metered at a feed rate of 3.67 g/min. into the second reactor over a period of 150 minutes at a reaction temperature maintained at approximately 90°C. With the emulsion monomer feed, 0.3% ammonium persulfate solution (aqueous solution wt./wt.) is simultaneously metered into the reaction mixture in the second reactor. After completion of the monomer addition the resulting reaction mixture is held at a temperature of about 90°C for an additional two and half hours to complete the polymerization. The resulting polymer emulsion product is cooled to room temperature, discharged from the reactor and recovered. The monomer components and amounts utilized are set forth in Table 1.

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>EA</th>
<th>MAA</th>
<th>TMPTA</th>
<th>TMPDAE</th>
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<tr>
<td>1</td>
<td>65.30</td>
<td>34.5</td>
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</table>

Examples 2 to 15

[0247] The following crosslinked acrylic copolymers are polymerized in accordance with the procedure and conditions set forth in Example 1 from the monomer components set forth in Table 2. Polymer C-1 is polymerized as set forth in Example 1 except that only one crosslinking monomer is employed in the polymerization reaction.
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<tr>
<th>EA</th>
<th>MAA</th>
<th>AA</th>
<th>STY</th>
<th>ACE</th>
<th>h-BA</th>
<th>VND</th>
<th>t-BAM</th>
<th>MA</th>
<th>NVP</th>
<th>HEMA</th>
<th>MMA</th>
<th>TMPTA</th>
<th>TMPDAE</th>
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<td></td>
<td></td>
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<td>0.3</td>
</tr>
</tbody>
</table>

Table 2

Monomer Components (wt.%)
Example 18

[0248] The polymer of Example 1 and C-1 are separately formulated into a
dear body wash cleansing composition comprising a blend of an anionic and
amphoteric surfactant. The formulation components are set forth in Table 3.
Each component (except component nos. 12, 13, and 14) is added to a mixing
vessel in the order listed in the table. Components 12, 13, and 14 are
formulated into the body wash samples during the testing procedure described
below. The solubiizer (component 8) and fragrance (component 9) are
premixed before addition to the vessel. The components are blended under mild
agitation until a homogeneous body wash master batch formulation is obtained.

Table 3
(Clear Body Wash Formulation)

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (wt. %)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  D.I. Water</td>
<td>q.s. to 100</td>
<td>Diluent</td>
</tr>
<tr>
<td>2  Polymer (30% active polymer solids)</td>
<td>8.00</td>
<td>Rheology Modifier</td>
</tr>
<tr>
<td>3  Sulfacem™ ES-2 CWK Surfactant (26% active)</td>
<td>40.00</td>
<td>Detersive Surfactant</td>
</tr>
<tr>
<td>4  Chembetaine™ CAD Surfactant (35% active)</td>
<td>6.70</td>
<td>Amphoteric Surfactant</td>
</tr>
<tr>
<td>5  Merquat™ Plus Polymer (10% active)</td>
<td>2.10</td>
<td>Conditioning Polymer</td>
</tr>
<tr>
<td>6  Tetrasodium EDTA</td>
<td>0.05</td>
<td>Chelating Agent</td>
</tr>
<tr>
<td>7  Phenonip®</td>
<td>0.50</td>
<td>Antibacterial</td>
</tr>
<tr>
<td>8  Tween 20</td>
<td>0.50</td>
<td>Fragrance Solubilizer</td>
</tr>
<tr>
<td>9  Fragrance</td>
<td>0.50</td>
<td>Fragrance</td>
</tr>
<tr>
<td>10 FD&amp;C Blue No. 1</td>
<td>1.85</td>
<td>Dye</td>
</tr>
<tr>
<td>11 FD&amp;C Yellow No. 6</td>
<td>0.85</td>
<td>Dye</td>
</tr>
<tr>
<td>12 NaOH (18% aqueous wt./wt.)</td>
<td>q.s. to pH</td>
<td>pH adjusting agent</td>
</tr>
<tr>
<td>13 Citric Acid (50% aqueous wt./wt.)</td>
<td>q.s. to pH</td>
<td>pH adjusting agent</td>
</tr>
<tr>
<td>14 Lipopearl™ 0293 Beads</td>
<td>1.0</td>
<td>Vitamin E Delivery Beads</td>
</tr>
</tbody>
</table>

[0249] The pH of each of the body wash master batch formulations is
increased with NaOH (component 12) to a pH value of approximately 6.4, and
then reduced (via back-acid addition) with citric acid (component 13) to a pH
value of approximately 4.5. At each pH value, 100 g and 20 g aliquots of each
master batch body wash formulation is transferred into 4 oz. jars and 6 dram
vials, respectively, and centrifuged to remove any entrained air bubbles. The
sample jars and vials containing tine centrifuged formulations are capped and held for 24 hrs. after which rheology and clarity property measurements are made. Viscosity and yield value measurements are carried out on the 100 g samples and clarify (turbidity) measurements are completed on the 20 g samples. The test formulation samples in the 6 dram vials are evaluated for suspension stability in accordance with the suspension stability test protocol set forth above. The data are presented in Table 4.

Table 4

<table>
<thead>
<tr>
<th>Polymer No. (Example No.)</th>
<th>Ex. C-1</th>
<th>Ex. 1</th>
<th>Ex. C-1</th>
<th>Ex. 1</th>
</tr>
</thead>
<tbody>
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<td>pH</td>
<td>6.44</td>
<td>6.41</td>
<td>4.50</td>
<td>4.57</td>
</tr>
<tr>
<td>Viscosity (mPa·s)</td>
<td>3.100</td>
<td>3.710</td>
<td>8.050</td>
<td>9.550</td>
</tr>
<tr>
<td>Yield Value (dynes/cm²)</td>
<td>94</td>
<td>105</td>
<td>412</td>
<td>500</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>4.31</td>
<td>7.77</td>
<td>90.5</td>
<td>67.6</td>
</tr>
<tr>
<td>Bead Suspension</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Example 17

[0250] The polymers of Examples 3 to 15 are each formulated into a clear bath gel cleansing composition comprising a sodium based anionic surfactant and an amphoteric surfactant. A food grade preservative, sodium benzoate, is added in place of alkyl parabens. The formulation components are set forth in Table 5. Components 1 through 11 are added to a vessel with mixing in the order listed in the table. Components 12, 13, and 14 are added to the bath gel formulations during the testing procedure described below. The fragrance (component 7) and solubilizer (component 8) are premixed before addition to the vessel. The components are blended under gentle agitation until a homogeneous bath gel master batch mixture is obtained.
The pH of each master batch formulation is adjusted to 6.5 with NaOH (component 11), and then reduced with citric acid (component 12) to an interim pH value of 5.0. Sodium benzoate (component 13) is added to each sample before additional citric acid is added to achieve the final pH value of 4.0.

Example 18

The polymers of Examples 1, 2, and 15 are separately formulated into a clear conditioning shampoo composition comprising an ammonium based anionic surfactant, an amphoteric surfactant and a subsequently added pearizing agent. The formulation is prepared from the components listed in Table 6.
Components 1 through 4 are added to a vessel in the order listed in the table and mixed under slow agitation until homogeneous. The pH of each formulation is adjusted to approximately 6.5 with NaOH (component 8), and then components 5 to 7 are added to each batch and homogeneously mixed. The pH of each batch is then sequentially reduced with citric acid (component 9) to pH values of 5.5. An alkyl paraben (component 10) is added to each sample at pH 5.5 before additional citric acid is added to achieve a final pH value of 5.0.

Example 19

The polymers of Examples 1 through 15 are formulated into a pearlized conditioning shampoo composition comprising a cationic polymer conditioning agent and a silicone conditioning agent. The formulation is prepared from the components listed in Table 7.
The components are formulated as set forth in Example 18, except that a cationic conditioning polymer (component 5) is utilized in addition to the silicone conditioning agent (component 7). The pH of the polymer formulations are immediately adjusted with NaOH (component 9) to 6.5, and then downward with citric acid (component 10) to 5.5 where the preservative is added. The pH is then adjusted to a final value of 5.0 with addition citric acid.

Example 20

A soap based shower gel composition is formulated from the components are set forth in the Table 8.
Table 8
(Soap Based Shower Gel)

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Deionized Water</td>
<td>q.s. to 100</td>
<td>Diluent</td>
</tr>
<tr>
<td>2 Potassium Hydroxide (87.5% aqueous wt./wt.)</td>
<td>6.60</td>
<td>Neutralizer</td>
</tr>
<tr>
<td>Part B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Deionized Water</td>
<td>q.s. to 100</td>
<td>Diluent</td>
</tr>
<tr>
<td>4 Glycerin</td>
<td>6.00</td>
<td>Humectant</td>
</tr>
<tr>
<td>5 Lauric Acid</td>
<td>12.00</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td>6 Myristic Acid (1499)</td>
<td>6.50</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td>7 Palmitic Acid (1898)</td>
<td>1.50</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td>8 Polymer No. 2 (30% active polymer solids)</td>
<td>7.0</td>
<td>Rheology Modifier</td>
</tr>
<tr>
<td>Part C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 Mineral Oil, Type #26 (24-28 mm2/s)</td>
<td>10.00</td>
<td>Emollient</td>
</tr>
<tr>
<td>10 Propylene Glycol</td>
<td>2.00</td>
<td>Humectant</td>
</tr>
<tr>
<td>11 Neolone® 950</td>
<td>0.05</td>
<td>Preservative</td>
</tr>
</tbody>
</table>

Part A is prepared by dissolving potassium hydroxide in D.I. wafer and heating the composition to 80°C. Part B is separately prepared by adding glycerin and the fatty acids (components 5, 6, and 7) to D.L water and mixing until the fatty acids fully melt. Once the fatty acids melt and are homogeneously mixed, the polymer of Example 1 is added to the mixture. Part A is slowly added to Part B under agitation while the temperature is maintained at 80°C. The Part AB composition is mixed for 30 to 60 minutes. Upon attaining a homogeneous mixture, the Part AB composition is allowed to cool at ambient room temperature (20-21°C). Mineral oil (component 9) is added to the AB composition at a temperature of about 60-70°C. Upon further cooling to 40°C, components 10 and 11 are added and uniformly mixed into the formulation. The formulation is allowed to cool under gentle agitation until ambient room temperature is reached.

While this example exemplifies the in situ saponification of the fatty acid(s) with a base, a pre-neutralized fatty acid salt can also be employed in the formulation of the cleansing formulation. In addition, high clarity soap based shower gel can also be made without the mineral oil component.
Example 21

[0259] A pear!ized soap/surfactant blend based shower gel composition is formulated from the components are set forth in the Table 9.

Table 9
(Soap/Surfactant Blend Based Shower Gel)

<table>
<thead>
<tr>
<th>Part A</th>
<th>Component</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Deionized Water</td>
<td>q.s. to 100</td>
<td>Diluent</td>
</tr>
<tr>
<td>2</td>
<td>Potassium Hydroxide (91.5% aqueous wt./wt.)</td>
<td>4.35</td>
<td>Neutralizer</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part B</th>
<th>Component</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Deionized Water</td>
<td>25.42</td>
<td>Diluent</td>
</tr>
<tr>
<td>4</td>
<td>Glycerin</td>
<td>8.00</td>
<td>Humectant</td>
</tr>
<tr>
<td>5</td>
<td>Lauric Acid</td>
<td>7.20</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td>6</td>
<td>Myristic Acid</td>
<td>2.40</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td>7</td>
<td>Palmitic Acid</td>
<td>2.40</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td>8</td>
<td>Polymer No. 2 (30% active polymer solids)</td>
<td>7.0</td>
<td>Rheology Modifier</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part C</th>
<th>Component</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Sulfochem ES-2K (26.1% active)</td>
<td>15.00</td>
<td>Detersive Surfactant</td>
</tr>
<tr>
<td>10</td>
<td>Chembetaine™ CAD (35% active)</td>
<td>12.88</td>
<td>Amphoteric Surfactant</td>
</tr>
<tr>
<td>11</td>
<td>Neolone® 950</td>
<td>0.05</td>
<td>Preservative</td>
</tr>
<tr>
<td>12</td>
<td>Liposphere™ 0031 Beads</td>
<td>0.15</td>
<td>Cosmetic Bead</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Containing Moisturizer</td>
</tr>
<tr>
<td>13</td>
<td>Lipopearl™ 0091 Beads</td>
<td>0.15</td>
<td>Cosmetic Bead</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Containing Moisturizer</td>
</tr>
<tr>
<td>14</td>
<td>Citric Acid (50% aqueous wt./wt.)</td>
<td>0.5</td>
<td>pH Adjusting</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Agent</td>
</tr>
</tbody>
</table>

[0260] Part A is prepared by dissolving potassium hydroxide in D.I. water and heating the composition to SOX. Part B is separately prepared by adding glycerin and polymer no. 2 to D.I. water under mixing. The fatty acids (components 5, 8, and 7) are added to Part B, which is heated to 80°C and mixed until the fatty acids fully melt. Once the fatty acids melt and are homogeneously mixed, Part A is slowly added to Part B under agitation while maintaining the temperature at 80X. The Part AB composition is mixed for 30 to 60 minutes. Upon attaining a homogeneous mixture, the Part AB composition is allowed to cool at ambient room temperature (20-21 °C). The surfactant package (components 9 and 10) is added in the order listed to the AB
composiiion under agitation and mixed until uniform. Upon further cooling to 40°C, components 11 through 14 are added in order and uniformly mixed into the formulation. The formulation is allowed to cool under gentle agitation until ambient room temperature is reached.

Example 22

[0281] A high oil containing moisturizing body wash containing a food preservative is formulated from the components and procedure set forth in Table 10 below.

<table>
<thead>
<tr>
<th>Table 10</th>
<th>(Moisturizing Body Wash)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component</strong></td>
<td>Amount (wt.%)</td>
</tr>
<tr>
<td>Part A</td>
<td></td>
</tr>
<tr>
<td>1 Deionized Water</td>
<td>q.s. to 100</td>
</tr>
<tr>
<td>2 Versene™ 220 (Tetrasodium EDTA)</td>
<td>0.05</td>
</tr>
<tr>
<td>3 Sufochem™ ALS Surfactant (30% active)</td>
<td>15.00</td>
</tr>
<tr>
<td>4 Sufochem™* EA-3 (27% active)</td>
<td>25.00</td>
</tr>
<tr>
<td>Part B</td>
<td></td>
</tr>
<tr>
<td>5 Florasun® 90 Sunflower Oil</td>
<td>18.00</td>
</tr>
<tr>
<td>6 Polymer Ex. No. 2 (30% active polymer solids)</td>
<td>6.60</td>
</tr>
<tr>
<td>Part C</td>
<td></td>
</tr>
<tr>
<td>7 N-Hance® 3000</td>
<td>0.30</td>
</tr>
<tr>
<td>8 Glycerine 99.7% USP</td>
<td>5.00</td>
</tr>
<tr>
<td>Part D</td>
<td></td>
</tr>
<tr>
<td>9 NaOH (18% aqueous wt./wt.)</td>
<td>1.50</td>
</tr>
<tr>
<td>Part E</td>
<td></td>
</tr>
<tr>
<td>10 Sodium Benzoate</td>
<td>0.50</td>
</tr>
<tr>
<td>11 Citric Acid (100%)</td>
<td>0.25</td>
</tr>
<tr>
<td>12 Chambetaine™ CGF (35% active)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

[0262] The body wash is formulated in accordance with the following procedure:

1) Combine Part A components and mix until uniform. Adjust mixing speed to keep foaming to a minimum;

2) Add Part B components in the listed order to Part A with mixing and mix until uniform;

3) In a separate vessel, pre-mix Part C components and add to Part AB and mix until uniform;
4) Add Part D (NaOH) to Part ABC and increase mixing speed as needed to maintain a good vortex; and

5) Add Part E components one at a time in the order listed to Part ABCD with good mixing in between additions. Increase mixing speed as needed to maintain mixing vortex.

Example 23

A sulfate free bath gel is formulated from the components listed in Table 11 below. The polymer of Examples 1 and 2 are separately formulated as the rheology modifying component.

Table 11
(Sulfate Free Bath Gel)

| Components | Amount (wt.%) | Function
|------------|--------------|----------
| 1 Deionized Water | q.s. to 100 | Diluent
| 2 Polymer of Examples 1 and 2 (30% active polymer solids) | 8.0 | Rheology Modifier
| 3 NaOH (18% aqueous wt./wt.) | q.s. to pH | pH Adjusting Agent
| 4 Chemorly™ SFB-10SK Surfactant Blend (32% active) | 30.0 | Mild Detertive Surfactant Blend (sulfate free)
| 5 Cocamidopropyl Betaine (38 % active) | 8.0 | Amphoteric Detertive Surfactant
| 6 Sodium Benzoate | 0.5 | Preservative
| 7 Citric Acid (50% aqueous wt./wt.) | q.s. to pH | pH Adjusting Agent

The test polymer (component 2) is added to D.I. water (component 1) in a glass beaker and mixed gently. The pH of the formulation is adjusted with NaOH (component 3) to 6.5 and then the surfactants (component 4) and (component 5) are added to the contents of the beaker and mixed until homogeneous. The pH of the bath gel contents of the beaker is adjusted to 5.5 with citric acid (component 7). The pH of the bath gel in the beaker is again adjusted with citric acid (component 7) to 5.0. The recipe amount of sodium benzoate is added to the bath gel in the beaker (previously adjusted to pH 5.0), and a final pH adjustment is made with citric acid (component 7) to achieve a pH of 4.0.
Example 24

[0265] This example demonstrates the formulation of a facial scrub composition containing the polymer of Example 1. The formulation components are listed in Table 12.

Table 12
(Facial Scrub)

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Deionized Water</td>
<td>q.s. to 100</td>
<td>Diluent</td>
</tr>
<tr>
<td>2 Disodium EDTA</td>
<td>0.05</td>
<td>Chelating Agent</td>
</tr>
<tr>
<td>3 Polymer of Example 1 (30% active polymer solids)</td>
<td>6.72</td>
<td>Rheology Modifier</td>
</tr>
<tr>
<td>4 Sulfocem™ AOS Surfactant (40% active)</td>
<td>7.575</td>
<td>Detergent Surfactant</td>
</tr>
<tr>
<td>5 NaOH (18% aqueous wt/wt.)</td>
<td>q.s. to pH</td>
<td>pH Adjusting Agent</td>
</tr>
<tr>
<td>6 Chemoryl™ SFB-10SK Surfactant (32% Active)</td>
<td>31.70</td>
<td>Amphoteric Surfactant</td>
</tr>
<tr>
<td>7 Tween 20</td>
<td>1.0</td>
<td>Solubilizer</td>
</tr>
<tr>
<td>8 Lebermuth Fragrance Oil (No. 90-3000-62)</td>
<td>0.45</td>
<td>Fragrance</td>
</tr>
<tr>
<td>9 Glucam™ E-10 Methyl Glucoside</td>
<td>0.50</td>
<td>Non-ionic Surfactant/Humectant</td>
</tr>
<tr>
<td>10 Geogard™ Ultra (sodium benzoate)</td>
<td>1.00</td>
<td>Preservative</td>
</tr>
<tr>
<td>11 Chembetaine LEC (35% active)</td>
<td>8.00</td>
<td>Amphoteric Surfactant</td>
</tr>
<tr>
<td>12 Citric Acid (50% aqueous wt/wt.)</td>
<td>q.s. to pH</td>
<td>pH Adjusting Agent</td>
</tr>
<tr>
<td>13 Florabeads™ Jojoba 28/60 Sonora Sand</td>
<td>0.10</td>
<td>Exfoliating Agent</td>
</tr>
<tr>
<td>14 Florabeads™ Jojoba 28/60 Gypsy Rose</td>
<td>0.10</td>
<td>Exfoliating Agent</td>
</tr>
</tbody>
</table>

[0266] The facial scrub is formulated in accordance with the following procedure:

1) With gentle mixing add disodium EDTA (component 2) to D.L water (component 1) warmed to 30 to 40°C until the disodium EDTA is fully dissolved;
2) Add polymer (component 3) to the mixture until fully dispersed and then add the detergentsurfactant (component 4) and continue mixing until homogeneous;
3) Under continuous stirring, neutralize the formulation with NaOH (component 5) to raise the pH of the formulation in the range of 6.6 to 8.8;
4) Add the amphoteric surfactant (component 8) and mix until homogeneous;
5) In a separate container pre-blend Polysorbate 20 (component 7) and the fragrance oil (component 8) and add the blend to the formulation and mix until homogeneous;
6) Add the non-ionic surfactant/humectant, the preservative, and the amphoteric surfactant (components 9, 10, and 11, respectively) in the order listed and mix until homogeneous;

7) Adjust the pH to 5.3 to 5.4 with citric acid (component 12) and add the exfoliating agents (components 13 and 14) and mix until homogeneous.

Example 25

[0267] This example illustrates the formulation of a facial scrub containing the cosmeceutical agent, salicylic acid. The formulation components are listed in Table 13.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Deionized Water</td>
<td>q.s. to 100</td>
<td>Diluent</td>
</tr>
<tr>
<td>2 Disodium EDTA</td>
<td>0.050</td>
<td>Chelating Agent</td>
</tr>
<tr>
<td>3 Polymer of Example 2 (30% active polymer solids)</td>
<td>6.72</td>
<td>Rheology Modifier</td>
</tr>
<tr>
<td>4 Sulfochem™ AOS Surfactant (40% active)</td>
<td>22.50</td>
<td>Detergent Surfactant</td>
</tr>
<tr>
<td>5 NaOH (18% aqueous wt./wt.)</td>
<td>q.s. to pH</td>
<td>pH Adjusting Agent</td>
</tr>
<tr>
<td>6 Chembetaine™ CAD Surfactant (35% active)</td>
<td>5.70</td>
<td>Amphoteric Surfactant</td>
</tr>
<tr>
<td>7 Lebermuth Fragrance Oil (No. 50-8001-30)</td>
<td>0.40</td>
<td>Fragrance</td>
</tr>
<tr>
<td>8 Deionized Water</td>
<td>12.53</td>
<td>Diluent</td>
</tr>
<tr>
<td>9 Zema™ propanediol</td>
<td>2.00</td>
<td>Diluent</td>
</tr>
<tr>
<td>10 Sulfochem™ AOS Surfactant (40% active)</td>
<td>7.50</td>
<td>Detergent Surfactant</td>
</tr>
<tr>
<td>11 Salicylic Acid</td>
<td>2.00</td>
<td>Cosmeceutical</td>
</tr>
<tr>
<td>12 Chembetaine™ CAD Surfactant (35% active)</td>
<td>5.70</td>
<td>Amphoteric Surfactant</td>
</tr>
<tr>
<td>13 Glucam™ E-10 Methyl Glucoside</td>
<td>0.50</td>
<td>Non-ionic Surfactant/Humectant</td>
</tr>
<tr>
<td>14 Geogard® Ultra (sodium benzoate)</td>
<td>1.00</td>
<td>Preservative</td>
</tr>
<tr>
<td>15 Citric Acid (50% aqueous wt./wt.)</td>
<td>q.s. to pH</td>
<td>pH Adjusting Agent</td>
</tr>
<tr>
<td>16 Unispheres™ NLT-2312 Cosmetic Beads</td>
<td>0.20</td>
<td>Cosmeceutical/Exfoliant</td>
</tr>
</tbody>
</table>

[0268] The facial scrub is formulated as follows:

1) With gentle mixing add disodium EDTA (component 2) to D.I. water (component 1) warmed to 30 to 40°C until the disodium EDTA is fully dissolved;

2) Add Polymer No. 2 (component 3) to the mixture until fully dispersed and then add the detersive surfactant (component 4) and continue mixing until homogeneous;
3) Under continuous stirring, neutralize the formulation with NaOH (component 5) to raise the pH of the formulation in the range of 6.8 to 6.8;
4) In a separate container pre-blend the amphoteric surfactant (component 8) and the fragrance oil (component 7) and add the pre-blend to the master batch formulation and mix until homogeneous;
5) In a separate vessel pre-blend D.I. water (component 8), propane diol (component 9), anionic surfactant (component 10), salicylic acid (component 11), amphoteric surfactant (component 12) and the non-ionic surfactant/humectant component 13) and mix until uniform;
8) Add the pre-blend to the master batch formulation and mix until homogeneous;
7) Add sodium benzoate (component 14) and adjust the pH to 4.0 to 4.4 with citric acid (component 15);
8) Add the exfoliating agent (component 16) and mix until homogeneous.

Example 28
[0269] The following example demonstrates a liquid dishwashing cleanser formulated with a polymer of the invention. The formulation components are set forth in Table 14.

**Table 14**
(Liquid Dishwashing Cleanser)

<table>
<thead>
<tr>
<th>Components</th>
<th>Amount (wt.%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D.I. Water</td>
<td>q.s. to 100</td>
</tr>
<tr>
<td>2</td>
<td>Polymer of Example 1 (30 wt.% active solids)</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>Sulfocem™ SLS Surfactant (30% active)</td>
<td>37.39</td>
</tr>
<tr>
<td>4</td>
<td>Sulfocem™ ES-70 Surfactant (70% active)</td>
<td>12.05</td>
</tr>
<tr>
<td>5</td>
<td>Chemoxide™ CAW Surfactant (30% active)</td>
<td>3.11</td>
</tr>
<tr>
<td>6</td>
<td>Geogard® Ultra (sodium benzoate)</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>NaOH (18% aqueous wt./wt.)</td>
<td>q.s. to pH</td>
</tr>
<tr>
<td>8</td>
<td>Citric Acid (50% aqueous wt./wt.)</td>
<td>q.s. to pH</td>
</tr>
</tbody>
</table>

[0270] The dish washing liquid is formulated as in accordance with the following procedure:
1) Into a beaker equipped with a magnetic stir bar, add the polymer (component 2) to D.I. water (component 1) and mix under slow agitation (200 rpm);

2) Add surfactants (components 3, 4, and 5) in order listed to the beaker and adjust stirring rate to avoid excessive foam generation;

3) Add preservative (component 8) and mix until uniform and homogeneous;

4) Adjust the pH of the composition with NaOH (component 7) and/or citric acid (component 8) to pH 5.5.
What Is Claimed Is:
1. A surfactant composition comprising:
   i) at least one surfactant selected from anionic, zwitterionic or amphoteric, cationic, or non-ionic surfactant, and combinations thereof;
   ii) a crosslinked acrylic copolymer polymerized from a monomer composition comprising:
      a) from about 10% to about 80% by weight of a first monomeric component selected from one or more ethylenically mono-unsaturated monomers containing at least one carboxylic acid group;
      b) from about 90% to about 15% by weight of a second ethylenically mono-unsaturated monomeric component selected from at least one linear or branched \( C_1 \) to \( C_5 \) hydroxyalkyl ester of (meth)acrylic acid, at least one \( C_1 \) to \( C_5 \) hydroxyalkyl ester of (meth)acrylic acid, and mixtures thereof;
      c) from about 0.01% to about 5% by weight of crosslinking component selected from a first polyunsaturated crosslinking monomer and a second polyunsaturated crosslinking monomer, wherein said first crosslinking monomer is selected from at least one polyfunctional acrylate having at least two polymerizable ethylenically unsaturated double bonds and said second crosslinking monomer is selected from at least one polyalkenyl polyether having at least two polymerizable ethylenically unsaturated double bonds; and optionally
      d) from about 1% to about 35% by weight of at least one other ethylenically mono-unsaturated monomer component different from monomeric components a) and b), wherein all monomer weight percentages are based on the weight of the total monomer composition;

2. A surfactant composition of claim 1, wherein said first crosslinking monomer is selected from the esterification product of (meth)acrylic acid and a linear and branched polyol having 2 to 12 carbon atoms.

3. A surfactant composition of claim 2, wherein said polyol is selected from alkyiene glycol, polyalkylene glycol, trimethyleneolthane and dimers thereof,
trimethylolethane and dimers thereof, triethylolethane and dimers thereof, tetramethylolethane (pentaerythritol), dipentaerythritol, and mixtures thereof.

4. A surfactant composition of claim 3, wherein said esterification product contains 2 to 6 unsaturated ester groups per molecule.

5. A surfactant composition of claim 1, wherein said second crosslinking monomer is selected from the etherification product of allyl alcohol and a linear and branched polyol having 2 to 12 carbon atoms.

6. A surfactant composition of claim 5, wherein said polyol is selected from sucrose, pentaerythritol, dipentaerythritol, trimethylolethane and dimers thereof, trimethylolethane and dimers thereof, triethylolethane and dimers thereof, and mixtures thereof.

7. A surfactant composition of claim 6, wherein said etherification product contains 2 to 8 allyl groups per molecule.

8. A surfactant composition of claim 1, wherein said at least one other ethylenically mono-unsaturated monomeric component is selected from a monomer represented by the formulas:

\[
\text{d1) } \text{CH}_2=\text{C(R)}\text{C(0)OR}^1, \\
\text{d2) } \text{CH}_2=\text{C(R)}\text{X}, \\
\text{d3) } \text{CH}_2=\text{CHOC(R)OR}^2, \\
\text{d4) } \text{CH}_2=\text{C(R)}\text{C(0)AOOR}^2,
\]

wherein \( R \) is selected from hydrogen or methyl; and \( R^1 \) is selected from \( \text{C}_{5-10} \) alkyi, \( \text{C}_6 \) to \( \text{C}_{10} \) hydroxyalkyl, \( -(\text{CH}_2)_{10}\text{CH}_2\text{CH}_3 \), and \( -(\text{CH}_2)_{2}\text{C(0)OH} \).

\[
\text{d2) } \text{CH}_2=\text{C(R)X}, \\
\text{d3) } \text{CH}_2=\text{CHOC(R)OR}^2, \\
\text{d4) } \text{CH}_2=\text{C(R)}\text{C(0)AOOR}^2,
\]

wherein \( R^1 \) is linear or branched \( \text{C}_{1-18} \) alkyi; and

\[
\text{d4) } \text{CH}_2=\text{C(R)}\text{C(0)AOOR}^2,
\]
wherein A is a divalent radical selected from -CH₂CH(OH)CH₂⁻ and
-CH₂CH(CH₂OH)-, R is selected from hydrogen or methyl, and R² is an acyl
residue of a linear or branched, saturated or unsaturated C₁₀ to C₂₂ fatty acid.

9. A surfactant composition of any of claims 1 to 8, wherein the weight ratio
of said first crosslinking monomer to said second crosslinking monomer ranges
from about 1:100 to about 100:1.

10. A surfactant composition of any of claims 1 to 9, wherein said first
crosslinking monomer is selected from ethylene glycol di(meth)acrylate,
polyethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-
butylene glycol di(meth)acrylate, 1,6-butylene glycol di(meth)acrylate, 1,6-
hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,9-nonanediol
di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane
di(meth)acrylate, tetramethylolethane tricarboxylate, trimethylolpropane
di(meth)acrylate, trimethylolmelamine tri(meth)acrylate, ditrimethylolpropane
tetra(meth)acrylate, tetramethylolethane tetra(meth)acrylate (pentaerythritol
tetra(meth)acrylate); dipentaerythritol hexa(meth)acrylate and mixtures thereof.

11. A surfactant composition of any of claims 1 to 10, wherein said second
crosslinking monomer is selected from polyalyl ethers of sucrose having from 2
to 8 alyl groups per molecule, pentaerythritol diallyl ether, pentaerythritol triallyl
ether, and pentaerythritol tetraallyl ether; trimethylolpropane diallyl ether,
trimethylolpropane triallyl ether, and mixtures thereof.

12. A surfactant composition of any of claims 1 to 11, further comprising:
at least one component selected from hair and skin conditioning agents,
emollients, emulsifiers, auxiliary rheology modifiers, thickening agents, vitamins,
hair growth promoters, self-tanning agents, sunscreens, skin lighteners, anti-
aging compounds, anti-wrinkle compounds, anti-cellulite compounds, anti-acne
compounds, anti-dandruff agents, anti-inflammatory compounds, analgesics,
antiperspirant agents, deodorant agents, particulates, abrasives, moisturizers,
antioxidants, keratolytic agents, anti-static agents, foam boosters, hydrotropes, solubilizing agents, antimicrobial agents, antifungal agents, chelating agents, buffering agents, botanicals, hair colorants, oxidizing agents, reducing agents, propellants, insoluble components, thermochromic dyes, hair and skin bleaching agents, pigments, anticaries, anti-tartar agents, anti-plaque agents, solvents, preservatives; and combinations thereof; and water.

13. A surfactant composition of any of claims 1 to 12 further comprising a pH adjusting agent selected from at least one alkalinity adjusting agent, at least one acidity adjusting agent, and combinations thereof.

14. A surfactant composition of claim 13, wherein said pH adjusting agent is selected from at least one alkalinity adjusting agent.

15. A surfactant composition of claim 13, wherein said pH adjusting agent is selected from at least one acidity adjusting agent.

18. A personal care cleansing composition comprising:
   i) at least one surfactant selected from anionic and a zwitterionic or amphoteric, surfactant, and combinations thereof;
   ii) a crosslinked acrylic copolymer polymerized from a monomer composition comprising:
       a) from about 10% to about 80% by weight of a first monomeric component selected from one or more ethylenically mono-unsaturated monomers containing at least one carboxylic acid group;
       b) from about 90% to about 15% by weight of a second ethylenically mono-unsaturated monomeric component selected from at least one linear or branched C₁ to C₅ hydroxyalkyl ester of (meth)acrylic acid, at least one C₁ to C₅ hydroxyalkyl ester of (meth)acrylic acid, and mixtures thereof;
       c) from about 0.01% to about 5% by weight of crosslinking component
selected from a first polyunsaturated crosslinking monomer and a second
polyunsaturated crosslinking monomer, wherein said first crosslinking monomer
is selected from at least one polyfunctional acrylate having at least two
polymerizable ethylenically unsaturated double bonds and said second
crosslinking monomer is selected from at least one polyalkenyl polyether having
at least two polymerizable ethylenically unsaturated double bonds; and optionally
d) from about 1% to about 35% by weight of at least one other
ethylenically mono-unsaturated monomer component different from monomeric
components a) and b), wherein all monomer weight percentages are based on
the weight of the total monomer composition;
   iii) water; and
   iv) a neutralizer.

17. A composition of claim 16, wherein said at least one other ethylenically
mono-unsaturated monomeric component is selected from a monomer
represented by the formulas:
   d1) \( CH_2=CR(0)OR \)
wherein \( R \) is selected from hydrogen or methyl; and \( R^1 \) is selected from \( C_6 \) to \( C_{10} \) hydroxyalkyl, \( C_6 \) to \( C_{10} \) hydroxyalkyl, \( -(CH_2)_20CH_2CH_3 \), and \( -(CH_2)_22C(0)OH \)
   d2) \( CH_2=CRX \)
wherein \( R \) is hydrogen or methyl; and \( X \) is selected from \( -CeHg \), \( -CN \),
-\( C(0)NH \) 2, \( -NC_4H_60 \), \( -C(0)NH(CCH_3)_3 \), \( -C(0)NO(CH_3)_2 \),
-\( C(0)NH(CCH_3)_2(CH_2)_4CH_3 \), and \( -C(0)NH(CCH_3)_2CH_2S(0)(0)OH \);
   d3) \( CH_2=CHO(C(0)R \)
wherein \( R \) is linear or branched \( C_1 \) to \( C_{18} \) alkyl; and
   d4) \( CH_2=CR(0)OAOR \)
wherein \( A \) is a divalent radical selected from \( -CH_2CH(OH)CH_2 \) and
-\( CH_2CH(CH_2OH)_2 \). \( R \) is selected from hydrogen or methyl, and \( R^2 \) is an acyl
residue of a linear or branched, saturated or unsaturated \( C_7 \) to \( C_{22} \) fatty acid.
18. A composition of claim 16 or 17, wherein said first crosslinking monomer is selected from the esterification product of (meth)acrylic acid and a linear and branched polyol having 2 to 12 carbon atoms.

19. A composition of claim 18, wherein said polyol is selected from alkylene glycol, poyiaikylene glycol, trimethylolethane and dimers thereof, trimethyolpropane and dimers thereof, triethyolpropane and dimers thereof, tetramethylolmethane (pentaerythritoi), dipentaerythritol, and mixtures thereof.

20. A composition of claim 18, wherein said esterification product contains 2 to 6 unsaturated ester groups per molecule.

21. A composition of claim 16 or 17, wherein said second crosslinking monomer is selected from the etherification product of allyl alcohol and a linear and branched polyol having 2 to 12 carbon atoms.

22. A composition of claim 18, wherein said polyol is selected from sucrose, pentaerythritoi, dipentaerythritol, trimethylolethane and dimers thereof, trimethyolpropane and dimers thereof, triethyolpropane and dimers thereof, and mixtures thereof.

23. A composition of claim 22, wherein said etherification product contains 2 to 8 allyl groups per molecule.

24. A composition of any of claims 16 to 23 further comprising:
   at least one component selected from hair and skin conditioning agents, emollients, emulsifiers, auxiliary rheology modifiers, thickening agents, vitamins, hair growth promoters, self-tanning agents, sunscreens, skin lighteners, anti-aging compounds, anti-wrinkle compounds, anti-cellulite compounds, anti-acne compounds, anti-dandruff agents, anti-inflammatory compounds, analgesics, antiperspirant agents, deodorant agents, particulates, abrasives, moisturizers,
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antioxidants, keratolytic agents, anti-static agents, foam boosters, hydrotropes, solublizing agents, antimicrobial agents, antifungal agents, chelating agents, buffering agents, botanicals, hair colorants, oxidizing agents, reducing agents, propellants, insoluble components, thermochromic dyes, hair and skin bleaching agents, pigments, anticaries, anti-tartar agents, anti-plaque agents, solvents, preservatives; and combinations thereof.

25. A composition of any of claims 16 to 24 further comprising a pH adjusting agent selected from at least one alkalinity adjusting agent, at least one acidity adjusting agent, and combinations thereof.

26. A composition of claim 25, wherein said pH adjusting agent is selected from at least one alkalinity adjusting agent.

27. A composition of claim 25, wherein said pH adjusting agent is selected from at least one acidity adjusting agent.

28. A composition of any of claims 16 to 25 further comprising a surfactant selected from a cationic surfactant, a non-ionic surfactant, and mixtures thereof.

29. A personal care cleansing composition comprising:
   i) at least one fatty acid salt;
   ii) at least one crosslinked acrylic copolymer polymerized from a monomer composition comprising:
      a) from about 10% to about 80% by weight of a first monomeric component selected from one or more ethylenically mono-unsaturated monomers containing at least one carboxylic acid group;
      b) from about 90% to about 15% by weight of a second ethylenically mono-unsaturated monomeric component selected from at least one linear or branched C_1 to C_5 alkyl ester of (meth)acrylic acid, at least one C_1 to C_5 hydroxyalkyl ester of (meth)acrylic acid, and mixtures thereof;
c) from about 0.01 % to about 5% by weight of crosslinking component
selected from a first polyunsaturated crosslinking monomer and a second
polyunsaturated crosslinking monomer, wherein said first crosslinking monomer
is selected from at least one polyfunctional acrylate having at least two
double bonds and said second crosslinking monomer is selected from at least one polyalkenyl polyether having
at least two polymerizable ethylenically unsaturated double bonds; and optionally
d) from about 1% to about 35% by weight of at least one other
ethylenically mono-unsaturated monomer component different from monomeric components a) and b), wherein all monomer weight percentages are based on
the weight of the total monomer composition; and optionally
iii) a surfactant selected from an anionic surfactant, a non-ionic surfactant,
amphoteric surfactant, and mixtures thereof.

3(3. A composition of claim 29, wherein said at least one other ethylenically
mono-unsaturated monomeric component is selected from a monomer represented by the formulas:
   d1) \( \text{CH}_2=\text{C}(\text{R})\text{C}(0)\text{R} \)
wherein \( \text{R} \) is selected from hydrogen or methyl; and \( \text{R}^1 \) is selected from \( \text{C}_6^\text{C}_1^0 \)
alkyl, \( \text{C}_6^\text{C}_1^0 \) to \( \text{C}_{10}^\text{C}_1^0 \) hydroxyalkyl, -(CH\(_2\))\(_{20}\)CH\(_2\)CH\(_3\), and -(CH\(_2\))\(_{2c}\)C(0)OH
   d2) \( \text{CH}_2=\text{C}(\text{R})\text{X} \)
wherein \( \text{R} \) is hydrogen or methyl; and \( \text{X} \) is selected from -CeH\(_2\), -CN,
-\( \text{C}(0)\text{NH}_2 \), -\( \text{C}(0)\text{NHC}(\text{CH}_3)_3 \), -\( \text{C}(0)\text{NCH}_3 \),
\( \text{C}(0)\text{NHC}(\text{CH}_3)_2\text{CH}_2\text{S}(0)(0)\text{OH} \);
   d3) \( \text{CH}_2=\text{CHOCH}(0)\text{R} \)
wherein \( \text{R}^1 \) is linear or branched \( \text{C}_1^\text{C}_1^0 \) alkyl; and
   d4) \( \text{CH}_2=\text{C}(\text{R})(0)\text{AOOR} \)
wherein \( \text{A} \) is a divalent radical selected from \( \text{-CH}_2\text{CH(OH)}\text{CH}_2- \) and
\( \text{-CH}_2\text{CH(CH}_2\text{OH)}- \), \( \text{R} \) is selected from hydrogen or methyl, and \( \text{R}^2 \) is an acyl residue of a linear or branched, saturated or unsaturated \( \text{C}_1^\text{C}_1^0 \) to \( \text{C}_{22}^\text{C}_1^0 \) fatty acid.
31. A composition of claim 29 or 33, wherein said first crosslinking monomer is selected from the esterification product of (meth)acrylic acid and a linear and branched polyol having 2 to 12 carbon atoms.

32. A composition of claim 31, wherein said polyol is selected from alkylene glycol, poiyalkylene glycol, trimethylolmethane and dimers thereof, trimethyolpropane and dimers thereof, triethyolpropane and dimers thereof, tetramethylo methane (pentaerythritol), dipentaerythritol, and mixtures thereof.

33. A composition of claim 32, wherein said esterification product contains 2 to 6 unsaturated ester groups per molecule.

34. A composition of claim 29 or 30, wherein said second crosslinking monomer is selected from the esterification product of allyl alcohol and a linear and branched polyol having 2 to 12 carbon atoms.

35. A composition of claim 31, wherein said polyol is selected from sucrose, pentaerythritol, dipentaerythritol, trimethylolmethane and dimers thereof, trimethyolpropane and dimers thereof, triethyolpropane and dimers thereof, and mixtures thereof.

36. A composition of claim 35, wherein said esterification product contains 2 to 8 allyl groups per molecule.

37. A composition of any of claims 29 to 36, wherein said fatty acid salt is selected from the alkali metal and/or ethanoamide salt of a C₈ to C22 fatty acid.

38. A composition of any of claims 29 to 37, further comprising:
   D) at least one component selected from hair and skin conditioning agents, emollients, emulsifiers, auxiliary rheology modifiers, thickening agents, vitamins, hair growth promoters, sunscreens, skin lighteners, anti-aging
compounds, anti-wrinkle compounds, anti-cellulite compounds, anti-acne compounds, anti-dandruff agents, antiperspirant agents, deodorant agents, particulates, abrasives, moisturizers, antioxidants, keratolytic agents, anti-static agents, foam boosters, hydrotrpores, solubilizing agents, chelating agents, antimicrobial agents, antifungal agents, buffering agents, botanicals, hair colorants, oxidizing agents, reducing agents, propelants, insoluble components, thermochromic dyes, hair and skin bleaching agents, pigments, solvents, preservatives; and combinations thereof.

39. A composition of any of claims 29 to 38, wherein the pH ranges from about 7 to about 12.

40. A method for thickening an aqueous surfactant containing composition comprising a crosslinked acrylic copolymer, said method comprising: adding to said aqueous composition a pH adjusting agent selected from an acidic material, an alkaline material, and mixtures thereof, wherein said crosslinked acrylic copolymer is polymerized from a monomer composition comprising:

a) from about 10% to about 80% by weight of a first monomeric component selected from one or more ethylenically mono-unsaturated monomers containing at least one carboxylic acid group;

b) from about 90% to about 15% by weight of a second ethylenically mono-unsaturated monomeric component selected from at least one linear or branched C₁ to C₅ alkyl ester of (meth)acrylic acid, at least one C₁ to C₅ hydroxyalkyl ester of (meth)acrylic acid, and mixtures thereof;

c) from about 0.01% to about 5% by weight of crosslinking component selected from a first polyunsaturated crosslinking monomer and a second polyunsaturated crosslinking monomer, wherein said first crosslinking monomer is selected from at least one polyfunctional acrylate having at least two polymerizable ethylenically unsaturated double bonds and said second crosslinking monomer is selected from at least one polyalkenyl polyether having at least two polymerizable ethylenically unsaturated double bonds; and optionally
d) from about 1% to about 35% by weight of at least one other ethylenically mono-unsaturated monomer component different from monomeric components a) and b), wherein all monomer weight percentages are based on the weight of the total monomer composition.

41. A method of claim 40, wherein said at least one other ethylenically mono-unsaturated monomeric component is selected from a monomer represented by the formulas:

\[ \text{d1)} \ CH_2=CR(C(0)O)R' \]

wherein \( R \) is selected from hydrogen or methyl; and \( R' \) is selected from \( C_6-C_{10} \) alkyl, \( C_6-C_{10} \) hydroxyalkyl, -(CH\(_2\))\(_2\)CH\(_2\)CH\(_3\), and -(CH\(_2\))\(_2\)C(0)OH

\[ \text{d2)} \ CH_2=C(R)X \]

wherein \( R \) is hydrogen or methyl; and \( X \) is selected from -CeHs, -CN, -C(0)NH\(_2\), -NC\(_2\)H\(_4\)O\(_2\), -C(0)NHC(CH\(_3\))\(_3\), -C(0)N(CH\(_3\))\(_2\), -C(0)NHC(CH\(_3\))\(_3\)H\(_2\)CH\(_2\)S(0)(0)OH;

\[ \text{d3)} \ CH_2=CHO(0)R' \]

wherein \( R' \) is linear or branched \( C_1-C_{18} \) alkyl; and

\[ \text{d4)} \ CH_2=CR(C(0)O)AOR \]

wherein \( A \) is a divalent radical selected from -CH\(_2\)CH(OH)CH\(_2\)- and -CH\(_2\)CH(CH\(_2\)OH)-, \( R \) is selected from hydrogen or methyl, and \( R' \) is an acyl residue of a linear or branched, saturated or unsaturated \( C_{10} \) to \( C_{22} \) fatty acid.

42. A method of claim 41, wherein said surfactant is selected from an anionic surfactant, an amphoteric surfactant, a non-ionic surfactant, a cationic surfactant, and mixtures thereof.

43. A method of claim 42, wherein said surfactant is selected from an anionic surfactant, an amphoteric surfactant, and mixtures thereof.

44. A method of claim 43, wherein said surfactant is selected from at least one anionic surfactant and at least one amphoteric surfactant.
45. A method of claim 42, 43, or 44, wherein an alkaline pH adjusting agent is added to said composition.

48. A method of claim 42, 43, or 44, wherein an acidic pH adjusting agent is added to said composition.

47. A method of claim 46, wherein an alkaline and an acidic pH adjusting agent is added to said composition.

48. A method of claim 47, wherein said alkaline pH adjusting agent is added to said composition before said acidic pH adjusting agent is added.

49. A method of claim 48, wherein the pH of said composition is adjusted with said alkaline pH adjusting agent to about 0.5 to about 2 pH units above the initial pH of the composition and subsequently reducing the alkaline adjusted pH of the composition by adding said acidic pH adjusting agent in a sufficient amount to obtain a final pH value ranging from about 3.5 to about 5.5.

50. A method of claim 49 wherein the initial pH of said composition is at least about 5.0.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/81 A61Q5/02 A61Q5/12 A61Q19/10 C11D3/37

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 C11D

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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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See patent family annex.

Date of the actual completion of the international search
9 February 2012

Date of mailing of the international search report
17/02/2012

Authorized officer
Klier, Eric
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