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(71) Applicant: THE PROCTER & GAMBLE COMPANY

[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(72) Inventors: NGUYEN-MEYER, Thuy, T; One Procter &

Gamble Plaza, Cincinnati, Ohio 45202 (US). DRIA, Jamie, Lynn; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US). LYNCH, Matthew, Lawrence; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US). LINSER, Matthew, Joseph; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US). NEAL, Taylor, Allen; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(74) Agent: KREBS, Jay A; c/o The Procter & Gamble Com-

pany, Global IP Services, One Procter & Gamble Plaza, C9, Cincinnati, Ohio 45202 (US).

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(54) Title: STRUCTURED RHEOLOGICAL SOLID COMPOSITIONS

(57) Abstract: A rheological solid composition comprises a crystallizing agent, 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester, cosolvent and water.

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STRUCTURED RHEOLOGICAL SOLID COMPOSITIONS

FIELD OF THE INVENTION

Described herein is a rheological solid comprising 3-[N-n-butyl-N-acetyl] aminopropionic acid
5 ethylester and more than about 55% water having a crystallizing agent with an elongated, fiber-
like crystal habit. Wherein the rheological solid composition allows for a unique skin feel “crunch”
and/or glide when rubbed on the skin; and provides an enhanced evaporative cooling for a
refreshing/cooling sensation, even in the absence of sensate.

BACKGROUND OF THE INVENTION

10 Insect bites, in particular mosquito bites, remain a source of discomfort and a vector for disease.
Vector control and prevention of mosquito bites are particularly based on the safe and efficacious
use of chemicals. Because mosquitoes become resistant, it is essential to develop new strategies
against insects to increase treatment efficacy and to circumvent resistance mechanisms. Chemicals
15 which have been classically used, up to now, are classified into two main categories, according to
their mode of action. In the first category are insect repellent molecules which prevent mosquitoes
of approaching their target and in the second category are insecticide molecules which "kill" the
mosquitoes. In the repellent molecule category, are insect repellents such as IR3535® (3-[N-Butyl-
N-acetyl]-aminopropionic acid ethyl ester). To be effective against most mosquitoes implies that
20 they have to be usually employed at relatively high concentrations in the compositions to be applied
for instance on clothes or nets. On-body insect repellents, such as those featuring the active
IR3535, currently exist, but are typically in the form of an aerosol spray, pump spray, lotion or
wipe. These forms do not allow for accurate application and can get into eyes and cause irritation;
they can also be difficult to apply (lotions or wipes can leave an unwanted residue on applicator's
25 hands) and potentially spill or leak during use or when stored.

Conventional soap-type gel-sticks are commonly used as deodorant for underarm application, and
typically incorporate sodium stearate (C18) gelling agents (which are really a mixture of chain
lengths derived from the natural source of stearate – typically tallow). The use of sodium stearate
30 requires the inclusion of high levels of polyols (e.g. propylene glycol and glycerin) as a solubility
aid for the gelling agent during processing, even at high process temperatures. Typical
compositions include about 50% propylene glycol, 25% glycerin and only 25% water (EP2170257
and EP2465487). This eliminates the crunch and mutes the glide feel and cooling sensation of the

solid stick. Finally, this may require high levels of gelling agent, including gelling agents other than sodium stearate, to produce gel-sticks and particularly translucent gel-sticks.

Attempts have been made to provide rheological solid compositions similar in composition to those embodied in this invention, comprising insoluble active agents such as perfume capsules, solid particles, or oil droplets because rheological solid compositions provide a way for a user to quickly and easily apply a rheological solid composition to a particular surface. However, these compositions do not form a rheological solid when the insect repellent 3-[N-Butyl-N-acetyl]-aminopropionic acid ethyl ester is incorporated in the compositions, resulting in the composition being liquid. There is a need for a rheological solid composition containing the insect repellent 3-[N-Butyl-N-acetyl]-aminopropionic acid ethyl ester. It would be rather advantageous for said rheological solid composition to remain a rheological solid after exposure to elevated storage conditions, such as those experienced during supply chain shipping and/ or storage by a consumer (e.g., stored in a hot car).

There is a need for a vehicle to deliver insect repellent to the skin of a user, and that can pass the EPA required accelerated ageing test (2 weeks at 54 C) required for registration.

SUMMARY OF THE INVENTION

A rheological solid composition is provided that comprises from about 2 wt. % to about 20 wt. % of at least one of sodium stearate, sodium palmitate, or sodium myristate; from 0 wt. % to about 6 wt. % sodium chloride; from about 1 wt. % to about 40 wt. % 3-[N-Butyl-N-acetyl]-aminopropionic acid ethyl ester; from about 3 wt. % to about 40 wt. % of a cosolvent that is at least one of glycerol, 1,2-hexanediol, propylene glycol, ethanol, or isopropyl alcohol; and about 30% to about 75% water; wherein the weight ratio of sodium stearate and sodium chloride to water is from about 17 to about 45; wherein the rheological solid remains a solid after 14 days of ageing at 54°C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention includes a rheological solid composition comprising a crystalline mesh and insect repellent 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester (Tradename IR3535®). The crystalline mesh ("mesh") comprises a relatively rigid, three-dimensional, interlocking crystalline skeleton frame of fiber-like crystalline particles (formed from crystallizing agents), having voids or openings containing aqueous solution and optionally one or more actives. The mesh provides a self-supporting structure, such that a rheological solid composition may 'stand on its own' when resting on a surface. If compressed above a critical stress, the mesh allows the

rheological solid composition to express the entrapped aqueous solution, and optionally one or more actives. The rheological solid compositions of the present invention may include 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester, crystallizing agent(s), cosolvent(s), insoluble active(s), and water, and may be combined with a device to enable application.

The combination of high levels of sodium stearate and sodium chloride along with the inclusion of a hydroxyl containing molecule (e.g., glycerol, 1,2-hexanediol, propylene glycol, ethanol, and isopropyl alcohol) and 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester, produce a rheological solid composition that remains solid after 2 weeks of rapid ageing at 54 °C. In embodiments the weight ratio of sodium stearate to sodium chloride to water can be from about 17 to about 45, from about 17 to 41, from about 17 to about 36, or from about 17 to 32, or from about 17 to about 29. If the amount of crystallizing agent is too low (below ratio of 17) then the rheological solid composition does not remain solid after two weeks at 54 °C (as in SAMPLES 25-33, TABLE 2 and 3). Above about ratio of 45, the composition would not solubilize completely during the making and would crystallize inconsistently (hard spots/soft spots).

As used herein, “composition” refers to compositions intended for topical application to the skin, including topical prescription medications, over-the-counter medications, behind-the-counter medications, cosmetics, consumer goods, and combinations thereof.

CRYSTALLIZING AGENT(S)

In the present invention, the mesh of a rheological solid composition includes fiber-like crystalline particles formed from crystallizing agents; wherein “crystallizing agent” as used herein includes sodium salts of fatty acid with shorter chain length (C12-C20), such as sodium palmitate (C16) in majority of water. The rheological solid compositions are best achieved with a ‘narrow’ distribution of crystallizing agent chain lengths, further best achieved in the absence of very short chain lengths (C12 or shorter) and measurable amounts of unsaturation on the chains of the fatty acid sodium salts, coupled with controlled crystallization processing. One skilled in the art recognizes crystalline particles as exhibiting sharp scattering peaks between 0.25 – 60 deg. 2θ in powdered x-ray diffraction measurements. This is in sharp contrast to compositions in which these materials are used as gelling agents, which show broad amorphous scattering peaks emanating from poorly formed solids.

Rheological solid compositions can comprise greater than about 30% water, greater than about 55% water, greater than about 60%, greater than about 65%, greater than about 70% water, or

greater than about 80% water, and are 'structured' by a mesh of interlocking, fiber-like crystalline particles of mostly single-chain length, as described above. The term "fiber-like crystalline particle" refers to a particle in which the length of the particle in the direction of its longest axis is greater than 10x the length of the particle in any orthogonal direction. The fiber-like crystalline particles produce a mesh at very low concentrations (~ 0.5 wt%) that create a solid that yields only with a minimum applied stress – i.e. rheological solid. The suspension agent(s), 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester, cosolvent(s), insoluble active(s) and aqueous phase (water) primarily reside in the open spaces of the mesh. In preparing these compositions, the crystallizing agent is dissolved in water using heat. The fiber-like crystalline particles form into the mesh as the mixture cools over minutes to hours. Preferred compositions have a phase stability grade of 'Y' as determined by the PHASE STABILITY TEST METHOD, described herein.

Without being limited to theory, it is thought that potassium or sodium salts of fatty acid with high chain length can function as crystallizing agents in the present invention. The inclusion of shorter chain length (C12 or shorter) crystallizing agents can make the compositions too soluble at room temperature, such that the fiber-like crystalline particles do not form. The inclusion of unsaturation in chains of the sodium salts of fatty acid adds too many 'kinks' for crystallization, such that the fiber-like crystalline particles do not form and the compositions are mush or liquid. The crystallizing agent should be present in sufficient quantity to create a rheological solid with a firmness between about 0.1 N and about 50.0 N, more preferably between about 0.5 N – about 40.0 N, more preferably between about 1.0 N – about 30.0 N and most preferably between about 2.5 N – about 15.0 N, where the lower value sets a minimum 'softness' to the composition and the upper value sets a maximum 'hardness' to the composition, both of which are influenced by the consumer product application. In some aspects, the crystallizing agent is present in an amount from about 2% to about 20%, by weight of the rheological solid composition. The crystallizing agent may be present in an amount of from about 3% to about 15%, by weight of the rheological solid composition, from about 4% to about 12%, by weight of the rheological solid composition, or from about 5% to about 11%, by weight of the rheological solid composition.

The crystallizing agent should form elongate fiber-like crystalline particles, in which the length of the particle in the direction of its longest axis is preferably greater than 10x the length of the particle in any orthogonal direction, more preferably greater than 15x, and most preferably greater than 20x, as assessed by standard Scanning Electron Microscopy (SEM) methods. Not wishing to be bound by theory, but longer crystalline particles are thought to intertwine more efficiently creating

efficient mesh structures. This contrasts with fatty acid crystals (protonated version of the sodium salt of fatty acid) of magnesium salt of fatty acid which are not-elongated and generally exhibit a ratio of 1x to 2x. The composition of the fiber-like crystalline particles should be thermally stable at room temperature, with preferred temperatures greater than about 30°C, more preferably greater than about 35°C, more preferably greater than about 40°C, more preferably greater than about 50°C, most preferably greater than about 60°C, as determined by the THERMAL STABILITY TEST METHOD, as described herein. Finally, the fiber-like crystalline particles combine to form a mesh, such that the aqueous phase and insoluble actives can be expressed from the rheological solid composition with a defined applied stress. The work required to express aqueous phase from 15% of the volume of the structure of the rheological solid composition is preferably between about 100 J m⁻³ and about 6000 J m⁻³, alternatively from about 100 J m⁻³ and about 3000 J m⁻³, alternatively between about 300 J m⁻³ and about 2000 J m⁻³, alternatively between about 500 J m⁻³ and about 1500 J m⁻³, as determined by the WATER-EXPRESSION TEST METHOD, as described herein.

In some aspects, the crystallizing agent can be a metal salt. Non-limiting examples of metals salts can include sodium stearate, sodium palmitate, potassium stearate, potassium palmitate, sodium myristate. One of skill in the art would understand that the rheological solid composition can be made using the acid form of the salt in combination with a base, such as sodium hydroxide, to form the metal salt.

SUSPENSION AGENT(S)

The suspension agent prevents the separation of insoluble actives in the preparation of the rheological solid composition. Inventive compositions are heated until the crystallizing agent is dissolved leaving a dispersed active in a low viscosity fluid. When the compositions are cooled, the crystallizing agent begins to form fiber-like crystalline particles which weave together into the mesh, which eventually traps the actives. This process can take minutes to hours. Not wishing to be bound by theory, it is believed that the suspension agents increase viscosity or create a yield stress that holds the actives from creaming or sedimenting during the crystallization of the crystallizing agent and formation of the mesh. Preferred suspension agents are effective at low concentrations to prevent potential negative effects on the mesh and performance of the consumer product. Preferred levels are below about 2 wt. %, alternatively below about 1 wt. %, alternatively below about 0.5 wt. %, alternatively below about 0.1 wt. %. In some aspects, the rheological solid composition can comprise from about 0.01 to about 2 wt. % of a suspension agent, alternatively

from about 0.05 to about 1 wt. %, alternatively from about 0.1 to about 0.5 wt. %, alternatively from about 0.25 to about 0.35 wt.%, all by weight of the rheological solid composition.

5 Suitable suspension agents include gums, polymers, microfiber particles, clay particles, and combinations thereof, and unexpectedly must be selected for a composition such that their addition does not have a negative effect on the mesh.

Gums

10 The rheological solid composition may include at least one suspension agent to keep insoluble materials (i.e. solids or oils) suspended during preparation. The suspension agent may include one or more biopolymers. Non-limiting examples of such biopolymers include polysaccharides such as polymers of glucose, fructose, galactose, mannose, rhamnose, glucuronic acid, and mixtures thereof.

15 The suspension agent may be in the form of a polysaccharide or mixture of polysaccharides. Preferable polysaccharide suspension agents include xanthan gum, glucomannan, galactomannan, and combinations thereof. The glucomannan may be derived from a natural gum such as konjac gum. The galactomannan may be derived from natural gums such as locust bean gum. Polysaccharide suspension agents may also include carrageenan. Suspension agent gums may be
20 modified such as by deacetylation.

The rheological solid composition may comprise a polysaccharide suspension agent system comprising at least two polysaccharides, such as a first polysaccharide and a second polysaccharide. The first polysaccharide may be xanthan gum. The second polysaccharide may
25 be selected from the group consisting of glucomannan, galactomannan, and combinations thereof. The second polysaccharide may be selected from the group consisting of konjac gum, locust bean gum, tara bean, and combinations thereof.

Inventive Samples 11, 12, 13 and 14 contain xanthan gum and form solid water that pass the
30 THERMAL STABILITY TEST METHOD. Comparative Sample 25 does not form a rheological solid initially nor does it pass the THERMAL STABILITY TEST METHOD. Comparative Samples 27, 28, 29, 31, and 32 contain xanthan gum and form a rheological solid initially but the level of cosolvent is insufficient to pass the THERMAL STABILITY TEST METHOD.

The total concentration of polysaccharide present in the rheological solid composition may be between about 0.01 – about 1.0 wt. %, or more preferably between about 0.03 – about 1.0 wt. %, or more preferably between about 0.05 – about 0.8 wt. %, more preferably between about 0.07 – about 0.75 wt. %, and most preferably between about 0.09 – about 0.5 wt. %, all by weight of the rheological solid composition. Without wishing to be bound by theory, it is believed that minimizing the total polysaccharide level in the composition ensures stability of the dispersed active agents during preparation while minimizing the effect of the suspension agent on the mesh structure.

The polysaccharide suspension agent system may have a weight-average molecular weight in the range of about 10,000 Daltons to about 15,000,000 Daltons, alternatively about 200,000 Daltons to about 10,000,000 Daltons, alternatively about 300,000 Daltons to about 6,000,000 Daltons, alternatively about 300,000 Daltons to about 500,000 Daltons.

The polysaccharide suspension agent system may be characterized by the average ratio of acetylation, wherein the average ratio of acetylation is the number of acetylated hydroxyl groups in the polysaccharide divided by the number of free hydroxyl groups in the polysaccharide. The average ratio of acetylation may be in the range of about 2.0 to about 0.5, preferably in the range of about 1.5 to about 0.5.

Microfibers

Any microcrystalline cellulose may be employed in the compositions of the present invention. Suitable feedstocks include, for example, wood pulp such as bleached sulfite and sulfate pulps, corn husks, bagasse, straw, cotton, cotton linters, flax, kemp, ramie, fermented cellulose, etc. The amounts of microcrystalline cellulose and hydrocolloid may be varied over a wide range depending upon the properties desired in the final composition. Suitable microfibers include Rheocrysta c-2sp (WASE COSFA USA, Inc.).

3-[N-N-BUTYL-N-ACETYL] AMINOPROPIONIC ACID ETHYLESTER

3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester (trade name IR3535®) is an insect repellent which is applied topically to prevent bites and stings from mosquitos, ticks, and other insects. It is a colorless and almost odorless oil, has efficacy against a broad range of insects, and is reasonably biodegradable. In embodiments, 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester may be present in an amount from about 1% to about 40%, from about 3% to about 40%, from about 5%

to about 40%, from about 5% to about 35%, from about 10% to about 35%, from about 7.5% to about 30%, or from about 7.5% to about 20%, by weight of the rheological solid composition. 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester has a published water solubility limit of about 6 wt. % in water. Without wishing to be bound by theory, it is believed that the cosolvent(s),
5 described in detail below, may increase the solubility limit of 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester in the rheological solid composition.

Unencapsulated Perfume

The rheological solid composition may include unencapsulated perfume comprising one or more
10 perfume raw materials that solely provide a hedonic benefit (i.e. that do not neutralize malodors yet provide a pleasant fragrance). Suitable perfumes are disclosed in US 6,248,135.

Where perfumes are formulated into the rheological solid composition, the total amount of perfumes may be from about 0.015 wt. % to about 2 wt. %, alternatively from about 0.01 wt. % to
15 about 1.0 wt. %, alternatively from about 0.015 wt. % to about 0.5 wt. %, by weight of the rheological solid composition.

Essential and Natural Oils

The insoluble active particle may include individual mixtures of insoluble oils such as essential
20 and natural oils. The term “essential oils” as used herein refers to oils or extracts distilled or expressed from plants and constituents of these oils. Typical essential oils and their main constituents are those obtained for example from thyme (thymol, carvacrol), oregano (carvacrol, terpenes), lemon (limonene, terpinene, phellandrene, pinene, citral), lemongrass (citral, methylheptenone, citronellal, geraniol), orange flower (linalool, β -pinene, limonene), orange
25 (limonene, citral), anise (anethole, safrol), clove (eugenol, eugenyl acetate, caryophyllene), rose (geraniol, citronellol), rosemary (borneol, bornyl esters, camphor), geranium (geraniol, citronellol, linalool), lavender (linalyl acetate, linalool), citronella (geraniol, citronellol, citronellal, camphene), eucalyptus (eucalyptol); peppermint (menthol, menthyl esters), spearmint (carvone, limonene, pinene), wintergreen (methyl salicylate), camphor (safrole, acetaldehyde, camphor), bay
30 (eugenol, myrcene, chavicol), cinnamon (cinnamaldehyde, cinnamyl acetate, eugenol), tea tree (terpinen-4-ol, cineole), eucalyptus oil, nutmeg oil, turpentine oil, chamomile oil, neroli oil, cedar leaf (α -thujone, β -thujone, fenchone), and combinations thereof. Essential oils are widely used in perfumery and as flavorings, medicine, and solvents. Essential oils, their composition and production, are described in detail in Kirk-Othmer Encyclopedia of Chemical Technology, 4th

Edition and in The Merck Index, 13th Edition.

In some aspects, the rheological solid composition can comprise from about 0.1 to about 20 wt. % insoluble oils, alternatively from about 0.5 to about 15 wt. %, alternatively from about 1 to about 12 wt. %, alternatively from about 4 to about 15 wt. %, alternatively from about 5 to about 10 wt. %, all by weight of the rheological solid composition.

Feel Modifiers

The rheological solid composition may also include insoluble active agents designed to alter the feel properties of the composition when applied to surfaces, such as skin. This may include starches (e.g. tapioca starch, rice starch, or the like), talc, fumed silica (Aerosil® 200), titanium dioxide, dimethicone, iron oxide, mica, charcoal, colloidal oatmeal, colloidal cellulose, kaolin, and combinations thereof.

Skin Care Agents

Skin care agents may be added to deliver a therapeutic and/or skin protective benefit. It will be recognized that of the numerous materials useful in the compositions delivered to skin, those that have been deemed safe and effective skin care agent and mixtures thereof are logical materials for use herein. Such materials include Category I actives as defined by the U.S. Food and Drug Administration's (FDA) Tentative Final Monograph on Skin Protectant Drug Products for Over-the-Counter Human Use (21 C.F.R. § 347), which presently include: allantoin, aluminum hydroxide gel, calamine, cocoa butter, dimethicone, cod liver oil (in combination), glycerine, kaolin, petrolatum, lanolin, mineral oil, shark liver oil, white petrolatum, talc, topical starch, zinc acetate, zinc carbonate, zinc oxide, and the like. Other potentially useful materials are Category DI actives as defined by the U.S. Food and Drug Administration's Tentative Final Monograph on Skin Protectant Drug Products for Over-the-Counter Human Use (21 C.F.R. § 347), which presently include: live yeast cell derivatives, aldioxa, aluminum acetate, microporous cellulose, cholecalciferol, colloidal oatmeal, cysteine hydrochloride, dexpantenol, Peruvian balsam oil, protein hydrolysates, racemic methionine, sodium bicarbonate, Vitamin A, buffered mixture of cation and anion exchange resins, corn starch, trolamine, and the like. Further, other potential materials are Category II actives as defined by the U.S. Food and Drug Administration's Tentative Final Monograph on Skin Protectant Drug Products for Over-the-Counter Human Use (21 C.F.R. § 347), which include: bismuth subnitrate, boric acid, ferric chloride, polyvinyl pyrrolidone - vinyl acetate copolymers, sulfur, tannic acid, and the like. The skin care agent may be selected from

these materials and mixtures thereof. As mentioned above, the materials for use should be safe. The rheological solid composition may include between about 0.001 wt. % and about 20 wt. %, by weight of the rheological solid composition, of the skin care agent. The concentration range of the skin care agents in the composition varies from material to material.

5

Topical Drug Actives

The rheological solid composition may comprise topical drug actives which are insoluble. In some aspects, the rheological solid composition can comprise from about 0.01 to about 20 wt. % of a topical drug active, alternatively from about 0.025 to about 10 wt. %, alternatively from about 0.1
10 to about 7 wt. %, alternatively from about 0.25 to about 5 wt. %, alternatively from about 1 to about 3 wt. %, all by weight of the rheological solid composition. Non-limiting examples of topical drug actives can include analgesics like methyl salicylate, ibuprofen, lidocaine, diphenylhydramine, methyl nicotinate and diclofenac sodium, melatonin, capsaicin, capsicum, camphor, menthol, anesthetics like benzocaine, corticosteroids like hydrocortisone and
15 hydrocortisone acetate, and combinations thereof.

Sensate

In some aspects, soluble active agents can include one or more components that provide a sensory benefit, often called a sensate. Sensates can have sensory attributes such as a warming, tingling,
20 or cooling sensation. Suitable sensates can include, for example, menthol, menthyl lactate, leaf alcohol, camphor, clove bud oil, eucalyptus oil, anethole, methyl salicylate, eucalyptol, cassia, 1-8 menthyl acetate, eugenol, oxanone, alpha-irisone, propenyl guaethol, thymol, linalool, benzaldehyde, cinnamaldehyde glycerol acetal known as "CGA", N-[(ethoxycarbonyl)methyl]-p-menthane-3-carboxamide, known as "WS-5", supplied by Renessenz-Symrise, and mixtures
25 thereof.

In some aspects, the sensate comprises a coolant. The coolant can be any of a wide variety of materials. Included among such materials are carboxamides, menthol, ketals, diols, and mixtures thereof. Some examples of carboxamide coolants include, for example, paramenthan
30 carboxamide agents such as N-ethyl-p-menthan-3-carboxamide, known commercially as "WS-3", N,2,3-trimethyl-2-isopropylbutanamide, known as "WS-23," and N-(4-cyanomethylphenyl)-p-menthanecarboxamide, known as "G-180" and supplied by Givaudan. G-180 generally comes as a 7.5% solution in a flavor oil, such as spearmint oil or peppermint oil. Examples of menthol coolants include, for example, menthol; 3-1-menthoxypropane-1,2-diol, known as TK-10 and

manufactured by Takasago; menthone glycerol acetal, known as “MGA” and manufactured by Haarmann and Reimer; and menthyl lactate, known as Frescolat® and manufactured by Haarmann and Reimer. The terms menthol and menthyl as used herein include dextro- and levorotatory isomers of these compounds and racemic mixtures thereof.

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In some aspects, the sensate comprises a coolant selected from the group consisting of menthol; 3-1-menthoxypropane-1,2-diol; menthyl lactate; N,2,3-trimethyl-2-isopropylbutanamide; N-ethyl-p-menthan-3-carboxamide; N-(4-cyanomethylphenyl)-p-menthanecarboxamide; menthyl ethylamido oxalate; and combinations thereof. In some aspects, the sensate comprises menthol;
10 N,2,3-trimethyl-2-isopropylbutanamide; N-(4-cyanomethylphenyl)-p-menthanecarboxamide; menthyl ethylamido oxalate, and combinations thereof.

In some aspects, the sensate comprises a warming sensates. Non-limiting examples of warming sensates can include vanillyl alcohol n-butyl ether (sold as TK-1000 by Takasago International),
15 vanillyl butyl ether (commercially available as HotFlux® from Corum, Inc., Taipei, Taiwan), capsaicin, nonivamide, ginger, capsicum (commercially available as Vegetol® Capsicum LC481 from Gattefossé, Lyon, France), and combinations thereof.

In some aspects, the sensate comprises a tingling sensate. Non-limiting examples of tingling
20 sensates can include sichuan pepper, hydroxy alpha sanshool, jambu extracts, spilanthol, and combinations thereof. A suitable sensory enhancer can include a neuro-soother such as Mariliance™ available from Givaudan, Vernier, Switzerland.

One advantage to including a sensate is that they can provide a topical sensory effect. When the
25 rheological solid composition having one or more sensates is applied to the skin, it can provide an on-skin sensation that can work in unison with the smell to provide an increased perception of product strength.

The rheological solid composition can comprise from about 0.001 to about 1.5 wt. % of a sensate,
30 alternatively from about 0.01 to about 1 wt. %, alternatively from about 0.1 to about 0.75 wt. %, alternatively from about 0.2 wt. % to about 0.5 wt. %, all by weight of the rheological solid composition.

Surfactant

In some aspects, soluble active agents can include one or more surfactants. These include cationic, anionic, zwitterionic and non-surfactants. Surfactants may help emulsify or stabilize perfumes oils, natural oils, or other water insoluble or hydrophobic actives.

5

Preservatives

In some aspects, soluble active agents can include a preservative. The preservative may be present in an amount sufficient to prevent spoilage or prevent growth of inadvertently added microorganisms for a specific period of time, but not sufficient enough to contribute to the odor neutralizing performance of the rheological solid composition. In other words, the preservative is not being used as the antimicrobial compound to kill microorganisms on the surface onto which the rheological solid composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is being used to prevent spoilage of the rheological solid composition in order to increase the shelf-life of the rheological solid composition.

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The preservative can be any organic preservative material which will not cause damage to skin or clothing appearance, e.g., discoloration, coloration, bleaching. Suitable water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, parabens, propane diol materials, isothiazolinones, quaternary compounds, benzoates, low molecular weight alcohols, dehydroacetic acid, phenyl and phenoxy compounds, or mixtures thereof.

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Non-limiting examples of commercially available water-soluble preservatives include a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Co.; 5-bromo-5-nitro-1,3-dioxane, available under the tradename Bronidox L® from Henkel; 2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol® from Inolex; 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and digluconic acids; a 95:5 mixture of 1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione and 3-butyl-2-iodopropynyl carbamate, available under the trade name Glydant Plus® from Lonza; N-[1,3-bis(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxy-methyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall® II from Sutton Laboratories, Inc.; N,N"-methylenebis{N'-[1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as

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imidazolidinyl urea, available, e.g., under the trade name Abiol® from 3V-Sigma, Unicide U-13® from Induchem, Germall 115® from Sutton Laboratories, Inc.; polymethoxy bicyclic oxazolidine, available under the trade name Nuosept® C from Hüls America; formaldehyde; glutaraldehyde; polyaminopropyl biguanide, available under the trade name Cosmocil CQ® from ICI Americas, Inc., or under the trade name Mikrokil® from Brooks, Inc; dehydroacetic acid; and benzisothiazolinone available under the trade name Koralone™ B-119 from Rohm and Hass Corporation; 1,2-Benzisothiazolin-3-one; Acticide MBS.

Suitable levels of preservative are from about 0.0001 wt. % to about 0.5 wt. %, alternatively from about 0.0002 wt. % to about 0.2 wt. %, alternatively from about 0.0003 wt. % to about 0.1 wt. %, by weight of the rheological solid composition.

The rheological solid composition may include an aqueous carrier. The aqueous carrier which is used may be distilled, deionized, or tap water. Water may be present in any amount for the rheological solid composition to be an aqueous solution. Water may be present in an amount of about 30 wt. % to 80 wt. %, alternatively about 40 wt. % to about 75 wt. %, alternatively about 45 wt. % to about 70 wt. %, alternatively about 45 wt. % to about 65 wt. %, by weight of the rheological solid composition.

Cosolvents

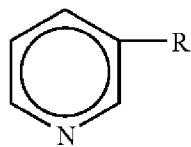
The rheological solid composition can include a hydroxyl containing cosolvent that serves to dissolve and improve thermal phase stability of rheological solid compositions comprising 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester (IR3535®). Non-limiting examples of cosolvents can include ethanol, glycerol, 1, 2-hexanediol, propylene glycol, polyethylene glycol 400, polyethylene glycol 200, isopropyl alcohol, and mixtures thereof. In some aspects, the rheological solid composition can comprise cosolvent from about 3 wt % to about 40 wt %; about 4 wt % to about 30 wt %; about 5 wt % to about 20 wt %; from about 6 wt. % to about 18 wt. % cosolvent; about 7 wt. % to about 16 wt. %.

Vitamins

As used herein, “xanthine compound” means one or more xanthines, derivatives thereof, and mixtures thereof. Xanthine compounds that can be useful herein include, but are not limited to, caffeine, xanthine, 1-methyl xanthine, theophylline, theobromine, derivatives thereof, and mixtures

thereof. Among these compounds, caffeine is preferred in view of its solubility in the composition. The composition can contain from about 0.05 wt. %, preferably from about 2.0 wt. %, more preferably from about 0.1 wt. %, still more preferably from about 1.0 wt. %, and to about 0.2 wt. %, preferably to about 1.0 wt. %, more preferably to about 0.3 wt. % by weight of a xanthine
 5 compound.

As used herein, “vitamin B3 compound” means a one or more compounds having the formula:



10 wherein R is —CONH_2 (i.e., niacinamide), —COOH (i.e., nicotinic acid) or $\text{—CH}_2\text{OH}$ (i.e., nicotinyl alcohol); derivatives thereof; mixtures thereof; and salts of any of the foregoing.

Exemplary derivatives of the foregoing vitamin B3 compounds include nicotinic acid esters, including non-vasodilating esters of nicotinic acid (e.g. tocopherol nicotinate, and myristyl
 15 nicotinate), nicotinyl amino acids, nicotinyl alcohol esters of carboxylic acids, nicotinic acid N-oxide and niacinamide N-oxide. The composition can contain from about 0.05 wt. %, preferably from about 2.0 wt. %, more preferably from about 0.1 wt. %, still more preferably from about 1.0 wt. %, and to about 0.1 wt. %, preferably to about 0.5 wt. %, more preferably to about 0.3 wt. %, by weight of a vitamin B3 compound.

20 As used herein, the term “panthenol compound” is broad enough to include panthenol, one or more pantothenic acid derivatives, and mixtures thereof. Panthenol and its derivatives can include D-panthenol ([R]-2,4-dihydroxy-N-[3-hydroxypropyl]-3,3-dimethylbutamide), DL- panthenol, pantothenic acids and their salts, preferably the calcium salt, panthenyl triacetate, royal jelly,
 25 panthetine, pantotheine, panthenyl ethyl ether, pangamic acid, pantoyl lactose, vitamin B complex, or mixtures thereof. The composition can contain from about 0.01 wt. %, preferably from about 0.02 wt. %, more preferably from about 0.05 wt. %, and to about 3 wt. %, preferably to about 1 wt. %, more preferably to about 0.5 wt. % by, weight of a panthenol compound.

Salts

In some aspects, the rheological solid composition may comprise a salt, which can help with thermal stability. Non-limiting examples of salts can include sodium chloride, sodium sulfate, and combinations thereof. In some aspects, the rheological solid composition can comprise from about 0.1 to about 10 wt. % of a salt, alternatively from about 1 to about 7 wt. %, alternatively 3 to about 6 wt. %, all by weight of the rheological solid composition. In embodiments a rheological solid composition may comprise sodium chloride in an amount of from about 2% to about 7%, from about 3% to about 6%, from about 4% to about 5%.

10 CONSUMER PRODUCT/ RHEOLOGICAL SOLID COMPOSITION

The rheological solid composition can be applied to the skin of a user on the hands, arms, back, neck, forehead, face, legs, feet and/or chest. The user can place a desired amount of the rheological solid composition on his or her skin and rub it in for about 5 seconds to about 3 minutes, alternatively for about 20 seconds to about 90 seconds, alternatively for about 30 seconds to about 60 seconds.

A dose of the rheological solid composition can be applied to the skin and/or clothing once daily, or twice daily, or three times per day. In one aspect, a dose of the rheological solid composition can be applied to the skin up to three times per day. The rheological solid composition can be applied to the skin and/or clothing on a daily basis or only as needed. Preferably the rheological solid composition is applied to and allowed to dry before subjecting to contact such as with clothing or other objects. The rheological solid composition is preferably applied to the desired area that is dry or has been dried prior to application.

A dose of the rheological solid composition can comprise from about 0.05g to about 10g, alternatively from about 0.1g to about 5g, alternatively from about 0.2g to about 3g, alternatively from about 0.5g to about 2g.

Another aspect of the present invention includes a method of providing one or more health benefits, cosmetic benefits, and/or consumer benefits by administering the rheological solid composition to a user in need thereof. Non-limiting examples of the one or more health benefits can include providing relief of muscle aches and pain, improving the quality of sleep to a user suffering from

insect bites, providing topical analgesic effects, providing relief from rash, pain, and/or itching, reducing redness and combinations thereof. Non-limiting examples of the one or more cosmetic benefits can include moisturizing, cleansing, beautifying, and combinations thereof.

- 5 The compositions of the present invention make it possible to obtain superior consumer aesthetics without compromising stability across a range of storage temperatures. The preferred ratios and weight percentages identified above provide sufficient medium coverage of product without being perceived as dry or flakey and provide a nice smoothing/evening effect of the skin. They also provide a pleasant fresh feel on the skin upon application of the composition.

10

The present invention also envisages kits and/or prepackaged materials suitable for consumer use containing one or more compositions according to the description herein. The packaging and application device for any subject of the invention may be chosen and manufactured by persons skilled in the art on the basis of their general knowledge; and adapted according to the nature of
15 the composition to be packaged. Indeed, the type of device to be used can be in particular linked to the consistency of the composition, in particular to its viscosity; it can also depend on the nature of the constituents present in the composition, such as the presence of volatile compounds.

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The rheological solid compositions of the present invention may also be combined with a device, such as a container, non-woven sheet or roller, given the soft-solid nature of the material.

PROPERTIES

PHASE STABILITY TEST METHOD

- 25 Phase stability, as used herein, is a measure of the composition to be a rheological solid at a specified temperature. The presence or absence of a rheological solid is determined by eye. A phase stability value of 'N' means the composition is not a rheological solid at the specified. A value of 'Y' means the composition is a rheological solid at the specified temperature.

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Firmness

Depending on the intended application, such as a stick, firmness of the composition may also be considered. The firmness of a composition may, for example, be expressed in Newtons of force. For example, compositions of the present invention comprising from about 5 wt% to about 11 wt.% crystallizing agent may give values of about 4 – 12 N, in the form of a solid stick or coating on a

sheet. As is evident, the firmness of the composition according to embodiments of the present invention may, for example, be such that the composition is advantageously self-supporting and can release liquids and/or actives easily to form a satisfactory deposit on a surface, such as the skin and/or superficial body growths, such as keratinous fibers. In addition, this firmness may impart good impact strength to the inventive compositions, which may be molded or cast, for example, in stick or sheet form, such as a wipe or dryer sheet product. The rheological solid composition may also be transparent or clear, including for example, a composition without pigments. Preferred firmness is between about 0.1 N and about 50.0 N, more preferably between about 0.5 N – about 40.0 N, more preferably between about 1.0 N – about 30.0 N, and most preferably between about 2.5 N – about 15.0 N. The firmness may be measured using the FIRMNESS TEST METHOD, as described below.

Liquid Expression

Depending on the intended application, such as a stick, liquid expression of the composition may also be considered. This is a measure of the amount of work need per unit volume to express water from the compositions, with larger values meaning it becomes more difficult to express water. A low value might be preferred, for example, when applying the composition to the skin. A high value might be preferred, for example, when applied to a substrate that requires ‘dry-to-the-touch-but-wet-to-the-wipe’ properties. Preferred values are between about 100 J m⁻³ and about 6000 J m⁻³, alternatively between about 100 J m⁻³ and about 3000 J m⁻³, alternatively between about 300 J m⁻³ and about 2000 J m⁻³, alternatively between about 500 J m⁻³ and about 1500 J m⁻³. The liquid expression may be measured using the WATER-EXPRESSION TEST METHOD, as described herein.

FIRMNESS TEST METHOD

All samples and procedures are maintained at room temperature ($25 \pm 3^\circ\text{C}$) prior to and during testing, with care to ensure little or no water loss.

All measurements were made with a TA-XT2 Texture Analyzer (Texture Technology Corporation, Scarsdale, N.Y., U.S.A.) outfitted with a standard 45° angle penetration cone tool (Texture Technology Corp., as part number TA-15).

To operate the TA-XT2 Texture Analyzer, the tool is attached to the probe carrier arm and cleaned with a low-lint wipe. The sample is positioned and held firmly such that the tool will contact a representative region of the sample. The tool is reset to be about 1 cm above the product sample.

- 5 The sample is re-position so that the tool will contact a second representative region of the sample. A run is done by moving the tool at a rate of 2 mm/second exactly 10 mm into the sample. The “RUN” button on the Texture Analyzer can be pressed to perform the measurement. A second run is done with the same procedure at another representative region of the sample at sufficient distance from previous measurements that they do not affect the second run. A third run is done with the
- 10 same procedure at another representative region of the sample at sufficient distance from previous measurements that they do not affect the third run.

The following Firmness values are returned from this measurement:

- 15 If the mixture fails to crystallize completely (e.g. remains clear or mushy) at Room Temperature, return a value of “NOT SOLID”; if the mixture is in excess of 48 N and too hard to measure, return a value of “TOO HARD”; otherwise a numeric value which is the average of the maximum value of three measurements is returned.

20 THERMAL STABILITY TEST METHOD

All samples and procedures are maintained at room temperature ($25 \pm 3^\circ\text{C}$) prior to testing.

- Samples for testing are stored in sealed glass jars. Jars are placed in a constant temperature oven set to $54 \pm 1^\circ\text{C}$ and stored for two weeks. After two weeks, samples are removed from oven, stored
- 25 at $25 \pm 3^\circ\text{C}$ for 24 hours and then visually assessed for being or not being a rheological solid.

WATER-EXPRESSION TEST METHOD

All samples and procedures are maintained at room temperature ($25 \pm 3^\circ\text{C}$) prior to testing.

- 30 Measurements for the determination of Water-Expression were made with a TA Discovery HR-2 Hybrid Rheometer (TA Instruments, New Castle, Delaware, U.S.A.) and accompanying TRIOS software version 3.2.0.3877, or equivalent. The instrument is outfitted with a DHR Immobilization Cell (TA Instrument) and 50 mm flat steel plate (TA Instruments). The calibration is done in

accordance with manufacturer's recommendations, with special attention to measuring the bottom of the DHR Immobilization Cell, to ensure this is established as gap = 0.

5 Samples are prepared in accordance with EXAMPLE procedures. It is critical that the sample be prepared in Speed Mixer containers (Flak-Tech, Max 60 Cup Translucent, Cat # 501 222t), so that the diameter of the sample matches the diameter of the HR-2 Immobilization Cell. The sample is released from the containers by running a thin spatula between the edge of the container and the sample. The container is gently turned over and placed on a flat surface. A gentle force is applied to the center of the bottom of the overturned container, until the sample releases and gently glides
10 out of the container. The sample is carefully placed in the center ring of the DHR Immobilization Cell. Care is used to ensure that the sample is not deformed and re-shaped through this entire process. The diameter of the sample should be slightly smaller than the inner diameter of the ring. This ensures that force applied to the sample in latter steps does not significantly deform the cylindrical shape of the sample, instead allowing the fluid to escape through the bottom of the
15 sample. This also ensures that any change in the height of the sample for the experiment is equivalent to the amount of aqueous phase expressed during the test. At the end of the measurement, one should confirm that the aqueous phase is indeed expressed from the sample through the measurement, by looking for water in the effluent tube connected to the Immobilization Cell. If no aqueous phase is observed, the sample is deemed not to express water and is not
20 inventive.

Set the instrument settings as follows. Select Axial Test Geometry. Then, set "Geometry" options: Diameter = 50 mm; Gap = 45000 um; Loading Gap = 45000 um; Trim Gap Offset = 50 um; Material = 'Steel'; Environmental System = "Peltier Plate". Set "Procedure" options: Temperature
25 = 25°C; Soak Time = 0 sec; Duration = 2000 sec; Motor Direction = "Compression"; Constant Linear Rate = 2 um sec-1; Maximum Gap Change = 0 um; Torque = 0 uN·m; Data Acquisition = 'save image' every 5 sec.

30 Manually move the steel tool within about 1000 um of the surface of the sample, taking care that the tool does not touch the surface. In the "Geometry" options, reset Gap to this distance.

Start the run.

The data is expressed in two plots:

- 1) Plot 1: Axial Force (N) on the left-y-axis and Step Time (s) on the x-axis;
- 2) Plot 2: Gap (um) on the right-y-axis and Step Time (s) on the x-axis.

The Contact Time – T(contact), is obtained from Plot 1. The T(contact) is defined as the time when the tool touches the top of the sample. The T(contact) is the Step Time when the first Axial Force data point exceeds 0.05 N.

The Sample Thickness – L, is the gap distance at the Contact Time, and expressed in units of meters.

The Time of Compression – T(compression), is the Step Time at which the gap is $0.85 \cdot L$, or 15 % of the sample.

The Work required to squeeze the water from the structure is the area under the Axial Force curve in Plot 1 between T(contact) and T(compression) multiplied by Constant Linear Rate, or $2e-6 \text{ m s}^{-1}$ normalized by dividing the total volume of expressed fluids, and is expressed in units of Joules per cubic meter (J m^{-3}).

If Water-Expression cannot be measured because the sample is a rheological solid but too soft to handle for testing, then a sample is assigned a value of 'SOFT'.

EXAMPLES

Materials List

1. Sodium Stearate – TCI Chemicals, Cambridge, MA, Cat. # S0081
2. Sodium Chloride – VWR, Radnor, PA. Cat.# BDH9286-500G
3. Propylene Glycol- THE DOW CHEMICAL COMPANY, Midland, MI, Cat. #360603
4. NovaGum- Archer Daniels Midland, Minneapolis, MN. Cat.# 99543283
5. Glycerol - Alfa Aesar, Havehill, MA. Cat. # A16205
6. 1,2 Hexanediol-Thermo Fisher Scientific, Waltham, MA. Cat. # L06864.18
7. Ethanol-EMD Millipore Corp., Burlington, MA. Cat.#EX0276
8. Isopropyl alcohol- EMD Millipore Corp., Burlington, MA. Cat.#PX1835
9. IR3535-EMD Performance Materials Corp., Philadelphia, PA. Cat. #111887
10. Stearic Acid-Sigma Aldrich, St. Louis, MO Cat#. 175366

11. Water – Millipore, Burlington, MA (18 m-ohm resistance)

SAMPLES 1-24 formed rheologically solid compositions at 25 °C according to the PHASE STABILITY TEST METHOD which included varying amounts of crystalizing agent, cosolvents, and insect repellent active. Inventive samples remained a rheological solid material after aging for 2 weeks at an elevated temperature according to the THERMAL STABILITY TEST METHOD. Comparative SAMPLE 25 did not form a rheological solid material at 25 °C according to the PHASE STABILITY TEST METHOD, demonstrating the need to overcome the negative impact which the insect repellent active has on crystallization. Comparative SAMPLES 26-33 formed rheologically solid compositions at 25 °C according to the PHASE STABILITY TEST METHOD which did not remain solid at an elevated temperature according to the THERMAL STABILITY TEST METHOD.

Each Sample was prepared according to the following procedure and with the material weights listed in TABLES 1 and 2. Water was heated to boiling using a benchtop kettle (Hamilton Beach Professional Digital Kettle type K58 120 V-60 Hz 1500 W Model : 41028 Serial: A2591ER). All constituent materials were weighed accurately using a Mettler-Toledo balance Moel E02140 (Mettler Toledo LLC, Columbus, OH.). Sodium stearate, sodium chloride, stearic acid, and the heated water were weighed and added to a glass jar of sufficient size with a sealing lid (40z jar or 16 Oz Jar.). The lid was affixed, and the jar placed into a Binder oven FD115-UL (Binder Inc., Bohemia, NY) set to 85°C± 2°C for a period of about two hours, until the sodium stearate and sodium chloride were fully solubilized and the mixture is visually clear. If the sodium stearate and sodium chloride did not fully solubilize, the composition making was stopped. The solution was removed from the oven and placed onto a hot/stir plate (Corning Stirrer/Hot plate model PC-420 120 VC-698W-60 HZ; Corning Inc., Corning NY). A magnetic stir bar of appropriate size was added to the solution and the heating and stir functionalities turned on to form a vortex in the solution with moderate heating. The jar lid was reaffixed to prevent evaporative loss except when materials were added. Propylene glycol was weighed, and qif a suspension agent was used, it was weighed and added to the propylene glycol, then mixed using a disposable spatula. The suspension agent/propylene glycol mixture was then added to the main mixing vessel. If no suspension agent was used, the propylene glycol alone was added to the main mixing vessel. The heating functionality of the hot plate was turned off. The cosolvents and 3-[N-n-butyl-N-acetyl] aminopropionic acid ethylester (IR3535) were weighed and added to the main mixing vessel. The mixture was left to stir for a period of about 1 minute. The stir bar was removed from the jar and

Rheological solid composition@ 25 C (after making)	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N
Rheological solid composition@ 25 C (after 2wks @ 54 C)	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N

TABLE 3 illustrates comparative examples where the composition remained solid at 54 °C initially but liquify after 2 weeks of ageing (Examples 29-33) while Examples (25-28) melt at 54 °C initially and do not recover to a solid.

5

TABLE 3

	26	27	28	29	30	31	32	33
Sodium Stearate	6	6	6	6	8	6	6	7
Sodium Chloride	4	4	4	4	5	4	4	4
Propylene Glycol	3	5	3	5	3	10	10	10
NovaGum	0.3	--	0.3	0.3	0.3	--	0.3	0.3
Ethanol	--	4	4	4	--	4	--	--
IR3535	10	10	10	10	10	10	10	10
Stearic Acid	--	--	--	--	--	--	--	--
Water	77	71	73	71	74	66	70	69
(SS+NaCl)/H ₂ O	13	14	14	14	18	15	14	16
Hydroxyl wt. %	3	9	7	9	3	14	10	10
Rheological solid @ 25 C (after making)	Y	Y	Y	Y	Y	Y	Y	Y
Rheological solid @ 25 C (after 2wks @ 54 C)	N	N	N	N	N	N	N	N

All samples (inventive and comparative) initially formed Rheological Solid Compositions (hardness quantified for some examples in Table below). Inventive examples that remained solid after 2 weeks of ageing at elevated temperature exhibit a pH drop of 1.15 units or less while the comparative examples had a pH drop greater than 1.15 units. As shown in TABLE 4.

10

TABLE 4

Example	pH after making	pH on day 14	pH Shift	Hardness after making (N)	Rheological solid composition @ 25 C (after making)	Rheological Solid composition @ 25 C (after 2wks @ 54 C)
1	7.66	7.52	0.14	22.7	Y	Y
2	7.72	7.05	0.67	22.1	Y	Y
9	7.63	7.38	0.25	16.6	Y	Y
11	7.99	6.96	1.03	17.6	Y	Y

12	7.87	7.22	0.65	19.3	Y	Y
13	7.89	7.44	0.45	5.8	Y	Y
14	7.83	6.75	1.08	22.3	Y	Y
15	7.61	7.69	-0.08	22.5	Y	Y
16	7.69	7.69	0	8.9	Y	Y
24	7.45	7.73	-0.28	29.3	Y	Y
25	7.94	5.55	2.39	5.3	Y	N
26	7.82	6.06	1.76	11.3	Y	N
27	7.84	5.89	1.95	10.8	Y	N
28	7.99	6.08	1.91	11.3	Y	N
29	7.89	6.27	1.62	--	Y	N
30	7.61	6.4	1.21	13.14	Y	N
31	7.94	5.95	1.99	11	Y	N
32	7.83	6.41	1.42	12.9	Y	N

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

Values disclosed herein as ends of ranges are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each numerical range is intended to mean both the recited values and any real numbers including integers within the range. For example, a range disclosed as “1 to 10” is intended to mean “1, 2, 3, 4, 5, 6, 7, 8, 9, and 10” and a range disclosed as “1 to 2” is intended to mean “1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, and 2.”

Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover
5 in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

What is claimed is:

1. A population of capsules comprising:

5 a core comprising a benefit agent;

a shell surrounding the core;

wherein the shell surrounding the core comprises a substantially inorganic first shell;

wherein the substantially inorganic first shell comprises a condensed layer comprising a condensation product of a mixture of precursors;

10 wherein the mixture of precursors comprises a silica precursor and a crosslinking metal-oxide precursor.

2. The population of capsules according to claim 1, wherein the silica precursor comprises at least one compound of formula (I) or formula (II):

15 SiY_4 (formula I)

Where each Y is independently selected from OH, -OR₂, halo, , NH₂, -

NHR₂, -N(R₂)₂, and 

wherein R₂ is a C₁ to C₂₀ alkyl, C₁ to C₂₀ alkylene, C₆ to C₂₂ aryl, or a 5-12 membered heteroaryl comprising from 1 to 3 ring heteroatoms selected from O, N, and S;

20 R₃ is a H, C₁ to C₂₀ alkyl, C₁ to C₂₀ alkylene, C₆ to C₂₂ aryl, or a 5-12 membered heteroaryl comprising from 1 to 3 ring heteroatoms selected from O, N, and S;

(SiO_zY_n)_w (formula II)

Where z is from 0.5 to 1.6,

25 each Y is independently selected from

OH, -OR₂, halo, , NH₂, -NHR₂, -N(R₂)₂, and 

wherein R₂ is a C₁ to C₂₀ alkyl, C₁ to C₂₀ alkylene, C₆ to C₂₂ aryl, or a 5-12 membered heteroaryl comprising from 1 to 3 ring heteroatoms selected from O, N, and S;

R3 is a H, C1 to C20 alkyl, C1 to C20 alkylene, C6 to C22 aryl, or a 5-12 membered heteroaryl comprising from 1 to 3 ring heteroatoms selected from O, N, and S;
n is from 0.7 to 4; and
w is from 2 to 2000.

5

3. The population of capsules according to claim 2, wherein the crosslinking metal-oxide comprises at least one compound of formula (III),
[M_aL_bX_c] (formula (III))

10

Where M is a metal that includes d-block and f-block elements;
each L independently includes mono- bi- or tri-dentate chelating ligands;
each X independently includes alkoxy ligands or halo ligand;
(a) is an integer from 1 to 3;
(b) is an integer from 1 to 6x(a); and
(c) is an integer from 0 to 4x(a).

15

4. The population of capsules according to claim 3, where M comprises Titanium or Zirconium, L comprises at least one of aldehydes, esters or alkoxides, preferably wherein the alkoxide group has eleven or more carbon atoms, and wherein (b) is larger than (c).

20

5. The population of capsules according to any of the preceding claims, wherein the Molecular weight of the compound of formula (II) is between 1000 Da and 6000 Da.

25

6. The population of capsules according to any of the previous claims, wherein the compound of formula (II) is a poly ethoxy siloxane.

7. A population of capsules comprising:

a core comprising a benefit agent;
a mixed-oxide shell surrounding the core;

30

wherein the mixed-oxide shell comprises silica and a crosslinking metal-oxide;
wherein the crosslinking metal-oxide is present in an amount of about 10ppm to about 10wt% based on the total weight of the mixed-oxide shell, preferably between 100ppm and 1%, more preferably between 500ppm and 0.5%.

8. The population of capsules according to claim 7, wherein the crosslinking metal oxide is at least one of zirconium oxide or titanium oxide.
9. A process of making capsules, the process comprising the following steps:
 - 5 a. preparing an oil phase comprising a benefit agent;
 - b. adding a precursor of formula(I) and formula (II);
 - c. adding a precursor for formula (III-a) or adding a metal-alkoxide to form in-situ the compound of formula (III-a);
 - d. forming an oil-in-water emulsion between said oil phase and a water phase optionally
10 comprising nanoparticles and optionally comprising an acid;
 - e. subjecting the oil-in-water emulsion to heat to form capsules.
10. The method according to claim 9 further comprising the step of adding a second-shell component solution to the capsules to form capsules with a second-shell component.
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11. The process of making capsules according to claim 9 or 10, wherein the benefit agent comprises an aldehyde or an ester and wherein the compound of formula(III-a) is formed in-situ between a metal alkoxide and the aldehyde or ester.
- 20 12. The process of making capsules according to any of claims 9 to 11, wherein the precursor of formula (II) has a molecular weight between 1000Da an 6000Da.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. A01P17/00 A01N37/46 A01N25/04 A01N25/30 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) A01P		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, CHEM ABS Data, WPI Data, BIOSIS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2021/207440 A1 (PROCTER & GAMBLE [US]) 14 October 2021 (2021-10-14) claims 1-14 page 33, lines 11-28 example 3 -----	1-12
A	US 2021/315783 A1 (LYNCH MATTHEW LAWRENCE [US] ET AL) 14 October 2021 (2021-10-14) claims 1-26 example 3 paragraphs [0075], [0078], [0085] -----	1-12
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 17 April 2024		Date of mailing of the international search report 08/05/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Marie, Gérald

INTERNATIONAL SEARCH REPORT

Information on patent family members

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