SURFACTANT AND SOLVENT-FREE HEAVY DUTY SKIN CLEANSER

FIELD

The present invention relates to the field of skin and surface cleansing formulations, more specifically to surfactant-free and solvent-free heavy duty skin cleansers.

BACKGROUND

Heavy duty skin cleansers are used for removing difficult to eliminate hydrophobic stains such as waterproof make-up, oil, grease, and tar to mention just a few. These formulations combine surfactants (to emulsify) and/or solvents (to solubilize), and sometimes fine abrasives particles (for example synthetic microbeads, ground fruit stones, minerals, vegetable fibers) with mechanical properties. The combination of the three modes of action – emulsification, solubilisation and scrubbing – makes these products particularly effective.

A typical composition of heavy duty skin cleanser consists of 5 to 20% of surfactants (anionics, and/or amphoterics and/or non-ionics), 1 to 30% of a solvent (for example white spirits, vegetable oils, esters, paraffin oil, glycols and terpenes) and 1 to 10% of microbeads (from vegetable, synthetic or mineral origins).

Surfactants and non-polar or semi-polar solvents have various levels of human and environmental toxicity. For instance, some surfactants may be irritating to the skin (i.e. sodium lauryl sulfate, and alkaline soaps) and solvents may be neurotoxic (i.e. hydrocarbons), hematotoxic (i.e. glycol ethers), allergising (i.e. oxidized terpenes, lactone sesquiterpenes), mutagenic (i.e. aromatics).

Therefore, one way to improve the toxicological and environmental profile of skin cleansers would be to reduce significantly their total amount of active matter (surfactants and solvents), assuming that highly synergistic associations of ingredients may be formulated; this is easier said than done, simply because thousands of formulators have already been working on such projects for the last 50 years, all over the world.

Thus it would be very beneficial to develop a totally new concept of hydrophobic stain removers by using a safe substitute to surfactants and solvents.

SUMMARY

In one aspect, there is provided a hand cleanser formulation, the formulation comprising: a gel; and lipophilic polymeric particles selected from the group consisting of a polymer of norbornane, a polymer of norbornene, a polymer of norbordiene, and a polymer of a derivative of norbornane, norbornene or norbordiene, wherein said derivative of norbornane, norbornene or norbordiene is one in which a hydrogen atom of one or more C-H bonds of norbornane, norbornene or norbordiene is substituted with a hydrocarbyl group;, the particles being suspended in the gel and present in a concentration from about 0.1 % w/w to about 99% w/w of the formulation, wherein: the gel comprises at least one non-Newtonian thickener present in an amount sufficient to provide the formulation with a yield value of at least 30 dynes/cm^2 (3 Pa); the formulation is optionally free of lipophilic solvent; and the formulation is optionally free of surfactant.

In another embodiment, there is provided a skin cleansing formulation, comprising: a gel; and lipophilic particles comprising cellulose acetate; orlipophilic particles comprising aggregates of fumed silica, the particles being suspended in the gel and present in a concentration from about 0.1 % w/w to about 99% w/w of the formulation, wherein: the gel comprises at least one non-Newtonian thickener present in an amount sufficient to provide the formulation with a yield value of at least 30 dynes/cm^2 (3 Pa); the formulation is optionally free of lipophilic solvent; and the formulation is optionally free of surfactant.

In another embodiment there is provided the formulation as disclosed above for use as a hand cleanser.

Also provided herein are skin cleansing formulations particularly useful for cleaning heavy duty oil/dirt from skin based on lipophilic particles as a hydrophobic stain-removing agent for the replacement of all or part of the surfactants and solvents normally involved in greasy stain-removing heavy duty skin cleansers.

An embodiment of a skin cleansing formulation is a gel in which lipophilic polymeric particles are suspended. The particles are present in a concentration from about 0.1 % w/w to about 99% w/w of the formulation, and the gel comprises at least

one non-Newtonian thickener present in an amount sufficient to provide the formulation with a yield value of at least 30 dynes/cm^2.

In embodiments, the formulation is free of lipophilic solvents and/or is free of surfactants.

A non-Newtonian thickener can be any one or more of acrylates/C10-30 alkyl acrylate crosspolymer, carbomer, xanthan gum, guar gum, quaternised guar gum, alginate, bentonite, and is typically present in a concentration totalling from about 0.01 to about 10% w/w of the formulation.

The polymer particles are often present in the formulation in a range from about 0.5 to about 20% w/w of the formulation, for example, or range from about 1 to about 10% w/w of the formulation.

While lipohilic particles may themselves act as scrubbing particles, a formulation may additionally include other scrubbing particles in a concentration from about 0.1 to about 95% w/w, more likely in a concentration from about 0.5 to about 20% w/w, or from about 1 to about 10% w/w of the formulation. Such scrubbing particles can be any one or any combination of vegetable based, organic based and mineral based scrubbing agents, such as, for example, vegetable based particles e.g., one or more of ground cornmeal, ground fruit stones, ground walnuts, or other organic based scrubbing particles such as wood dust, polyethylene and/or polypropylene, or mineral based scrubbing particles such as pumice and/or ground shellfish.

One or more preservatives having bacteriostatic and/or fungistatic properties can be included in a formulation.

A formulation can also include one or more than one chelating agent, typically in a concentration of from 0.01 to 5% w/w, or more likely from about 0.1 to about 0.5% w/w of the formulation.

A formulation can include skin conditioner(s) such as polyols (glycerin, polyglycerol, sorbitol, and propylene glycol), allantoin, quaternised polymers or gums (polyquaterniums, dihydroxypropyl PEG-5 linoleammonium chloride, guar hydroxypropyltrimonium chloride, behentrimonium chloride), butylene glycol, hydrogenated vegetal oils, and toxopherols. Typical conditioner(s) concentrations are from about 0.01 to about 10% w/w or from about 0.1 to about 5% w/w of the formulation.

As discussed further below, a formulation can include one or more hydrotrope in a concentration of from about 0.01 to about 10% w/w, or from about 0.1 to about 5% w/w of the formulation.

Lipophilic particles of a formulation generally have a size in a range from about 10 to about 3000 μm, or from about 50 μm to about 1000 μm. An average size of the particles can be in the range of from 50 μm to 2000 μm, or they can be microparticles having an average size in the range of from 50 μm to 900 μm, 100 μm to 700 μm, or from 200 μm to 600 μm.

A formulation can thus be substantially free of lipophilic solvent and/or substantially free of surfactant.

Formulations to which no water has been added are also possible.

Where water is a component of a gel formulation, it may be present in amount of from about 0% to about 85% w/w or more of the formulation.

A pH adjuster may also be present, to bring the pH of the formulation into a range of e.g., between about 4 and about 9, more typically from about 5 to about 7.

Lipophilic particles include one or more polymers of a norbornane, norbornene, norbornadiene, or derivatives of any of these, cellulose acetate; aggregates of fumed silica, or a combination of any of the foregoing.

A derivative of norbornane, norbornene or norbornadiene include those in which a hydrogen atom of one more C-H bonds of norbornane, norbornene or norbornadiene is substituted with a hydrocarbyl group, as discussed further below.

An example described in greater detail below involves a formulation containing poly(norbornene), a homopolymer of of bicyclo[2.2.1]hept-2-ene (norbornene).

Another embodiment of a skin cleansing formulation comprises a gel and particles of a polymer comprised of any one of norbornadiene, its derivatives, norbornane and its derivatives, with the particles being suspended in the gel and present in a concentration from about 0.1% to about 99% w/w of the formulation.

Another embodiment of the invention is a skin cleansing formulation comprising lipophilic polymeric particles wherein the formulation is substantially free of lipophilic solvent, substantially free of surfactant, and particles form from 0.1% to about 100% of the formulation.

Water can be included in such a formulation in an amount of about 1% to about 95.5% w/w, about 10% to about 95%, about 15% to about 95%, about 20% to about 95%, about 30% to about 95%, about 40% to about 95%, about 50% to about 95%, about 1% to about 90%, about 1% to about 80%, about 1% to about 70%, about 1% to about 60%, about 5% to about 95%, about 5% to about 80%, about 20% to about 95%, about 20% to about 80%, about 30% to about 95%, about 30% to about 80%, about 40% to about 99%, about 40% to about 95%, about 40% to about 80%, or about 50% to about 95%, w/w of the formulation.

The formulation can include scrubbing particles, as described above, e.g., in a concentration from about 0.5 to about 20% w/w of the formulation.

The formulation can include preservative(s) as described in connection with gel formulations.

The formulation can include chelating agent(s), as described above.

The formulation can include one or more skin conditioners as described elsewhere herein.

The formulation can also include at least one hydrotrope as described below.

Lipophilic particles of the formulation can have a size in a range from about 10 to about 3000 μm and can be microparticles having a size in a range from about 50 μm to about 1000 μm, or as elsewhere described herein.

A formulation containing water may include a pH-adjuster.

The lipophilic particles can comprise any of those described above or as set out in the detailed description, including a polymer of a norbornane, norbornene, norbornadiene, or a derivative of norbornane, norbornene or norbornadiene; cellulose acetate; aggregates of fumed silica, or a combination of any of these.

In aspects, the polymer particles are present in the formulation in a range from about 0.5 to about 20% w/w or from about 1 to about 10% w/w of the formulation.

The invention includes a composition comprising a formulation as described herein for use as a hand cleanser, particularly a heavy duty cleanser, including a method of cleansing hands using such a composition.

A further understanding of the functional and advantageous aspects of the disclosure can be realized by reference to the following detailed description and drawings.

BRIEF DESCRIPTION OF THE TABLES

Table 1 shows a formulation used to test effectiveness of heavy duty hand cleansers;

Table 2 shows an exemplary test formulation;

Table 3 summarizes the final scores used to rate different formulations;

Table 4 shows non-limiting examples of water-based formulations that can be used as formulations for a gritty foam dispenser in accordance with the present invention; and

Tables 5 to 10 show non-limiting examples of water-less formulations.

DETAILED DESCRIPTION

Various embodiments and aspects of the disclosure will be described with reference to details discussed below. The following description and drawings are illustrative of the disclosure and are not to be construed as limiting the disclosure. The drawings are not necessarily to scale. Numerous specific details are described to provide a thorough understanding of various embodiments of the present disclosure. However, in certain instances, well-known or conventional details are not described in order to provide a concise discussion of embodiments of the present disclosure.

As used herein, the terms, "**comprises**" and "**comprising**" are to be construed as being inclusive and open ended, and not exclusive. Specifically, when used in this specification including claims, the terms, "comprises" and "comprising" and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

As used herein, the term "**exemplary**" or "**example**" means "serving as an example, instance, or illustration," and should not be construed as preferred or advantageous over other configurations disclosed herein.

As used herein, the terms "**about**" and "**approximately**", when used in conjunction with ranges of dimensions of particles, compositions of mixtures or other physical properties or characteristics, are meant to cover slight variations that may exist in the upper and lower limits of the ranges of dimensions so as to not exclude embodiments where on average most of the dimensions are satisfied but where statistically dimensions may exist outside this region. It is not the intention to exclude embodiments such as these from the present disclosure.

As used herein, the phrase "**non-Newtonian thickener**" or "non-Newtonian thickening agent" means a category of fluids whose viscosity (resistance to deformation or shear forces) is influenced by the shear stress and/or by the time this force is applied.

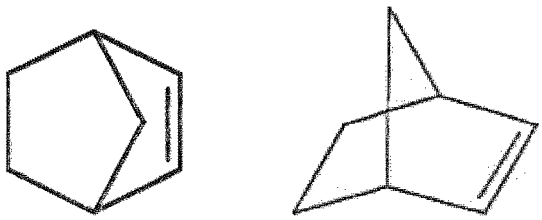
As used herein, the phrase "**critical strain force**" (also referred to as "**yield value**") refers to a term used in rheology in which the 'critical strain force' is the minimum force that must be applied to a material to induce viscous flow. The critical strain force is a measurable quantity (expressed in dynes/cm^2). More particularly, both phrases are referring to the same phenomenon which is that up to a certain force exerted (the critical strain force), a visco-elastic material will exhibit "solid like" or "elastic" properties, i.e. it will not have a net flow. Above the critical strain force (or above the "yield value") the same material will exhibit viscous properties, i.e. it will flow.

The present formulation strategy to find a replacement for surfactants and solvents was to identify some oil-absorbing and lipophilic ingredients (see below)

with the potential to replace all or part of the surfactants and solvents usually involved in formulations of heavy duty hand cleansers.

Oil-absorbers such as polynorbornenes are used mainly in the rubber industry for anti-vibration (rail, building), anti-impact (personal protective equipment, shoe parts, bumpers) and grip improvement (toy tires, racing tires, transmission systems, transports systems for copiers, feeders, etc.). They are also useful for other applications such as oil-binding system with absorption capability (10 times of own weight) of hydrocarbons to treat pollutions from oil spills. It has been surprisingly found that the invention is able to provide high levels of skin cleansing efficacy with only 5% of norbornene polymer suspended in an aqueous gel.

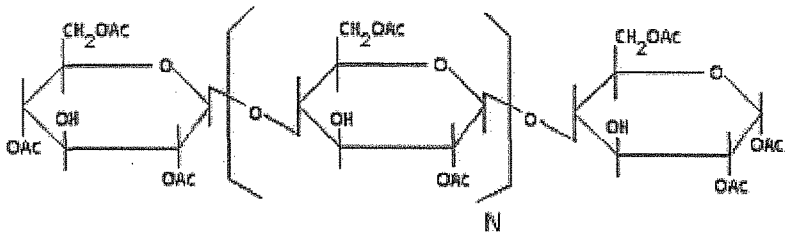
The norbornene molecule carries a double bond which induces significant ring strain and significant reactivity: It is made by a Diels-Alder reaction of cyclopentadiene and ethylene:



The IUPAC name of the molecule is bicyclo[2.2.1]hept-2-ene, its CAS Number is 498-66-8, and its chemical formula is C_7H_{10}. The norbornene molecule (also called norbornylene or norcamphene) is not toxic to humans and aquatic life. It is comprised of a cyclohexene ring bridged with a methylene group in the 'para' position.

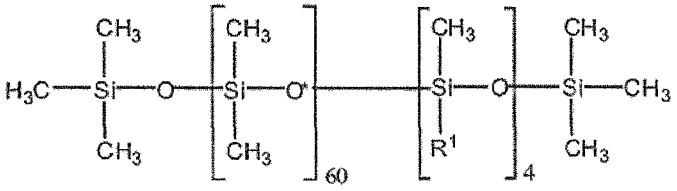
In addition to norbornene, the present formulations instead of using norbornene includes derivatives of norbornene and may also include separately or in combination related bicyclics of norbornene including norbornadiene which has the same carbon skeleton but with two double bonds, and derivatives of norbornadiene and norbornane which is completely saturated without double bonds, and its derivatives.

Formulations may also contain, alone or in combination with norbornyl-related polymeric particles, other lipophilic absorbent particles such as cellulose acetate:



Cellulose acetate is also known as zyl, zylonite, Cellon and Rhodoid.

Formulations may also include aggregates of hydrophobic (fumed) silica which hydrophobic groups are alkyl or polydimethylsiloxane chains such as in the following structure:



Fumed silica, also called 'pyrogenic silica' consists of amorphous three-dimensional particles, and is characterized by an extremely low density and a very high specific surface area (500 to 2000 m^2/g).

Norbornene based polymer particles have a size ranging from 50 to 1000 µm, which is an appropriate granulometry and the right hardness also serve as a scrubbing agent. Preferred norbornene particles are available from the manufacturers Astrotech Advanced Elastomerproducts GmbH. Such particles are microparticles e.g., the product Norsorex® APX.

An embodiment of the skin cleansing formulation comprises a gel and particles of a polymer comprised of any one of bicyclo[2.2.1]hept-2-ene, homopolymer (norbornene) and/or its derivatives. Other embodiments may contain norbornadiene and its derivatives or and norbornane and its derivatives.

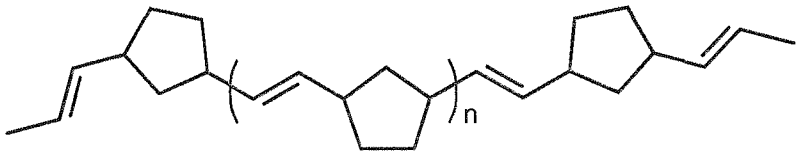
Embodiments include formulations containing derivatives of norbornane, norbornene, norbornadiene include those in which a hydrogen atom of one more C-H bonds of norbornane, norbornene or norbornadiene is substituted with a hydrocarbyl group. The term "hydrocarbyl", when referring to groups attached to the remainder of a molecule, refers to a radical group made up of carbon and hydrogen

atoms. Such groups include: C1-C20 hydrocarbyl groups that are straight chain and branched alkyl groups, C2-C20 alkenyl and alkynyl groups containing one or more or both type of said unsaturations, C3-C20 hydrocarbyl groups containing one or more rings, and which may also contain one or more alkenyl or alkynyl unsaturations. Examples of hydrocarbon groups include methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, n-pentyl, branched pentyl, hexyl, branched hexyl, heptyl, branched heptyl, octyl, branched octyl, and any of C9-, C10-, C11-, C12-, C13-, C14-, C15-, C16-, C17-, C18-, C19- and C20- straight chain and branched alkyl groups. Alkenyl and alkynyl groups include those corresponding to the foregoing alkyl groups of ethyl, n-propyl, i-propyl, etc. containing one or more double bonds (C=C) or triple bonds (C≡C) or combinations of double and triple bonds. Cyclic hydrocarbyl groups include cyclopropyl, cycobutyl, cyclopentyl, norbornyl, and the like, and these may be appended by a diradical formed by replacing a hydrogen atom of a linear or branched hydrocarbyl group with such a cyclic group. Cyclic groups themselves can include one or more double and/or triple bonds.

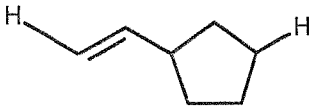
In the context of this invention, the term "microparticle" refers to a solid or amorphous particle 1 µm to about 1 mm in diameter. Lipophilic particles of a formulation can extend to particles in the range from 1 µm to 3,000 µm, 10 µm to 3,000 µm, 10 µm to 2,000 µm, but more likely ranges are 10 µm to 1,000 µm, 20 µm to 900 µm or 40 to 900 µm or about 50 to about 800 µm. Particle size is readily determined by techniques well known in the art, such as e.g., photon correlation spectroscopy, laser diffractometry and/or scanning electron microscopy. The term "microparticles" means a collection of particles whose average size is less than 1 mm, more likely less than 800 µm. This includes collections having an average size in the range of from 50 µm to 800 µm, 50 µm to 700 µm, 100 µm to 700 µm, 150 µm to 700 µm, 200 µm to 700 µm, 250 µm to 700 µm, 300 µm to 700 µm, 400 µm to 700 µm, 50 µm to 600 µm, 100 µm to 600 µm, 150 µm to 600 µm, 200 µm to 600 µm, 250 µm to 600 µm, 300 µm to 600 µm, 350 µm to 600 µm, 100 µm to 500 µm, 200 µm to 500 µm, or 300 µm to 500, or collections having an average size of about 100 µm, 150 µm, 200 µm, 250 µm, 275 µm, 300 µm, 325 µm, 350 µm, 375 µm, 400 µm, 425 µm, 450 µm, 475 µm, 500 µm, 525 µm, 550 µm, 575 µm, 600 µm, 625 µm, 650 µm, 675 µm, or 700 µm.

"Lipophilic" microparticles or particles of compositions have an affinity for e.g., hydrocarbons and absorb these in use as part of the cleansing process. This has been found to reduce or even eliminate the need for a solvent, as the term is used in the art, as part of the cleanser. As mentioned above such cleaning solvents include white spirits, vegetable oils, esters, paraffin oil, and terpenes.

A particle is a solid particle that does not dissolve in a liquid such as water or toluene. Particles composed of monomeric units that are lipophilic when isolated are themselves said to be lipophilic particles. For the purposes of this definition, an isolated monomeric unit of e.g., the homopolymer polynorbornene can be obtained by replacing the single bonds to neighboring units of polymer by hydrogen atoms to obtain compound **A**.



polynorbornene



A

Compound **A** does not dissolve to an appreciable extent in or mix with water i.e., is not miscible with water, so is lipophilic, and so polymeric particles composed of the monomer are said to be lipophilic. Compound **A** does dissolve in or is miscible with a lipophilic solvent e.g., white spirits (petroleum distillates), paraffin oil, terpenes, etc. Fumed silica particles are often referred to in the art as hydrophobically-modified silica and are lipophilic particles. Norbornene has exemplary oil-binding capabilities with respect to hydrocarbons, absorbing up to ten times its own weight.

In another context, cleansing formulations are said to be substantially free of lipophilic solvents. Such solvents are not appreciably miscible with water i.e., less than 1 mg/ml (preferably less than 0.5 mg/ml) is miscible with water at 15°C, but such solvents are miscible with other lipophilic solvents such as white spirits, paraffin oil, terpenes, benzene, toluene, etc. A formulation is substantially free of lipophilic solvent when lipophilic solvent(s) make up no more than about 5 % w/w of the formulation, more preferably less than about 4 % w/w, 3 % w/w, 2 % w/w, 1 % w/w, 0.5% w/w, or less than 0.1 % w/w of a formulation. In the examples described here,

no lipophilic solvent is added to the formulation, so these formulations contain at most trace amounts of such solvent(s) as may be present in components of the formulation as sourced. Such formulations are referred to as solvent-free formulations. As water is not a lipophilic liquid, but rather a hydrophilic liquid, it is not considered a solvent in this context.

The particles are suspended in the gel and present in a concentration from about 0.1% to about 99 % w/w of the formulation. More preferably the polymer particles are present in a range from about 0.5 to about 20% w/w, and more preferably they are present in a range from about 1 to about 10% w/w. The particles have a size in a range from about 10 to about 3000 µm, and more preferably in the range from about 100 to 1000 µm.

The gel includes at least one non-Newtonian thickener able to provide the formulation with a yield value of 30 dynes/cm² or more, the non-Newtonian thickener being any one or combination of acrylates/C10-30 alkyl acrylate crosspolymer, carbomer, xanthan gum, guar gum, quaternised guar gum, alginate and bentonite, in a concentration of from about 0.01 to about 10% w/w of the formulation, more likely in a range from about 0.1 to about 10%, or 0.1 and 5%, or 0.1 and 4%, or 0.1 and 3%, or 0.1 and 2%, or 0.1 and 1% w/w of the gel formulation.

The non-Newtonian thickener able to provide the formulation with a yield value of 30 dynes/cm² or more, the non-Newtonian thickener being any one or combination of acrylates/C10-30 alkyl acrylate crosspolymer, carbomer, xanthan gum, guar gum, quaternised guar gum, alginate, bentonite.

In order to provide the structure to suspend the particles, the gel must also have a yield value superior or equal to 30 dynes / cm² associated or not to non-Newtonian rheological behaviour, and it must have more particularly plastic or thixotropic properties (pseudoplastic fluids being excluded from this requirement). The rheology of this form of gel must be viscoplastic (Casson, or Bingham, or dilatant, or thixotropic, or rheopectic fluids) with a yield value which is preferably greater than or equal to 30 dynes/cm². The Yield value is defined as that stress which must be applied before flow will start and, although related to viscosity, it is more dependent on the characteristics of the rheological additive used. Yield value has traditionally been determined by measuring the viscosity of the material at two

speeds using a Brookfield Viscometer. As the speed of rotation of the spindle is increased materials that undergo shear thinning give a lower viscosity measurement.

The soap's yield value or the required yield value may be calculated as follows:

Yield Value (in dynes/cm²) = ($V_{0.5rpm}$ – V_{1rpm}) / 100

Required Yield Value (in dynes/cm²) = [4/3 R(D-Do)g]

Where:

R = particle radius (cm)

D = particle density (g/cm³) Do = medium density (g/cm³)

g = acceleration due to gravity = 980 cm/s²

The non-Newtonian thickener may be present in a range from about 0.1 to about 10% w/w, of the formulation. Viscosity can be in the range e.g., of from 500 to 100,000 cP (centipoise), more preferably in the range of 1,000 to 20,000, or 2,000 to 10,000 cP.

The formulation lipophilic particles may be present in a concentration from about 0.1 to about 95% w/w, or more preferably they may be present in a concentration from about 0.5 to about 20% w/w. More preferably the particles are present in a concentration from about 1 to about 10% w/w.

The formulation can additionally include scrubbing particles that are vegetable based, organic based and/or mineral based scrubbing agents. The vegetable based scrubbing particles may include any one or more of ground cornmeal, ground fruit stones, ground walnuts; the organic based scrubbing particles may include any one or more of wood dust, polyethylene and polypropylene; and the mineral based scrubbing particles may include one or both of pumice and ground shellfish.

The formulation may include at least one preservative having bacteriostatic and fongistatic properties. Non-limiting examples of the preservative includes any one or combination of benzoic acid, benzyl alcohol, bromo-nitro-propanediol, chloroxylenol, diazolidinyl urea, dehydroacetic acid, dichloro-benzyl alcohol, imadazolidinyl urea, iodopropynylbutyl carbamate, methyl-chloro-isothiazolinone and methyl-isothiazolinone, paraben methyl and/or ethyl and/or butyl and/or isobutyl, phenoxyethanol, poly(hexa-methylene biguanide)-hydrochloride, propionic acid, sodium hydroxymethyl glycinate and sorbic acid.

The formulation may include at least one chelating agent. Non-limiting examples of chelating agents include any one or combination of sodium tripolyphosphate, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), 2-hydroxyethyliminodiacetic acid (HEIDA), aminobenzoic acid, iminodisuccinic acid, polyaspartic acid, gluconic acid, and salts thereof, in a concentration of from 0.01 to 5% w/w. More preferably the chelating agent is present from about 0.1 to about 0.5% w/w.

The formulation may include at least one skin conditioner. Non-limiting examples of the skin conditioner includes any one or combination of polyols (glycerin, polyglycerol, sorbitol, propylene glycol), allantoin, quaternised polymers or gums (polyquaterniums, dihydroxypropyl PEG-5 linoleammonium chloride, guar hydroxypropyltrimonium chloride, behentrimonium chloride), butylene glycol, hydrogenated vegetal oils, toxopherols, present in a concentration from about 0.01 to about 10% w/w. More preferably the at least one skin conditioner is present in a concentration from about 0.1 to about 5% w/w. Certain of these compounds e.g., polyquaternium-7 have surfactant properties, however, are included as part of a formulation for skin conditioning properties. As such, they are incorporated into a composition at a level at which they contribute little, if anything, to the cleansing properties of a formulation. In this sense, a formulation is said to be surfactant-free and to be substantially free of surfactant. Examples of such levels are less than 1 %, or less than 0.9 %, or less than 0.8 %, or less than 0.7 %, or less than 0.6 %, or less than 0.5 %, or less than 0.4 %, or less than 0.3 %, or less than 0.2 %, or less than 0.1 %, or less than 0.09 %, or less than 0.08 %, or less than 0.07 %, or less than 0.06 %, or less than 0.05 %, or less than 0.04 %, or less than 0.03 %, or less than 0.02 %, or about 1 %, or about 0.9 %, or about 0.8 %, or about 0.7 %, or about 0.6 %, or about 0.5 %, or about 0.4 %, or about 0.3 %, or about 0.2 %, or about 0.1 %, or about 0.09 %, or about 0.08 %, or about 0.07 %, or about 0.06 %, or about 0.05 %, or about 0.04 %, or about 0.03 %, or about 0.02 %, or about 0.01 % w/w of a formulation.

A formulation may include at least one hydrotrope, but is surfactant-free, or at least substantially free of surfactant as discussed above. Surfactants are compounds

that lower surface tension between two liquids or a liquid and a solid and can act as detergents. One or more hydrotropes can be included in a cleansing a composition to aid stabilization of the gel. A hydrotrope, although amphiphilic like a surfactant, is distinct from a surfactant in this setting in that a hydrotrope does not self-aggregate as a surfactant. Non-limiting examples of the hydrotrope include any one or combination of sodium xylene sulfonate, ammonium xylene sulfonate, calcium xylene sulfonate, potassium xylene sulfonate, sodium toluene sulfonate, ammonium toluene sulfonate, sodium cumene sulfonate, ammonium cumene sulfonate, phosphate polyether ester, alkyldiphenyloxide disulfonate, present in a concentration of from about 0.01 to about 10% w/w. More preferably the at least one hydrotrope is present in a concentration from about 0.1 to about 5% w/w.

The formulation may include at least one pH-adjuster for adjusting the pH of the formulation between about pH 4 and about pH 9, and more preferably between about pH 5 and pH 7. Non-limiting examples of the pH-adjuster include an acidic or alkaline pH-adjuster and is any one or combination of citric acid, phosphoric acid, lactic acid, tartaric acid, sodium hydroxide, potash, aminomethyl propanol, triethanolamine.

The formulation may include any one or combination of colouring dyes, pigments and perfumes.

The formulation may include water, or it may be waterless. A composition that is "substantially free of water" is one to which water has not been added during its formulation, so that it contains at most water contained in ingredients used to make up the composition. The term "waterless" means that a composition contains from 0 up to 5%, preferably less than 3%, most preferably less than 1% by weight of water, based on the total weight of the composition.

EXAMPLES

A simple preliminary test was conducted as follows: Three (3) test subjects washed their hands with soap and dried them well to remove any soiling already present on the skin. The testers soiled their hands with 0.4 g of a reference greasy stain called 'Black Gunge' having ingredients shown in **Table 1**, all around their hands, covering all areas up to their wrists.

Table 1

Black Gunge Formulation	% w/w
Hydraulic Oil	40
Charcoal Powder	20
Hydrocarbon solvent (Premium Burning Oil®)	10
Sunflower seed oil	5
Kaolin	5
Lanolin Ester	20

Without pre-wetting their hands, the test subjects applied 2 ml of a test-product containing ingredients shown in **Table 2** and rubbed it around hands for 30 seconds, insisting on the backs of the hands and between the fingers.

Table 2

Ingredients	% w/w
Water	Qs 100
Acrylates Copolymer (Aqua SF1®)	6.00
Norbonene polymer (Norsorex APX®)	5.00
Sodium hydroxide	Qs pH 7 +/- 0.5

They washed their hands were thoroughly to remove product and soiling and then dried.

The test was repeated with a very effective reference heavy duty hand cleanser 'Swarfega Orange®' from the Deb Group Ltd's international range. Eventual soiling left was assessed by a technician and results were scored with results shown in **Table 3**.

Table 3

Sum of 1 and 2	Final Score	Interpretation of Final Score
0	5	Complete removal of gunge
40	4	Some removal of gunge
80	3	Some removal of gunge
120	2	Some removal of gunge
160	1	Some removal of gunge
200	0	No removal of gunge

Unexpectedly, an average final score of 4.66 was obtained for both test-product and reference product, which means that the test-product was as effective as the reference heavy duty hand cleanser 'Swarfega Orange®' which contains 15-20% of active matter (surfactant, polygrains and solvent).

Table 4 shows non-limiting examples of water-based formulations.

Table 4

Ingredients	Concentrations % w/w					
Water	Qs to 100					
Norbornene polymer	5	10	20	40	80	99
Acrylic polymer	0.40					
Sodium cumene sulfonate	1.00					
Glycerin	3.00					
Polyquaternium-7	0.50					
Phenoxyethanol	1.00					
Diazolidinyl urea	0.50					
Sodium imminodisuccinate	0.40					
sodium xylene sulfonate	2.00					
Perfume	0.20					
CI 19140	0.01					
CI 42090	0.02					
Sodium hydroxide or citric acid	Qs to pH 7+/-0.5					

Tables 5 to 10 show non-limiting examples of water-less formulations.

Table 5

Ingredients	Concentrations % w/w					
Norbornene polymer	5	10	20	40	80	100
Vegetable polygrains	Qs 100					0
Sodium cumene sulfonate	1.00					0
Glycerin	3.00					0
Polyquaternium-7	0.50					0
Perfume	0.20					0
sodium xylene sulfonate	2.00					0

Table 5

Ingredients	Concentrations % w/w					
Norbornene polymer	5	10	20	40	80	100
Vegetable polygrains	Qs 100	Qs 100	Qs 100	Qs 100	Qs 100	0
Sodium cumene sulfonate	1.00	1.00	1.00	1.00	1.00	0
Glycerin	3.00	3.00	3.00	3.00	3.00	0
Polyquaternium-7	0.50	0.50	0.50	0.50	0.50	0
Perfume	0.20	0.20	0.20	0.20	0.20	0
sodium xylene sulfonate	2.00	2.00	2.00	2.00	2.00	0

Table 6

Ingredients	Concentrations % w/w					
Cellulose acetate	5	10	20	40	80	100
Vegetable polygrains	Qs 100	Qs 100	Qs 100	Qs 100	Qs 100	0
Sodium cumene sulfonate	1.00	1.00	1.00	1.00	1.00	0
Glycerin	3.00	3.00	3.00	3.00	3.00	0
Polyquaternium-7	0.50	0.50	0.50	0.50	0.50	0
Perfume	0.20	0.20	0.20	0.20	0.20	0
Sodium xylene sulfonate	2.00	2.00	2.00	2.00	2.00	0

Table 7

Ingredients	Concentrations % w/w					
Hydrophobic fumed silica	5	10	20	40	80	100
Vegetable polygrains	Qs 100	Qs 100	Qs 100	Qs 100	Qs 100	0
Sodium cumene sulfonate	1.00	1.00	1.00	1.00	1.00	0
Glycerin	3.00	3.00	3.00	3.00	3.00	0
Polyquaternium-7	0.50	0.50	0.50	0.50	0.50	0
Perfume	0.20	0.20	0.20	0.20	0.20	0
Sodium xylene sulfonate	2.00	2.00	2.00	2.00	2.00	0

Table 8

Ingredients	Concentrations % w/w					
Norbornene polymer and cellulose acetate (50:50)	5	10	20	40	80	100
Vegetable polygrains	Qs 100	Qs 100	Qs 100	Qs 100	Qs 100	0
Sodium cumene sulfonate	1.00	1.00	1.00	1.00	1.00	0
Glycerin	3.00	3.00	3.00	3.00	3.00	0
Polyquaternium-7	0.50	0.50	0.50	0.50	0.50	0
Perfume	0.20	0.20	0.20	0.20	0.20	0
Sodium xylene sulfonate	2.00	2.00	2.00	2.00	2.00	0

Table 9

Ingredients	Concentrations % w/w					
Norbornene polymer and hydrophobic fumed silica (50:50)	5	10	20	40	80	100
Vegetable polygrains	Qs 100	Qs 100	Qs 100	Qs 100	Qs 100	0
Sodium cumene sulfonate	1.00	1.00	1.00	1.00	1.00	0
Glycerin	3.00	3.00	3.00	3.00	3.00	0
Polyquaternium-7	0.50	0.50	0.50	0.50	0.50	0
Perfume	0.20	0.20	0.20	0.20	0.20	0
Sodium xylene sulfonate	2.00	2.00	2.00	2.00	2.00	0

Table 10

Ingredients	Concentrations % w/w					
Norbornene polymer and cellulose acetate and hydrophobic fumed silica (1/3:1.3:1/3)	5	10	20	40	80	100
Vegetable polygrains	Qs 100	Qs 100	Qs 100	Qs 100	Qs 100	0
Sodium cumene sulfonate	1.00	1.00	1.00	1.00	1.00	0
Glycerin	3.00	3.00	3.00	3.00	3.00	0
Polyquaternium-7	0.50	0.50	0.50	0.50	0.50	0
Perfume	0.20	0.20	0.20	0.20	0.20	0
Sodium xylene sulfonate	2.00	2.00	2.00	2.00	2.00	0

The specific embodiments described above have been shown by way of example, and it should be understood that these embodiments may be susceptible to various modifications and alternative forms. It should be further understood that the claims are not intended to be limited to the particular forms disclosed, but rather to cover all modifications, equivalents, and alternatives falling within the spirit and scope of this disclosure.

THEREFORE WHAT IS CLAIMED IS:

1. A hand cleanser formulation comprising:

a gel; and

lipophilic polymeric particles selected from the group consisting of a polymer of a norbornane, a polymer of a norbornene, a polymer of a norbornadiene, or a polymer of a derivative of norbornane, norbornene or norbornadiene, wherein said derivative of norbornane, norbornene or norbornadiene is one in which a hydrogen atom of one or more C-H bonds of norbornane, norbornene or norbornadiene is substituted with a hydrocarbyl group;

the particles being suspended in the gel and present in a concentration from about 0.1 % w/w to about 99% w/w of the formulation,

wherein:

the gel comprises at least one non-Newtonian thickener present in an amount sufficient to provide the formulation with a yield value of at least 30 dynes/cm^2 (3 Pa);

the formulation is optionally free of lipophilic solvent; and

the formulation is optionally free of surfactant.

2. The formulation according to claim 1, wherein the at least one non-Newtonian thickener is any one or combination of acrylates/C10-30 alkyl acrylate crosspolymer, carbomer, xanthan gum, guar gum, quaternised guar gum, alginate, bentonite, in a concentration of from about 0.01 to about 10% w/w of the formulation.

3. The formulation according to claim 1 or 2, wherein the non-Newtonian thickener is present in a range from about 0.1 to about 5% w/w of the formulation.

4. The formulation according to claim 1, 2 or 3, wherein the polymer particles are present in the formulation in a range from about 0.5 to about 20% w/w of the formulation.

5. The formulation according to claim 4, wherein the polymer particles are present in the formulation in a range from about 1 to about 10% w/w of the formulation.

6. The formulation according to any one of claims 1 to 5, further comprising scrubbing particles in a concentration from about 0.1 to about 95% w/w of the formulation.

7. The formulation according to claim 6, wherein the scrubbing particles are present in a concentration from about 0.5 to about 20% w/w of the formulation.

8. The formulation according to claim 7, wherein the scrubbing particles are present in a concentration from about 1 to about 10% w/w of the formulation.

9. The formulation according to any one of claims 6 to 8, wherein said scrubbing particles are any one or any combination of vegetable based, organic based and mineral based scrubbing agents.

10. The formulation according to claim 9, wherein said vegetable based scrubbing particles include any of ground cornmeal, ground fruit stones, ground walnuts, wherein said organic based scrubbing particles include any of wood dust, polyethylene and polypropylene, and wherein said mineral based scrubbing particles include any of pumice and ground shellfish.

11. The formulation according to any one of claims 1 to 10, further comprising at least one preservative having bacteriostatic and fungistatic properties.

12. The formulation according to claim 11, wherein the at least one preservative is any one or a combination of benzoic acid, benzyl alcohol, bromo-nitro-propanediol,

chloroxylenol, diazolidinyl urea, dehydroacetic acid, dichloro-benzyl alcohol, imadazolidinyl urea, iodopropynylbutyl carbamate, methyl-chloro-isothiazolinone and methyl-isothiazolinone, paraben methyl and/or ethyl and/or butyl and/or isobutyl, phenoxyethanol, poly(hexa-methylene biguanide)-hydrochloride, propionic acid, sodium hydroxymethyl glycinate and sorbic acid.

13. The formulation according to any one of claims 1 to 12, further comprising at least one chelating agent.

14. The formulation according to claim 13, wherein the at least one chelating agent is any one or combination of sodium tripolyphosphate, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-(hydroxyethyl)-ethylenediami- netriacetic acid (HEDTA), 2-hydroxyethyliminodiacetic acid (HEIDA), aminobenzoic acid, iminodisuccinic acid, polyaspartic acid, gluconic acid, and salts thereof, in a concentration of from 0.01 to 5% w/w of the formulation.

15. The formulation according to claim 14, wherein the at least one chelating agent is present from about 0.1 to about 0.5% w/w of the formulation.

16. The formulation according to any one of claims 1 to 15, further comprising at least one skin conditioner, the at least one skin conditioner being any one or a combination of one or more allantoin, quaternised polymers or gums (polyquaterniums, dihydroxypropyl PEG-5 linoleammonium chloride, guar hydroxypropyltrimonium chloride, behentrimonium chloride).

17. The formulation according to claim 16, wherein said at least one skin conditioner is present in a concentration from about 0.01 to about 10% w/w of the formulation.

18. The formulation according to claim 17, wherein said at least one skin conditioner is present in a concentration from about 0.1 to about 5% w/w of the formulation.

19. The formulation according to any one of claims 1 to 18, the formulation further comprising at least one hydrotrope.

20. The formulation according to any one of claims 1 to 18, the formulation further comprising at least one hydrotrope that is any one or a combination of sodium xylene sulfonate, ammonium xylene sulfonate, calcium xylene sulfonate, potassium xylene sulfonate, sodium toluene sulfonate, ammonium toluene sulfonate, sodium cumene sulfonate, ammonium cumene sulfonate, phosphate polyether ester, alkyldiphenyloxide disulfonate, present in a concentration of from about 0.01 to about 10% w/w.

21. The formulation according to claim 20, wherein the at least one hydrotrope is present in a concentration from about 0.1 to about 5% w/w of the formulation.

22. The formulation according to any one of claims 1 to 21, the formulation further comprising any one or a combination of colouring dyes, pigments and perfumes.

23. The formulation according to any one of claims 1 to 22, wherein said lipophilic particles have a size in a range from about 10 to about 3000 µm.

24. The formulation according to claim 23, wherein said lipophilic particles are microparticles having a size in a range from about 50 µm to about 1000 µm.

25. The formulation according to claim 23, wherein said lipophilic particles have an average size in the range of from 50 µm to 2000 µm.

26. The formulation according to claim 25, wherein said lipophilic particles are microparticles having an average size in the range of from 50 µm to 900 µm.

27. The formulation according to claim 26, wherein said microparticles have an average size in the range of from 100 µm to 700 µm.

28. The formulation according to claim 27, wherein said microparticles have an average size in the range of from 200 µm to 600 µm.

29. The formulation according to any one of claims 1 to 28, wherein said formulation is substantially free of lipophilic solvent.

30. The formulation according to any one of claims 1 to 29, wherein said formulation is substantially free of surfactant.

31. The formulation according to any one of claims 1 to 30, wherein said formulation is substantially free of water.

32. The formulation according to any one of claims 1 to 30, the formulation further comprising water.

33. The formulation according to claim 32, wherein the water is present in amount of from about 0% to about 85% w/w of the formulation.

34. The formulation according to claim 32 or 33, the formulation further comprising at least one pH-adjuster and wherein the formulation has a pH between about 4 and about 9.

35. The formulation according to claim 34, wherein the formulation has a pH between about 5 and about pH 7.

36. The formulation according to claim 34 or 35, wherein the pH-adjuster is an acidic or alkaline pH-adjuster and is any one or a combination of citric acid, phosphoric acid, lactic acid, tartaric acid, sodium hydroxide, potash, aminomethyl propanol, and triethanolamine.

37. The formulation according to claim 1, wherein said the polymer of a norbornane, norbornene or norbornadiene is a homopolymer.

38. The formulation according to claim 1, wherein said polymer of norbornane, norbornene or norbornadiene is poly(norbornene).