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(54) LIQUID HAND DISHWASHING DETERGENT COMPOSITION

(57) The need for a liquid hand dishwashing composition which provides for a multi-phase hand dish-washing composition which is more readily emulsified and re-separate upon standing and provides improvements in skin-care, especially moisturisation during use, is met by formulating the liquid hand dishwashing composition as a multi-phase composition comprising a first phase and a second phase comprising vegetable oil which comprises glycerides formed from fatty acids having a number average alkyl chain length of less than 14 carbon atoms.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to multi-phase liquid hand dishwashing detergent compositions, which are readily emulsified by shaking temporarily and re-separate upon standing, and which provide improved skin care, beyond good sudsing and grease cleaning performance.

BACKGROUND OF THE INVENTION

[0002] Hand-dishwashing remains the most popular method of cleaning dishes. However, such manual dishwashing methods can leave the hands feeling dry, especially for people with sensitive skin. Typical liquid hand dishwashing compositions are usually homogeneous stable isotropic solutions. However, hydrophobic components can be added to provide skin benefits. Such prior art hydrophobic components have typically resulted in the composition becoming cloudy, leading to lower consumer acceptance, considering product clarity is typically associated by consumers with stronger cleaning performance. Moreover, it has been challenging to stably incorporate high levels of skin-benefit providing hydrophobic components into an isotropic liquid hand dishwashing composition.

[0003] As such, an approach has been to form an aqueous multi-phase liquid hand dishwashing detergent composition having the skin-benefit providing hydrophobic component in a separate layer, with the composition being temporary emulsified by shaking before use, while re-separating after use upon standing. Such compositions can be formulated having a high homogeneity within the layers, with the improved clarity resulting in improved consumer acceptance. However, it has been found that such compositions can require very vigourous and time-consuming shaking in order to emulsify the hydrophobic component, especially at high levels of the hydrophobic component. To reduce the effort to emulsify the composition, high levels of salt or other electrolyte can be used. However, such means can reduce the skin-care efficacy of the multi-phase composition. Moreover, high levels of salts and electrolytes can affect the clarity of the first phase, or result in a less sharp transition between the phases.

[0004] As such, a need remains for a multi-phase hand dish-washing composition which is more readily emulsified upon shaking and provides improvements in skin-care, especially moisturisation during use, without the need of high levels of salts and electrolytes.

[0005] EP0158108A1 relates to a detergent composition or the skin and hair cleaning comprising a mixture of: a greater proportion of one or more oils of the group comprising mineral, vegetable, animal and synthetic oils, and a minor proportion of at least one emulsifying agent, preferably a mixture of emulsifying agents, one of which is a saccharose ester, whereby the cleaning action is improved but a protecting lipidic layer is left onto the skin. The composition may also contain a bentonite or montmorillonite clay to improve the hydrating and restoring effects thereof.

[0006] WO200130958 relates to an aqueous multiple phase detergent containing a nonionic surfactant, especially a manual dishwashing detergent, comprising at least two continuous phases. The detergent has at least one lower, aqueous phase I and an upper, aqueous phase II which is not miscible with the first, and can be temporarily converted into an emulsion by shaking. Said detergent contains more than 2 wt. % of at least one organic solvent, can be used for cleaning hard surfaces, especially crockery, and is produced by directly mixing the raw materials, then re-mixing them and finally, allowing the product to stand in order to separate the temporary emulsion. WO2001010996A1, WO2000071665A1, WO200039270A1, WO9947635A1, WO200121752A1, WO9947634A1, WO200121751A1, WO200121754A1, WO200121753A1, WO200121755A1, WO200244314A1, WO200248308A1 all also relate to an aqueous, liquid, multi-phase cleaning agents which contains surfactants and has at least two continuous phases. Said cleaning agent has at least one lower aqueous phase I and an upper aqueous phase II which is immiscible with this phase, can be converted temporarily into an emulsion by shaking. DE10106712A1 relates to liquid aqueous detergent composition, including multi-phase compositions, comprising one or more surfactants and enzymes includes a carbohydrate. WO200344150A1 relates to a process of cleaning household surfaces comprising applying to the surface a temporary emulsion which is formed by the agitation of a composition comprising at least two immiscible liquids, the liquids having at least one liquid-liquid interface with an interfacial tension of at least 5 mN/m, and in which the concentration of the most polar liquid in the composition is from 10 to 90% by volume. The process is especially effective for the removal of particulate soil from household surfaces such as carpets and tiles. JP2007177128A relates to a liquid detergent composition separable in two layers, having excellent detergency, as well as being excellent in external appearance because of good layer separation condition, and to provide a liquid detergent held in a container using the composition. US20150203799A1 relates to a multiphase liquid detergent composition comprising at least two visually distinct liquid phases and a surfactant, at least one of the visually distinct phases has a high shear viscosity between about 100 cps and 15,000 cps at 20° C., a medium shear viscosity between about 5,000 cps and about 60,000 at 20° C., and a low shear viscosity between about 10,000 cps and 500,000 cps at 20° C, the visually distinct non-lamellar liquid phases has a yield stress and a high low shear viscosity and hence maintains two visually distinct layers and also do not readily re-separate into two distinct layers after shaking.

SUMMARY OF THE INVENTION

[0007] The present invention relates to a multi-phase liquid hand dishwashing detergent composition comprising: from 5% to 50% by weight of the total composition of a surfactant system, and from 5.0% to 60% of vegetable oil, wherein the vegetable oil is selected from vegetable oils which comprise glycerides formed from fatty acids having a number average alkyl chain length of less than 14 carbon atoms; wherein the low shear viscosity of each phase of the composition is from 10 mPa·s to 1,000 mPa·s, measured at 0.01s^{-1} at 20°C.

[0008] The present invention further relates to a method of cleaning dishware using the cleaning product, comprising the steps of: optionally pre-wetting the dishware; homogenizing the multiphase liquid cleaning composition upon shaking, applying the homogenized cleaning composition onto the dishware; optionally scrubbing the dishware; and rinsing the dishware, and allowing the homogenized cleaning composition to re-separate layers upon standing after the cleaning step.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The need for a liquid multi-phase hand dish-washing composition which is more readily emulsified upon shaking while re-separating upon standing and provides improvements in skin-care, especially moisturisation, during use, while still offering strong sudsing and grease cleaning performance, is met by formulating the hand dish-washing composition using a surfactant system and a vegetable oil, wherein the vegetable oil is selected from vegetable oils which comprise glycerides formed from fatty acids having a number average alkyl chain length of less than 14.

[0010] As used herein, articles such as "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

[0011] The term "comprising" as used herein means that steps and ingredients other than those specifically mentioned can be added. This term encompasses the terms "consisting of' and "consisting essentially of." The compositions of the present invention can comprise, consist of, and consist essentially of the essential elements and limitations of the invention described herein, as well as any of the additional or optional ingredients, components, steps, or limitations described herein.

[0012] The term "dishware" as used herein includes cookware and tableware made from, by non-limiting examples, ceramic, china, metal, glass, plastic (e.g., polyethylene, polypropylene, polystyrene, etc.) and wood.

[0013] The term "grease" or "greasy" as used herein means materials comprising at least in part (*i.e.,* at least 0.5 wt% by weight of the grease) saturated and unsaturated fats and oils, preferably oils and fats derived from animal sources such as beef, pig and/or chicken.

[0014] The terms "include", "includes" and "including" are meant to be non-limiting.

[0015] The term "particulate soils" as used herein means inorganic and especially organic, solid soil particles, especially food particles, such as for non-limiting examples: finely divided elemental carbon, baked grease particle, and meat particles.

[0016] The term "sudsing profile" as used herein refers to the properties of a detergent composition relating to suds character during the dishwashing process. The term "sudsing profile" of a detergent composition includes suds volume generated upon dissolving and agitation, typically manual agitation, of the detergent composition in the aqueous washing solution, and the retention of the suds during the dishwashing process. Preferably, hand dishwashing detergent compositions characterized as having "good sudsing profile" tend to have high suds volume and/or sustained suds volume, particularly during a substantial portion of or for the entire manual dishwashing process. This is important as the consumer uses high suds as an indicator that sufficient detergent composition has been dosed. Moreover, the consumer also uses the sustained suds volume as an indicator that sufficient active cleaning ingredients (e.g., surfactants) are present, even towards the end of the dishwashing process. The consumer usually renews the washing solution when the sudsing subsides. Thus, a low sudsing detergent composition will tend to be replaced by the consumer more frequently than is necessary because of the low sudsing level.

[0017] In all embodiments of the present invention, all percentages are by weight of the total composition, as evident by the context, unless specifically stated otherwise. All ratios are weight ratios, unless specifically stated otherwise, and all measurements are made at 25°C, unless otherwise designated.

Detergent composition

[0018] The detergent composition is a multi-phase hand dishwashing detergent composition in liquid form. As such, the detergent composition comprises a first phase and a second phase.

[0019] The first phase can comprise polar solvents. Suitable polar solvents include water and/or polar organic solvents. Non-limiting examples of polar organic solvents include short chain protic organic solvents comprising O-H or N-H bonds, and hence can participate in hydrogen bonding and as such being soluble in water.

[0020] The first phase can optionally comprise a small amount of non-polar solvent dissolved therein, since the first phase also comprises surfactant. Preferably, the first phase comprises less than 5.0% preferably less than 3.0% more preferably less than 1.0%, by weight of the first phase of a non-polar solvent. In the most preferred embodiments, the first phase is free of non-polar solvents.

[0021] The first phase can comprise at least 5.0 % preferably at least 7.0% most preferably at least 10% by weight of the first phase of a polar solvent. Suitable polar solvents include water and optionally polar organic solvents. Such polar organic solvents have a solubility in demineralised water of at least 5.0%, preferably at least 10%, more preferably at least 20% by weight of the polar organic solvent in demineralised water at 25 °C. Non-polar organic solvents have a solubility in demineralised water of less than 5.0% by weight of the non-polar organic solvent in demineralised water at 25 °C.

[0022] The composition can comprise from 1% to 50%, preferably from 3% to 35%, more preferably from 5% to 25% by weight of the total composition of water. The composition can comprise from 1.0% to 25%, or preferably from 5.0% to 20%, or more preferably from 8.0% to 15% by weight of the total composition of polar organic solvent.

[0023] Suitable polar organic solvents can be selected from the group consisting of: alcohols, glycols, glycol ethers, and mixtures thereof, preferably alcohols, glycols, and mixtures thereof. Ethanol is the preferred alcohol. Polyalkyleneglycols, especially polypropyleneglycol (PPG), are the preferred glycol. The polypropyleneglycol can have a molecular weight of from 400 to 3000, preferably from 600 to 1500, more preferably from 700 to 1300. The polypropyleneglycol is preferably poly-1,2-propyleneglycol. High levels of ether solvents are not preferred. As such, the composition preferably comprises less than 3.0%, preferably less than 1.0%, more preferably less than 0.1% of ether solvent.

[0024] The addition of the organic solvent at such levels improves the sharpness of the split between the first phase and second phase, in addition to improving low temperature stability.

[0025] The second phase comprises the vegetable oil. The second phase can optionally comprise a non-polar solvent. Preferably, at least 70%, more preferably at least 80%, most preferably at least 90% by weight of the vegetable oil is present in the second phase. The second phase typically comprises less than 5.0% preferably less than 3.0% most preferably less than 1.0% of water by weight of the second phase. The second phase typically comprises less than 5.0% preferably less than 3.0% more preferably less than 1.0% by weight of polar solvent.

[0026] The exact composition of the first phase and the second phase depends on the overall composition of the hand dishwashing detergent composition, such as type and level of solvents and hydrotropes. As such, the first phase can comprise trace amounts of non-polar components and the second phase can comprise trace amounts of polar components such as water, polar organic solvents or other water-soluble components. The first phase and the second phase can be readily mixed upon shaking but re-separate into separate layers upon standing after shaking. As such, preferably the first phase and the second phase both have a yield stress of less than 0.001 Pa, or even less than 0.0001 Pa.

[0027] The first phase and the second phase can be present as a bilayer (biphasic composition). The composition preferably consists of two layers, though further layers can be present in less preferred embodiments.

[0028] The detergent composition comprises a surfactant system. Since the surfactant system is water-soluble, the surfactant system is predominantly present in the first phase. Typically, at least 70%, preferably at least 80%, more preferably at least 90% by weight of the surfactant system is present in the first phase.

[0029] Preferably, the pH of the composition is from 5.0 to 12, preferably from 5.5 to 10, or more preferably from 7 to 9. The pH of the composition can be adjusted using pH modifying ingredients known in the art.

[0030] The compositions of the present invention can be Newtonian or non-Newtonian, preferably Newtonian. Without wishing to be bound by theory, it is believed that re-separation of polar and second phases is more difficult for compositions having a non-Newtonian viscosity. Each phase of the composition has a low shear viscosity of from 10 mPa·s to 1,000 mPa·s, preferably from 30 mPa·s to 500 mPa·s, and more preferably from 50 mPa·s to 200 mPa·s. Such low shear viscosities are preferred as the compositions are easier to homogenise with shaking and have quicker re-separation of the phases upon standing. Preferably, the composition has a low shear viscosity after homogenization of from 10 mPa·s to 1,000 mPa·s, preferably from 30 mPa·s to 500 mPa·s, and more preferably from 50 mPa·s to 200 mPa·s

Vegetable oil

[0031] The composition comprises from 5.0% to 60%, preferably from 15% to 55%, more preferably from 25% to 50% of the vegetable oil, with the vegetable oil being comprised predominantly in the second phase. As such, at least 70%, preferably at least 80%, more preferably at least 90% by weight of the vegetable oil is present in the second phase.

[0032] The vegetable oil is selected from vegetable oils which comprise glycerides formed from fatty acids having a number average alkyl chain length of less than 14.0 carbon atoms or 12.0 or less, preferably from 6.0 to 12.0, more preferably from 8.0 to 10.0 carbon atoms. The vegetable oils are preferably glycerides formed from fatty acids, wherein less than 20%, preferably less than 10%, more preferably less than 5% by number of the fatty acids have an alkyl chain comprising 12 or more carbon atoms. Without wishing to be bound by theory it is believed that oils comprising fatty acids with shorter alkyl chains will interact less with the typical longer alkyl chains of the surfactant system, resulting in a more clean split between the layers of the multiphase liquid hand dishwashing detergent composition.

[0033] Due to the low number average alkyl chain lengths of the fatty acids comprised in the glycerides of the vegetable oil, and the low shear viscosity, the phases of the multi-phase hand dishwashing detergent composition are readily mixed together by simple hand-shaking of the container in which it is comprised.

[0034] As such, the compositions are typically fully homogenised after shaking, with less than 10%, preferably less than 5% of the total composition being non-emulsified after shaking, and preferably the composition being fully emulsified after shaking. In addition, the phases re-separate in to separate layers within less than 12 hours preferably less than 6 hours, more preferably less than 3 hours after cessation of shaking.

[0035] Vegetable oils are generally obtained by processing oil seeds. Crude vegetable oils can be obtained from vegetable seeds by forming an emulsion comprising the oil and centrifuging the oil. Additional pre-treatments can be used in order to break the emulsion and aid centrifugation, such as freeze-thawing, fermentation, enzymatic extraction, or heating.

[0036] During freeze-thaw processes, the stability of the oil-water emulsion is broken by chilling, freezing and thawing, and the thawed cream separated by centrifugation. The emulsion is typically centrifuged before chilling and thawing to allow better packing of the oil globules. In fermentation, an inoculum, typically comprising a *lactobacillus* strain, can be used to assist the rapid breakage of emulsion, prior to centrifugation. Alternatively, the oil can be partially separated by the action of an enzyme blend.

[0037] The crude vegetable oils generally contain neutral glycerides, predominantly triglycerides and a host of natural oil seed-derived contaminants including phosphatides, sulphurous compounds, free fatty acids, carbohydrates, peptides, proteins, nucleic acids, oxidized lipids, traces of lower aldehydes and ketones, glycosides of sterols and terpenes, and diverse types of color bodies or dyestuffs. Many of these contaminants can be removed from the crude vegetable oils in the course of refining to render the vegetable oils food-grade and to ensure that the vegetable oils are more compatible with sensitive or delicate skin.

[0038] The vegetable oil comprises glycerides which can be selected from mono-glycerides, diglycerides, triglycerides, and mixtures thereof. More typically, the vegetable oil comprises glycerides which are a blend of mono-glycerides, diglycerides, and triglycerides, with the proportions of the mono-, di-, and tri-glycerides being dependent on the vegetable oil source and any processing such as fractionation. Typically, the glycerides are predominantly triglycerides (also referred to as triacylglycerols), with such triglycerides forming at least 90%, more typically at least 95% of the content by weight of the oil.

[0039] Preferred sources of suitable vegetable oils are high in glycerides formed from fatty acids having the desired number average alkyl chain lengths. Hence, the vegetable oil is preferably derived from vegetable oils selected from the group consisting of: coconut oil, palm kernel oil, and mixtures thereof. Coconut oil is particularly preferred as a source for the vegetable oil, since it is particularly high in glycerides formed from fatty acids having a number average alkyl chain length of from 4.0 to 12.0, and especially 8.0 to 10.0.

[0040] The vegetable oils typically should be fractionated, in order to yield the desired fatty acid chain lengths of the glycerides. Fractionation of vegetal oils is a well known process, and typically involves a first step of partial crystallization of oils and fats under the controlled gradual cooling to the desired temperature in a crystallizer, followed by the separation of solid and liquid fractions by means of filtration, centrifugation, or distillation. Fractionation applied in the industrial scale can be classified into three groups, dry fractionation, detergent fractionation, distillation, and solvent fractionation, depending on the procedures and separation systems. Fractionation technologies have been used to produce cooking and frying oils from palm kernel oil, specialty fats from tropical solid fats, soft butter from anhydrous milk fat and so on.

[0041] Preferably, at least 80%, preferably at least 90%, more preferably at least 95% by weight of the fatty acids that form the vegetable oil are saturated fatty acids. Without wishing to be bound by theory, it is believed that oils having a high level of saturation, due to their high degree of linearity within the fatty acid chains comprising the glycerides, show improved packing and hence lead to a more defined split between the different layers of the multi-phase liquid hand dishwashing cleaning composition.

Surfactant System

[0042] The liquid hand dishwashing detergent composition comprises from 5% to 50%, preferably from 10% to 40%, more preferably from 15% to 35%, by weight of the total composition of a surfactant system.

[0043] For improved sudsing, the surfactant system preferably comprises anionic surfactant. The surfactant system preferably comprises from 50% to 90% by weight of the surfactant system of the anionic surfactant. Alkyl sulphated anionic surfactants are preferred, particularly those selected from the group consisting of: alkyl sulphate, alkyl alkoxy sulphate, and mixtures thereof. More preferably, the anionic surfactant consists of alkyl sulphated anionic surfactant selected from the group consisting of: alkyl sulphate, alkyl alkoxy sulphate, and mixtures thereof. For further improvements in sudsing, the surfactant system can comprise less than 30%, preferably less than 15%, more preferably less than 10%

of further anionic surfactant beyond the alkyl sulphated surfactant, and most preferably the surfactant system comprises no further anionic surfactant.

[0044] The alkyl sulphated anionic surfactant can have a number average alkyl chain length of from 8 to 18, preferably from 10 to 14, more preferably from 12 to 14, most preferably from 12 to 13 carbon atoms.

[0045] The alkyl sulphated anionic surfactant can have an average degree of alkoxylation of less than 3.5, preferably from 0.5 to 2.0, most preferably from 0.5 to 0.9. Preferably, the alkyl sulphated anionic surfactant is ethoxylated.

[0046] The average degree of alkoxylation is the mol average degree of alkoxylation (*i.e.,* mol average alkoxylation degree) of all the alkyl sulphate anionic surfactant. Hence, when calculating the mol average alkoxylation degree, the mols of non-alkoxylated sulphate anionic surfactant are included:

$$\text{Mol average alkoxylation degree} = (x1 * \text{alkoxylation degree of surfactant } 1 + x2 * \text{alkoxylation degree of surfactant } 2 + \ldots.) / (x1 + x2 + \ldots.)$$

wherein x1, x2, ... are the number of moles of each alkyl (or alkoxy) sulphate anionic surfactant of the mixture and alkoxylation degree is the number of alkoxy groups in each alkyl sulphate anionic surfactant.

[0047] The alkyl sulphate anionic surfactant can have a weight average degree of branching of more than 10%, preferably between 20% and 60%, more preferably between 30% and 50%. The alkyl sulphate anionic surfactant can comprise at least 5%, preferably at least 10%, most preferably at least 25%, by weight of the alkyl sulphate anionic surfactant, of branching on the C2 position (as measured counting carbon atoms from the sulphate group for non-alkoxylated alkyl sulphate anionic surfactants, and the counting from the alkoxy-group furthest from the sulphate group for alkoxylated alkyl sulphate anionic surfactants). More preferably, greater than 75%, even more preferably greater than 90%, by weight of the total branched alkyl content consists of C1-C5 alkyl moiety, preferably C1-C2 alkyl moiety. It has been found that formulating the inventive compositions using alkyl sulphate surfactants having the aforementioned degree of branching results in improved low temperature stability. Such compositions require less solvent in order to achieve good physical stability at low temperatures. As such, the compositions can comprise lower levels of organic solvent, of less than 5.0% by weight of the detergent composition of organic solvent, while still having improved low temperature stability. Higher surfactant branching also provides faster initial suds generation, but typically less suds mileage. The weight average branching, described herein, has been found to provide improved low temperature stability, initial foam generation and suds longevity.

[0048] The weight average degree of branching for an anionic surfactant mixture can be calculated using the following formula:

$$\text{Weight average degree of branching (\%)} = [(x1 * \text{wt\% branched alcohol 1 in alcohol 1} + x2 * \text{wt\% branched alcohol 2 in alcohol 2} + \ldots.) / (x1 + x2 + \ldots.)] * 100$$

wherein x1, x2, ... are the weight in grams of each alcohol in the total alcohol mixture of the alcohols which were used as starting material before (alkoxylation and) sulphation to produce the alkyl (alkoxy) sulphate anionic surfactant. In the weight average degree of branching calculation, the weight of the alkyl alcohol used to form the alkyl sulphate anionic surfactant which is not branched is included.

[0049] The weight average degree of branching and the distribution of branching can typically be obtained from the technical data sheet for the surfactant or constituent alkyl alcohol. Alternatively, the branching can also be determined through analytical methods known in the art, including capillary gas chromatography with flame ionisation detection on medium polar capillary column, using hexane as the solvent. The weight average degree of branching and the distribution of branching is based on the starting alcohol used to produce the alkyl sulphate anionic surfactant.

[0050] The alkyl chain of the alkyl sulphated anionic surfactant preferably has a mol fraction of C12 and C13 chains of at least 50%, preferably at least 65%, more preferably at least 80%, most preferably at least 90%. Suds mileage is particularly improved, especially in the presence of greasy soils, when the C13/C12 mol ratio of the alkyl chain is at least 50/50, preferably at least 57/43, preferably from 60/40 to 90/10, more preferably from 60/40 to 80/20, most preferably from 60/40 to 70/30, while not compromising suds mileage in the presence of particulate soils.

[0051] Suitable counterions include alkali metal cation earth alkali metal cation, alkanolammonium or ammonium or substituted ammonium, but preferably sodium.

[0052] Suitable examples of commercially available alkyl sulphate anionic surfactants include, those derived from alcohols sold under the Neodol® brand-name by Shell, or the Lial®, Isalchem®, and Safol® brand-names by Sasol, or some of the natural alcohols produced by The Procter & Gamble Chemicals company. The alcohols can be blended in order to achieve the desired mol fraction of C12 and C13 chains and the desired C13/C12 ratio, based on the relative fractions of C13 and C12 within the starting alcohols, as obtained from the technical data sheets from the suppliers or from analysis using methods known in the art.

[0053] In order to improve surfactant packing after dilution and hence improve suds mileage, the surfactant system can comprise a co-surfactant. Preferred co-surfactants are selected from the group consisting of an amphoteric surfactant, a zwitterionic surfactant, and mixtures thereof. The co-surfactant is preferably an amphoteric surfactant, more preferably an amine oxide surfactant. The co-surfactant is included as part of the surfactant system.

[0054] The composition preferably comprises from 0.1% to 20%, more preferably from 0.5% to 15% and especially from 2% to 10% by weight of the total detergent composition of a co-surfactant selected from amphoteric surfactants, zwitterionic surfactants, or mixtures thereof. The surfactant system of the detergent composition of the present invention preferably comprises from 5% to 40%, preferably from 7% to 35%, more preferably from 10% to 30%, by weight of the surfactant system of a co-surfactant selected from amphoteric surfactants, zwitterionic surfactants, or mixtures thereof. The anionic surfactant to the co-surfactant weight ratio can be less than 9:1, preferably from 1:1 to 8:1, more preferably from 2:1 to 6:1, most preferably from 2.5:1 to 5:1.

[0055] Amine oxide surfactants are preferred for use as a co-surfactant. The amine oxide surfactant can be linear or branched, though linear are preferred. Suitable linear amine oxides are typically water-soluble, and characterized by the formula R1 - N(R2)(R3) O wherein R1 is a C8-18 alkyl, and the R2 and R3 moieties are selected from the group consisting of C1-3 alkyl groups, C1-3 hydroxyalkyl groups, and mixtures thereof. For instance, R2 and R3 can be selected from the group consisting of: methyl, ethyl, propyl, isopropyl, 2-hydroxethyl, 2-hydroxypropyl and 3-hydroxypropyl, and mixtures thereof, though methyl is preferred for one or both of R2 and R3. The linear amine oxide surfactants in particular may include linear C10-C18 alkyl dimethyl amine oxides and linear C8-C12 alkoxy ethyl dihydroxy ethyl amine oxides.

[0056] Preferably, the amine oxide surfactant is selected from the group consisting of: alkyl dimethyl amine oxide, alkyl amido propyl dimethyl amine oxide, and mixtures thereof. Alkyl dimethyl amine oxides are preferred, such as C8-18 alkyl dimethyl amine oxides, or C10-16 alkyl dimethyl amine oxides (such as coco dimethyl amine oxide). Suitable alkyl dimethyl amine oxides include C10 alkyl dimethyl amine oxide surfactant, C10-12 alkyl dimethyl amine oxide surfactant, C12-C14 alkyl dimethyl amine oxide surfactant, and mixtures thereof. C12-C14 alkyl dimethyl amine oxide are particularly preferred.

[0057] Alternative suitable amine oxide surfactants include mid-branched amine oxide surfactants. As used herein, "mid-branched" means that the amine oxide has one alkyl moiety having n1 carbon atoms with one alkyl branch on the alkyl moiety having n2 carbon atoms. The alkyl branch is located on the α carbon from the nitrogen on the alkyl moiety. This type of branching for the amine oxide is also known in the art as an internal amine oxide. The total sum of n1 and n2 can be from 10 to 24 carbon atoms, preferably from 12 to 20, and more preferably from 10 to 16. The number of carbon atoms for the one alkyl moiety (n1) is preferably the same or similar to the number of carbon atoms as the one alkyl branch (n2) such that the one alkyl moiety and the one alkyl branch are symmetric. As used herein "symmetric" means that | n1 - n2 | is less than or equal to 5, preferably 4, most preferably from 0 to 4 carbon atoms in at least 50 wt%, more preferably at least 75 wt% to 100 wt% of the mid-branched amine oxides for use herein. The amine oxide further comprises two moieties, independently selected from a C1-3 alkyl, a C1-3 hydroxyalkyl group, or a polyethylene oxide group containing an average of from about 1 to about 3 ethylene oxide groups. Preferably, the two moieties are selected from a C1-3 alkyl, more preferably both are selected as C1 alkyl.

[0058] Alternatively, the amine oxide surfactant can be a mixture of amine oxides comprising a mixture of low-cut amine oxide and mid-cut amine oxide. The amine oxide of the composition of the invention can then comprises:

a) from about 10% to about 45% by weight of the amine oxide of low-cut amine oxide of formula R1R2R3AO wherein R1 and R2 are independently selected from hydrogen, C1-C4 alkyls or mixtures thereof, and R3 is selected from C10 alkyls and mixtures thereof; and

b) from 55% to 90% by weight of the amine oxide of mid-cut amine oxide of formula R4R5R6AO wherein R4 and R5 are independently selected from hydrogen, C1-C4 alkyls or mixtures thereof, and R6 is selected from C12-C16 alkyls or mixtures thereof

[0059] In a preferred low-cut amine oxide for use herein R3 is n-decyl, with preferably both R1 and R2 being methyl. In the mid-cut amine oxide of formula R4R5R6AO, R4 and R5 are preferably both methyl.

[0060] Preferably, the amine oxide comprises less than about 5%, more preferably less than 3%, by weight of the amine oxide of an amine oxide of formula R7R8R9AO wherein R7 and R8 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R9 is selected from C8 alkyls and mixtures thereof. Limiting the amount of amine oxides of formula R7R8R9AO improves both physical stability and suds mileage.

[0061] Suitable zwitterionic surfactants include betaine surfactants. Such betaine surfactants includes alkyl betaines, alkylamidobetaine, amidazoliniumbetaine, sulphobetaine (INCI Sultaines) as well as the Phosphobetaine, and preferably meets formula (I):

$$R^1\text{-}[CO\text{-}X(CH_2)_n]_x\text{-}N^+(R^2)(R_3)\text{-}(CH_2)_m\text{-}[CH(OH)\text{-}CH_2]_y\text{-}Y^-$$

wherein in formula (I),

R1 is selected from the group consisting of: a saturated or unsaturated C6-22 alkyl residue, preferably C8-18 alkyl residue, more preferably a saturated C10-16 alkyl residue, most preferably a saturated C12-14 alkyl residue;
X is selected from the group consisting of: NH, NR4 wherein R4 is a C1-4 alkyl residue, O, and S,
n is an integer from 1 to 10, preferably 2 to 5, more preferably 3,
x is 0 or 1, preferably 1,
R2 and R3 are independently selected from the group consisting of: a C1-4 alkyl residue, hydroxy substituted such as a hydroxyethyl, and mixtures thereof, preferably both R2 and R3 are methyl,
m is an integer from 1 to 4, preferably 1, 2 or 3,
y is 0 or 1, and
Y is selected from the group consisting of: COO, SO3, OPO(OR5)O or P(O)(OR5)O, wherein R5 is H or a C1-4 alkyl residue.

[0062] Preferred betaines are the alkyl betaines of formula (IIa), the alkyl amido propyl betaine of formula (IIb), the sulphobetaines of formula (IIc) and the amido sulphobetaine of formula (IId):

$$R^1\text{-}N(CH_3)_2\text{-}CH_2COO^- \qquad (IIa)$$

$$R^1\text{-}CO\text{-}NH\text{-}(CH_2)_3\text{-}N^+(CH_3)_2\text{-}CH_2COO^- \qquad (IIb)$$

$$R^1\text{-}N^+(CH_3)_2\text{-}CH_2CH(OH)CH_2SO_3^- \qquad (IIc)$$

$$R^1\text{-}CO\text{-}NH\text{-}(CH_2)_3\text{-}N^+(CH_3)_2\text{-}CH_2CH(OH)CH_2SO_3^- \qquad (IId)$$

in which R1 has the same meaning as in formula (I). Particularly preferred are the carbobetaines [i.e. wherein Y^-=COO- in formula (I)] of formulae (IIa) and (IIb), more preferred are the alkylamidobetaine of formula (IIb).

[0063] Suitable betaines can be selected from the group consisting or [designated in accordance with INCI]: capryl/capramidopropyl betaine, cetyl betaine, cetyl amidopropyl betaine, cocamidoethyl betaine, cocamidopropyl betaine, cocobetaines, decyl betaine, decyl amidopropyl betaine, hydrogenated tallow betaine / amidopropyl betaine, isostearamidopropyl betaine, lauramidopropyl betaine, lauryl betaine, myristyl amidopropyl betaine, myristyl betaine, oleamidopropyl betaine, oleyl betaine, palmamidopropyl betaine, palmitamidopropyl betaine, palm-kernelamidopropyl betaine, stearamidopropyl betaine, stearyl betaine, tallowamidopropyl betaine, tallow betaine, undecylenamidopropyl betaine, undecyl betaine, and mixtures thereof. Preferred betaines are selected from the group consisting of: cocamidopropyl betaine, cocobetaines, lauramidopropyl betaine, lauryl betaine, myristyl amidopropyl betaine, myristyl betaine, and mixtures thereof. Cocamidopropyl betaine is particularly preferred.

[0064] Preferably, the surfactant system of the composition of the present invention further comprises from 5% to 50%, preferably from 10% to 40%, more preferably from 20% to 35%, by weight of the surfactant system, of a non-ionic surfactant.

[0065] Suitable nonionic surfactants can be selected from the group consisting of: alkoxylated non-ionic surfactant, alkyl polyglucoside ("APG") surfactant, and mixtures thereof.

[0066] Suitable alkoxylated non-ionic surfactants can be linear or branched, primary or secondary alkyl alkoxylated non-ionic surfactants. Alkyl ethoxylated non-ionic surfactant are preferred. The ethoxylated non-ionic surfactant can comprise on average from 9 to 15, preferably from 10 to 14 carbon atoms in its alkyl chain and on average from 5 to 12, preferably from 6 to 10, most preferably from 7 to 8, units of ethylene oxide per mole of alcohol. Such alkyl ethoxylated nonionic surfactants can be derived from synthetic alcohols, such as OXO-alcohols and Fisher Tropsh alcohols, or from naturally derived alcohols, or from mixtures thereof. Suitable examples of commercially available alkyl ethoxylate nonionic surfactants include, those derived from synthetic alcohols sold under the Neodol® brand-name by Shell, or the Lial®, Isalchem®, and Safol® brand-names by Sasol, or some of the natural alcohols produced by The Procter & Gamble Chemicals company.

[0067] The compositions of the present invention can comprise alkyl polyglucoside ("APG") surfactant. The addition of alkyl polyglucoside surfactants have been found to improve sudsing beyond that of comparative nonionic surfactants such as alkyl ethoxylated surfactants. Preferably the alkyl polyglucoside surfactant is a C8-C16 alkyl polyglucoside surfactant, preferably a C8-C14 alkyl polyglucoside surfactant. The alkyl polyglucoside preferably has an average degree of polymerization of between 0.1 and 3, more preferably between 0.5 and 2.5, even more preferably between 1 and 2.

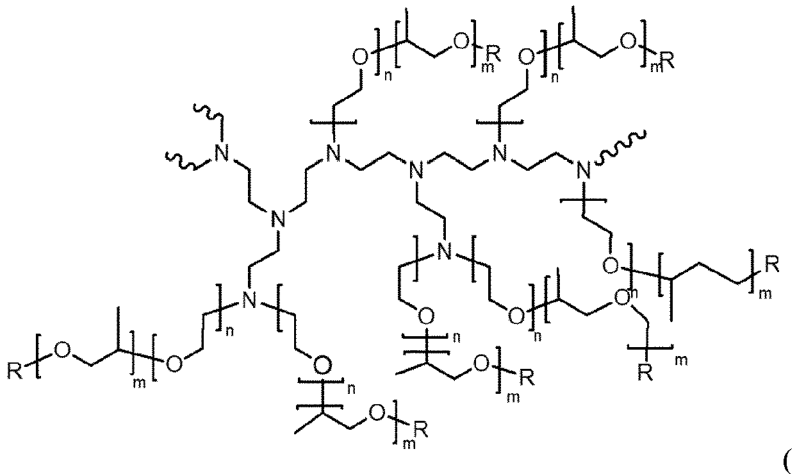
Most preferably, the alkyl polyglucoside surfactant has an average alkyl carbon chain length between 10 and 16, preferably between 10 and 14, most preferably between 12 and 14, with an average degree of polymerization of between 0.5 and 2.5 preferably between 1 and 2, most preferably between 1.2 and 1.6. C8-C16 alkyl polyglucosides are commercially available from several suppliers (e.g., Simusol® surfactants from Seppic Corporation; and Glucopon® 600 CSUP, Glucopon® 650 EC, Glucopon® 600 CSUP/MB, and Glucopon® 650 EC/MB, from BASF Corporation).

Further ingredients:

[0068] The composition can comprise further ingredients such as those selected from: amphiphilic alkoxylated polyalkyleneimines, cyclic polyamines, triblock copolymers, hydrotropes, organic solvents, other adjunct ingredients such as those described herein, and mixtures thereof.

[0069] Amphiphilic alkoxylated polyalkyleneimine:
The composition of the present invention may further comprise from 0.05% to 2%, preferably from 0.07% to 1% by weight of the total composition of an amphiphilic polymer. Suitable amphiphilic polymers can be selected from the group consisting of: amphiphilic alkoxylated polyalkyleneimine and mixtures thereof. The amphiphilic alkoxylated polyalkyleneimine polymer has been found to reduce gel formation on the hard surfaces to be cleaned when the liquid composition is added directly to a cleaning implement (such as a sponge) before cleaning and consequently brought in contact with heavily greased surfaces, especially when the cleaning implement comprises a low amount to nil water such as when light pre-wetted sponges are used.

[0070] A preferred amphiphilic alkoxylated polyethyleneimine polymer has the general structure of formula (I):



(I)

wherein the polyethyleneimine backbone has a weight average molecular weight of 600, n of formula (I) has an average of 10, m of formula (I) has an average of 7 and R of formula (I) is selected from hydrogen, a C_1-C_4 alkyl and mixtures thereof, preferably hydrogen. The degree of permanent quaternization of formula (I) may be from 0% to 22% of the polyethyleneimine backbone nitrogen atoms. The molecular weight of this amphiphilic alkoxylated polyethyleneimine polymer preferably is between 10,000 and 15,000 Da.

[0071] More preferably, the amphiphilic alkoxylated polyethyleneimine polymer has the general structure of formula (I) but wherein the polyethyleneimine backbone has a weight average molecular weight of 600 Da, n of Formula (I) has an average of 24, m of Formula (I) has an average of 16 and R of Formula (I) is selected from hydrogen, a C_1-C_4 alkyl and mixtures thereof, preferably hydrogen. The degree of permanent quaternization of Formula (I) may be from 0% to 22% of the polyethyleneimine backbone nitrogen atoms and is preferably 0%. The molecular weight of this amphiphilic alkoxylated polyethyleneimine polymer preferably is between 25,000 and 30,000, most preferably 28,000 Da.

[0072] The amphiphilic alkoxylated polyethyleneimine polymers can be made by the methods described in more detail in PCT Publication No. WO 2007/135645.

Cyclic Polyamine

[0073] The composition can comprise a cyclic polyamine having amine functionalities that helps cleaning. The composition of the invention preferably comprises from 0.1% to 3%, more preferably from 0.2% to 2%, and especially from 0.5% to 1%, by weight of the total composition, of the cyclic polyamine.

[0074] The cyclic polyamine has at least two primary amine functionalities. The primary amines can be in any position in the cyclic amine but it has been found that in terms of grease cleaning, better performance is obtained when the primary amines are in positions 1,3. It has also been found that cyclic amines in which one of the substituents is -CH3 and the rest are H provided for improved grease cleaning performance.

[0075] Accordingly, the most preferred cyclic polyamine for use with the cleaning composition of the present invention are cyclic polyamine selected from the group consisting of: 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof. These specific cyclic polyamines work to improve suds and grease cleaning profile through-out the dishwashing process when formulated together with the surfactant system of the composition of the present invention.

[0076] Suitable cyclic polyamines can be supplied by BASF, under the Baxxodur tradename, with Baxxodur ECX-210 being particularly preferred.

[0077] A combination of the cyclic polyamine and magnesium sulphate is particularly preferred. As such, the composition can further comprise magnesium sulphate at a level of from 0.001 % to 2.0 %, preferably from 0.005 % to 1.0 %, more preferably from 0.01 % to 0.5 % by weight of the composition.

Triblock Copolymer

[0078] The composition of the invention can comprise a triblock copolymer. The triblock copolymers can be present at a level of from 1% to 20%, preferably from 3% to 15%, more preferably from 5% to 12%, by weight of the total composition. Suitable triblock copolymers include alkylene oxide triblock co-polymers, defined as a triblock co-polymer having alkylene oxide moieties according to Formula (I): (EO)x(PO)y(EO)x, wherein EO represents ethylene oxide, and each x represents the number of EO units within the EO block. Each x can independently be on average of from 5 to 50, preferably from 10 to 40, more preferably from 10 to 30. Preferably x is the same for both EO blocks, wherein the "same" means that the x between the two EO blocks varies within a maximum 2 units, preferably within a maximum of 1 unit, more preferably both x's are the same number of units. PO represents propylene oxide, and y represents the number of PO units in the PO block. Each y can on average be from between 28 to 60, preferably from 30 to 55, more preferably from 30 to 48.

[0079] Preferably the triblock co-polymer has a ratio of y to each x of from 3:1 to 2:1. The triblock co-polymer preferably has a ratio of y to the average x of 2 EO blocks of from 3:1 to 2:1. Preferably the triblock co-polymer has an average weight percentage of total E-O of between 30% and 50% by weight of the tri-block co-polymer. Preferably the triblock co-polymer has an average weight percentage of total PO of between 50% and 70% by weight of the triblock co-polymer. It is understood that the average total weight % of EO and PO for the triblock co-polymer adds up to 100%. The triblock co-polymer can have an average molecular weight of between 2060 and 7880, preferably between 2620 and 6710, more preferably between 2620 and 5430, most preferably between 2800 and 4700. Average molecular weight is determined using a 1H NMR spectroscopy *(see* Thermo scientific application note No. AN52907).

[0080] Triblock co-polymers have the basic structure ABA, wherein A and B are different homopolymeric and/or monomeric units. In this case A is ethylene oxide (EO) and B is propylene oxide (PO). Those skilled in the art will recognize the phrase "block copolymers" is synonymous with this definition of "block polymers".

[0081] Triblock co-polymers according to Formula (I) with the specific EO/PO/EO arrangement and respective homopolymeric lengths have been found to enhances suds mileage performance of the liquid hand dishwashing detergent composition in the presence of greasy soils and/or suds consistency throughout dilution in the wash process.

[0082] Suitable EO-PO-EO triblock co-polymers are commercially available from BASF such as Pluronic® PE series, and from the Dow Chemical Company such as Tergitol™ L series. Particularly preferred triblock co-polymer from BASF are sold under the tradenames Pluronic® PE6400 (MW ca 2900, ca 40wt% EO) and Pluronic® PE 9400 (MW ca 4600, 40 wt% EO). Particularly preferred triblock co-polymer from the Dow Chemical Company is sold under the tradename Tergitol™ L64 (MW ca 2700, ca 40 wt% EO).

[0083] Preferred triblock co-polymers are readily biodegradable under aerobic conditions.

[0084] The composition of the present invention may further comprise at least one active selected from the group consisting of: hydrotrope, organic solvent, and mixtures thereof.

[0085] Hydrotrope:

The composition of the present invention can comprise from 0.1% to 2.0%, preferably from 0.2% to 1.0%, more preferably from 0.3% to 0.5% by weight of the total composition of a hydrotrope or a mixture thereof, wherein the hydrotrope preferably is selected from sodium cumene sulphonate, sodium xylene sulphonate, sodium toluene sulphonate, and mixtures thereof, preferably sodium cumene sulphonate. At such levels, low temperature stability of the composition is improved while avoiding the formation of a third intermediate phase. Where a third intermediate phase is desired, the composition can comprise higher levels of the hydrotrope.

[0086] Dyes:

The composition can comprise a dye, with water-soluble (and hence hydrophilic) dyes being preferred. Water-soluble dyes are fully soluble in polar solvents such as water, at the levels used in the composition. As such the hydrophilic dye will predominantly or entirely colour the first phase and will make the first phase visually distinct from the lightly or non-coloured second phase. Water-soluble dyes are preferred for liquid hand dishwashing applications in order to avoid dye staining on soiled-dishware. Hydrophobic dyes, which could be used to also colour the second phase, are less preferred since they are soluble in grease and oils. As such, hydrophobic dyes can result in more visible grease stains on dishware, dispersed in the wash solution, as well as visible stains on the skin. In addition, such hydrophobic dyes can also be solubilised in the first phase as it comprises surfactant, which results in less visible differentiation of the two or more phases. The composition can comprise the dye at a level of from 0.1 ppm to 100 ppm, preferably from 0.5 ppm to 50 ppm, more preferably from 1 ppm to 30 ppm.

Adjunct Ingredients

[0087] The cleaning composition may optionally comprise a number of other adjunct ingredients such as builders (such as citrate), chelants, conditioning polymers, other cleaning polymers, surface modifying polymers, emollients, humectants, skin rejuvenating actives, enzymes, carboxylic acids, scrubbing particles, perfumes, malodor control agents, pigments, opacifiers, pearlescent particles, inorganic cations such as alkaline earth metals such as Ca/Mg-ions, anti-bacterial agents, viscosity adjusters (e.g., salt such as NaCl, and other mono-, di- and trivalent salts) and pH adjusters and buffering means (e.g. carboxylic acids such as citric acid, HCl, NaOH, KOH, alkanolamines, carbonates such as sodium carbonates, bicarbonates, sesquicarbonates, and alike). However, inorganic salts, chelants and carboxylates are less preferred since they can lead to reduced low temperature stability. As such, the composition preferably comprises less than 5.0%, preferably less than 3.0%, more preferably less than 1.0% by weight of the composition of inorganic salts, chelants and carboxylates. Most preferably, the composition is free of inorganic salts, chelants and carboxylates, apart from residues that may be entrained with raw materials such as the surfactant used to make the composition.

[0088] Since the compositions of the present invention preferably can be readily emulsified, the present compositions preferably comprise less than 0.5%, more preferably less than 0.1% by weight of structurant, and most preferably are free of structurants. Such structurants raise the lowshear viscosity of the composition outside the desired range for compositions of the present invention, and also can result in the composition having a yield point. As such, such external structurants result in both poor homogenisation after shaking and also inhibit the reforming of the separate phase layers once shaking of the composition has ceased.

Packaged product

[0089] The hand dishwashing detergent composition can be packaged in a container. Suitable containers comprise an orifice. Typically, the container comprises a cap, with the orifice typically comprised on the cap. The cap can comprise a spout, with the orifice at the exit of the spout. The spout can have a length of from 0.5 mm to 10 mm

[0090] The orifice can have an open cross-sectional surface area at the exit of from 3 mm^2 to 20 mm^2, preferably from 3.8 mm^2 to 12 mm^2, more preferably from 5 mm^2 to 10 mm^2, wherein the container further comprises the composition according to the invention. The cross-sectional surface area is measured perpendicular to the liquid exit from the container (that is, perpendicular to the liquid flow during dispensing).

[0091] The container can typically comprise from 200 ml to 5,000 ml, preferably from 350 ml to 2000 ml, more preferably from 400 ml to 1,000 ml of the liquid hand dishwashing detergent composition.

Method of Washing

[0092] Before use, the composition is preferably shaken to homogenize the composition and emulsify the oil comprising phase.

[0093] The present invention provides for a method of neat application of a liquid detergent composition which comprises the step of contacting said composition in its neat form, with the dish. Said composition may be poured directly onto the dish from its container. Alternatively, the composition may be applied first to a cleaning device or implement such as a brush, a sponge, a nonwoven material, or a woven material. The cleaning device or implement, and consequently the liquid dishwashing composition in its neat form, is then directly contacted to the surface of each of the soiled dishes, to remove said soiling. The cleaning device or implement is typically contacted with each dish surface for a period of time range from 1 to 10 seconds, although the actual time of application will depend upon factors such as the degree of soiling of the dish. The contacting of said cleaning device or implement to the dish surface is preferably accompanied by concurrent scrubbing. Alternatively, the device or implement may be immersed in the liquid hand dishwashing detergent composition in its neat form, in a small container that can accommodate the cleaning device.

[0094] By "in its neat form", it is meant herein that said composition is applied directly onto the surface to be treated, or onto a cleaning device or implement such as a brush, a sponge, a nonwoven material, or a woven material, without undergoing any significant dilution by the user (immediately) prior to application. "In its neat form", also includes slight dilutions, for instance, arising from the presence of water on the cleaning device, or the addition of water by the consumer to remove the remaining quantities of the composition from a bottle. Therefore, the composition in its neat form includes mixtures having the composition and water at ratios ranging from 50:50 to 100:0, preferably 70:30 to 100:0, more preferably 80:20 to 100:0, even more preferably 90:10 to 100:0 depending on the user habits and the cleaning task. For the avoidance of doubt, a ratio of 100:0 is most preferred.

[0095] Prior to the application of said composition, the soiled dish may be immersed into a water bath, or held under running water, to wet the surface of the dish.

[0096] The method may comprise an optional rinsing step, after the step of contacting the liquid detergent composition with the dishes.

[0097] Alternatively, the method can comprise the steps of delivering a composition of the present invention to a volume of water to form a wash solution and immersing the dishware in the solution. The wash solution is preferably at a temperature of greater than 30 °C, more preferably greater than 35 °C, most preferably greater than 40 °C. The wash solution is typically at a temperature of less than 70 °C, more typically less than 60 °C. The dishware is to be cleaned with the composition in the presence of water. Optionally, the dishware can be rinsed. By "rinsing", it is meant herein contacting the dishware cleaned with the process according to the present invention with substantial quantities of appropriate solvent, typically water. By "substantial quantities", it is meant usually about 1 to about 20 L, or under running water.

[0098] The composition herein can be applied in its diluted form. Soiled dishware is contacted with an effective amount, typically from about 0.5 mL to about 20 mL (per about 25 dishes being treated), preferably from about 3 mL to about 10 mL, of the detergent composition, preferably in liquid form, of the present invention diluted in water. The actual amount of detergent composition used will be based on the judgment of the user and will typically depend upon factors such as the particular product formulation of the detergent composition, including the concentration of active ingredients in the detergent composition, the number of soiled dishes to be cleaned, the degree of soiling on the dishes, and the like. Generally, from about 0.01 mL to about 150 mL, preferably from about 3 mL to about 40 mL of a detergent composition of the invention is combined with from about 2,000 mL to about 20,000 mL, more typically from about 5,000 mL to about 15,000 mL of water in a sink. The soiled dishware are immersed in the sink containing the diluted detergent compositions then obtained, before contacting the soiled surface of the dishware with a cloth, sponge, or similar cleaning implement. The cloth, sponge, or similar cleaning implement may be immersed in the detergent composition and water mixture prior to being contacted with the dishware, and is typically contacted with the dishware for a period of time ranged from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of cloth, sponge, or similar cleaning implement to the dishware is accompanied by a concurrent scrubbing of the dishware.

METHODS:

[0099]

A) Flow viscosity:

The viscosity is measured at 20°C, with a Brookfield RT Viscometer using spindle 18 with the RPM of the viscometer adjusted to achieve a torque of between 40% and 60%. The viscosity is measured after homogenisation. That is, the multi-phase liquid detergent composition is first homogenised through aggressive shaking before measuring the viscosity. If the viscosity is higher than achievable using spindle 18 in the torque range described herein, an alternative spindle such as spindle 31 can be selected, per the guidance in the Brookfield RT Viscometer manual.

B) Low shear viscosity

The low shear viscosity of the composition is measured after homogenisation. That is, the multi-phase liquid detergent composition is first homogenised through mixing with a stirrer sufficiently aggressively so as to ensure good mixing, while avoiding air entrainment.

The low shear viscosity of each phase is measured after extracting sufficient amounts of each phase using a pipette, making sure not to extract parts of the adjacent phase(s).

The low shear viscosity is determined using an AR G2 rheometer from TA instruments using a steel spindle at 40 mm diameter and a gap size of 500 μιη., using a logarithmic shear rate sweep at 20 °C, as is known in the art. The low shear viscosity is measured at 0.01 s^{-1}, the medium shear viscosity at 0.1 s^{-1} and the high shear viscosity at 10 s^{-1} during the logarithmic shear rate sweep. The procedure consists of 3 steps including a pre-conditioning, a peak hold step at 0.01 s-1 and a flow ramp up from 0.01 s^{-1} to 100 s^{-1}. The pre-conditioning step consists of a pre-shear at 10 s^{-1} for 30 s. The peak hold step at 0.01 s^{-1} follows immediately, taking a sample point every 10 s. The step reaches equilibrium if the viscosity of 8 consecutive sample points is within a 2 % tolerance. The flow ramp up follows immediately and consists in shearing the sample at increasing shear rates in steady state flow mode from 0.01 to 100 s^{-1}, for 5 points per decade on a logarithmic scale, allowing measurements to stabilize for a period of from 2 s for up to 20 s with a tolerance of 2 per cent. The logarithmic plot of the viscosity vs. shear rate of the last step is used to determine the low shear viscosity at 0.01 s-1, the medium shear viscosity at 0.1 s^{-1} and the high shear viscosity at 10 s^{-1}.

C) Yield stress:

The dynamic yield stress is conducted as follows: a sample is placed in an AR G2 Stress Controlled Rheometer equipped with double concentric cylinder geometry from TA Instruments ("Rheometer") and subjected to a range of shear from 100 s"1 to 0.001 s"1. Fifty measurements spaced apart evenly in a logarithmic scale (as determined by the Rheometer) are performed at varying shear rates within the range stated, and the steady state viscosity and applied stress are measured and recorded for each imposed level of shear rate. The applied stress vs. imposed shear rate data are plotted on a chart and fitted to a modified Hershel-Bulkley model to account for the presence of a constant viscosity at high shear rate provided by the surfactant and adjunct ingredients present in the liquid matrix.

[0100] The following equation is used to model the stress of the liquid matrix:

$$\sigma = PI + P2 * fn + PA * \gamma$$

where: σ : Stress, dependent variable; PI : Yield stress, fit parameter; P2 : Viscosity term in Hershel-Bulkley model, fit parameter; f : Shear rate, independent variable; P : Exponent in the Hershel-Bulkley model, fit parameter; and P : Asymptotic viscosity at high shear rate, fit parameter. One of ordinary skill will understand that the fitting procedure due to the Hershel-Bulkley model to the data collected from the sample will output the PI to PA parameters, which include the yield stress (PI). The Herschel Bulkley model is described in "Rheometry of Pastes Suspensions and Granular Material" page 163, Philippe Coussot, John Wiley & Sons, Inc., Hoboken, New Jersey (2005).

[0101] C) Homogenisation and re-separation:

The composition is mixed using a mixer blade, at a sufficiently high rpm to achieve full homogenization, while avoiding air-entrainment. Full homogenization is indicated by an absence of a visual separation layer 10 seconds after end of mixing, after which 400 ml of the homogenized composition is quickly transferred into a 500 ml glass jar (dimensions: 145mm height, 76mm diameter, commercially available from the VWR company) and left closed for at least 24 hours to fully separate out into two visually distinct layers. The height of the top layer formed is measured.

[0102] The jar is then shaken by hand vertically 20 times up and down over a distance of 20cm up and 20 cm down at a rate of 2 cycles per second (1 cycle being 1 time up and 1 time down movement). The composition is checked for homogeneity after 10 seconds (absence of a visible top layer remaining). The hand shaken step is repeated until no remaining top layer is visually observed. The time taken after cessation of shaking for the top layer to re-separate is recorded using a stopwatch. The end-point is defined as when 90% of the initial height of the top layer has been recovered.

[0103] The test is repeated twice (for a total of three replicates) and the results are averaged over the three sets of measurements and reported.

[0104] D) pH:

The multi-phase liquid cleaning composition is first homogenized through aggressive shaking before diluting in demineralised water to provide a 10% solution and measuring the pH. As such, the pH is measured as a 10% solution of the finished product in demineralized water at 20 °C.

EXAMPLES

[0105] The following comparative test was made, using example 3 of WO200130958 A as the comparative example (example A). The phases of all of the compositions had a low shear viscosity of from 10 mPa·s to 1,000 mPa·s measured at 20 °C and a shear rate of 0.01 s^{-1}, as did the full compositions after homogenisation. None of the compositions exhibited a yield stress.

Table 1: Compositions of the present invention (examples 1 to 6) and comparative example A (example 3 of WO200130958 A)

Wt% (100% active basis)	Ex A* wt%	Ex 1 wt%	Ex 2 wt%
Sodium C14-C17 alkyl sec. sulfonate[1]	20	20	
C12-C13 alkyl ethoxylated (EO0.6) sulphate			18.0
C8-C18 alkyl polyglucoside[2]	4	4	-
Cocamidopropyl betaine	4	4	-
C12-C14 dimethyl amine oxide	-	-	4.1
di-n-octyl ether	5	-	-
C8-C10 coconut oil[3]	-	5	40
Ethanol	10	10	10
Citric acid monohydrate	13	13	13
Sodium cumene sulphonate			
Monoethanolamine	9.4	9.4	9.9
Red dye	0.00091	0.00091	0.00091
water	to 100%	to 100%	to 100%
pH (10% solution)	5.7	5.7	7.9

* Example 3 of WO200130958 A
[1] Hostapur SAS60, supplied by Clariant
[2] Glucopon 600CSUP, supplied by BASF
[3] Refined, Captex 355, supplied by Abitec

Wt% (100% active basis)	Ex 3 wt%	Ex 4 wt%	Ex 5 wt%	Ex 6 wt%
Sodium C14-C17 alkyl sec. sulfonate[1]	-	-	-	-
C12-C13 alkyl ethoxylated (EO0.6) sulphate	18.0	18.0	18.0	18.0
C8-C18 alkyl polyglucoside[2]	-	-	-	-
Cocamidopropyl betaine	-	-	-	4.1
C12-C14 dimethyl amine oxide	4.1	4.1	4.1	-
C9-11 EO8 nonionic surfactant[4]	-	-	10	-
EO-PO-EP copolymer5	-	10	-	10
di-n-octyl ether	-	-	-	-
C8-C10 coconut oil[3]	40	40	40	40
Ethanol	12	12	12	12
Citric acid monohydrate	0	0	0	0
Sodium cumene sulphonate	0.4	0.4	0.4	0.4
Monoethanolamine	9.9	9.9	9.9	9.9
Red dye	0.00091	0.00091	0.00091	0.00091
water	to 100%	to 100%	to 100%	to 100%

(continued)

Wt% (100% active basis)	Ex 3 wt%	Ex 4 wt%	Ex 5 wt%	Ex 6 wt%
pH (10% solution)	7.9	7.9	7.9	7.9
[4] Neodol® 91-8, supplied by Shell [5] Tergitol® L64, supplied by DOW				

[0106] In comparative example A, di-n-octyl ether is used to provide the second, top phase with a high level of citric acid being used to induce the phase split. As such, comparative example A using a combination of an apolar organic solvent as a phase separating agent, in combination with a high ionic strength component (citric acid) to separate out a second phase. The top phase of comparative example A comprised roughly 90% by volume of the composition. As such, it was not possible to formulate higher that 5% of the di-n-octyl ether, for instance, to provide increased skin care, while maintaining a highly visible dual-phase. Moreover, since di-n-octyl ether is soluble in first phases comprising the surfactant system, changes in the surfactant system can result in substantial changes in the relative sizes of the different phases.

[0107] Comparative example A had poor low temperature stability, which is believed to be due to the high levels of citrate present. When example A was formulated without citrate (replacing the citrate with water), the resultant composition had only one phase.

[0108] The red dye was present in both phases since both phases were aqueous. As a result, the presence of the dye had a relatively small impact on the visibility of the different phases.

[0109] In contrast, the compositions of the present invention use a vegetable oil having a defined alkyl chain length in order to provide the second phase with skin care benefit.

[0110] Inventive examples 1 comprised a second phase on top of at least one predominantly first phase. Inventive example 1 had essentially the same formulation as comparative example A, but with the di-n-octyl ether replaced by a C8-C10 coconut oil. Since inventive example 1 comprised a second phase which was predominantly oil, the red dye, being a water-soluble dye, was present only in the first phase, leading to a sharper differentiation and visualization between the two phases. Moreover, vegetable oils such as the C8-C10 coconut provide improved skin mildness in comparison to di-alkyl ethers.

[0111] As can be seen from Example 2, the amount of the C8-C10 coconut oil could be increased, both to improve the skin care benefit but also to provide a more balanced 2-phase structure. In addition, since the oil is in a different phase form the surfactant, it is relatively simple to modify the surfactant system while avoiding substantial changes to the overall visual impression of the composition.

[0112] Example 3 shows that the citric acid can be reduced or even eliminated without impacting the phase behaviour. An increase in solvent (ethanol) and introduction of hydrotrope (sodium cumene sulphonate) both lead to an improvement in low temperature stability and sharpness of the split between the phases.

[0113] As can be seen from examples 4 to 6, the use of a vegetable oil having a defined alkyl chain length in order to provide the second phase with skin care benefit, means that the composition can be readily reformulated without undue effort.

[0114] For examples 1 to 6, and comparative example A, the compositions could be converted into emulsions by simple shaking and separated into separate phases once left standing.

[0115] 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."

Claims

1. A multi-phase liquid hand dishwashing detergent composition comprising a first phase and a second phase, wherein the multi-phase liquid hand dishwashing detergent composition comprises:

   a. from 5% to 50% by weight of the total composition of a surfactant system; and
   b. from 5.0% to 60% by weight of the total composition of vegetable oil, wherein the vegetable oil is selected from vegetable oils which comprise glycerides formed from fatty acids having a number average alkyl chain length of less than 14.0 carbon atoms;

wherein the low shear viscosity of each phase of the composition is from 10 mPa·s to 1,000 mPa·s, measured at $0.01s^{-1}$ at 20°C.

2. The composition according to claim 1, wherein the composition comprises from 15% to 55%, preferably from 25% to 50% by weight of the total composition of the vegetable oil.

3. The composition according to any of the preceding claims, wherein the vegetable oil comprises glycerides, wherein the glycerides are formed from fatty acids having a number average alkyl chain length of 12.0 or less, preferably from 6.0 to 12.0, more preferably from 8.0 to 10.0 carbon atoms.

4. The composition according to any of the preceding claims, wherein the vegetable oil is selected from coconut oil, palm kernel oil, and mixtures thereof, most preferably coconut oil.

5. The composition according to any of the preceding claims, wherein the vegetable oil comprises glycerides, wherein less than 20%, preferably less than 10%, more preferably less than 5% by number of the fatty acids of the glycerides have an alkyl chain comprising 12 or more carbon atoms.

6. The composition according to any of the preceding claims, wherein at least 80%, preferably at least 90%, more preferably at least 95% by number of the fatty acids that form the glycerides of the vegetable oil are saturated fatty acids.

7. The composition according to any preceding claim, wherein the liquid hand dishwashing detergent composition comprising from 10% to 40%, preferably from 15% to 35%, by weight of the total composition of the surfactant system.

8. The composition according to any preceding claim, wherein the surfactant system comprises anionic surfactant, preferably wherein the anionic surfactant comprises alkyl sulphated anionic surfactant selected from the group consisting of: alkyl sulphate, alkyl alkoxy sulphate, and mixtures thereof.

9. The composition according to claim 8, wherein the surfactant system comprises a co-surfactant selected from the group consisting of an amphoteric surfactant, a zwitterionic surfactant and mixtures thereof, preferably wherein the surfactant system comprises the anionic surfactant and the co-surfactant in a weight ratio of less than 9:1.

10. The composition according to claim 9, wherein the co-surfactant is an amphoteric surfactant selected from amine oxide surfactant, preferably wherein the amine oxide surfactant is selected from the group consisting of: alkyl dimethyl amine oxide, alkyl amido propyl dimethyl amine oxide, and mixtures thereof.

11. The composition according to claim 9, wherein the co-surfactant is a zwitterionic surfactant selected from betaine surfactant, preferably wherein the betaine surfactant is selected from the group consisting of: cocamidopropyl betaine, cocobetaines, lauramidopropyl betaine, lauryl betaine, myristyl amidopropyl betaine, myristyl betaine, and mixtures thereof; more preferably cocamidopropyl betaine.

12. The composition according to any preceding claim, wherein the low shear viscosity of the composition after homogenization is from 30 mPa·s to 500 mPa·s, preferably from 50 mPa·s to 200 mPa·s, measured at $0.01s^{-1}$ at 20°C.

13. The composition according to any preceding claim, wherein the composition further comprises a hydrotrope, preferably at a level of from 0.1% to 2.0%, more preferably from 0.2% to 1.0%, most preferably from 0.3% to 0.5% by weight of the composition.

14. The composition according to any preceding claim, wherein the composition further comprises organic solvent, preferably at a level of from 1.0% to 25%, or preferably from 5.0% to 20%, or more preferably from 8.0% to 15% by weight of the total composition.

15. The composition according to any preceding claim, wherein the first phase and the second phase both have a yield stress of less than 0.001 Pa, preferably less than 0.0001 Pa.

16. The composition according to any preceding claim, wherein after shaking, the first phase and second phase re-separate into separate layers within less than 12 hours preferably less than 6 hours, more preferably less than 3 hours.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 21 6734

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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