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(54) LIQUID HAND DISHWASHING COMPOSITIONS

(57) The need for a liquid hand dishwashing composition and method of washing dishes at temperatures of less than 30°C, at which the liquid detergent composition provides improved sudsing in the presence of greasy soils, is met by formulating the liquid hand dishwashing detergent composition to comprise a quaternized acrylic copolymer and a surfactant system, wherein the surfactant system comprises an anionic surfactant system comprising alkyl sulfated anionic surfactant, wherein the alkyl sulfated anionic surfactant has an average degree of alkoxylation of less than 0.1.

Description

FIELD OF THE INVENTION

[0001] The present invention relates to liquid hand dishwashing detergent compositions and methods of cleaning dishes.

BACKGROUND OF THE INVENTION

[0002] Hand dishwashing compositions should provide good grease cleaning and sudsing. Typically, dishes and the like are washed at elevated temperatures in order to more effectively clean dishes. In particular, greasy soils are softened at elevated temperatures. As such, dishes and the like are typically cleaned at temperatures of 35°C or higher.

[0003] However, there is a greater desire to wash dishes in a more sustainable manner, and more cost-effective manner. Heating the water used when washing dishes is one of the steps in the hand dishwashing process that is the least environmentally desirable, and is also one of the steps that adds most to the cost of washing dishes. As such, there is a greater desire to wash dishes at colder temperatures. However, there remains a high degree of scepticism from users that hand dishwashing detergents provide effective grease removal at low temperatures. As the amount of residual suds (suds mileage) is typically seen by users as an indication of cleaning efficacy, especially for greasy soils, improving sudsing performance at reduced dishwashing temperatures is a way to reassure users that washing at lower water temperatures still results in good cleaning of the dishware.

[0004] As such, a need remains for a method of washing dishes at temperatures of less than 30°C, at which the liquid detergent composition provides improved sudsing in the presence of greasy soils.

[0005] WO2017110773A1 relates to liquid detergent composition for hard surfaces, including dishware, and its use for cleaning the aforementioned hard surface at low temperatures. JP2013100461A discloses a liquid detergent composition hand-washing tableware at a low temperature (10 to 35 ° C.). WO201691688A relates to a liquid cleaning agent for hard surfaces, in particular for washing dishes by hand, containing an α amylase for cleaning starch stains at low temperature (< 40 degrees C). JP2015010141A relates to a tableware washing detergent which provides detergency, foaming and rinsibility at low temperatures and aroma and reduced aroma variation at low temperatures. WO2014117973A relates to relates to anionic sulfonated cyclic surfactants of specific formula with lower cmc, for providing cleaning at low temperatures. EP3971270A relates to a liquid hand dishwashing cleaning compositions that comprise alkyl sulfate anionic surfactant having little or no ethoxylation, which provides improved low temperature stability while also achieving the desired product viscosity, suds mileage and overall cleaning. EP3971271A relates to a hand-dishwashing composition which is highly effective at removing grease, providing long-lasting suds under soiled conditions, while having a Newtonian viscosity which is less sensitive to changes on surfactant and solvent levels, the liquid hand dishwashing cleaning composition comprising a surfactant system having a combination of alkyl sulphate anionic surfactant having little or no alkoxylation and an alkyl polyglucoside surfactant. EP3971273A relates to a hand-dishwashing composition which is highly effective at removing grease, while also having good suds mileage, and avoiding negatives on physical stability, especially at low temperatures, the hand dishwashing composition comprising a surfactant system, the surfactant system comprising an alkyl sulfate anionic surfactant comprising little or no branching and having a low degree of alkoxylation, or no alkoxylation, and a co-surfactant, in combination with polypropylene glycol of a defined molecular weight, as described herein. EP3919594A relates to a liquid detergent composition suitable for washing dishes, fitting both in-sink as well as direct application habits, which provides reduced smearing when used in direct application dishwashing methods, while having good suds mileage especially under in-sink application habit, and good viscosity, the liquid detergent composition comprises a surfactant system, which comprises an alkyl sulfate anionic surfactant comprising C13 alkyl sulfate anionic surfactant, the C13 alkyl sulfate anionic surfactant comprising a specific fraction of 2-branched C13 alkyl sulfate anionic surfactant, with a specific distribution of the 2-branching. EP3971275A relates to a hand-dishwashing composition which is highly effective at emulsifying grease, the liquid hand dishwashing cleaning composition comprising a surfactant system having a combination of alkyl sulphate anionic surfactant and a co-surfactant comprising at least 70% by weight of the co-surfactant of a betaine, in combination with a polypropyleneglycol having a weight average molecular weight from 500 g/mol to 1800 g/mol. WO201836864A relates to hard surface treatment compositions comprising quaternised acrylic copolymer and amphoteric modified polysaccharide, wherein the weight ratio of the quaternised acrylic copolymer to the amphoteric modified polysaccharide is from 0.75:1 to 3:1 and the quaternised acrylic copolymer is different from the amphoteric modified polysaccharide. EP3835399A1 relates to hard surface cleaning composition comprising a surfactant system; a first polymer; and a second polymer, the first polymer being a polyethyleneimine, as well as to the use of the composition to clean a glass surfaces. US20030134770A relates to liquid detergent compositions comprising a polymeric material which is a suds enhancer and a suds volume extender, said compositions having increased effectiveness for preventing re-deposition of grease during hand washing, the polymeric material being suitable as suds volume and suds endurance enhancers and comprising an effective amount of a quaternary nitrogen-containing monomeric unit and/or zwitterionic monomeric unit-containing polymeric suds enhancer. US7741265B relates to a cleaning composition for a hard surface which provides for initial cleaning of the hard surface and provision of a hydrophilic coating or barrier layer on the surface which provides residual cleaning to the hard surface for an extended number of rinsings. The composition includes a hydrophilic polymer, at least one nonionic surfactant, at least one solvent, an acid and water, wherein the acid provides the composition with a pH of about 2 to 3.5 and the composition is provided in the absence of any anionic, cationic or amphoteric surfactant. US7741265B teaches the use of hydrophilic cationic polymers, including acrylic based polymers, for providing a residual cleaning benefit through numerous rinsings. US20120028872A relates to a method of cleaning dishware with a liquid detergent composition having a hydrophobic emollient and a crystalline structurant to provide improved hand skin care benefits and superior grease cleaning and/or suds mileage. US20120028872A discloses cationic polymers, and their use for enhancing skin benefits. US20220081649A relates to a hand-dishwashing composition for removing grease, providing long-lasting suds under soiled conditions, while having a Newtonian viscosity which is less sensitive to changes on surfactant and solvent levels. US20220081649A teaches the provision of such benefits through the use of a combination of alkyl sulfate surfactant and short-chain alkyl polyglucoside.

SUMMARY OF THE INVENTION

[0006] The present invention relates a liquid hand dishwashing cleaning composition comprising: from 6% to 50% by weight of the total composition of a surfactant system, and a quaternised acrylic copolymer, wherein the surfactant system comprises: at least 40% by weight of the surfactant system of anionic surfactant, wherein the anionic surfactant comprises at least 50% by weight of the anionic surfactant of alkyl sulfated anionic surfactant, wherein the alkyl sulfated anionic surfactant has an average degree of alkoxylation of less than 0.1.

[0007] The present invention further relates to methods of cleaning dishware, using such compositions, wherein the method comprises the step of: contacting dishware with the liquid hand dishwashing detergent composition and water, wherein the water has a temperature of 30 °C or less.

DETAILED DESCRIPTION OF THE INVENTION

[0008] It has been found that methods using liquid hand dishwashing detergent compositions, as described herein, and contrary to methods using more traditionally used compositions comprising ethoxylated alkyl sulfate anionic surfactants, provide more effective sudsing, especially in the presence of greasy soil during low temperature dishwashing. As such, the user is more incentivised to wash their dishware at lower temperatures. Moreover, the incorporation of a quaternised acrylic copolymer within a liquid hand dishwashing detergent composition as described herein further improves sudsing during low temperature washing of dishware.

Definitions

[0009] 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.

[0010] 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.

[0011] 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.

[0012] 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.

[0013] The terms "include", "includes" and "including" are meant to be non-limiting.

[0014] 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.

[0015] The term "sudsing profile" as used herein refers to the properties of a cleaning composition relating to suds character during the dishwashing process. The term "sudsing profile" of a cleaning composition includes suds volume generated upon dissolving and agitation, typically manual agitation, of the cleaning composition in the aqueous washing solution, and the retention of the suds during the dishwashing process. Preferably, hand dishwashing cleaning 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 cleaning 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 cleaning composition will tend to be replaced by the consumer more frequently than is necessary because of the low sudsing level.

[0016] It is understood that the test methods that are disclosed in the Test Methods Section of the present application must be used to determine the respective values of the parameters of Applicants' inventions as described and claimed herein.

[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.

Cleaning Composition

[0018] The cleaning composition is a liquid hand dishwashing cleaning composition. The cleaning composition is preferably an aqueous cleaning composition. As such, the composition can comprise from 50% to 85%, preferably from 50% to 75%, by weight of the total composition of water.

[0019] Preferably, the pH of the composition is from about 6 to about 14, preferably from about 7 to about 12, or more preferably from about 7.5 to about 10, as measured at 10% dilution in distilled water at 20°C. The pH of the composition can be adjusted using pH modifying ingredients known in the art.

[0020] The composition of the present invention can be Newtonian or non-Newtonian, preferably Newtonian in the usage shear rate range of from 0.1 s^{-1} to 100 s^{-1}. Preferably, the composition has a viscosity of from 10 mPa·s to 10,000 mPa·s, preferably from 100 mPa·s to 5,000 mPa·s, more preferably from 300 mPa·s to 2,000 mPa·s, or most preferably from 500 mPa·s to 1,500 mPa·s, alternatively combinations thereof. The viscosity is measured at 20°C with a Brookfield RT Viscometer using spindle 31 with the RPM of the viscometer adjusted to achieve a torque of between 40% and 60%.

Surfactant System

[0021] The liquid cleaning composition comprises from 6.0% to 50%, preferably from 6.0% to 40%, most preferably from 15% to 35%, by weight of the total composition of a surfactant system.

Anionic surfactant:

[0022] The liquid hand dishwashing detergent composition comprises a surfactant system, wherein the surfactant system comprises an anionic surfactant system comprising alkyl sulfated anionic surfactant, wherein the alkyl sulfated anionic surfactant has an average degree of alkoxylation of less than 0.1 and is more preferably free of any alkoxylation. If alkoxylation is present, the alkyl sulfate anionic surfactant is preferably ethoxylated.

[0023] The average degree of alkoxylation is the mol average degree of alkoxylation (*i.e.*, mol average alkoxylation degree) of all the alkyl sulfate anionic surfactant. Hence, when calculating the mol average alkoxylation degree, the mols of non-alkoxylated sulfate 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) sulfate anionic surfactant of the mixture and alkoxylation degree is the number of alkoxy groups in each alkyl sulfate anionic surfactant.

[0024] For improved sudsing, the surfactant system comprises at least 40%, preferably from 60% to 90%, more preferably from 70 to 80% by weight of the surfactant system of the anionic surfactant.

[0025] The anionic surfactant comprises at least 50%, preferably at least 70%, more preferably at least 90% by weight of the anionic surfactant of alkyl sulfated anionic surfactant. Most preferably, the anionic surfactant consists of alkyl sulfated surfactant, most preferably primary alkyl sulfated anionic surfactant. As such, while the surfactant system may comprise small amounts of further anionic surfactant, including sulfonates such as HLAS, or sulfosuccinate anionic surfactants, the surfactant system preferably comprises no further anionic surfactant beyond the alkyl sulfated anionic surfactant.

[0026] The alkyl sulfated anionic surfactant has an alkyl chain comprising an average of from 8 to 18 carbon atoms, preferably from 10 to 14 carbon atoms, more preferably from 12 to 13 carbon atoms.

[0027] The alkyl chain of the alkyl sulfated 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 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.

[0028] The alkyl sulfated anionic surfactant can have an average degree of branching of at least 5.0%, preferably from 10% to 50%, more preferably from 15% to 40%. As such, the alkyl sulfated anionic surfactant can comprise a mixture of linear and branched alkyl sulfated anionic surfactant.

[0029] The alkyl chains of the alkyl sulphated anionic surfactant can be derived from natural or synthetic origins. The linear chains can be natural alkyl chains which are preferably derived from coconut oil, coconut oil being more sustainably derivable while having a preferred chain length. The linear alkyl chains can be blended with a highly branched alkyl chain so that less branched alkyl chains need to be added in order to arrive at the desired degree of branching.

[0030] The overall degree of branching (as well as how the branching is achieved) affects not just the sustainability of the sourcing material, but also impacts the amount of organic solvent required to physically stabilise the liquid hand dishwashing composition. The branching of the alkyl sulfated anionic surfactant also affects the viscosity as well as the viscosity upon dilution, avoiding viscosity thickening upon dilution and ensuring that the composition is readily dispersible in the water.

[0031] The level of branching in the branched alkyl sulfate or alkyl alkoxy sulfate used in the detergent composition is calculated on a molecular basis. Commercially available non-alkoxylated alkyl sulfate anionic surfactant blends that are sold as "branched" will typically comprise a blend of linear alkyl sulfate as well as branched alkyl sulphate molecules. Commercially available alkyl alkoxy sulfate anionic surfactant blends that are sold as "branched" will typically comprise a blend of linear alkyl sulfate, branched alkyl sulfate, as well as linear alkyl alkoxy sulfate and branched alkyl alkoxy sulfate molecules. The actual calculation of the degree of branching is done based on the starting alcohol (and alkoxylated alcohols for alkyl alkoxy sulfate blends), rather than on the final sulfated materials, as explained in the weight average degree of branching calculation below:

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

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) sulfate anionic surfactant. In the weight average degree of branching calculation, the weight of the alkyl alcohol used to form the alkyl sulfate anionic surfactant which is not branched is included.

[0032] 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 sulfated anionic surfactant.

[0033] The branched alkyl sulfated anionic surfactant can comprise C2-branched alkyl sulfated anionic surfactant and optionally non-C2-branched alkyl sulfated anionic surfactant. The branched alkyl sulfated anionic surfactant can comprise at least 90%, preferably at least 95%, more preferably at least 98% by weight of the branched alkyl sulfated anionic surfactant of C2-branched alkyl sulfated anionic surfactant and at most 10%, preferably at most 5%, most preferably at most 2% by weight of the branched alkyl sulfated anionic surfactant of non-C2 branched alkyl sulfate anionic surfactant.

[0034] C2-branched means the alkyl branching is a single alkyl branching on the alkyl chain of the alkyl sulfated anionic surfactant and is positioned on the C2 position, as measured counting carbon atoms from the sulfate group for non-alkoxylated alkyl sulfate anionic surfactants, or counting from the alkoxy-group furthest from the sulfate group for alkoxylated alkyl sulfate anionic surfactants.

[0035] Non-C2 branching means the alkyl chain comprises branching at multiple carbon positions along the alkyl chain backbone, or a single branching group present on a branching position on the alkyl chain other than the C2 position.

[0036] The non-C2 branched alkyl sulfated anionic surfactant can comprise less than 30%, preferably less than 20%, more preferably less than 10% by weight of the non-C2 branched alkyl sulfated anionic surfactant of C1-branched alkyl sulfated anionic surfactant, most preferably the non-C2 branched alkyl sulfated anionic surfactant is free of C1-branched alkyl sulfated anionic surfactant.

[0037] The non-C2 branched alkyl sulfated anionic surfactant can comprise at least 50%, preferably from 60 to 90%, more preferably from 70 to 80% by weight of the non-C2 branched alkyl sulfated anionic surfactant of isomers comprising a single branching at a branching position greater than the 2-position. That is, more than 2 carbons atoms away from the hydrophilic headgroup, as defined above. The non-C2 branched alkyl sulfated anionic surfactant can comprise from 5% to 30%, preferably from 7% to 20%, more preferably from 10% to 15% by weight of the non-C2 branched alkyl sulfated anionic surfactant of multi-branched isomers. The non-C2 branched alkyl sulfated anionic surfactant can comprise from 5% to 30%, preferably from 7% to 20%, more preferably from 10% to 15% by weight of non-C2 branched alkyl sulfated anionic surfactant of cyclic isomers. If present, the acyclic branching groups can be selected from C1 to C5 alkyl groups, and mixtures thereof.

[0038] It has been found that formulating the compositions using alkyl sulfated anionic surfactants having the aforementioned branching distribution and reduced to nil ethoxylation results in reduced viscosensitivity to variations in temperature and, as such, a more consistent dosage experience, compared to compositions comprising alkyl sulfated anionic surfactants with a comparative branching distribution. Moreover, the composition maintains a Newtonian viscosity profile for a broader shear rate range, which means less dosage variation and a more consistent user experience, regardless of how hard the container is squeezed.

[0039] Suitable counterions for the anionic surfactant include alkali metal cation earth alkali metal cation, alkanolammonium or ammonium or substituted ammonium, but preferably sodium.

[0040] Suitable examples of commercially available alkyl sulfated 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 average alkyl chain, average degree of branching and type of branching distribution according to the invention. Considering the targeted branched alkyl sulfated anionic surfactant according to the invention has a high dominance of C2 branched alkyl sulfated anionic surfactant content, preferably the alkyl sulfated anionic surfactant comprises an OXO derived alkyl sulfated anionic surfactant, such as commercially available under the lial and isalchem brandname from the Sasol company, and Neodol from the Shell company, OXO derived alkyl sulfated anionic surfactants comprising branched alkyl sulfated anionic surfactant consisting essentially of C2 branched alkyl sulfate anionic surfactant. OXO alcohols are alcohols that are prepared by adding carbon monoxide (CO) and hydrogen (usually combined together as synthesis gas) to an olefin to obtain an aldehyde using the hydroformylation reaction and then hydrogenating the aldehyde to obtain the alcohol. More preferably the alkyl sulfated anionic surfactant comprises from 60% to 85%, preferably from 75% to 85% by weight of the alkyl sulfate anionic surfactant of OXO-derived alkyl sulfated anionic surfactant, wherein OXO alcohols are alcohols that are prepared by adding carbon monoxide (CO) and hydrogen to an olefin to obtain an aldehyde using the hydroformylation reaction and then hydrogenating the aldehyde to obtain the alcohol. Alternative processes yielding alkyl sulfated anionic surfactants comprising branched alkyl sulfated anionic surfactant with high dominance of C2 branched alkyl sulfated anionic surfactant are also considered suitable for the invention. An example of such an alternative process is described in US applications 63/035125 and 63/035131. As such the alkyl sulfated anionic surfactant then comprises at least 30%, preferably from 40% to 95%, more preferably from 50% to 85% by weight of alkyl sulfated anionic surfactant of this alternative process derived alkyl sulfate anionic surfactant, or of a mixture of OXO derived and this alternative process derived alkyl sulfate anionic surfactant.

[0041] If ethoxylated alkyl sulfate is present, without wishing to be bound by theory, through tight control of processing conditions and feedstock material compositions, both during alkoxylation especially ethoxylation and sulfation steps, the amount of 1,4-dioxane by-product within alkoxylated especially ethoxylated alkyl sulfates can be reduced. Based on recent advances in technology, a further reduction of 1,4-dioxane by-product can be achieved by subsequent stripping, distillation, evaporation, centrifugation, microwave irradiation, molecular sieving or catalytic or enzymatic degradation steps. Processes to control 1,4-dioxane content within alkoxylated/ethoxylated alkyl sulfates have been described extensively in the art. Alternatively 1,4-dioxane level control within detergent formulations has also been described in the art through addition of 1,4-dioxane inhibitors to 1,4-dioxane comprising formulations, such as 5,6-dihydro-3-(4-morpholinyl)-1-[4-(2-oxo-1-piperidinyl)-phenyl]-2-(1-H)-pyridone, 3-α-hydroxy-7-oxo stereoisomer-mixtures of cholinic acid, 3-(N-methyl amino)-L-alanine, and mixtures thereof.

Co-surfactant

[0042] In order to improve surfactant packing after dilution and hence improve suds mileage, the surfactant system can comprise a co-surfactant in addition to the anionic surfactant.

[0043] The co-surfactant can be selected from the group consisting of an amphoteric surfactant, a zwitterionic surfactant, and mixtures thereof.

[0044] The weight ratio of anionic surfactant to the co-surfactant can be from 2.0:1 to 8.0:1, preferably from 2.0:1 to 5.0:1, more preferably from 2.5:1 to 4.0:1, in order to provide improved grease cleaning, sudsing and viscosity build.

[0045] The surfactant system can comprise from 0.1% to 20%, preferably from 0.5% to 15%, more preferably from 2% to 10% by weight of the cleaning composition of the co-surfactant. The surfactant system of the cleaning composition of the present invention can comprise from 10% to 40%, preferably from 15% to 35%, more preferably from 20% to 30%, by weight of the surfactant system of the co-surfactant.

[0046] The co-surfactant can be an amphoteric surfactant, such as an amine oxide 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.

[0047] 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. Preferably, the alkyl chain of the alkyl dimethyl amine oxide is a linear alkyl chain, preferably a C12-C14 alkyl chain, more preferably a C12-C14 alkyl chain derived from coconut oil or palm kernel oil.

[0048] 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 1 to 3 ethylene oxide groups. Preferably, the two moieties are selected from a C1-3 alkyl, more preferably both are selected as C1 alkyl.

[0049] 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 10% to 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

[0050] 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.

[0051] Preferably, the amine oxide comprises less than 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.

[0052] The co-surfactant can be zwitterionic surfactants such as a betaine surfactant. Such betaine surfactants include 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(ORS)O or P(O)(OR5)O, wherein R5 is H or a C1-4 alkyl residue.

[0053] 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).

[0054] 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.

Nonionic Surfactant:

[0055] The surfactant system can further comprise nonionic surfactant, preferably alkoxylated alcohol nonionic surfactant.

[0056] The surfactant system can comprise at least 0.5%, preferably at least 1.0% more preferably at least 2.0% by weight of the composition of the alkoxylated alcohol nonionic surfactant. The anionic surfactant and alkoxylated alcohol nonionic surfactant can be present in a weight ratio of less than 10:1. The anionic surfactant and alkoxylated alcohol nonionic surfactant are preferably present in a weight ratio of from 0.8:1 to 6.0:1, more preferably from 3.5:1 to 5.5:1. Alternatively the composition can comprise greater than 3.0%, preferably from 3.5% to 10%, more preferably from 4.0% to 7.5% by weight of the liquid hand dishwashing detergent composition of an alkoxylated alcohol nonionic surfactant.

[0057] Preferably, the alkoxylated alcohol non-ionic surfactant is a linear or branched, preferably linear, primary or secondary alkyl alkoxylated non-ionic surfactant, preferably an alkyl ethoxylated non-ionic surfactant, preferably comprising 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 alkylene oxide per mole of alcohol. The alkoxylated alcohol non-ionic surfactant is preferably ethoxylated and/or propoxylated, more preferably ethoxylated.

[0058] The surfactant system can comprise a further nonionic surfactant such as an alkyl polyglucoside nonionic surfactant:
A combination of alkylpolyglucoside and anionic surfactant especially alkyl sulfate anionic surfactant, has been found to improve polymerized grease removal, suds mileage performance, reduced viscosity variation with changes in the surfactant and/or system, and a more sustained Newtonian rheology.

[0059] The alkyl polyglucoside surfactant can be selected from C6-C18 alkyl polyglucoside surfactant. The alkyl polyglucoside surfactant can have a number average degree of polymerization of from 0.1 to 3.0, preferably from 1.0 to 2.0, more preferably from 1.2 to 1.6. The alkyl polyglucoside surfactant can comprise a blend of short chain alkyl polyglucoside surfactant having an alkyl chain comprising 10 carbon atoms or less, and mid to long chain alkyl polyglucoside surfactant having an alkyl chain comprising greater than 10 carbon atoms to 18 carbon atoms, preferably from 12 to 14 carbon atoms.

[0060] Short chain alkyl polyglucoside surfactants have a monomodal chain length distribution between C8-C10, mid to long chain alkyl polyglucoside surfactants have a monomodal chain length distribution between C10-C18, while mid chain alkyl polyglucoside surfactants have a monomodal chain length distribution between C12-C14. In contrast, C8 to

C18 alkyl polyglucoside surfactants typically have a monomodal distribution of alkyl chains between C8 and C18, as with C8 to C16 and the like. As such, a combination of short chain alkyl polyglucoside surfactants with mid to long chain or mid chain alkyl polyglucoside surfactants have a broader distribution of chain lengths, or even a bimodal distribution, than non-blended C8 to C18 alkyl polyglucoside surfactants. Preferably, the weight ratio of short chain alkyl polyglucoside surfactant to long chain alkyl polyglucoside surfactant is from 1:1 to 10:1, preferably from 1.5:1 to 5:1, more preferably from 2:1 to 4:1. It has been found that a blend of such short chain alkyl polyglucoside surfactant and long chain alkyl polyglucoside surfactant results in faster dissolution of the detergent solution in water and improved initial sudsing, in combination with improved suds stability.

[0061] 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). Glucopon® 215UP is a preferred short chain APG surfactant. Glucopon® 600CSUP is a preferred mid to long chain APG surfactant.

[0062] If present, the alkyl polyglucoside can be present in the surfactant system at a level of from 0.5% to 20%, preferably from 0.75% to 15%, more preferably from 1% to 10%, most preferably from 1% to 5% by weight of the surfactant composition. Alkyl polyglucoside nonionic surfactants are typically more sudsing than other nonionic surfactants such as alkyl ethoxlated alcohols.

[0063] In other preferred compositions, the alkyl polyglucoside is present at a level of less than 2.0%, preferably less than 1.0%, more preferably less than 0.5% by weight of the composition.

[0064] In even more preferred compositions, the composition is free of any further nonionic surfactant.

Quaternised acrylic copolymer

[0065] The liquid hand dishwashing detergent comprises a quaternised acrylic copolymer. "Copolymer" as used herein refers to a polymer comprising at least two different monomer compositions. Quaternised polymers comprise quaternary ammonium groups, which are positively charged polyatomic ions of the structure NR_4^+, R being an alkyl group or an aryl group. Unlike the ammonium ion (NH_4^+) and the primary, secondary, or tertiary ammonium cations, the quaternary ammonium cations are permanently charged, independent of the pH of their solution.

[0066] The composition preferably comprises from 0.01% to 3.0%, preferably from 0.05% to 2.0%, more preferably from 0.1% to 1.0% by weight of the composition of the quaternised acrylic copolymer.

[0067] The quaternised acrylic copolymer can have a weight average molecular weight (Mw), measured by aqueous gel permeation chromatography (GPC) with light scattering detection (SEC-MALLS), in the range of from 5,000 to 500,000 Da, preferably from 15,000 to 300,000 Da and even more preferably from 25,000 to 75,000 Da.

[0068] The quaternised acrylic copolymer may be characterized by a cationic charge density. Cationic charge density is typically expressed as milliequivalents of charge per gram of compound (mEq/g). The hydrophobically modified cationic polyvinyl alcohols of the present disclosure may be characterized by a cationic charge density (or "CCD") ranging from 0.10 mEq/g to 4.0 mEq/g, preferably from 1.0 mEq/g to 3.50 mEq/g, more preferably from 1.75 mEq/g to 2.75 mEq/g.

[0069] Preferably the different types of monomer units are randomly distributed over the quaternised acrylic copolymer.

[0070] The quaternised acrylic copolymer is preferably derived from cationic monomer units and ethylenically unsaturated monomer units.

[0071] The cationic monomer units can be selected from:

$$CH_2{=}CR^1\text{-}Y\text{-}(CH_2)_n\text{-}N^+R^2R^3R^4X^- \qquad \text{(a);}$$

wherein:

- each R^1 are independently selected from a hydrogen or a methyl, preferably a methyl;
- each R^2 is independently selected from a C1 to C4 alkyl(ene), preferably $CH_2CH{=}CH_2$ or methyl, more preferably methyl;
- each R^3, R^4 are independently selected from a C1 to C4 alkyl, preferably C1 to C3 alkyl, more preferably methyl;
- each Y is a linking group independently selected from: $CO\text{-}NR'\text{-}(CH_2)_n$, $CO\text{-}O\text{-}(CH_2)_n$, or $(CH_2)_n$, preferably $CO\text{-}NR^5\text{-}(CH_2)_n$, or $(CH_2)_n$, more preferably $CO\text{-}NR^5\text{-}(CH_2)_n$,
  wherein:
  - each R^5 is independently selected from hydrogen or methyl, preferably hydrogen,
  - n is an average of from 1 to 4, preferably 1 or 3, more preferably 3; and

[0072] X^- is a suitable counterion, preferably X^- is independently selected from a halide counterion, more preferably Cl^-.

[0073] The choice of linking group Y is dependent on the reaction scheme used to make the quaternised acrylic copolymer. Preferably, all Y are the same. Preferably, all R^5 are the same.

[0074] The cationic monomer units can be selected from the group consisting of: acrylamidopropyl trimethylammonium chloride (APTAC), methacrylamidopropyltrimethylammonium chloride (MAPTAC), diallyl dimethyl ammonium chloride (DADMAC), acryloyloxyethyltrimethylammonium chloride (AETAC), methyloyloxyethyltrimethyl ammonium chloride (METAC), and mixtures thereof. Particularly preferred cationic monomers are (meth)acrylamidopropyltrimethylammonium chloride (APTAC or MAPTAC) or diallyldimethylammonium chloride (DADMAC), with methacrylamidopropyltrimethylammonium chloride (MAPTAC) being most preferred. Two polymeric structures are possible when polymerizing DADMAC: N-substituted piperidine structure or N-substituted pyrrolidine structure. The pyrrolidine structure is favored (see John, Wilson; et al. (2002), Synthesis and Use of PolyDADMAC for Water Purification).

[0075] The ethylenically unsaturated monomers can be selected from the group consisting of: C3-C8 ethylenically unsaturated acids and/or salts thereof, C3-C8 hydroxyalkyl acrylates, and mixtures thereof. By C3-C8, it is meant that the ethylenically unsaturated acids and/or salts thereof, or C3-C8 hydroxyalkyl acrylate comprises from 3 to 8 carbon atoms.

[0076] Suitable C3-C8 ethylenically unsaturated acids and/or salts thereof include (meth)acrylic acid and mixtures thereof, with acrylic acid being preferred. Suitable salts include alkali metal and ammonium salts.

[0077] Suitable C3-C8 hydroxyalkyl acrylates can be selected from the group consisting of: ethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxy-2-methylethyl (meth)acrylate, 2-hydroxy-1-methylethyl (meth)acrylate, and mixtures thereof, preferably ethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and mixtures thereof, more preferably ethyl (meth)acrylate, with ethyl acrylate being most preferred.

[0078] The quaternised acrylic copolymer can further comprise additional monomers selected from the group consisting of: ethyl acrylate, 2-acrylamido-2-methylpropane-sulfonic acid, N-isopropylamide, vinylpyrrolidone, and mixtures thereof, as polymerized monomers, with ethyl acrylate and/or vinylpyrrolidone being preferred, with ethyl acrylate being particularly preferred.

[0079] The additional monomer is preferably present at a level of less than 20 mol%, preferably less than 15 mol%, more preferably less than 10% of the total monomers present in the quaternised acrylic.

[0080] The quaternised acrylic copolymer can comprise diallyldimethylammonium chloride (DADMAC) as the cationic monomer with hydroxyethylacrylate as the ethylenically unsaturated monomer. Such quaternised acrylic copolymers can comprise vinylpyrrolidone as an additional monomer. Such quaternised acrylic copolymers include those sold under the tradename of Mirapol® SURF-S FAST DRY by Solvay.

[0081] More preferably, the quaternised acrylic copolymer can comprise (meth)acrylamidopropyltrimethylammonium chloride (APTAC or MAPTAC) as the cationic monomer, with acrylate and/or ethyl acrylate as the ethylenically unsaturated monomer. Such quaternised acrylic copolymers can comprise ethyl acrylate as an additional monomer. Such quaternised acrylic copolymers include those sold under the tradename of Polyquart® by BASF, with Polyquart149A ® being particularly preferred.

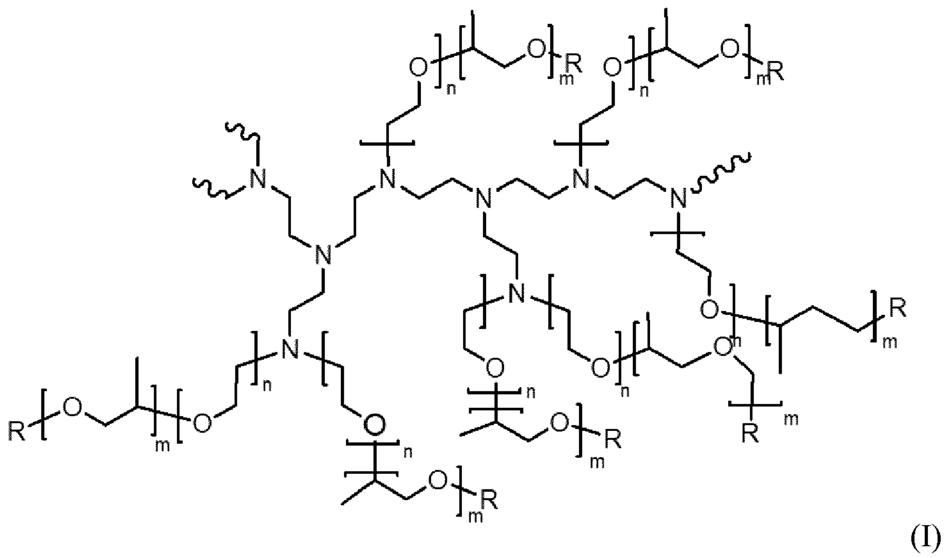
Further ingredients:

[0082] The composition can comprise further ingredients such as those selected from: amphiphilic alkoxylated polyalkyleneimines, cyclic polyamines, triblock copolymers, salts, hydrotropes, organic solvents, other adjunct ingredients such as those described herein, and mixtures thereof.

[0083] 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.

[0084] 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.

[0085] 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.

[0086] The amphiphilic alkoxylated polyethyleneimine polymers can be made by the methods described in more detail in PCT Publication No. WO 2007/135645.

Cyclic Polyamine

[0087] 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 composition, of the cyclic polyamine.

[0088] 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.

[0089] 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.

[0090] Suitable cyclic polyamines can be supplied by BASF, under the Baxxodur tradename, with Baxxodur ECX-210 being particularly preferred.

[0091] 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 Co-Polymer

[0092] The composition of the invention can comprise a triblock copolymer. The triblock co-polymers can be present at a level of from 0.1% to 10%, preferably from 0.5% to 7.5%, more preferably from 1% to 5%, 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.

[0093] 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 EO 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).

[0094] 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".

[0095] 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.

[0096] 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).

[0097] Preferred triblock co-polymers are readily biodegradable under aerobic conditions.

[0098] The composition of the present invention may further comprise at least one active selected from the group consisting of: salt, hydrotrope, organic solvent, and mixtures thereof.

Salt:

[0099] The composition of the present invention may comprise from 0.05% to 2%, preferably from 0.1% to 1.5%, or more preferably from 0.5% to 1%, by weight of the total composition of a salt, preferably a monovalent or divalent inorganic salt, or a mixture thereof, more preferably selected from: sodium chloride, sodium sulfate, and mixtures thereof. Sodium chloride is most preferred.

Hydrotrope:

[0100] The composition of the present invention may comprise from 0.1% to 10%, or preferably from 0.5% to 10%, or more preferably from 1% to 10% by weight of the total composition of a hydrotrope or a mixture thereof, preferably sodium cumene sulfonate.

Organic Solvent:

[0101] The composition can comprise from 0.1% to 10%, or preferably from 0.5% to 10%, or more preferably from 1% to 10% by weight of the total composition of an organic solvent. Suitable organic solvents include organic solvents 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.

Adjunct Ingredients

[0102] The cleaning composition may optionally comprise a number of other adjunct ingredients such as builders (preferably citrate), chelants, conditioning polymers, other cleaning polymers, surface modifying polymers, structurants, emollients, humectants, skin rejuvenating actives, enzymes, carboxylic acids, scrubbing particles, perfumes, malodor control agents, pigments, dyes, opacifiers, pearlescent particles, inorganic cations such as alkaline earth metals such as Ca/Mg-ions, antibacterial agents, preservatives, 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).

Packaged product

[0103] The hand dishwashing detergent composition can be packaged in a container, typically plastic containers. 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.

[0104] 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).

[0105] 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

[0106] The compositions of use in the present invention are used in methods of manually washing dishware. The method comprises the step of: contacting dishware with a liquid hand dishwashing detergent composition and water, wherein: the liquid hand dishwashing detergent composition comprises a quaternized acrylic copolymer and a surfactant system, wherein the surfactant system comprises an anionic surfactant system comprising alkyl sulfated anionic surfactant, wherein the alkyl sulfated anionic surfactant has an average degree of alkoxylation of less than 0.1, and the water has a temperature of 30 °C or less, preferably wherein the water has a temperature of from 20 °C to 30 °C.

[0107] The water present in usual households can typically have a hardness of up to 3.0 mmol/l $CaCO_3$ equivalence. As such, the method described herein is suitable for use when washing with water having a hardness of up to 3.0 mmol/l, preferably 0.3 mmol/l to 2.7 mmol/l, more preferably from 0.75 mmol/l to 2 mmol/l $CaCO_3$ equivalence.

[0108] Suitable methods can include the steps of delivering a liquid hand dishwashing composition to a volume of water to form a wash solution and immersing the dishware in the wash solution. The dishware is cleaned with the composition in the presence of water.

[0109] The wash solution can comprise the liquid hand dishwashing detergent composition at a level of from 100 ppm to 10,000 ppm, preferably from 200 ppm to 5000 ppm, more preferably from 500 ppm to 2000 ppm.

[0110] Typically, from 0.5 ml to 50 ml, preferably from 1.0 ml to 25 ml, more preferably from 2.5 ml to 10 ml of the liquid hand dishwashing detergent composition is combined with 1.0 1 to 15 l, preferably from 1.5 l to 10 1, more preferably from 2.5 to 7.5 l of water to form the wash solution. 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.

[0111] The soiled dishware is immersed in the wash liquor obtained, before scrubbing the soiled surface of the dishware with a cloth, sponge, or similar cleaning implement. The cloth, sponge, or similar cleaning implement is typically contacted with the dishware for a period of time ranged from 1 to 10 seconds, although the actual time will vary with each application and user preferences. Scrubbing can sometimes also take place after a period of soaking, for instance, after about 30 minutes of soaking.

[0112] Alternatively, prior to contacting the dishware with the liquid hand dishwashing detergent composition and the water, the liquid hand dishwashing detergent composition and the water are combined on a device, preferably wherein the device is a brush, a sponge, a nonwoven material, or a woven material, more preferably wherein the device is a sponge. The liquid hand dishwashing detergent composition and water can be combined on or in the device at ratios of from 25:75 to 1:99, preferably 15:85 to 1:99, more preferably 10:90 to 1:99.

[0113] The cleaning device or implement, and consequently the liquid dishwashing composition and the water, is directly contacted to the surface of each of the soiled dishes, to remove the soiling. The cleaning device or implement is typically contacted with each dishware 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

[0114] The dishware can be subsequently rinsed. By "rinsing", it is meant herein contacting the dishware cleaned with the process according to the present invention with substantial quantities of water. By "substantial quantities", it is meant usually from 1.0 to 20 L, or under running water.

TEST METHODS

Molecular weight determination by Gel Permeation Chromatography:

[0115] Gel Permeation Chromatography (GPC) with Multi-Angle Light Scattering (MALS) and Refractive Index (RI) Detection (GPC-MALS/RI) is a well known system to directly measure the weight average molecular weight, M_w, and number average molecular weight, M_n, of a polymer without the need for comparisons with known reference standards.

[0116] The true number-average molecular weight, M_n, of polymers can be obtained by GPC coupled with light-scattering detection and refractive index detection even if the composition and therefore the refractive index increment varies with elution volume, provided slices taken are sufficiently monodisperse with respect to molecular weight and composition.

[0117] For example, the molecular weight distribution of polymer can be measured using a Liquid Chromatography system such as an Agilent 1260 Infinity pump system with OpenLab Chemstation software (from Agilent Technology, Santa Clara, CA, USA) provided with two ultrahydrogel linear columns, 7.8mm ID x 300 mm length used in series (S/N 002C180181 VE077 and 005C180181 VE084, supplied by Waters Corporation of Milford, Mass., USA) and an ultrahydrogel guard column (6mm ID x 40mm length, S/N2016260401BE105, also supplied Waters Corporation of Milford, Mass., USA) installed between the injector and the analytical column to prevent any impurities and suspended solids from reaching the analytical column, operated at 40°C. A multiangle light scattering (MALS) detector DAWN® and a differential refractive index (RI) detector (Wyatt Technology of Santa Barbara, Calif., USA) controlled by Wyatt Astra® software can be used for the detection.

[0118] Since the analytes are spread over a relatively narrow time window, an isocratic rather than gradient elution method can be used. Isocratic means that the mixture of your mobile phase is consistent over the complete testing time. Using a gradient implies that the compounding of the eluent mixture is changed during measurement and so influences the retention of analytes. The separation can be either accelerated or decelerated when using a gradient method.

[0119] 0.1M sodium nitrate in water containing 0.02% sodium azide is used as the mobile phase. Samples are prepared by dissolving the polymer in the mobile phase at ~1.0 mg per ml and by mixing the solution overnight at room temperature to ensure full hydration of the polymer. The sample is then filtered through a 0.8 μm Versapor membrane filter (AP4189, supplied by PALL, Life Sciences, NY, USA) into the LC autosampler vial using a 3-ml syringe. The sample is then pumped into the columns at a flow rate of 1.0 mL/min.

[0120] The number average and weight average molecular weights of the polymer are calculated from the dn/dc (differential change of refractive index with concentration) measurements, as provided by the Astra detector software.

Suds mileage

[0121] The objective of the Suds Mileage Test is to compare the evolution over time of suds volume generated for different test formulations at specified water hardness, solution temperatures and formulation concentrations, while under the influence of periodic soil injections. Data are compared and expressed versus a reference composition or test condition as a suds mileage index (reference composition or test condition has suds mileage index of 100). The steps of the method are as follows:

1. 0.12 wt% of the test composition is dispensed through a plastic pipette at a flow rate of 0.67 mL/ sec at a height of 37 cm above the bottom surface of a sink (dimension: 300 mm diameter and 288 mm height) into a water stream having the desired water hardness and the desired water temperature, that is filling up the sink to 4 L at a constant pressure of 4 bar.
2. An initial suds volume generated (measured as average foam volume X above the liquid in the sink (expressed in cm^3) is recorded immediately after end of filling.
3. A fixed amount (6 mL) of a soil with the defined composition below is immediately injected into the middle of the sink.
4. The resultant solution is mixed with a metal blade (10 cm x 5 cm) positioned in the middle of the sink at the air liquid interface under an angle of 45° rotating at 85 RPM for 20 revolutions.
5. Another measurement of the total suds volume is recorded immediately after end of blade rotation.
6. Steps 3-5 are repeated until the measured total suds volume reaches a level of 400 cm^3 or less. The amount of added soil that is needed to get to the 400 cm^3 level is considered as the suds mileage for the test composition.
7. Each test composition is tested 4 times per testing condition (i.e., water temperature, composition concentration, water hardness, soil type).
8. The average suds mileage is calculated as the average of the 4 replicates for each sample for a defined test condition.
9. The Suds Mileage Index is calculated by comparing the average mileage of a test composition sample at 25 °C versus the same test sample at 40 °C at the same targeted water hardness. The calculation is as follows:

$$\text{Suds Mileage Index} = \frac{\text{Average number of soil additions of test composition at 25 °C}}{\text{Average number of soil additions of reference composition at 40 °C}} \text{ X } 100$$

[0122] The greasy soil composition used in the test is produced through standard mixing of the components described in Table 1.

Table 1: Greasy Soil

Ingredient	Weight %
Crisco Oil	12.730
Crisco shortening	27.752
Lard	7.638
Refined Rendered Edible Beef Tallow	51.684
Oleic Acid, 90% (Techn)	0.139
Palmitic Acid, 99+%	0.036
Stearic Acid, 99+%	0.021

EXAMPLES

[0123] The following compositions were prepared and evaluated for suds mileage benefit in the presence of greasy soil, at a water hardness of 1.25 mmol/L equivalence of Ca, and wash water temperatures of 25 °C (inventive wash method) and 40 °C (comparative and reference wash method), as described herein.

[0124] Example 1 comprised both a quaternised acrylic copolymer and unalkoxylated alkyl sulfate anionic surfactant and hence was of the invention. Example A was similar to example 1 but did not comprise a quaternised acrylic copolymer. Example B was similar to example 1 but comprised ethoxylated alkyl sulfate anionic surfactant instead of unalkoxylated alkyl sulfate anionic surfactant. Example C was similar to example 1 but comprised ethoxylated alkyl sulfate anionic surfactant instead of unalkoxylated alkyl sulfate anionic surfactant and did not comprise a quaternised acrylic copolymer. As such, examples A, B and C were comparative compositions.

[0125] For all the compositions, the resultant suds mileage in the presence of greasy soil is given in table 1.

Table 1: Comparative and inventive liquid hand dishwashing detergent compositions, and resultant suds mileage in the presence of greasy soil

wt% (100% active basis)	Ex 1	Ex A*	Ex B*	Ex C*
C12-13 alkyl sulfate (18% branching)[1]	20.7	20.7	-	-
C12-13 alkyl EO2 sulfate (18% branching)[2]	-	-	20.7	20.7
C12-14 dimethyl amine oxide	6.9	6.9	6.9	6.9
C9-11 EOS nonionic surfactant[3]	0.8	0.8	0.8	0.8
NaCl	0.7	0.7	0.7	0.7
PPG (MW2000)	0.5	0.5	0.5	0.5
Citric acid (pH trimming agent)	0.82	0.73	0.26	0.20
Alkoxylated polyethyleneimine[4]	0.5	0.5	0.5	0.5
Ethanol (viscosity trimming agent)	-	-	1.0	1.0
MIT preservative	0.0035	0.0075	0.0075	0.0075
Phenoxyethanol	0.08	0.08	0.08	0.08

(continued)

wt% (100% active basis)	Ex 1	Ex A*	Ex B*	Ex C*
Acrylate/ethyl acrylate/methacrylamidopropyl trimethyl ammonium chloride copolymer[5]	0.5	-	0.5	-
Water and minors (perfume, dye)	bal.	bal.	bal.	bal.
pH (10% solution in demi water)	9.0	9.0	9.0	9.0
Suds mileage	138	130	104	101

* Comparative

[1] made by sulfating C12-13 alkyl alcohol, sold under the tradename of Neodol 23® and supplied by Shell

[2] made by sulfating ethoxylated C12-13 alkyl alcohol, sold under the tradename of Neodol 23-2® and supplied by Shell

[3] sold under the tradename of Neodol®, supplied by Shell

[4] Polyethyleneimine with a PE1 backbone having a weight average molecular weight of 600g/mol and 24EO and 16PO units per alkoxylation chain, supplied by BASF

[5] a quaternised acrylic copolymer of use in the present invention, sold under the tradename of Polyquart® 149A, supplied by BASF

[0126] As can be seen from the results above, the presence of quaternised acrylic copolymer in compositions comprising alkyl ethoxylated sulfate anionic surfactant provides a negligible improvement in suds mileage in the presence of greasy soil (comparing the results from comparative example B to that of comparative example C), when washing dishware using water at cold temperatures relative to when washing dishware using water at warm temperatures.

[0127] By comparing the results from comparative example A with that of comparative example C, it can be seen that formulating the composition using unalkoxylated alkyl sulfate surfactant instead of ethoxylated alkyl sulfate, without the presence of quaternised acrylic copolymer, results in a surprising improvement in suds mileage during low temperature cleaning of dishware, even though ethoxylated alkyl sulfate surfactant containing compositions are typically more stable at low temperatures than similar compositions formulated using unalkoxylated alkyl sulfate anionic surfactant.

[0128] By comparing the results from example 1 with that from example A, it can be seen that formulating the composition with the quaternised acrylic copolymer on top of a surfactant system comprising unalkoxylated alkyl sulfate anionic surfactant results in a further improvement in suds mileage at decreased versus increased temperatures.

[0129] 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 liquid hand dishwashing cleaning composition comprising: from 6% to 50% by weight of the total composition of a surfactant system, and a quaternised acrylic copolymer,
wherein the surfactant system comprises:
at least 40% by weight of the surfactant system of anionic surfactant, wherein the anionic surfactant comprises at least 50% by weight of the anionic surfactant of alkyl sulfated anionic surfactant, wherein the alkyl sulfated anionic surfactant has an average degree of alkoxylation of less than 0.1.

2. The composition according to claim 1, wherein the composition comprises from 0.01% to 3.0%, preferably from 0.05% to 2.0%, more preferably from 0.1% to 1.0% by weight of the composition of the quaternised acrylic copolymer.

3. The composition according to any preceding claim, wherein the quaternised acrylic copolymer has a weight average molecular weight (Mw), measured by aqueous gel permeation chromatography (GPC) with light scattering detection (SEC- MALLS), in the range of from 5,000 to 500,000 Da, preferably from 15,000 to 300,000 Da and even more preferably from 25,000 to 75,000 Da.

4. The composition according to any preceding claim, wherein the quaternised acrylic copolymer has an average cationic charge density of from 0.01 to 2.8, preferably from 0.1 to 2.75, more preferably from 0.75 to 2.25 cationic units per 100 mEq/g.

5. The composition according to any preceding claim, wherein the quaternised acrylic copolymer is derived from:

a. cationic monomer units selected from:

i.

$$CH_2=CR^1\text{-}Y\text{-}N^+R^2R^3R^4X^- \qquad (a);$$

wherein:

each R^1 are independently selected from a hydrogen or a methyl, preferably a methyl;
each R^2 is independently selected from a C1 to C4 alkyl(ene), preferably $CH_2CH=CH_2$ or methyl, more preferably methyl;
each R^3, R^4 are independently selected from a C1 to C4 alkyl, preferably C1 to C3 alkyl, more preferably methyl;
each Y is a linking group selected from: $CO\text{-}NR^5\text{-}(CH_2)_n$, $CO\text{-}O\text{-}(CH_2)_n$, or $(CH_2)_n$, preferably $CO\text{-}NR^5\text{-}(CH_2)_n$, or $(CH_2)_n$, more preferably $CO\text{-}NR^5\text{-}(CH_2)_n$,
wherein:

R^5 is hydrogen or methyl, preferably hydrogen,
n is an average of from 1 to 4, preferably 1 or 3, more preferably 3; and X^- is a suitable counterion, preferably a halide counterion, more preferably Cl^-; and

b. ethylenically unsaturated monomer units.

6. The composition according to claim 5, wherein the cationic monomer unit is selected from the group consisting of: acrylamidopropyl trimethylammonium chloride (APTAC), diallyl dimethyl ammonium chloride (DADMAC); acryloyloxyethyltrimethylammonium chloride (AETAC); methacrylamidopropyltrimethylammonium chloride (MAPTAC); methyloyloxy ethyl trimethyl ammonium chloride (METAC), and mixtures thereof, preferably (meth)acrylamidopropyltrimethylammonium chloride (APTAC or MAPTAC) or diallyldimethylammonium chloride (DADMAC), more preferably methacrylamidopropyltrimethylammonium chloride (MAPTAC).

7. The composition according to claim 5 or 6, wherein the ethylenically unsaturated monomer units are selected from the group consisting of: C3-C8 ethylenically unsaturated acids and/or salts thereof, C3-C8 hydroxyalkyl acrylates, and mixtures thereof.

8. The composition according to any preceding claims, wherein the quaternised acrylic copolymer further comprises additional monomers selected from the group consisting of: ethyl acrylate, 2-acrylamido-2-methylpropane-sulfonic acid, N-isopropylamide, and mixtures thereof, as polymerized monomers, preferably ethyl acrylate.

9. The composition according to any preceding claims, wherein the composition comprises from 6.0% to 40%, preferably from 15% to 35%, by weight of the total composition of the surfactant system.

10. The composition according to any of the preceding claims, wherein the surfactant system comprises at least 50%, preferably from 50% to 80%, more preferably from 55% to 70% by weight of the surfactant system of an anionic surfactant.

11. The composition according to any of the preceding claims, wherein the anionic surfactant comprises at least 70%, preferably at least 85%, more preferably 100% by weight of the anionic surfactant of the alkyl sulphated anionic surfactant.

12. The composition according to any preceding claims, wherein the alkyl sulfated anionic surfactant is free of alkoxylation.

13. The composition according to any preceding claims, wherein the surfactant system comprises nonionic surfactant, wherein the nonionic surfactant comprises alkoxylated alcohol nonionic surfactant.

14. The composition according to any preceding claim, wherein the surfactant system further comprises a co-surfactant selected from the group consisting of: amphoteric co-surfactant, zwitterionic co-surfactant, and mixtures thereof.

15. A method of cleaning dishes, the method comprising the step of: contacting dishware with a liquid hand dishwashing detergent composition according to any preceding claim, and water, wherein: the water has a temperature of 30 °C or less.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 20 2400

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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	**6 March 2024**	**Goodman, Marco**

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