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(71) Applicant: **The Procter & Gamble Company**
Cincinnati, OH 45202 (US)

(72) Inventors:

- **BETTIOL, Jean-Luc Philippe**
1853 Strombeek-Bever (BE)
- **MODREGO RUIZ, Jara Bienvenida**
1853 Strombeek-Bever (BE)
- **MORAN, Mary Teresa**
Egham, TW20 9NW (GB)

(74) Representative: **P&G Patent Belgium UK**

N.V. Procter & Gamble Services Company S.A.
Temselaan 100
1853 Strombeek-Bever (BE)

(54) **LIQUID CLEANING COMPOSITION**

(57) The need for a liquid cleaning composition, and especially a liquid hand dishwashing detergent composition, which provides effective cleaning, good sudsing, and improved preservation at a pH of from 6.0 or greater is met when the composition is formulated with a dipyrithione and a surfactant system which comprises at least

40% by weight of the surfactant system of an anionic surfactant, with the anionic surfactant comprising at least 70% by weight of the anionic surfactant of alkyl sulphate anionic surfactant, and the surfactant system is free of fatty acid or salt thereof.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a liquid cleaning composition, especially a liquid hand dishwashing cleaning composition.

BACKGROUND OF THE INVENTION

10 **[0002]** Liquid cleaning compositions, especially for use in manual dishwashing applications have to be able to clean a variety of soils from dishes and tableware, be highly sudsing, and have a pleasant odour. However, many of the ingredients used in these compositions are susceptible to microbes, leading to the build-up of undesired microbes in the composition, malodour, and possibly reduced performance. As such, liquid detergent compositions are typically preserved using a biocide in order to avoid microbial contamination such as from bacteria, fungi and the like. While there are preservatives available for liquid hand dishwashing products, there remains a need to have alternative preservatives that can be used to preserve to detergent compositions.

15 **[0003]** Such preserved hand dish formulations should come without the loss of cleaning efficacy and sudsing benefit. Sudsing is particularly important for liquid hand dishwashing compositions since good sudsing connotes good cleaning. As such, liquid hand dishwashing compositions are preferably formulated without suds suppressors and other ingredients such as fatty acids and their salts, which are known to suppress suds.

20 **[0004]** Alternative biocides have typically been cationic and hence incompatible with anionic surfactants which are needed to produce sudsing and provide good cleaning. Moreover, the antimicrobial efficacy of cationic antimicrobial agents is sharply reduced by the presence of anionic surfactants. As such, neutral or anionically charged antimicrobial agents are preferred. However, such neutral and anionically charged antimicrobial agents are typically less effective than their cationic counterparts.

25 **[0005]** Liquid hand dishwashing formulations are ideally formulated with a pH that is from slightly acidic to alkaline pH in order to provide good cleaning and sudsing. Therefore, suitable biocides should be both stable and effective in such a pH range.

30 **[0006]** In addition, the liquid hand dishwashing detergent has to be formulated to be safe for consumers and the environment, when being used as intended.

[0007] Hence, a need remains for safe liquid hand dishwashing detergent composition which provides effective cleaning, good sudsing, and improved preservation in the desired pH range.

35 **[0008]** GB970955A relates to a germicidal detergent composition which comprises a soap and at least 0.05% by weight based on the weight of the soap of a pyridine thione. Such compositions comprising soaps are unsuitable for washing dishes since they are low sudsing, especially during in-sink washing conditions, and have poor suds longevity especially in the presence of hard water, and are prone to leaving unsightly residues, especially on glass. WO92/17285A relates to a method for imparting biocidal protection to clothing or other fabrics which comprises contacting the clothing or other fabrics with a biocidally effective amount of pyriithione acid, or salt(s) thereof, or combinations thereof, in an automatic laundry dryer. Also disclosed is a transfer substrate containing a biocide consisting essentially of pyriithione acid, or salt(s) thereof, or combinations thereof, said biocide being present in or on said transfer substrate in an amount sufficient to impart antimicrobial activity to clothing or other fabric in an automatic clothes dryer. US3583999A relates to a process for preparing 2-pyridinethiol n-oxides and derivatives thereof. WO2014/059417A relates to an antimicrobial composition that decreases the bioavailability of iron by introducing a higher-affinity iron-selective chelating agent capable of competing with microbial siderophores. WO2011/039088A relates to a microbicidal composition in the form of a concentrate which comprises a) one or more isothiazolin-3-ones, b) one or more organic amines with an alkyl group having at least 8 carbon atoms and c) one or more oxidizing agents. GB9923253A relates to the use of combinations of bactericides in detergent compositions.

SUMMARY OF THE INVENTION

50 **[0009]** The present invention relates to a liquid cleaning composition comprising from 5.0% to 50% by weight of the total composition of a surfactant system, wherein the surfactant system comprises at least 40% by weight of the surfactant system of an anionic surfactant, wherein the anionic surfactant comprises at least 70% by weight of the anionic surfactant of alkyl sulphate anionic surfactant, wherein the surfactant system is free of fatty acid or salt thereof, wherein the composition further comprises a dipyriithione preservative, wherein the liquid cleaning composition has a pH from 6.0 or greater, measured as a 10% aqueous solution in demineralized water at 20 degrees °C.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Formulating the liquid cleaning composition with a pH of from 6.0 or greater, measured as a 10% aqueous solution in demineralized water at 20 degrees °C, using a dipyrithione preservative as described herein, has been found to provide a well preserved, liquid cleaning composition which provides effective cleaning and good sudsing.

[0011] 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.

[0012] 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.

[0013] 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.

[0014] 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 in the material) saturated and unsaturated fats and oils, preferably oils and fats derived from animal sources such as beef, pig and/or chicken.

[0015] The terms "include", "includes" and "including" are meant to be non-limiting.

[0016] 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.

[0017] 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 initial 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 initial 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 enough cleaning composition has been dosed. Moreover, the consumer also uses the sustained suds volume as an indicator that enough 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.

[0018] 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.

[0019] 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.

Liquid cleaning composition

[0020] The cleaning composition is a liquid cleaning composition, preferably a liquid hand dishwashing cleaning composition, and hence is in liquid form. The liquid 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.

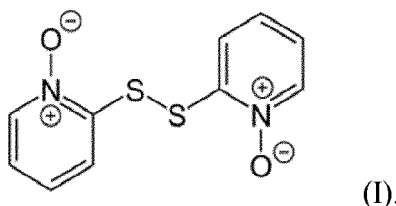
[0021] The liquid cleaning composition has a pH from 6.0 or greater, or a pH of from 6.0 to 12.0, preferably from 7.0 to 11.0, more preferably from 8.0 to 10.0, measured as a 10% aqueous solution in demineralized water at 20 degrees °C.

[0022] When the pH exceeds a pH of 7.0, the reserve alkalinity can be from 0.1 to 1.0, more preferably from 0.1 to 0.5. Reserve alkalinity is herein expressed as grams of NaOH/100 ml of composition required to titrate product from a pH 7.0 to the pH of the finished composition. This pH and reserve alkalinity further contribute to the cleaning of tough food soils.

[0023] The liquid cleaning composition of the present invention can be Newtonian or non-Newtonian, preferably Newtonian. 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%.

Dipyrithione

[0024] The liquid cleaning composition comprises a dipyrithione preservative according to formula I:



[0025] The dipyrithione preservative can be present at a level of from 10 ppm to 10000 ppm, preferably from 50 ppm to 5000 ppm, more preferably from 200 ppm to 2000 ppm in the composition, based on the fully ionised form of the dipyrithione, and hence excluding any counterions.

[0026] The dipyrithione preservative can be substituted or unsubstituted. Unsubstituted dipyrithione is shown in Formula (I) above. Preferably the dipyrithione preservative is unsubstituted dipyrithione. If substituted, the substitutions are preferably non-functional. That is, any substitution does not provide any further benefit. Examples of such substitutions include halogen atoms or lower alkyl or alkoxy groups having from 1 to 4 carbon atoms.

[0027] The dipyrithione preservative can be present as a salt, wherein the counterions of the salt are independently selected from the group consisting of: alkali metal ions, earth alkali metal ions, transition metal ions, ammonium ions, protonated alkanolamines, and mixtures thereof, preferably alkali metal ions selected from sodium, potassium, and mixtures thereof, more preferably sodium.

[0028] Most preferably the dipyrithione preservative used is disodium dipyrithione, as shown in formula I, having two sodium counterions to balance the negative charges on the individual pyrrithione subgroups.

[0029] It has been found that dipyrithiones have a biocidal efficacy which is less pH dependent than mono-pyrrithiones such as 1-hydroxy-2-pyridinethione.

[0030] The biocidal activity of mono-pyrrithione and its derivatives are well known, especially for acidic compositions. However, they are typically less effective in neutral or alkaline compositions, where the pH is above the pKa of the aromatic thiol (thiol protonation) of the mono-pyrrithione (pKa of around 4.7). In contrast, it has been found that dipyrithiones maintain their biocidal efficacy in liquid cleaning compositions even when formulated into compositions having a pH which is neutral or even alkaline. It is believed that this is due to the di-sulphur bridge of the dipyrithione increasing the bio-availability of the preservative to microbes in a detergent composition.

[0031] The preparation of dipyrithiones is well known. For instance, dipyrithiones can be prepared via oxidation of a pyrrithione using chlorine in the presence of NaOH, following the reaction scheme, as described in Unger, Thomas A. (1996). "Dipyrithione". Pesticide Synthesis Handbook. Noyes Publications. p. 853. ISBN 9780815518532.

Surfactant System

[0032] The liquid cleaning composition comprises from 5.0% 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

[0033] The surfactant system comprises an anionic surfactant. The surfactant system comprises at least 40%, or at least 50%, preferably from 60% to 90%, more preferably from 65% to 85% by weight of the surfactant system of the anionic surfactant. The surfactant system is free of fatty acid or salt thereof, since such fatty acids impede suds longevity, especially in the presence of hard water and can leave unsightly residues on dishware.

[0034] The anionic surfactant comprises at least 70%, preferably at least 85%, more preferably 100% by weight of the anionic surfactant of alkyl sulphate anionic surfactant.

[0035] The mol average alkyl chain length of the alkyl sulphate anionic surfactant can be from 8 to 18, preferably from 10 to 14, more preferably from 12 to 14, most preferably from 12 to 13 carbon atoms, in order to provide a combination of improved grease removal and enhanced speed of cleaning.

[0036] The alkyl chain of the alkyl sulphate anionic surfactant can have 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 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.

[0037] The relative molar amounts of C13 and C12 alkyl chains in the alkyl sulphate anionic surfactant can be derived from the carbon chain length distribution of the anionic surfactant. The carbon chain length distribution of the alkyl chains of the alkyl sulphate anionic surfactants can be obtained from the technical data sheets from the suppliers for the surfactant or constituent alkyl alcohol. Alternatively, the chain length distribution and average molecular weight of the fatty alcohols, used to make the alkyl sulphate anionic surfactant, can also be determined by methods known in the art. Such methods include capillary gas chromatography with flame ionisation detection on medium polar capillary column, using hexane as the solvent. The chain length distribution is based on the starting alcohol and alkoxyated alcohol. As such, the alkyl sulphate anionic surfactant should be hydrolysed back to the corresponding alkyl alcohol and alkyl alkoxyated alcohol before analysis, for instance using hydrochloric acid.

[0038] The alkyl sulphate surfactant can be alkoxyated or free of alkoxylation. When alkoxyated, the alkyl sulphate anionic surfactant can have an average degree of alkoxylation of less than 3.5, preferably from 0.3 to 2.0, more preferably from 0.5 to 0.9, in order to improve low temperature physical stability and improve suds mileage of the compositions of the present invention. When alkoxyated, ethoxylation is preferred.

[0039] 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-alkoxyated sulphate anionic surfactant are included:

$$\text{Mol average alkoxylation degree} = (x_1 * \text{alkoxylation degree of surfactant 1} + x_2 * \text{alkoxylation degree of surfactant 2} + \dots) / (x_1 + x_2 + \dots)$$

wherein $x_1, x_2, \dots$ 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.

[0040] Preferred alkyl alkoxy sulphates are alkyl ethoxy sulphates

[0041] The alkyl sulphate anionic surfactant can have a weight average degree of branching of more than 10%, preferably more than 20%, more preferably more than 30%, even more preferably between 30% and 60%, most preferably between 30% and 50%.

[0042] 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-alkoxyated alkyl sulphate anionic surfactants, and the counting from the alkoxy-group furthest from the sulphate group for alkoxyated 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 liquid cleaning 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.

[0043] The weight average degree of branching for an anionic surfactant mixture can be calculated using the following formula:

$$\text{Weight average degree of branching (\%)} = [(x_1 * \text{wt\% branched alcohol 1 in alcohol 1} + x_2 * \text{wt\% branched alcohol 2 in alcohol 2} + \dots) / (x_1 + x_2 + \dots)] * 100$$

wherein $x_1, x_2, \dots$ 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.

[0044] 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.

[0045] Suitable counterions include alkali metal cation earth alkali metal cation, alkanolammonium or ammonium or

substituted ammonium, but preferably sodium.

[0046] 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.

[0047] The performance can be affected by the width of the alkoxylation distribution of the alkoxyated alkyl sulphate anionic surfactant, including grease cleaning, sudsing, low temperature stability and viscosity of the finished product. The alkoxylation distribution, including its broadness can be varied through the selection of catalyst and process conditions when making the alkoxyated alkyl sulphate anionic surfactant.

[0048] If ethoxylated alkyl sulphate 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 sulphation steps, the amount of 1,4-dioxane by-product within alkoxyated especially ethoxylated alkyl sulphates 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 alkoxyated/ethoxylated alkyl sulphates 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.

[0049] The surfactant system may comprise further anionic surfactant, including sulphonate anionic surfactants such as HLAS, or sulphosuccinate anionic surfactants. However, the composition preferably comprises less than 30%, preferably less than 15%, more preferably less than 10% by weight of the surfactant system of further anionic surfactant. Most preferably, the surfactant system comprises no further anionic surfactant, other than the alkyl sulphate anionic surfactant.

Co-Surfactant

[0050] In order to improve surfactant packing after dilution and hence improve suds mileage, the surfactant system can comprise a co-surfactant. The co-surfactant can be selected from the group consisting of an amphoteric surfactant, a zwitterionic surfactant and mixtures thereof.

[0051] The alkyl sulphate anionic surfactant to the co-surfactant weight ratio can be from 1:1 to 8:1, preferably from 2:1 to 5:1, more preferably from 2.5:1 to 4:1.

[0052] 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 cleaning composition of the co-surfactant.

[0053] The surfactant system of the cleaning composition of the present invention preferably comprises up to 50%, preferably from 10% to 40%, more preferably from 15% to 35%, by weight of the surfactant system of a co-surfactant.

[0054] The co-surfactant is preferably an amphoteric surfactant, more preferably an amine oxide surfactant.

[0055] 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 $R_1 - N(R_2)(R_3)O$ wherein R_1 is a C8-18 alkyl, and the R_2 and R_3 moieties are selected from the group consisting of C1-3 alkyl groups, C1-3 hydroxyalkyl groups, and mixtures thereof. For instance, R_2 and R_3 can be selected from the group consisting of: methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl and 3-hydroxypropyl, and mixtures thereof, though methyl is preferred for one or both of R_2 and R_3 . 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 particularly 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 n_1 carbon atoms with one alkyl branch on the alkyl moiety having n_2 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 n_1 and n_2 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 (n_1) 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:

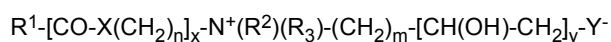
a) from about 10% to about 45% by weight of the amine oxide of low-cut amine oxide of formula R1R2R3AO wherein R1 and R2 are independently selected from hydrogen, C1-C4 alkyls or mixtures thereof, and R3 is selected from C10 alkyls and mixtures thereof; and

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):



[0062] 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,

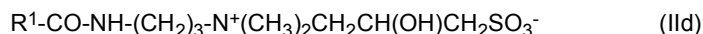
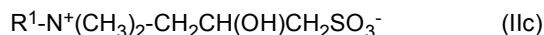
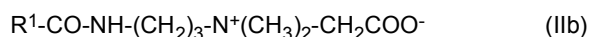
R2 and R3 are independently selected from the group consisting of: a C1-4 alkyl residue, hydroxy substituted such as a hydroxyethyl, and mixtures thereof, preferably both R2 and R3 are methyl,

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.

[0063] Preferred betaines are the alkyl betaines of formula (Ia), the alkyl amido propyl betaine of formula (Ib), the sulphobetaine of formula (Ic) and the amido sulphobetaine of formula (Id):



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 (Ia) and (Ib), more preferred are the alkylamidobetaine of formula (Ib).

[0064] 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, isostearyl-

amidopropyl 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:

[0065] The surfactant system can further comprise a nonionic surfactant. Suitable nonionic surfactants include alkoxylated alcohol nonionic surfactants, alkyl polyglucoside nonionic surfactants, and mixtures thereof.

Alkoxylated alcohol nonionic surfactant:

[0066] Preferably, the surfactant system of the composition of the present invention further comprises from 1% to 25%, preferably from 1.25% to 20%, more preferably from 1.5% to 15%, most preferably from 1.5% to 5%, by weight of the surfactant system, of an alkoxylated alcohol non-ionic surfactant.

[0067] Preferably, the alkoxylated alcohol non-ionic surfactant is a linear or branched, 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 ethylene oxide per mole of alcohol.

Alkyl polyglucoside nonionic surfactant:

[0068] The compositions of the present invention can comprise alkyl polyglucoside ("APG") surfactant. The addition of alkyl polyglucoside surfactants has been found to improve sudsing beyond that of comparative nonionic surfactants such as alkyl ethoxylated nonionic surfactants. 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. 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.

[0069] 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:

[0070] The composition can comprise further ingredients such as those selected from: further biocide, amphiphilic alkoxylated polyalkyleneimines, cyclic polyamines, triblock copolymers, inorganic mono-, di- or trivalent salts, hydrotropes, organic solvents, other adjunct ingredients such as those described herein, and mixtures thereof.

Further biocide:

[0071] The composition can comprise a further biocide, in order to improve preservation and/or antimicrobial activity. If present, the further biocide is preferably neutral or anionically charged. More preferably, the composition does not comprise an isothiazolinone or derivative thereof.

[0072] A particularly preferred further biocide for use as part of the preservative is phenoxyethanol. The combination of the dipyrithione preservative and phenoxyethanol has been found to improve the preservation efficacy of the liquid detergent composition, especially the long-term efficacy. If present, the composition can comprise phenoxyethanol at a level of from 100 ppm to 5000 ppm, more preferably from 250 ppm to 3500 ppm, most preferably from 500 ppm to 2500 ppm.

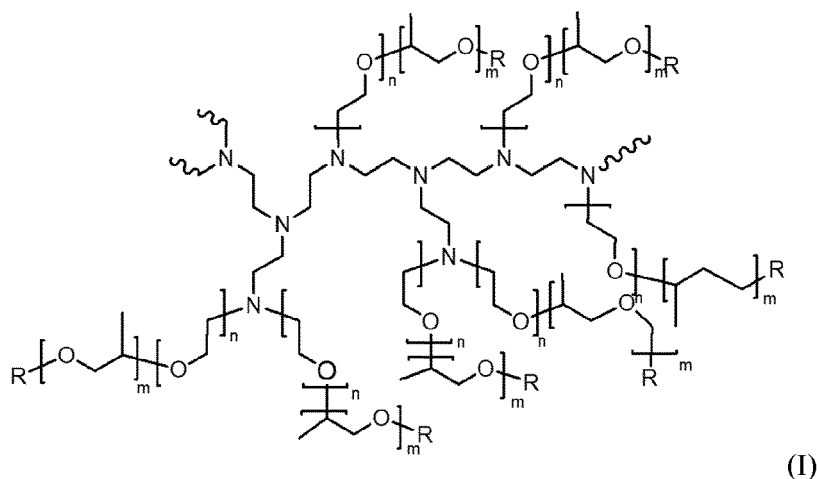
[0073] Preferably, the composition comprises no further biocide beyond the optional phenoxyethanol.

Amphiphilic alkoxylated polyalkyleneimine:

[0074] 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 alkoxyated polyalkyleneimine and mixtures thereof. The amphiphilic alkoxyated polyalkyleneimine polymer has been found to reduce gel formation on the hard surfaces to be cleaned when the liquid cleaning 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.

[0075] A preferred amphiphilic alkoxyated polyethyleneimine polymer has the general structure of formula (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 C₁-C₄ 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 alkoxyated polyethyleneimine polymer preferably is between 10,000 and 15,000 Da.

[0076] More preferably, the amphiphilic alkoxyated 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 C₁-C₄ 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 alkoxyated polyethyleneimine polymer preferably is between 25,000 and 30,000, most preferably 28,000 Da.

[0077] The amphiphilic alkoxyated polyethyleneimine polymers can be made by the methods described in more detail in PCT Publication No. WO 2007/135645.

Cyclic Polyamine

[0078] 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.

[0079] 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.

[0080] Accordingly, the most preferred cyclic polyamine for use with the liquid 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.

[0081] Suitable cyclic polyamines can be supplied by BASF, under the Baxxodur tradename, with Baxxodur ECX-210 being particularly preferred.

[0082] 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

[0083] 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.

[0084] 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).

[0085] 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".

[0086] Triblock co-polymers according to Formula (I) with the specific EO/PO/EO arrangement and respective homopolymeric lengths have been found to enhance suds mileage performance of the liquid cleaning composition in the presence of greasy soils and/or suds consistency throughout dilution in the wash process, especially when the liquid cleaning composition is a liquid hand dishwashing cleaning composition.

[0087] 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).

[0088] Preferred triblock co-polymers are readily biodegradable under aerobic conditions.

[0089] 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:

[0090] 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 sulphate, and mixtures thereof. Sodium chloride is most preferred.

Hydrotrope:

[0091] 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 sulphonate.

Organic Solvent:

[0092] 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

[0093] The liquid 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, 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).

[0094] The dipyrithione is typically produced from the respective mono-pyrithione via an oxidation reaction which is facilitated by the presence of metal ions. As such, re-hydrolysis of the disulphide bond of the dipyrithione is thought to be less likely in presence of metal ions. As such, the composition can comprise inorganic cations, and especially alkaline earth metal ions with magnesium and calcium ions being particularly preferred. If present, the composition comprises from 0.01% to 2.0%, preferably from 0.05% to 1.5%, or more preferably from 0.1% to 1.0%, by weight of alkaline earth metal ions, with magnesium and/or calcium ions being particularly preferred. Low levels of transition metal ions can also be present in the liquid detergent composition, such as up to 1.0%, or up to 0.5% by weight of the composition.

[0095] Since chelants sequester any metal ions that might be present, whether as part of the water added to make the composition, or added intentionally, the composition is preferably free of chelants.

Method of Washing

[0096] The invention is further directed to a method of manually washing dishware with the composition of the present invention. The method comprises 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 dishware is cleaned with the composition in the presence of water. 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.

[0097] The composition herein can be applied in its diluted form. Soiled dishware are 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 cleaning composition, preferably in liquid form, of the present invention diluted in water. The actual amount of cleaning 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 cleaning composition, including the concentration of active ingredients in the cleaning 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 cleaning 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 is immersed in the sink containing the diluted cleaning 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 cleaning 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.

[0098] Alternatively, the composition herein can be applied in its neat form to the dish to be treated. 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.

TEST METHODS

[0099]

A) pH:

The pH is measured as a 10% aqueous solution in demineralized water at 20 °C.

B) Reserve alkalinity:

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Reserve alkalinity is defined as the grams of NaOH per 100 g of composition required to titrate the test composition at pH 7.0 to come to the test composition pH. The reserve alkalinity for a solution is determined in the following manner.

A pH meter (for example an Orion Model 720A) with an Ag/AgCl electrode (for example an Orion sure flow Electrode model 9172BN) is calibrated using standardized pH 7 and pH 10 buffers. A 100g of a 10% solution in distilled water at 20°C of the composition to be tested is prepared. The pH of the 10% solution is measured and the 100g solution is titrated down to pH 10 using a standardized solution of 0.1 N of HCl. The volume of 0.1N HCl required is recorded in ml. The reserve alkalinity is calculated as follows:

$$\text{Reserve Alkalinity} = \text{ml 0.1N HCl} \times 0.1 \text{ (equivalent / liter)} \times \text{Equivalent weight NaOH (g/equivalent)} \times 10.$$

C) Microbial Susceptibility:

The following Microbial Susceptibility Test (MST) method is used to assess the preservative efficacy of a liquid cleaning composition.

[0100] The following lab equipment is used for the test:

- Petri dishes, automatic pipettors, serological pipettes, 25ml disposable syringe/pipette, autoclavable containers, sample containers with tight fitting lids, swabs, all sterilised;
- UV-Vis spectrophotometer (such as Mettler Toledo Cuvette Spectrophotometer)
- Autoclave (such as Phoenix 40 Autoclave, supplied by Rodwell)
- Incubators (supplied by Bioscience);
- Balance (0-200g range, at least 0.5g accuracy, such as supplied by Mettler Toledo)

[0101] The following test media are used:

- Modified letheen broth with polysorbate 80 and lecithin (MLBTL, supplied by BioMérieux FR under order code 44539)
- Modified letheen Agar with polysorbate 80 (MLAT, supplied by BioMérieux FR under order code 257607, MLAT will be cloudy and must be swirled immediately on removal from the autoclave prior to being cooled to re-suspend the polysorbate 80)
- Physiological saline 0.85% (NaCl 0.85%)
- Tryptic soy agar plates (TSA plates, supplied by BioMérieux FR)
- Sabouraud dextrose agar plates (SDA plates, supplied by BioMérieux FR)

[0102] The test inoculum preparations are prepared as follows. The preparations are used the day that they are prepared. The test organisms used are summarized in table 1 below.

[0103] Bacteria inoculum preparation:

Streak the surface of a TSA plate for each bacterial challenge organisms. Incubate at 30°C to 35°C for 18 to 24 hours in the incubator. After incubation, collect growth by gently rolling a dry sterile swab across confluent growth. Transfer the growth on the swab into a container of sterile saline (0.85% NaCl) to generate a turbid solution of cells. Thoroughly homogenise the resultant suspension to obtain an even dispersion. Measure the inoculum count. Adjust the bacterial challenge organism level or saline level to deliver a target inoculum count of between 5.0 - 7.0 log¹⁰ cfu/ml. The % transmission at a wavelength of 425nm (as measured using a uv-vis spectrophotometer) as shown in Table 1 should generate an inoculum count approximately in this range.

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Table 1: % transmittance range at 425nm for the challenge organisms

	Organism	Designation at Microbiologics Inc.	ATCC number	% transmittance (425nm)
Pooled Inoculum	<i>Staphylococcus aureus</i>	485	6538	23-25
	<i>Pseudomonas aeruginosa</i>	484	9027	31-33
	<i>Escherichia coli</i>	483	8739	31-33
	<i>Candida albicans</i>	443	10231	0.2-0.4
	<i>Burkholderia cepacia</i>	488	25416	25-30
	<i>Klebsiella pneumoniae</i>	556	-	31-33
	<i>Enterobacter gergoviae</i>	565	-	31-33
	<i>Serratia marcescens</i>	562	-	31-33

[0104] Yeast inoculum preparation:

Streak the surface of an SDA plate with the *C.albicans* organism. Incubate at 20°C to 25°C for between 44 and 52 hours. Collect the growth and adjust according to steps explained for bacteria above.

[0105] Pooled inoculum preparation and log count of the fresh pooled inoculum:

To create the pooled inoculum, mix equal parts of each of the bacteria and the yeast dispersions, as prepared above. Quantify the adjusted test inoculum preparations by preparing 10⁻⁵, 10⁻⁶, and 10⁻⁷ dilutions (the dilution factor) using MLBTL. Pour or spread 0.5mL aliquots of each dilution on to two plates using MLAT as plating medium. Evenly distribute the inoculum and allow the agar to sufficiently harden or dry before inverting. Incubate all inoculum plates at 30 to 35°C for 3 to 5 days.

[0106] Count the total number of colonies on both plates for each dilution. Select the set of two plates having between 50 to 250 colonies. Multiply the colony count of the selected plates by the relevant dilution factor. This is then multiplied by 0.01 to calculate the concentration of pooled inoculum in the product (in cfu/ml). This is the log count of the fresh pooled inoculum.

[0107] The inoculated liquid cleaning compositions are prepared and sampled as follows:

Aseptically weigh out 25 ± 0.5g of the liquid cleaning composition to be tested into a sterile container. Inoculate the liquid cleaning composition with 0.25mL of the earlier prepared pooled inoculum and mix thoroughly, such as by turning upside down repeatedly for 10 seconds or by using a homogenizer, while avoiding excessive bubble entrainment. The actual weights of liquid cleaning composition and inoculum can vary so long as the ratio of the inoculum to liquid cleaning composition remains at 1.0% by weight.

[0108] The inoculated samples are then stored at 20 to 25°C in the incubator for 7 days.

[0109] The activity of the liquid cleaning composition on the pooled inoculum is stopped using the following procedure: The samples are removed from the incubator and diluted in a 1:10 volume ratio of the sample into MLBTL (i.e. 1mL of sample into 9mL of MLBTL). Thoroughly mix the samples by any suitable means, such as described earlier. The sample is then further diluted in a volume ratio of 1:100 in MLBTL, to result in a 1:1000 volume ratio of the original inoculated liquid cleaning composition into MLBTL.

[0110] Remaining log count of the pooled inoculum:

Plate a 0.5mL aliquot of the dilutions into prepared agar plates comprising 15 to 25mL of MLAT. Evenly distribute the aliquot and allow the agar to sufficiently harden or dry before inverting. Incubate the inverted bacterial/yeast plates at 30°C to 35°C for 3 days.

[0111] Following the incubation, count the colonies on the plate and multiply by 2 and then multiply by the appropriate dilution factor to calculate the remaining concentration of pooled inoculum (cfu/ml). This is the remaining log count of the pooled inoculum after ageing in the finished product for 7 days.

[0112] Calculation of the log count reduction:

The log count reduction is calculated by subtracting the remaining log count of the pooled inoculum after ageing in the finished product for 7 days as described earlier, from the log count of the fresh pooled inoculum, as described earlier.

[0113] The higher the log count reduction the stronger the preservation action of the tested liquid cleaning composition.

EXAMPLES

[0114] The following comparative test demonstrates the improvement in preservation which is achieved by formulating

the liquid cleaning composition according to the present invention.

[0115] Three base compositions which did not comprise a biocide preservative were prepared through mixing of the individual raw materials (Table 2):

Table 2: Unpreserved base liquid cleaning compositions:

	Base 1 wt%	Base 2 wt%	Base 3 wt%
C12 AE2.0S ¹	13.2	13.2	13.2
Cocoamidopropylbetaine	4.4	4.4	-
C12-14 dimethyl amine oxide	-	-	4.4
NaCl	0.95	0.95	0.95
Water and minors (perfume, dyes)	to 100%	to 100%	to 100%
pH (as 10% aqueous solution) ²	5.0	9.0	9.0
¹ 7.92% sodium laureth 3 sulphate + 5.28% Tensopol S30LSHPH (% as wt% 100% active basis)			
² trimmed to target pH using HCl or NaOH			

[0116] Comparative examples A and B and C were made using Base 1 of Table 2. Inventive example 1 and comparative examples D and E were made using Base 2 of Table 2. Inventive example 2 and comparative examples F and G were made using Base 3 of Table 2.

[0117] Inventive example 1 was a composition according to the invention, comprising disodium dipyrithione as the biocide preservative with a composition pH of 9.0. Comparative examples A to C had a pH of 5.0 and was hence outside the scope of the invention. Comparative example A comprised disodium dipyrithione as the biocide preservative and had a composition pH of 5.0. Comparative example B also had a pH of 5.0 but did not comprise a preservative while comparative example C comprised mono-pyrithione as the preservative. Comparative examples D and E had a pH of 9.0. Comparative example D did not comprise a preservative while comparative example E comprised mono-pyrithione as the preservative. Inventive example 1 and comparative examples A to E had a surfactant system which comprised alkyl ether sulphate and cocoamidopropylbetaine.

[0118] The sodium pyrithione and disodium dipyrithione levels were chosen to provide an equal equivalent mol pyrithione level across the respective test legs. 1 mol dipyrithione delivers 2 mols of pyrithione upon hydrolysis of the disulphur bond. As such, 500 ppm of sodium pyrithione and 422 ppm of disodium dipyrithione both provide 0.00335 mol/kg equivalent of pyrithione in the liquid cleaning composition.

[0119] Inventive example 2 was the same as inventive example 1 but had a surfactant system which comprised alkyl ether sulphate and an amine oxide surfactant. Comparative examples F and G were the same as comparative examples D and E respectively but had a surfactant system which comprised alkyl ether sulphate and an amine oxide surfactant.

[0120] The ability of the inventive and comparative liquid cleaning compositions to preserve against microbial growth was evaluated using the microbial susceptibility test method described above, and the results are also given in table 3 in terms of log reduction in the microbial count after 7 days.

Table 3: Preserved inventive (examples 1 to 2) and comparative (examples A to G) liquid cleaning compositions:

	Ex 1	Ex A	Ex B	Ex C	Ex D	Ex E
C12 AE2.0S ¹	13.2	13.2	13.2	13.2	13.2	13.2
Cocoamidopropylbetaine	4.4	4.4	4.4	4.4	4.4	4.4
C12-14 dimethyl amine oxide	-	-	-	-	-	-
NaCl	0.95	0.95	0.95	0.95	0.95	0.95
Water and minors (perfume, dyes)	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%
pH (as 10% aqueous solution) ²	9.0	5.0	5.0	5.0	9.0	9.0
Disodium dipyrithione	422 ppm	422 ppm	-	-	-	-
Sodium pyrithione	-	-	-	500 ppm	-	500 ppm
Log reduction after 7 days	5.4	5.4	1.9	5.4	4.6	4.0

	Ex 2	Ex F	Ex G
C12 AE2.0S ¹	13.2	13.2	13.2
C12-14 dimethyl amine oxide	4.4	4.4	4.4
NaCl	0.95	0.95	0.95
Water and minors (perfume, dyes)	to 100%	to 100%	to 100%
pH (as 10% aqueous solution) ²	9.0	9.0	9.0

Disodium dipyrithione	422 ppm	-	-
Sodium pyrithione	-	-	500 ppm
Log reduction after 7 days	5.4	1.9	2.5

[0121] As can be seen from the results for comparative examples A, B and C, both sodium pyrithione and disodium dipyrithione provide good preservation in strongly acidic liquid cleaning compositions (pH 5.0). However, acidic formulae are typically less effective at removing grease, and hence less desired for use as liquid cleaning compositions, and especially as liquid hand dishwashing cleaning compositions. Hence, a pH of less than 6.0 is undesirable for liquid hand dishwashing compositions, and the like.

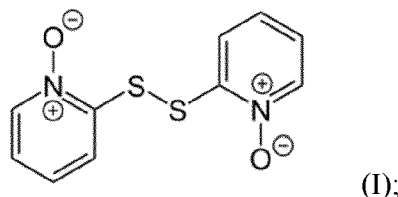
[0122] As can be seen from comparing the preservation of inventive example 1 with that of comparative example E, and inventive example 3 with that of comparative example G, disodium dipyrithione provides an improvement in preservation over equivalent compositions comprising sodium pyrithione as the preservative in alkaline compositions (pH 9.0). The improvement is present regardless of whether the surfactant system comprised a zwitterionic surfactant (a betaine) or an amphoteric surfactant (amine oxide) as co-surfactant, though the benefit is more pronounced where the surfactant system comprised an amphoteric surfactant. It is believed that the dipyrithione is better able to maintain preservation efficacy at a pH which is above the pKa of the aromatic thiol (thiol protonation) of the mono-pyrithione (pKa of around 4.7), with the relative improvement in preservation efficacy of the dipyrithione vs. mono-pyrithione increasing as the composition pH is increased.

[0123] 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 cleaning composition comprising from 5.0% to 50% by weight of the total composition of a surfactant system, wherein the surfactant system comprises at least 40% by weight of the surfactant system of an anionic surfactant, wherein the anionic surfactant comprises at least 70% by weight of the anionic surfactant of alkyl sulphate anionic surfactant, wherein the surfactant system is free of fatty acid or salt thereof, wherein the composition further comprises a dipyrithione preservative according to formula I:



wherein the liquid cleaning composition has a pH from 6.0 or greater, measured as a 10% aqueous solution in demineralized water at 20 degrees °C.

2. The composition according to claim 1, wherein the dipyrithione preservative is present at a level of from 10 ppm to 10000 ppm, preferably from 50 ppm to 5000 ppm, more preferably from 200 ppm to 2000 ppm in the composition, based on the fully ionised form of the dipyrithione.
3. The composition according to any preceding claim, wherein the composition further comprises phenoxyethanol, preferably at a level of from 100 ppm to 5000 ppm, more preferably from 250ppm to 3500 ppm, most preferably from 500 ppm to 2500 ppm.
4. The composition according to any preceding claim, wherein the composition has a pH of from 6.0 to 12.0, preferably from 7.0 to 11.0, more preferably from 8.0 to 10.0, measured as a 10% aqueous solution in demineralized water at 20 degrees °C.
5. The composition according to any preceding claim, wherein the composition comprises from 6.0% to 40%, preferably from 15% to 35%, by weight of the total composition of the surfactant system.
6. The composition according to any preceding claim, wherein the surfactant system comprises at least 50%, preferably from 60% to 90%, more preferably from 65% to 85% by weight of the surfactant system of an anionic surfactant.
7. The composition according to any preceding claim, wherein the anionic surfactant comprises at least 85%, preferably 100% by weight of the anionic surfactant of alkyl sulphate anionic surfactant.
8. The composition according to any preceding claim, wherein the alkyl sulphate anionic surfactant has 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.
9. The composition according to any preceding claim, wherein the alkyl sulphate anionic surfactant is an alkyl alkoxy sulphate anionic surfactant having an average degree of alkoxylation of less than 3.5, preferably from 0.3 to 2.0, more preferably from 0.5 to 0.9.
10. The composition according to any preceding claim, wherein the alkyl sulphate anionic surfactant has a weight average degree of branching of more than 10%, preferably more than 20%, more preferably more than 30%, even more preferably between 30% and 60%, most preferably between 30% and 50%.
11. The composition according to any preceding claim, wherein the surfactant system further comprises a co-surfactant

selected from an amphoteric co-surfactant, a zwitterionic co-surfactant, and mixtures thereof, preferably wherein the anionic surfactant and the co-surfactant are present in a weight ratio of from 1:1 to 8:1, preferably from 2:1 to 5:1, more preferably from 2.5:1 to 4:1.

- 5 **12.** The composition according to claim 11, wherein the co-surfactant is an amphoteric surfactant, preferably an amine oxide surfactant, more 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, most preferably alkyl dimethyl amine oxide.
- 10 **13.** The composition according to claim 11, wherein the co-surfactant is a zwitterionic surfactant, preferably a betaine surfactant, more preferably a betaine surfactant selected from the group consisting of alkyl betaines, alkylamidoalkyl-betaine, amidazoliniumbetaine, sulphobetaine (INCI Sultaines), phosphobetaine, and mixtures thereof, most preferably cocoamidopropylbetaine.
- 15 **14.** The composition according to any preceding claim, wherein the surfactant system further comprises a nonionic surfactant, preferably wherein the nonionic surfactants is selected from the group consisting of: alkoxylated alcohol nonionic surfactants, alkyl polyglucoside nonionic surfactants, and mixtures thereof.
- 20 **15.** A method of manually washing dishware using a composition according to any preceding claim, preferably comprising the step of delivering the composition to a volume of water to form a wash solution and immersing the dishware in the solution.

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