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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BIOCIDAL CLEANING COMPOSITION

(57) Abstract: The present invention relates to a biocidal cleaning composition comprising a biocide, a surfactant of formula R-O-(G)_n, and an amphoteric surfactant; wherein R is an alkyl group; G is a saccharide residue; and n is a number from 0-4 to 10.



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Biocidal cleaning composition

The invention relates to biocidal cleaning compositions and more particularly but not exclusively to mild liquid formulations having utility in the manual cleaning and sanitising of dishes and hard surfaces.

There exists a continuing need for mild surfactants suitable particularly for manual dishwashing and other light duty hard surface cleaning applications, and such products have been the subjects of much prior art.

These products have generally comprised anionic and non-ionic surfactant blends conferring on them good foaming and drain drying properties so that crockery and glassware are rendered sparkling clean and streak free.

Furthermore, since the world's population is now more hygiene conscious than ever before it is desirable to produce a composition, which in addition to cleaning properties, also possesses antibacterial properties, and as such is suitable for sanitising hard surfaces, floors, walls, work surfaces and the like, especially in catering, food processing and health and hygiene situations where major health problems can arise due to the growth and spread of pathogenic bacteria.

These products have generally combined non-ionic surfactants with cationic biocides and/or organic halides often with higher alcohol co-solvents and chelating agents. They tend to be characterised by having

relatively low foam and whilst they may have good grease removal, they are unsuitable for use in manual dishwashing applications as crockery and glassware are left with residual streaks and smears.

Previous attempts to combine both dishwashing and sanitising have met with limited success due to the incompatibility of anionic surfactants with cationic biocides such that their biocidal effectiveness has been much reduced. The use of organic halides or other biocides compatible with anionic surfactants has had limited success due to their ineffectiveness at high dilutions. Recent attempts to overcome these constraints have resulted in formulations having good dishwashing properties at normal use dilutions with biocidal properties when used neat or virtually neat .

Certain groups of non-ionic surfactants, particularly those based on sugars and vegetable oils for example alkyl polyglycosides (also known as alkyl polyglucosides and hereinafter referred to as APG's) are mild to the skin and have good foaming and rinsing properties. Moreover their detergency may be potentiated by combination with amphoteric surfactants. It is also known that they are compatible with some cationic surfactants. This has been utilised in the formulation of for example mouthwashes and skin and hair cleansers.

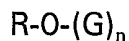
International Patent Application Nos. 94/05753, 95/31962 and European Patent Application No. 0911022A1 all teach of the use of APG's in such compositions.

APG'S have also been used as additives in manual dishwashing formulations to confer mildness usually in conjunction with anionic surfactants such as alkyl benzene sulphonate or sodium lauryl sulfate. The use of cationic biocides or biguanides in mouthwashes and skin cleansers and for example, surgical scrubs are also well known in the prior art and is described in US Patents Nos. 4022834 and 5719113.

However, the combination of sugar surfactants, amphoteric surfactants and quaternary biocides, or biguanides has not been previously applied to the production of a dishwashing composition having effective biocidal properties at normal use dilution.

Therefore, an object of the present invention is to provide a high performance surfactant solution with superior manual dish and glasswashing properties which also exhibits biocidal properties effective at normal use dilutions and is suitable for light duty hard surface cleaning/sanitising applications.

According to the present invention therefore, there is provided a biocidal cleaning composition comprising a biocide, a surfactant of formula I and an amphoteric surfactant.

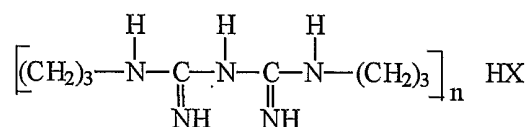
Formula I

wherein; R = alkyl (C₄ - C₂₄),

G = saccharide residue having 5 or 6 Carbon atoms,

n = a number from 0.4 to 10.

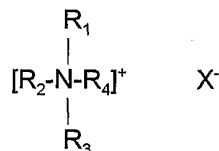
In a preferred embodiment of the invention the biocide is water soluble, typically has some cationic properties and is normally either a biguanide or a quaternary ammonium compound. Suitable biguanides are referred to in US patent Nos. 3,468,898 and 4,022,834 and are preferentially either a salt of chlorhexidine or polyhexamethylene biguanide (PHMB), as exemplified in formula II. Chlorhexidine is the common name for the antiseptic 1,1'-hexamethylene-bis-[-5-(4-chlorophenyl)-biguanide].

Formula II

wherein; HX is a salt forming anion

n is a No. between 4 and 50, but preferably 12.

Suitable quaternary ammonium biocides are of formula III.

Formula III

Where R_1 is selected from an alkyl group having 6 to 24 carbon atoms or aromatic, aryl or alkaryl groups having 6 to 24 carbon atoms; R_2 , R_3 and R_4 are independently selected from hydrogen, an alkyl group having 1 to 24 carbon atoms, or aromatic, aryl or alkaryl groups having from 6 to 24 carbon atoms; X is an anion selected from but not limited to chloride, bromide, iodide, acetate, phosphate, nitrate, sulphate, lactate, citrate, and mixtures thereof.

The glycolate, saccharinate and biocide may constitute from 0.1% to 10% of the composition. Preferably, the biocide of the present invention shall constitute from 0.2% to 5% of the composition. Most preferably, the biocide of the present invention shall constitute from 0.5% to 2% of the composition.

The non-ionic surfactant, in accordance with formula I, is an APG.

Suitable APG's have been described in US Patent No.s 3839318, 3772269, 3707535 and 3547828 also in German and European patents and are commercially produced by reacting glucose or oligosaccharides with alcohols containing from 4 to 24 carbon atoms under acid catalysis.

With higher alcohols high reaction temperatures and prolonged reaction times result in complex mixtures of mono-, di-, tri- and oligosaccharides and reference to APG's shall include complex mixtures as described.

A particular property of APG's is that although being formally classified as non-ionic surfactants they do exhibit very slight anionic behaviour. The APG's of the present invention may constitute from 5% to 35% of the composition. Preferably, the APG's of the present invention shall constitute from 10% to 20% of the composition.

It is well known in the art that amphoteric surfactants (also known as zwitterionic surfactants) show synergistic interactions with anionic surfactants.

The present invention utilises a non-ionic surfactant with very mild anionic properties and the use of an amphoteric surfactant has been shown to improve the cleaning performance of APG's (Henkel sales brochure on their Glucopon range in April 1996). Since most classes of amphoteric surfactant are broadly compatible with the aforesaid biocides the nature of the amphoteric surfactant suitable for use in the present invention is not limited. Although the amphoteric surfactant may originate from a wide variety of sources those most suitable are derived from secondary and tertiary amines wherein the alkyl groups can be straight or branched alkyl chains between 1 and 22 carbon atoms long and may contain other

functional groups, for example amido groups. Preferably the nitrogen of the amphoteric surfactant of the present invention shall be in a cationic state wherein, the number of cations present in the molecule shall not be limited.

At least one of the alkyl groups must contain an ionisable head group which can adopt a negative charge such as a carboxylate, sulphate, sulphonate, phosphate, phosphonate, succinate, or sulfosuccinate.

Preferably, the amphoteric surfactants shall be chosen from betaines, sultaines, hydroxysultaines, iminopropionates and iminodipropionates.

The amphoteric surfactant shall preferably constitute from 2% to 20% of the composition and advantageously from 5% to 15% of the composition.

The aforesaid constituents, (hereinafter referred to as the key formula) form the basis of the invention providing both washing ability and antibacterial activity, however, in order to optimise the performance of the present invention additional constituents may be added. Preferably, a non-ionic foam booster shall be added to the key formula for example, alkanolamides and amine oxides, for example alkyl amine oxides and ethoxylated amine oxides such as those available under the Aromox (RTM) range from Akzo Nobel Chemicals. The addition of these foam boosters has no detrimental effect on the biocidal efficacy of the present invention.

The foam booster may be added to the key formula in proportions not exceeding 10% of the composition.

Preferably, the foam booster shall be added to the key formula in proportions from 2% to 6% of the composition.

These classes of nitrogen containing nonionic surfactants are well known to show synergistic and foam boosting effects when used in conjunction with anionic surfactants. It has been found that they exhibit similar beneficial effects when used in conjunction with the mildly anionic APG's.

Preferably, anionic surfactants shall be added to the key formula in order to influence the feel, rinsing and foaming properties and without markedly reducing the bactericidal efficiency of the invention. The nature of the anionic surfactant is limited only by its compatibility with the key formula suitable anionic surfactants include sodium lauryl sulfate, sodium lauryl ether sulfate and sodium lauryl sarcosinate.

The aforesaid anionic surfactants may be tolerated by the key formula in proportions not exceeding 1% of the total.

Preferably, minor amounts of specific nonionic surfactants may be added to the key formula in order to improve grease removal. Suitable non-ionic surfactants include alcohol alkoxylates and alky phenol alkoxylates. Preferably, the non-ionic surfactants shall be an alcohol ethoxylate having a cloud point below 20°C according to DIN 53917. The non-ionic surfactant may be included in the key formula in proportions not exceeding 10%.

Preferably, the non-ionic surfactant shall be included in the key

formula in proportions not exceeding 5% of the total.

Advantageously, the non-ionic surfactant shall be included in the key formula in proportions between 1% and 3% of the total.

The pH of the composition shall be between 5 and 9, and may be adjusted by the additions of small amounts of acid or base.

Preferably, the pH of the composition shall be between 6 and 8.

The acid employed to adjust the pH of the composition is not limited but preferably shall be chosen from sulfamic, citric, hydrochloric, phosphoric, nitric, lactic, formic, acetic or gluconic but other mineral or organic acids may be used without detriment.

The base employed to adjust the pH of the composition is not limited but preferably shall be chosen from sodium or potassium hydroxide and mono-, di- or tri- ethanolamine but other bases may be used without detriment.

Furthermore, additional constituents may be added to the key formula including sequesterants, thickeners, perfume, dye and preservative. Careful selection of these ingredients is required since their inclusion is limited only by their compatability with the key formula.

The aforesaid additional constituents may be added to the key formula in proportions not exceeding 3% and preferably, not exceeding 1%.

It should be noted that common commercial detergents for manual dishwashing typically contain between 15% and 40% total surfactant

content and the guideline inclusion rates described above are relevant to those typical detergent strengths. However, it is possible to manufacture very weak or very strong detergent solutions and any limits described above should be amended accordingly for such detergents.

Furthermore, the present invention is not based on petroleum derived stocks but rather on renewable resources such as coconuts, palm kernals and vegetable starch, and is therefore significantly more environmentally friendly both in terms of biodegradability and sustainability.

It is to be understood that all percentage values are measured by weight, and are relative to the total composition, unless otherwise stated.

This invention will now be described further by reference to the following specific examples:-

Formulation A

CLASS OF COMPOUND	COMPOUND	AMOUNT ADDED (%)
Non-ionic surfactant	C ₈₋₁₆ alkyl glycoside	14.35
Amphoteric surfactant	Cocoamidopropyl betaine	10.62
Non-ionic foam booster	Coconut diethanolamide	3.00
Non-ionic surfactant	C ₉₋₁₁ alcohol ethoxylate (4EO)	1.50
Anionic surfactant	Sodium lauryl sulfate	0.24
Sequesterent	Tetrasodium EDTA	0.30
Biocide	PHMB hydrochloride	0.90
Cationic biocide	Alkyl trimethyl ammonium bromide	0.45
Acid	Sulfamic acid (to pH 6.5)	0.33
Perfume	Perfume	0.25
Dye	Dye	0.005
Water	Water	68.06

The antimicrobial efficacy of formulation A was determined using standard testing procedures (BS 6471). Formulation A passed the standard test at a dilution of 1 part product to 200 parts water by volume.

Formulation B

CLASS OF COMPOUND	COMPOUND	AMOUNT ADDED (%)
Non-ionic surfactant	C ₈₋₁₆ alkyl glycoside	14.32
Amphoteric surfactant	Cocoamidopropyl betaine	6.62
Non-ionic foam booster	Coconut diethanolamide	2.99
Non-ionic surfactant	C ₉₋₁₁ alcohol ethoxylate (4EO)	1.50
Non-ionic foam booster	Myristyl amine oxide	3.99
Anionic surfactant	Sodium lauryl sulfate	0.24
Sequesterent	Tetrasodium EDTA	0.30
Biocide	PHMB hydrochloride	0.90
Cationic biocide	Alkyl trimethyl ammonium bromide	0.45
Acid	Sulfamic acid (to pH 6.5)	0.53
Perfume	Perfume	0.25
Dye	Dye	0.005
Water	Water	67.91

The antimicrobial efficacy of Formulation B was determined using standard testing procedures (BS 6471). Formulation B passed the standard test at a dilution of 1 part product to 400 parts water by volume.

In use these formulations in aqueous solution at a 1% dilution give rise to at least a 99% reduction in microbial activity when tested in accordance with BS 6471.

It will be appreciated that the above formulations are given by way of example only and that many variations are possible within the scope of the invention.

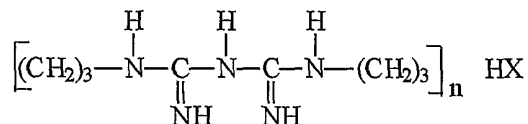
CLAIMS

1. A biocidal cleaning composition comprising a biocide, a surfactant of formula I and an amphoteric surfactant.

Formula I $R-O-(G)_n$

wherein R is an alkyl group
 G is a saccharide residue and
 n is a number from 0.4 to 10.

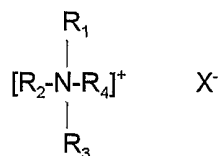
2. A biocidal cleaning composition according to claim 1 in which the saccharide residue has 5 or 6 carbon atoms.
3. A biocidal cleaning composition according to claim 1 or 2 in which the alkyl group has 4 to 24 carbon atoms.
4. A biocidal cleaning composition according to any preceding claim in which the biocide has cationic properties.
5. A biocidal cleaning composition according to any preceding claim in which the biocide is a biguanide.
6. A biocidal cleaning composition according to any of claims 1 to 4 in which the biocide is a quaternary ammonium compound.
7. A biocidal cleaning composition according to any of claims 1 to 5 in which the biguanide is a salt of chlorhexidine.
8. A biocidal cleaning composition according to any of claims 1 to 5 in which the biguanide is a salt of polyhexamethylene biguanide (PHMB) in accordance with formula II.

Formula II

wherein; HX is a salt forming anion

n is a No. between 4 and 50, but preferably 12.

9. A biocidal cleaning composition according to claim 6 in which the quaternary ammonium compound is of the following formula,



wherein; R₁ is alkyl (C₆ to C₂₄), aromatic, aryl or alkaryl (C₆ to C₂₄)

R₂ is hydrogen, alkyl (C₆ to C₂₄), aromatic, aryl or alkaryl (C₆ to C₂₄)

R₃ is hydrogen, alkyl (C₆ to C₂₄), aromatic, aryl or alkaryl (C₆ to C₂₄)

R₄ is hydrogen, alkyl (C₆ to C₂₄), aromatic, aryl or alkaryl (C₆ to C₂₄)

X is chloride, bromide, iodide, acetate, phosphate, nitrate, sulfate, lactate, citrate, glycolate, saccharinate and mixtures thereof.

10. A biocidal cleaning composition according to any one of the preceding claims in which the biocide constitutes from 0.1% to 10% of the composition.

11. A biocidal cleaning composition according to any of the preceding

claims in which the biocide constitutes from 0.2% to 5% of the composition.

12. A biocidal cleaning composition according to any of the preceding claims in which the biocide constitutes from 0.5% to 2% of the composition.

13. A biocidal cleaning composition according to any preceding claim in which the surfactant is an APG.

14. A biocidal cleaning composition according to claim 13 in which the APG constitutes from 5% to 35% of the composition.

15. A biocidal cleaning composition according to claims 13 or 14 in which the APG constitutes from 10% to 20% of the composition.

16. A biocidal cleaning composition according to claim 1 the amphoteric surfactant is derived from secondary or tertiary amines wherein the alkyl groups are straight or branched possessing between 1 and 22 carbon atoms.

17. A biocidal cleaning composition according to any preceding claim in which the amphoteric surfactant shall constitute from 2% to 20% of the composition.

18. A biocidal cleaning composition to any preceding claim in which the amphoteric surfactant shall constitute from 5% to 15% of the composition.

19. A biocidal cleaning composition according to any of the preceding claims which comprises a foam booster.

20. A biocidal cleaning composition according to claim 19 in which the foam booster comprises 10% or less of the composition.

21. A biocidal cleaning composition according to claims 19 and 20 in which the foam booster shall constitute from 2% to 6% of the composition.

22. A biocidal cleaning composition according to any of the preceding claims which comprises an anionic surfactant.

23. A biocidal cleaning composition according to claim 22 in which the

anionic surfactant comprises 1% or less of the composition.

24. A biocidal cleaning composition according to any preceding claim which comprises a non-ionic surfactant.

25. A biocidal cleaning composition according to claim 24 in which the non-ionic surfactant shall have a cloud point below 20°C.

26. A biocidal cleaning composition according to claims 24 or 25 in which the non-ionic surfactant comprises 10% or less of the composition.

27. A biocidal cleaning composition according to claims 24, 25 or 26 in which the non-ionic surfactant comprises from 1% to 3% of the composition.

28. A biocidal cleaning composition according to any of the preceding claims in which the pH of the composition lies between 5 and 9.

29. A biocidal cleaning composition according to any of the preceding claims in which the pH of the composition lies between 6 and 8.

30. A biocidal cleaning composition according to any of the preceding claims in which additional constituents shall be added, included sequesterants, thickeners, perfume, dye and preservative.

31. A biocidal cleaning composition according to claim 30 in which each additional constituent shall be added in a proportion not exceeding 3% of the composition.

32. A biocidal cleaning composition according to claims 30 or 31 in which each additional constituents shall be added in proportions not exceeding 1% of the composition.

33. A biocidal cleaning composition according to example A or B as described.

34. A biocidal cleaning composition according to any preceding claim in which a dilution of 1% of the composition in an aqueous solution produces a reduction of 99% in microbial activity.

INTERNATIONAL SEARCH REPORT

tional Application No
ru/GB 02/00710

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D1/94 C11D1/66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 911 022 A (UNILEVER PLC ;UNILEVER NV (NL)) 28 April 1999 (1999-04-28) claims 1-5; example 1 page 2, line 50,51 page 3, line 55 -page 4, line 29 page 6, line 40-45 ----	1-34
X	WO 95 31962 A (GOJO IND INC) 30 November 1995 (1995-11-30) page 3, line 3-5; claims 1-4,7-15,18-20; tables IV,VI,XII,XIV page 8, line 13-22 page 10, line 26 -page 11, line 21 page 12, line 3,4,16-21,30,31 ----- -/--	1-34



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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