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<p>(21) International Application Number: PCT/US94/13022 (22) International Filing Date: 14 November 1994 (14.11.94) (30) Priority Data: 93203307.9 26 November 1993 (26.11.93) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Protector and Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BOUTIQUE, Jean-Pol [BE/BE]; Rue Emile-Labarre 32, B-5800 Emage (BE). DELPLANCKE, Patrick, Firmin, A. [BE/BE]; Avelgemsestraat 38, B-8550 Zwevegem (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p>(81) Designated States: CA, JP, US. Published <i>With international search report.</i></p>
<p>(54) Title: N-ALKYL POLYHYDROXY FATTY ACID AMIDE COMPOSITIONS AND THEIR METHOD OF SYNTHESIS</p>		
<p>(57) Abstract</p>		
<p>The present invention concerns aqueous surfactant composition comprising poly hydroxy fatty acid amides of formula (A), wherein R2 is C11-C19 alkyl, alkenyl or mixtures thereof; Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain; and in a part of the total amide surfactant (a) R1 is a methyl group and in the remainder of the total amide surfactant (b) R1 is an alkyl group with from 3 to 8 carbon atoms; said composition further comprising (c) from 0 % to 15 % by weight of an organic solvent; wherein the ratio of N-methyl poly hydroxy fatty acid amide (a) to N-alkyl (C3-C8) polyhydroxy fatty acid amide (b), is from 25:1 to 1:1. In a preferred embodiment of the present invention, the surfactant composition is prepared by mixing N-methyl poly hydroxy fatty acid amine and N-propyl poly hydroxy fatty acid amine, and reacting said mixture with a fatty acid ester reactant in the presence of a base catalyst and, preferably, in the presence of a reaction solvent.</p>	$ \begin{array}{c} \text{O} \qquad \qquad \text{R1} \\ \parallel \qquad \qquad \\ \text{R2} - \text{C} - \text{N} - \text{Z} \end{array} \quad (\text{A}) $	

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N-ALKYL POLYHYDROXY FATTY ACID AMIDE COMPOSITIONS AND THEIR
METHOD OF SYNTHESIS

FIELD OF THE INVENTION

The present invention relates to certain mixtures of N-alkyl polyhydroxy fatty acid amide deterative surfactants and their method of synthesis.

BACKGROUND OF THE INVENTION

The formulation of detergent compositions presents a considerable challenge, since effective compositions are required to remove a variety of soils and stains from diverse substrates. In particular, the removal of greasy/oily soils quickly and efficiently can be problematic. While a review of the literature would seem to indicate that a wide selection of surfactants is available to the detergent manufacturer, the reality is that many such materials are specialty chemicals which are

not suitable in low unit cost items such as home-use detergent compositions. The fact remains that most home-use detergents still comprise one or more of the conventional ethoxylated nonionic and sulfated or sulfonated anionic surfactants, presumably due to economic considerations.

The challenge to the detergent manufacturer seeking improved fabric cleaning has been increased by various environmental factors. For example, some nonbiodegradable ingredients have fallen into disfavor. Effective phosphate builders have been banned by legislation in many countries.

Moreover, many surfactants are often available only from nonrenewable resources such as petrochemicals.

Accordingly, the detergent manufacturer is quite limited in the selection of surfactants which are effective cleaners, biodegradable and, to the extent possible, available from renewable resources such as natural fats and oils, rather than petrochemicals.

Considerable attention has lately been directed to nonionic surfactants which can be prepared by using mainly renewable resources, such as fatty esters and sugars. One such class of surfactants includes the N-alkyl polyhydroxy fatty acid amides. Moreover, the combination of such nonionic surfactants with conventional anionic surfactants such as the alkyl sulfates, alkyl benzene sulfonates, alkyl ether sulfates, and the like has also been studied. Indeed,

substantial success in the formulation of dishwashing compositions has recently been achieved using the N-alkyl polyhydroxy fatty acid amides. However, even these superior surfactants do suffer from some drawbacks. For example, their solubility is not as high as might be desired for optimal formulations and this is exacerbated at chain lengths of about C₁₆ and above. At high concentrations in water they can be difficult to handle, store and pump, so additives must be employed in manufacturing plants to control their viscosity and maintain their fluidity.

A suitable method for the manufacture of N-alkyl polyhydroxy fatty acid amides having desirable low color and little or no contamination with cyclized by-products, carried out in the presence of organic hydroxy solvents, is disclosed in U.S. Patent 5,194,639, Connor, Scheibel and Severson, issued March 16, 1993.

In order to prevent gelling or solidification of the liquid fatty acid amides, it has generally been found to be necessary to store them at elevated temperatures, and/or to add substantial quantities of organic solvents mentioned in US 5 194 639.

It has now been discovered that certain mixtures of N-alkyl polyhydroxy fatty acid amides can be prepared using low

levels of organic solvents, and can be stored at ambient temperatures.

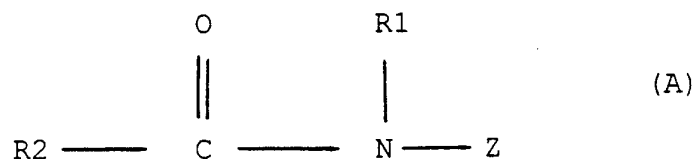
Accordingly, the present invention provides new, highly soluble, highly deterative surfactants which have the additional advantage that they can be prepared in an efficient and effective manner with reduced need for solvents, and which can be stored in the liquid state at ambient temperatures.

BACKGROUND ART

Japanese Kokai HEI 3[1991]-246265 Osamu Tachizawa, U.S. Patents 5,194,639, 5,174,927 and 5,188,769 and WO 9,206,171, 9,206,151, 9,206,150 and 9,205,764 relate to various polyhydroxy fatty acid amide surfactants and uses thereof.

SUMMARY OF THE INVENTION

The present invention concerns aqueous surfactant composition comprising poly hydroxy fatty acid amides of the formula (A):



wherein R2 is C11-C19 alkyl, alkenyl or mixtures thereof;

Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain; and

in a part of the total amide surfactant (a) R1 is a methyl group and in the remainder of the total amide surfactant

(b) R1 is an alkyl group with from 3 to 8 carbon atoms;

said composition further comprising (c) from 0% to 15% by weight of an organic solvent;

wherein the ratio of N-methyl poly hydroxy fatty acid amide (a) to N-alkyl (C3-C8) polyhydroxy fatty acid amide (b), is from 25:1 to 1:1.

In a preferred embodiment of the present invention, the surfactant composition is prepared by mixing N-methyl poly hydroxy fatty acid amine and N-propyl poly hydroxy fatty acid amine, and reacting said mixture with a fatty acid ester reactant in the presence of a base catalyst and, preferably, in the presence of a reaction solvent.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an aqueous surfactant composition which preferably comprises at least 30% by weight of N-methyl poly hydroxy fatty acid amide and which remains as a homogeneous liquid for at least 1 week when

stored at 25°C. Preferably the composition comprises at least 40% by weight of polyhydroxy fatty acid amides (in total)

In addition the aqueous surfactant composition preferably comprises

- (a) N-methyl poly hydroxy fatty acid amide;
- (b) N-alkyl poly hydroxy fatty acid amide, having an alkyl chain length of from 3 to 8 carbon atoms;

wherein (a) and (b) are both amides of the formula (A), and furthermore the weight ratio of (a) to (b) is from 15:1 to 2:1.

The surfactants of formula (A) are preferably based on the following groups: where R₂-CO-N< is preferably selected from the group consisting of cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide and mixtures of these, and Z is a glyceryl moiety.

R₁ preferably consists of methyl (a) and propyl (b) groups.

Any suitable organic solvent may be used, such as methanol, ethanol, propanol, iso-propanol, the butanols, glycerol, 1,2-propylene glycol, and 1,3-propylene glycol. Organic solvents are preferably used at a level of less than 5% by weight of the composition.

The most preferred compositions of the present invention comprise:

- (a) at least 40% by weight of N-methyl glucamide
- (b) from 2.5% to 15% by weight of N-propyl glucamide
- (c) from 2% to 8% by weight of propylene glycol

The following defines the terms used herein.

By "low-color" herein is meant a N-alkyl polyhydroxy fatty acid amide reaction product which is substantially white or light beige. On the standard Gardner scale, a color in the range of 0-4, preferably 0-2, most preferably 0, is secured.

By "cyclized by-products" herein is meant contaminants which undesirably form during the synthesis by internal cyclization of the polyol structure (e.g., glycityl) of the N-alkyl polyhydroxy fatty acid amides herein, presumably by a dehydration reaction. The term "cyclized by-products" does not refer to natural cyclic structures, such as those which may be present in di- and higher saccharide reducing sugars such as maltose. The process of this invention provides N-alkyl polyhydroxy fatty acid amides which are substantially free, i.e., which contain less than 10% preferably 1% or less, of undesirable "cyclized by-products".

By "ester amides" herein is meant N-alkyl polyhydroxy fatty acid amides whose polyol units have undesirably undergone a further reaction with the fatty acid ester reactant to form one or more fatty ester linkages. The process of this

invention provides N-alkyl polyhydroxy fatty acid amides which are substantially free, i.e., which contain less than 10%, preferably less than 5%, most preferably 1% or less, of such ester-amides.

It is to be understood that the polyhydroxy amines used herein can be derived from an alkoxy amine and any desired reducing sugar, such as glucose (preferred), xylose, maltose, fructose, and the like.

In a second aspect of the invention, a process is provided in which a mixture of amines is reacted with esters in the presence of a base catalyst.

The process herein is conducted under the following conditions.

Preferably, the base catalyst used in the process is an alkoxide material, especially sodium methoxide. The fatty acid "ester" can be a C₈-C₂₂ fatty acid alkyl ester or, for the sake of economy, a C₈-C₂₂ fatty acid mono-, di- or tri-glyceride ester. Thus, natural plant oils such as palm oil, soy oil, coconut oil, palm kernel oil, canola oil and the like, can be used in the process.

In a preferred mode of the reaction, the fatty acid ester is a C₁₁-C₁₉ fatty acid methyl ester and the N-alkyl polyhydroxy amine reactants are N-methyl glucamine and N-propyl glucamine.

In order to provide low-colour products, and to minimize ester amide or cyclic by-products formed by the polyol

substituent, the process herein is preferably conducted at a temperature below about 170°C, most preferably in the range from about 140°C to about 70°C. If desired, any unreacted N-alkoxyamino polyol remaining in the product can be acylated (50°C-85°C) with an acid anhydride, e.g., acetic anhydride, maleic anhydride, or the like, in water to minimize the overall level of such residual amines in the product. Residual sources of straight chain fatty acids, which can suppress suds, can be depleted by reaction with, for example, monoethanolamine (50°C-85°C).

In a most preferred mode of the reaction, a reaction solvent is present. Suitable reaction solvents include C1-C4 alcohol, ethylene glycol, alkoxyated alcohol, or mixtures thereof. Propylene glycol is most preferred.

Optional Components

Additional components which contribute to the prevention of gelling, precipitation or solidification may, optionally, be included in the compositions of the present invention. Such components include carboxylate and borate functional materials.

Useful carboxylate functional materials including citrates, oxydisuccinates, tartrates, tartrate monosuccinate, tartrate disuccinate, gluconate and saccharate have been

disclosed in the Applicants co-pending application no.
PCT/US9302066, filed on 8th March, 1993.

Useful borate functional materials include boric acid or its salts, such as metaborate or tetraborate, and borax. These have been disclosed in the Applicants co-pending Application EP92870164.8, filed on 13th October, 1992.

EXAMPLE

The following surfactant compositions were prepared :

	A	B	C	D	E
C12 N-methyl glucamide	30	30	30	40	50
C12 N-propyl glucamide	15	-	-	-	12
C12 N-butyl glucamide	-	15	15	2	-
Ethanol	-	-	-	2	3
1,2 Propanediol	5	-	5	8	7
Water	-----up to 100 parts-----				

All examples stay clear, transparent liquids after 1 week storage at 25°C.

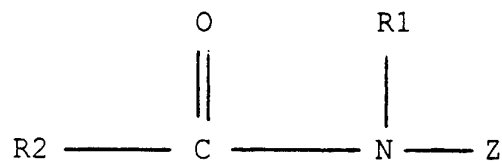
The compositions of Examples A to E were first prepared by mixing appropriate quantities of N-methyl glucamide, N-propyl or N-butyl glucamide, organic solvent and water.

The compositions of Examples A to E can also be prepared by mixing the appropriate proportions of N-methyl glucamine with either N-propyl glucamine (Examples A and E) or N-butyl glucamine (Examples B, C and D). The mixture of glucamine was reacted with C12 fatty acid methyl ester in the presence of sodium methoxide base catalyst and 1,2 propane diol where present (Examples A, C, D and E) at a temperature of 80°C. After completion of the amidation

reaction the glucamides were diluted with water and ethanol added were present (Examples D and E) to give the finished compositions.

CLAIMS

1. An aqueous surfactant composition comprising poly hydroxy fatty acid amides of the formula:



wherein R2 is C11-C19 alkyl, alkenyl or mixtures thereof;

Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain; and

in a part of the total surfactant (a), R1 is a methyl group; and in the remainder of the total surfactant (b), R1 is an alkyl group with from 3 to 8 carbon atoms;

said composition further comprising (c) from 0% to 15% by weight of an organic solvent;

characterised in that the ratio of N-methyl poly hydroxy fatty acid amide(a) to N-alkyl (C3-C8) polyhydroxy fatty acid amide (b), is from 25:1 to 1:1.

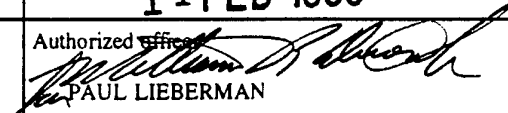
2. A composition according to claim 1 in which R₂-CO-N< is selected from the group consisting of cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide and mixtures of these, and Z is a glycityl moiety.
3. A composition according to either of claims 1 or 2 comprising
 - (a) N-methyl poly hydroxy fatty acid amide;
 - (b) N-alkyl poly hydroxy fatty acid amide, having an alkyl chain length of from 3 to 8 carbon atoms;wherein the weight ratio of (a) to (b) is from 15:1 to 5:1.
4. A composition according to any of the previous claims comprising at least 30% by weight of N-methyl poly hydroxy fatty acid amide (a) which remains as a homogeneous liquid for at least 1 weeks when stored at 25°C.
5. A composition according to any of the previous claims comprising at least 40% by weight of poly hydroxy fatty acid amide [(a)+(b)] which remains as a homogeneous liquid for at least 1 weeks when stored at 25°C.
6. A composition according to any of the previous claims wherein said N-alkyl poly hydroxy fatty acid amide having an alkyl chain length of from 3 to 8 carbon atoms (b) is predominantly N-propyl poly hydroxy fatty acid amide.

7. A composition according to any of the previous claims wherein said organic solvent comprises propylene glycol.
8. A composition according to any of the previous claims comprising:
- (a) at least 40% by weight of N-methyl glucamide
 - (b) from 2.5% to 15% by weight of N-propyl glucamide
 - (c) from 2% to 8% by weight of propylene glycol
9. A process for the preparation of a surfactant composition comprising the steps of mixing (a) N-methyl poly hydroxy fatty acid amine and (b) N-alkyl (C3-C8) poly hydroxy fatty acid amine, and reacting said mixture with a fatty acid ester reactant in the presence of a base catalyst and, preferably, in the presence of a reaction solvent, characterised in that the ratio of N-methyl poly hydroxy fatty acid amide(a) to N-alkyl (C3-C8) polyhydroxy fatty acid amide (b), is from 25:1 to 1:1.
10. A process according to claim 9 wherein the base catalyst is an alkoxide material.
11. A process according to either of claims 9 or 10 wherein the temperature of said reaction is maintained between 70°C and 140°C.

12 A process according to any of claims 9 to 11 wherein the reaction solvent comprises propylene glycol.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/13022

<p>A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C11D 1/66, 1/825 US CL : 252/548, 162, 170 According to International Patent Classification (IPC) or to both national classification and IPC</p>																				
<p>B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 252/548, 162, 170</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS search terms: glucamide, glucamine, polyhydroxy fatty acid (2w) (amide# or amine#)</p>																				
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US, A, 2,703,798 (SCHWARTZ) 8 MARCH 1955, col. 2 lines 38-47 and examples.</td> <td>1-3, 9-11</td> </tr> <tr> <td>Y,P</td> <td>US, A, 5,334,764 (SCHEIBEL ET AL.) 02 August 1994, see col. 2 lines 57-59, col. 9 lines 57-59, col. 10 lines 18-20, col. 10 lines 33-39, col. 10 lines 65-69</td> <td>1-3, 9-11</td> </tr> <tr> <td>A,P</td> <td>US, A, 5,283,009 (SPECKMAN ET AL.) 01 FEBRUARY 1994, see abstract</td> <td>1-3 and 9-11</td> </tr> <tr> <td>A,P</td> <td>US, A, 5,338,487 (CONNOR ET AL.) 16 August 1994, see abstract</td> <td>1-3 and 9-11</td> </tr> <tr> <td>A,P</td> <td>US, A, 5,338,486 (CONNOR ET AL.) 16 August 1994, see abstract</td> <td>1-3 and 9-11</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	US, A, 2,703,798 (SCHWARTZ) 8 MARCH 1955, col. 2 lines 38-47 and examples.	1-3, 9-11	Y,P	US, A, 5,334,764 (SCHEIBEL ET AL.) 02 August 1994, see col. 2 lines 57-59, col. 9 lines 57-59, col. 10 lines 18-20, col. 10 lines 33-39, col. 10 lines 65-69	1-3, 9-11	A,P	US, A, 5,283,009 (SPECKMAN ET AL.) 01 FEBRUARY 1994, see abstract	1-3 and 9-11	A,P	US, A, 5,338,487 (CONNOR ET AL.) 16 August 1994, see abstract	1-3 and 9-11	A,P	US, A, 5,338,486 (CONNOR ET AL.) 16 August 1994, see abstract	1-3 and 9-11
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<p><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p>																				
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>*T</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>*A document defining the general state of the art which is not considered to be of particular relevance</td> <td>*X</td> <td>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</td> </tr> <tr> <td>*E earlier document published on or after the international filing date</td> <td>*Y</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>*Z</td> <td>document member of the same patent family</td> </tr> <tr> <td>*O document referring to an oral disclosure, use, exhibition or other means</td> <td></td> <td></td> </tr> <tr> <td>*P document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*A document defining the general state of the art which is not considered to be of particular relevance	*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	*E earlier document published on or after the international filing date	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z	document member of the same patent family	*O document referring to an oral disclosure, use, exhibition or other means			*P document published prior to the international filing date but later than the priority date claimed		
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INTERNATIONAL SEARCH REPORT

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PCT/US94/13022

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