

LIQUID DETERGENT COMPOSITION

This invention relates to a liquid detergent composition, and has particular reference to a weakly acidic transparent liquid detergent composition, having a pH in the range of from 4.0 to 6.5, and which has excellent detergency, good foamability and excellent stability at lower temperatures.

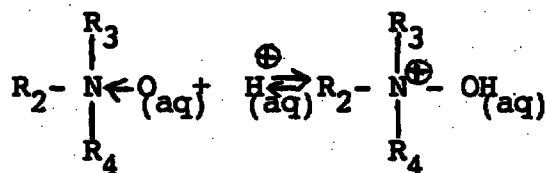
A liquid detergent composition such as, for example, a liquid detergent composition for use in washing-up dirty crockery and cutlery must have excellent detergency, foamability, and stability at low temperatures.

Furthermore, such a liquid detergent composition must exhibit "mildness" to the skin. In order to obtain such properties, prior art liquid detergent compositions comprise an anionic surfactant such as a polyoxyethylene alkylether sulfate or an alkylbenzene sulfonate as a main detergent and a sub-surfactant such as a tertiary amine oxide or a higher fatty acid alkanol amide.

It is well known in the prior art that the "mildness" to skin of polyoxyethylene alkylether sulfate increases with the number of moles of alkylene oxide per mole of surfactant. Although polyoxyethylene alkylether sulfate is widely used in many prior art liquid detergent compositions for its excellent detergency and mildness to skin, it suffers from the significant disadvantage, however, that its properties of detergency and foamability decrease in a generally inverse relationship to the proportion of alkylene oxide in the surfactant. Japanese Patent Gazettes

Nos. 38(1963) - 3264 and 38(1963) - 17467 each disclose the use of a tertiary amine oxide surfactant in a liquid detergent composition to reduce the stimulus to skin and thereby to permit the use of a polyoxyethylene alkylether sulfate surfactant as the main detergent.

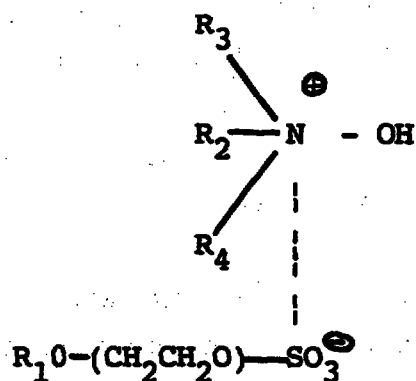
The effect of the addition of a tertiary amine oxide to a liquid detergent composition as a sub-surfactant is generally considered to be a result of the behaviour of the tertiary amine oxide in solution. In aqueous solution, a tertiary amine oxide exists in equilibrium with its conjugate acid in accordance with the following equilibrium:-



It is well known that the tertiary amine oxide shown on the left hand side of the equilibrium acts as a non-ionic surfactant, whilst its conjugate acid, shown on the right hand side of the equilibrium, acts as a cationic surfactant.

In solution, in the presence of an anionic surfactant such as, for example, polyoxyethylene alkylether sulfate, the tertiary amine oxide molecules associate with the anionic surfactant molecules by electrostatic interactions.

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Owing to the interactions between the anionic surfactant molecules and the tertiary amine oxide molecules, the electrostatic repulsions between anionic surfactant molecules are decreased thereby facilitating the formation of micelles. Furthermore, the critical micelle concentration (cmc) of the detergent composition shows a concomittant decrease thereby permitting foaming at lower concentrations of surfactant and thus increasing the detergency of the composition and the solubility of hydrophobic materials therein.

If the detergent composition is made more acidic, the above equilibrium is displaced towards the conjugate acid of the tertiary amine oxide, thereby promoting the association of anionic surfactant molecules and tertiary amine oxide molecules and thus enhancing the advantageous effects discussed above.

Increasing the acidity of the liquid detergent composition, however, also increases the viscosity of the composition owing to the interactions between the anionic surfactant and the tertiary amine oxide and thus reduces the stability of the composition at low temperatures. Furthermore, as the detergent composition becomes more hydrophobic, the detergency with respect to hydrophobic materials increases

but the foamability of the composition decreases significantly.

5 In order to facilitate dispensing, it is desirable that the viscosity of a liquid detergent composition should be within the range of from 100 to 500 Centipoise. Furthermore, it is desirable that the appearance of the detergent composition should not alter significantly at low temperatures down to about 10 -5°C. To this end, lower alcohols such as ethanol, lower alkylbenzene sulfonates such as p-toluene sulfonate, glycols such as ethylene glycol and propylene glycol, and urea are used. However, the effect of these hydrotopes in a weakly acidic mixture 15 is small and, thus, large amounts of these agents are required. This is uneconomical and, at high temperatures, the hydrotopes can decompose producing an unpleasant odour. Furthermore, although the inclusion of such agents in liquid detergent 20 compositions obviates the disadvantages of increased viscosity and decreased stability at low temperature, it has no effect on the decrease in the foamability of the composition.

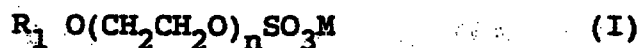
25 The present invention, therefore, seeks to provide a liquid detergent composition which does not exhibit a decrease in foamability even when such a composition has a weakly acidic pH, and has a suitable viscosity and an excellent stability at low temperatures. The present inventors have found that the addition of a 30 polypropylene oxide adduct of a polyhydric alcohol to a mixture of an anionic surfactant, a tertiary amine oxide and a higher fatty alkanol amide, said adduct having a specified molecular weight, produces a composition having a suitable viscosity, excellent 35 stability at low temperatures and, rather surprisingly, increased foamability.

According to the present invention, therefore, there is provided a transparent liquid detergent composition comprising:-

- 5 (a) 5% to 25% (w/w) of at least one anionic surfactant selected from polyoxyethylene alkylether sulphates, alkylbenzene sulfonates, α -olefin sulfonates and alkane sulfonates;
- 10 (b) 1 to 10% (w/w) of a tertiary amine oxide having a straight or branched chain alkyl group or an alkenyl group;
- (c) 1 to 15% (w/w) of at least one higher fatty
15 acid alkanolamide;
- (d) 0.5 to 10% (w/w) of at least one polypropylene oxide adduct of a polyhydric alcohol having an average molecular weight from 300 to 4000;

20 wherein the molar ratio of component (b) to component (a) $[(b)/(a)]$ is in the range of from 0.2 to 1.0, and the pH of the composition is in the range of from 4.0 to 6.5.

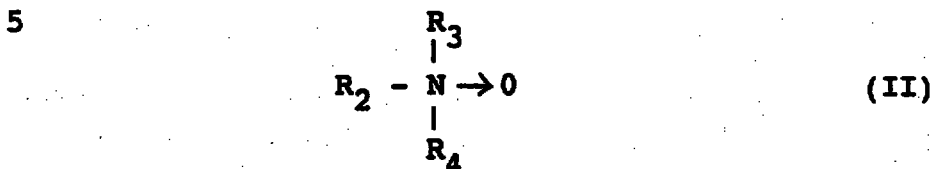
25 According to the present invention, anionic surfactant (a) may be one or more surfactants selected from polyoxyethylene alkylether sulfate, alkylbenzene sulfonate, α -olefin sulfonate, and alkane
30 sulfonate. In a preferred embodiment of the present invention, however, polyoxyethylene alkylether sulfate, which is represented by the following formula (I), is used because of its mildness to the hands and
35 skin;



5 In formula (I), R_1 represents a straight or branched chain alkyl group, n has an average value in the range of from 0.5 and 7, and M represents an alkali metal, an alkaline earth metal, an ammonium group or an alkanol substituted ammonium group. Preferably R_1 comprises from 9 to 15 carbon atoms; if the number of
10 carbons in R_1 is less than 9, the detergency of the composition may be insufficient, and if the number of carbons in R_1 is more than 15 the stability of the composition at low temperature may be significantly reduced. In a preferred embodiment of the present
15 invention, R_1 represents a straight or branch chain alkyl group having from 10 to 13 carbons. Furthermore, if the average number of ethylene oxide units, n , in (I) is less than 0.5, the stimulus to the hand and skin may increase, whilst if n is more than 7, the
20 detergency of the composition may be reduced. In a preferred embodiment of the present invention, the value of n is in the range of from 2.0 to 5.5.

25 The proportion of component (a) in the liquid detergent composition of the present invention is in the range of from 5 to 25% by weight of composition. If the proportion of component (a) is less than 5% by weight, both the detergency and foamability may be insufficient. If the proportion of component (a)
30 exceeds 25% by weight, however, the stability of the composition may be decreased. In a preferred embodiment of the present invention, the proportion of anionic surfactant in the composition of the present invention is in the range of from 10 to 20% by weight.

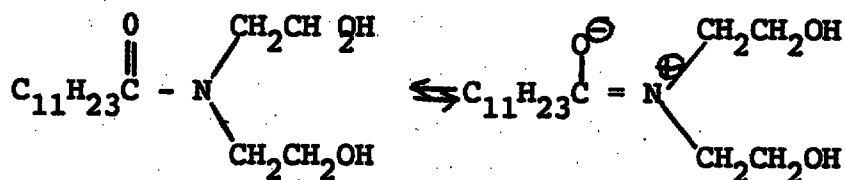
In a preferred embodiment of the present invention, component (b) is represented by the following formula (II):-



10 wherein R_2 represents a straight or branched chain alkyl group or an alkenyl group having from 10 to 16 carbons, and R_3 and R_4 each independently represent a methyl group or an ethyl group. If R_2 contains less than 10 carbons, the detergency of the liquid
15 composition may be low and, if R_2 contains more than 16 carbons, the stability of the composition at low temperatures may be significantly decreased. The liquid detergent composition of the present invention comprises from 1 to 10% by weight of the
20 tertiary amine oxide and, if a proportion of tertiary amine oxide falling outside this range is used, the detergency of the composition may be impaired or its stability may be reduced.

25 The higher fatty acid alkanolamide used as component (c) in the liquid detergent composition of the present invention is preferably synthesized from a mixture of more than one kind of a saturated or unsaturated fatty acid having from 10 to 18 carbons and an alkanolamine.
30 In a preferred embodiment of the present invention, palm oil fatty acid diethanolamide is used.

A higher fatty acid alkanolamide such as, for example, lauric acid diethanolamide, can be considered to exhibit the following resonance structure:-



From the above resonance structure, it can be seen that lauric acid diethanolamide exhibits a weak dipole which enables it to form weak electrostatic associations with anionic surfactant molecules. This interaction is weaker than the interaction of an anionic surfactant with a tertiary amine oxide as described herein and, in a weakly acidic composition, may not reduce the low temperature stability of the liquid detergent composition.

The effect of higher fatty acid alkanolamide on a detergent composition comprising an anionic surfactant and a tertiary amine oxide may be to hinder the formation of association complexes of the anionic surfactant and the tertiary amine oxide thereby improving the stability of the composition compared to a composition which comprises only an anionic surfactant and a tertiary amine oxide.

According to the present invention, the proportion of the higher fatty acid alkanolamide is in the range of from 1 to 15% by weight, and preferably in the range of from 2 to 8% by weight. If the proportion of higher fatty acid alkanolamide in the composition is less than 1% by weight, its effect may not be significant but, on the other hand, if the proportion exceeds 15% by weight, the stability of the composition may be impaired.

Component (d) of the composition, according to the present invention, is at least one polypropylene oxide adduct of a polyhydric alcohol. The polyhydric alcohol may be selected from dihydric alcohols such as ethylene glycol, propylene glycol, neopentyl glycol, etc, or from polyhydric alcohols such as glycerin, polyglycerin, trimethylol propane, pentaerythritol and sorbitol. Preferred polyhydric alcohols for use in the present invention are ethylene glycol and glycerine. Component (d), according to the present invention, may include more than one polypropylene oxide adduct of polyhydric alcohol. When component (d) is added to a weakly acidic detergent composition comprising an anionic active agent and a tertiary amine oxide together with a higher fatty acid alkanolamide, a significant decrease in the viscosity of the composition, an increase in the stability of the composition at low temperatures and an excellent foamability may result.

According to the present invention, the molecular weight of the polypropylene oxide adduct of a polyhydric alcohol is in the range of from 300 - 4000 and, preferably, from 500 to 2000. If a polypropylene oxide adduct of polyhydric alcohol having a molecular weight outside of the specified range is used, it is found that the decrease in the viscosity of the liquid detergent composition and the increase in the low temperature stability thereof may be small. Further, the detergent composition may not exhibit increased foamability. The proportion of component (d) in the detergent composition of the present invention is in the range of from 0.5 to 10% by weight and, preferably, from 2 to 5% by weight.

In the liquid detergent composition of the present invention, the anionic surfactant (a) and the tertiary amine oxide (b) may form a strong inter-molecular association as described above. Consequently, the ratio of component (b) to component (a) in the liquid detergent composition may influence the detergency of the composition. According to the present invention, the molar ratio of component (b) to component (a) is in the range of from 0.2 to 1.0 and, preferably, from 0.3 to 0.5. If the molar ratio of component (b) to component (a) is less than 0.2, a sufficient detergency may not be obtained even in an acidic composition. Further, if the molar ratio of (b) to (a) exceeds 1.0, the stability of the composition at low temperatures may be significantly reduced and, in an acidic composition, the majority of the free tertiary amine oxide molecules not associated with anionic surfactant molecules may be present in solution in the conjugate acid form, thereby increasing the stimulus to the hands and skin.

According to the present invention, the pH of the composition is in the range of from 4.0 to 6.5 and preferably in the range of from 4.0 to 6.0. If the pH of the composition is less than 4.0, the low temperature stability of the composition may be impaired and the stimulus to the hands and skin may be increased. On the other hand, if the pH of the composition exceeds 6.5, the detergency of the composition may be insufficient.

Furthermore, it has been found that the foamability of the composition according to the present invention may be reduced by the presence of water insoluble substances such as abrasives and the like. In view of this, such substances should not be used with the composition of the present invention.

To the liquid detergent composition of the present invention can be added a proportion of a surfactant for a commercially available liquid detergent composition as required and in an amount such that the performance of the composition is not impaired. Such surfactants may include non-ionic surfactants such as polyoxyethylene alkyl ether having an alkyl group of from 7 to 18 carbons and an average of from 4 to 20 oxyethylene units; amphoteric surfactants such as alkylbetaine; and anionic surfactants such as α -sulpho fatty acidic ester salts, N-acyl glutamate and monoalkyl phosphates.

Some embodiments of the present invention may comprise other components such as, for example, lower alcohols such as ethanol, lower alkylbenzene sulfonates such as p-toluene sulfonate, glycols such as ethylene glycol, polypropylene glycol etc, hydrotrope agents such as urea; pH buffer solutions such as citric acid and malic acid; organic or inorganic builders, agents to prevent hand irritation, enzymes, protein derivatives, coloring agents, perfumes, preservatives and the like.

The transparent liquid detergent composition of the present invention may have excellent detergency, a rich foamability and a suitable viscosity; further the detergent composition of the present invention may exhibit excellent stability at low temperatures. In view of these advantageous properties, the liquid detergent composition according to the present invention may be useful as a detergent in the kitchen and especially as a detergent for table-ware.

The following is a description by way of example only of carrying the invention into effect:

Example 1

Each of the liquid detergent compositions shown in Table 1 was prepared and the detergency, foamability, viscosity, and stability at low temperature of each composition was investigated. The measurement of the properties of the detergent compositions was conducted as follows:-

Detergency:-

0.1% by weight of Sudan II (red pigment) indicator was added to an amount of beef tallow. 5g of this was then coated on to a porcelain dish (25cm in diameter). The dish was then rubbed with a sponge saturated with a mixture of detergent composition and water. The detergency of the composition was measured by the number of dishes which could be cleaned such that no beef tallow remained on each dish.

Foamability:-

The foamability of the liquid detergent compositions was determined as follows: 0.1% weight of butter was added to an aqueous solution of a detergent solution containing 0.5% by weight of detergent composition. The measurement was carried out by adding the detergent solution containing the butter to a glass cylinder having a diameter of 5cm, stirring for 5 minutes, and then determining the height of foam in the cylinder.

Viscosity:-

Each composition was put into a viscosity beaker held at a temperature of 20°C and determined by the use of a B type viscosity meter (rotor no.3). If the viscosity of the composition exceeded 2,000 cp, rotor no.4 was used (60 rpm).

Stability at low temperature:-

The evaluation of the low temperature stability of the compositions was carried out after preserving the examples for 10 days in a thermostatic chamber at -5°C.

Evaluation	Content
o	: no change
Δ	: slightly opaque
X	: separation or precipitation

Example 2

The liquid detergent compositions in Table 2 were prepared and the detergency, foamability, viscosity, and stability at low temperature of each composition was evaluated.

Example 3

The liquid detergent compositions in Table 3 were prepared, and the detergency, foamability, viscosity and stability at low temperature of each composition was evaluated.

Table 1

Composition No.	This invention						Comparative example				
Component	1	2	3	4	5	6	7	8	9	10	11
Sodium polyoxyethylene-3-dodecylether sulfate	20	17	15	5	5	10	30	10	15	5	10
Sodium dodecylbenzene sulfonate				10						10	
α-sodium olefin sulfonate (average molecular weight 326)					10						
Sodium octadecane sulfonate (average molecular weight 356)						10					
Dodecyl-dimethylamine-oxide	5	4	7	2	2	2	7	0.5	2	2	7
Palm oil fatty diethanolamide	5	7	5	5	5	5	8	8	0.5	4	5
PPG2000 *1(diols type *2)	3	4	4	3	3	3	4	4	0.1	12	3
Water	Balance										
Molar ratio [(b)/(a)]	0.46	0.43	0.86	0.22	0.21	0.25	0.43	0.09	0.24	0.22	1.28
PH (controlled suitably by sulfuric acid or sodium hydroxide)	6.0	6.0	5.5	5.5	5.5	5.0	6.0	6.0	5.5	5.0	5.5
Detergency (number of dishes)	15	14	18	13	13	13	20	5	8	13	13
Foaming power (mm)	95	95	92	90	91	96	95	25	30	50	60
Viscosity (cp, 20°C)	150	100	200	180	110	100	1800	50	800	30	1300
Stability at low temperature	0	0	0	0	0	0	x	0	4	x	x

*1 The number represents an average molecular weight of the compound.

*2 PO adducts whose starting material is ethylene glycol.

Table 2

Composition No. Component	This invention						Comparative example					
	12	13	14	15	16	17	18	19	20	21	22	
Sodium polyoxyethylene-4-dodecylether sulfate	20	20	20	10	10	10	20	20	20	10	10	
Sodium dodecylbenzene sulfonate				10	10	10				10	10	
Dodecyl dimethylamine oxide	3	3	3	2	2	2	3	3	3	2	2	
Lauric acid diethanolamide	5	5	5	4	4	4	5	5	5	4	4	
PPG1000 *1(diols type *2)	5	5	5	3	3	3	5	5	5	3	3	
Water	Balance											
Molar ratio[(b)/(a)]	0.30	0.30	0.30	0.24	0.24	0.24	0.30	0.30	0.30	0.24	0.24	
PH (controlled suitably by sulfuric acid or sodium hydroxide)	4.0	5.0	6.0	4.0	5.0	6.0	3.0	7.0	10.0	3.5	7.0	
Detergency (number of dishes)	15	15	13	13	13	13	10	7	5	10	7	
Foaming power (mm)	92	93	93	91	91	90	76	92	87	70	92	
Viscosity (cp, 20°C)	150	120	120	150	150	150	860	85	80	670	180	
Stability at low temperature	0	0	0	0	0	0	x	0	0	x	0	

*1 The number represents an average molecular weight of the compound.

*2 PO adducts whose starting material is ethyleneglycol.

Table 3

Component	Composition No.						This invention						Comparative examples			
	23	24	25	26	27	28	29	30	31							
Sodium polyoxyethylene-4-dodecylether sulfate	15	15	15	15	15	15	1	15	15							
Dodecyl-dimethylamine-oxide	2	2	2	2	2	2	2	2	2							
Palm oil fatty diethanolamide	6	6	6	6	6	6	6	6	6							
PPG100 *1(diols type *2)																
PPG3000 *1(diols type *2)	3															
PPG2000 *1(triols type *3)		3														
PPG5000 *1(triols type *3)																
PO adduct of trimethylol propane (1500*1)			3													
PO adduct of sorbitol (3000*1)																
PO adduct of pentaerythritol (4000*1)																
PEG2000*1																
Water																
----- Balance -----																
Molar ratio [(b)/(a)]	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27							
pH (controlled suitably by sulfuric acid or sodium hydroxide)	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5							
Detergency (number of dishes)	13	13	13	13	13	13	13	13	13							
Foaming power (mm)	95	93	94	94	94	95	93	93	93							
Viscosity (cp, 20°C)	150	120	130	110	100	100	350	150	880							
Stability at low temperature	0	0	0	0	0	0	0	0	0							

*1 The number represents an average molecular weight of the compound.

*2 PO adducts whose starting material is ethylene glycol.

*3 PO adducts whose starting material is glycerine.

CLAIMS



1. A transparent liquid detergent composition comprising:-

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(a) 5 to 25% by weight of at least one anionic surfactant selected from polyoxyethylene alkylether sulfates, alkylbenzene sulfonates, α -olefin sulfonates and alkane sulfonates;

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(b) 1 to 10% by weight of a tertiary amine oxide having a straight or branched chain alkyl group or an alkenyl group;

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(c) 1 to 15% by weight of at least one higher fatty acid alkanolamide; and

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(d) 0.5 to 10% weight of at least one polypropylene oxide adduct of a polyhydric alcohol having an average molecular weight of from 300 to 4000;

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wherein the molar ratio of component (b) to component (a) $[(b)/(a)]$ is in the range of from 0.2 to 1, and the pH of the composition is in the range of from 4.0 to 6.5.

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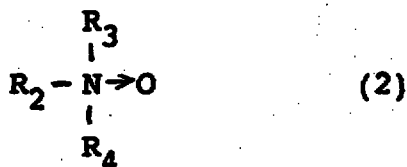
2. A transparent liquid detergent composition as claimed in Claim 1, wherein component (a) is a polyoxyethylene alkylether sulfate represented by the following formula (1):-



wherein R_1 represents a straight or branched chain alkyl group, n has an average value in the range of from 0.5 to 7, and M is an alkali metal, an alkaline-earth metal, an ammonium group or an alkanol substituted ammonium group.

3. A composition as claimed in Claim 2 wherein R_1 comprises from 9 to 15 carbon atoms.

4. A composition as claimed in Claim 1, Claim 2 or claim 3 wherein component (b) is a tertiary amine oxide represented by the following formula (2):-



Wherein R_2 represents a straight or branched chain alkyl group or an alkenyl group having from 10 to 16 carbons, and R_3 and R_4 each independently represent a methyl or ethyl group.

5. A transparent liquid detergent composition as claimed in any preceding claim wherein the polypropylene oxide adduct of a polyhydric alcohol is a polypropylene oxide adduct of ethylene glycol or glycerine.

6. A transparent liquid detergent composition substantially as described in Composition No. 1,2,3,4,5 or 6 of Example 1, Composition No. 12,13,14,15, 16 or 17 of Example 2, or Composition No. 23,24,25,26,27 or 28 of Example 3.