

LIQUID DETERGENT COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention:

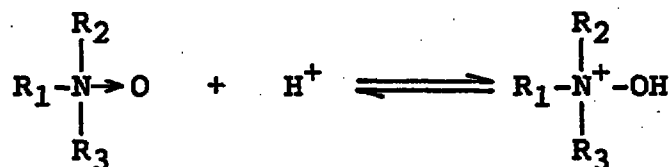
The present invention relates to a transparent and weakly acidic liquid detergent composition having a pH of 4.0 to 6.0, and, more particularly, to a transparent liquid detergent composition which possesses excellent detergency and foaming capability, as well as good stability at a low temperature.

Description of the Background

Excellent detergency and foaming capability as well as the characteristics imparting no irritation to the skin are fundamental properties demanded of liquid detergents such as dish-washing detergents. In order to satisfy these demands, detergents conventionally used rely their foaming capability upon anionic surfactants, such as polyoxyethylene alkyl ether sulfate, alkylbenzene sulfonate, α -olefin sulfonate, as the main detergent components. In order to supplement the detergency and foaming capability when used for removing oily dirt, or to reduce irritation to the skin, conventional detergent compositions contain, as an auxiliary component, nitrogen-containing amphoteric or non-ionic surfactants such as tertiary amine oxides, higher fatty acid alkanol amides, and alkyl-betaine. Among these auxiliary

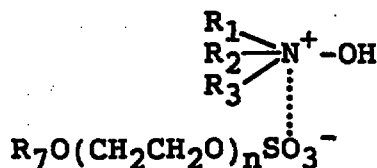
detergent components, tertiary amine oxides are known to bring about extremely good results (Japanese Patent Publication Nos. 14979/1964 and 3264/1963).

The effect of adding tertiary amine oxide as an auxiliary component is considered to be brought about by their dissolution behavior in an aqueous solution. In other words, a tertiary amine oxide exhibits dissociation equilibrium in an aqueous solution as shown by the following formula:



wherein R_1 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, and R_2 and R_3 independently represent an alkyl group having 1 to 2 carbon atoms.

Tertiary amine oxides are known to act as a non-ionic surfactant under alkaline conditions and, under acidic conditions, they act as a cationic surfactant. In addition, when present together with an anionic surfactant, for example, with polyoxyethylene alkyl ether sulfate, they form molecular association complexes shown below and neutralize the anionic charge of the surfactant,



wherein R_7 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, n has an average value of 1 to 7, and R_1 , R_2 , and R_3 have the same meanings as defined above.

The neutralization of the anionic charge decreases the electrical repellent force between the surfactant molecules which form the micelles, making the formation of the micelles easier. This, in turn, lowers the critical micelle concentration (CMC) and increases the number of the association. As a result, lathering takes place at a lower concentration, and oil solubilizing capability as well as oil emulsifying capability increase. The detergency is also promoted.

If the above-mentioned properties of tertiary amine oxides are considered, it can be predicted that the formation of a molecular association complex by a tertiary amine oxide and an anionic surfactant is promoted when the pH of the detergent compositions is adjusted to an acidic range. This would contribute to an even better performances of detergent compositions.

However, because of strong molecular association complexes in an acidic pH range, a detergent composition becomes remarkably viscous and unstable at a low temperature, and tends to produce liquid crystals. Particularly, at a low temperature, formation of a liquid crystal phase makes the composition turbid, thus making it difficult to obtain a clear, stable liquid detergent. Another problem of acidic compositions is that the detergent power towards oily dirt can be promoted only at the

sacrifice of the foaming ability, since the detergent compositions become hydrophobic in an acidic pH range.

In general, in order to ensure easy handling when taking out of the container, the viscosity of a liquid detergent has to be adjusted to a value of about 100 to 500 cp. In addition, in order for a detergent composition to be stable in winter time, its outward appearance must be kept unchanged at a temperature as low as -5°C. Because of this, hydrotropic agents such as lower alcohols, e.g. ethanol, lower alkylbenzene sulfonates, e.g. p-toluene sulfonate, glycols, e.g. ethylene glycol, propylene glycol, urea, are used individually or in combination. These hydrotropic agents, however, have only a slight effect in weakly acidic detergents, requiring the addition of a large amount. Even if low temperature stability is achieved, it is difficult to adjust the viscosity of the product to an appropriate value. The decrease in foaming capability can not be resolved only by addition of a hydrotropic agent.

In view of this situation, the present inventors have undertaken extensive studies in order to obtain a liquid detergent which has low temperature stability even in a weakly acidic pH range, as well as excellent foaming capability, and found that by adding a specific polypropylene oxide adduct of polyvalent alcohol and a specific sulfo-betaine to a composition including anionic surfactants and tertiary amine oxides, a proper degree of

viscosity and an excellent stability at low temperature could be obtained. It has been also found that such a formulation could bring about unexpected result in exhibiting remarkable increase in foaming effect even in weakly acidic conditions. These findings have led to the completion of this invention.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a liquid detergent composition having a pH of 4.0 to 6.0 and comprising:

(A) 10 to 40% by weight of at least one anionic surfactant selected from polyoxyethylene alkyl ether sulfate, alkylbenzene sulfonate, α -olefin sulfonate, alkane sulfonate, and polyoxyethylene alkyl ether carboxylate,

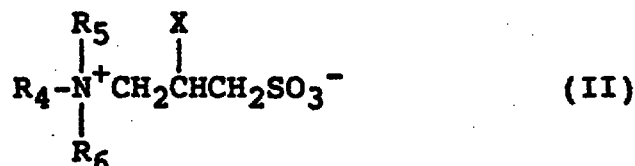
(B) 0.5 to 10% by weight of tertiary amine oxide represented by the following formula (I),



wherein R_1 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, and R_2 and R_3 independently represent an alkyl group having 1 to 2 carbon atoms,

(C) 0.5 to 10% by weight of a propylene oxide adduct of polyhydric alcohol having an average molecular weight of 300 to 4000, and

(D) 0.5 to 10% by weight of sulfo-betaine represented by the following formula (II),



wherein R_4 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, R_5 and R_6 independently represent an alkyl group having 1 to 2 carbon atoms, and X represents a hydroxide group or a hydrogen atom, and in which the molar ratio of component (B) to component (A) $[(\text{B})/(\text{A})]$ is in the range of 0.1 to 1.0.

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

As the anionic surfactant, component (A) of the present invention, one or more types of anionic surfactants selected from the following anionic surfactants can be used: polyoxyethylene alkyl ether sulfates, alkylbenzene sulfonates, α -olefin sulfonates, alkane sulfonates and polyoxyethylene alkyl ether carboxylates.

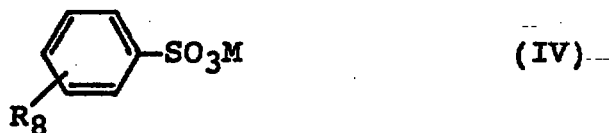
Among these compounds, polyoxyethylene alkyl ether sulfates are desirable because of their mildness to the skin. In particular, sulfates having the formula (III)

below are preferable.



wherein R_7 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, M is an alkali metal, ammonium, or alkanolamine, and n has an average value of 1 to 7. If the R_7 carbon number is less than 10, the performance of the detergent is inadequate, while if the carbon number is greater than 18, the low temperature stability of the compositions deteriorates remarkably. An especially desirable range for the number of carbons is 12 to 14. If the added molar number n for ethylene oxide in formula (III) is less than 1, skin irritability increases, while if the number is greater than 7, the detergent capability of the composition deteriorates remarkably. An especially preferable range for the added molar number for ethylene oxide is between 2 and 5.

On the other hand, in view of the detergency and the cost performance, alkylbenzene sulfonates shown of the following formula (IV) is desirable.



wherein R_8 represents an alkyl group having 10 to 16 carbon atoms and M has the same meaning as previously defined. If the R_8 carbon number is less than 10, the detergency is insufficient, while if it is greater than 16, the stability

of the compositions at a low temperature decreases remarkably. For these reasons these carbon numbers are not desirable. An especially desirable range for the number of carbons is 11 to 13.

The content of component (A) in the present invention is in the range of 10 to 40% by weight. If the content is below 10% by weight, the detergent power and foaming capability are insufficient, while if the content is above 40% by weight, the stability of the compositions deteriorates. Particularly desirable content range is 15 to 25% by weight.

The tertiary amine oxide, component (B) of the present invention, is a mono linear tertiary amine oxide as shown in formula (I). If the carbon number of R_1 is less than 10, the detergent efficiency of the compositions is low, while if the carbon number exceeds 18, the stability of the compositions at a low temperature deteriorates remarkably. A particularly desirable range for the carbon number is between 12 and 14. It is essential that the content of this mono linear tertiary amine oxide be 0.5 to 10% by weight of the detergent compositions. If the content deviates from this range, the combined use of component (C) with component (A) results in a decrease in detergent power or a loss of stability. The most desirable content range is from 1.5 to 5% by weight.

Component (C) of the compositions of the present invention is a polypropylene oxide adduct of polyhydric alcohol. Given as preferable examples of polyhydric

alcohols are bivalent alcohols such as ethylene glycol, propylene glycol, neopentyl glycol; and tri- or higher polyhydric alcohols such as glycerin, polyglycerin, trimethylolpropane, pentaerythritol, sorbitol.

Among these, polypropylene oxide adducts of ethylene glycol or polypropylene oxide adducts of glycerin are particularly desirable. These can be used alone or in combinations of 2 or more for component (C).

If component (C) is added to a weakly acidic detergent composition containing an anionic surfactant and a tertiary amine oxide, a remarkable decrease in viscosity and increase in low temperature stability are exhibited. In order to obtain this effect, however, the average molecular weight of the anionic surfactant must be 300 to 4,000, and more preferably 500 to 2,000. The decrease in viscosity and increase in low temperature stability is small outside this average molecular weight range. The content of component (C) in the composition is 0.5 to 10% by weight, with a preferable range being 2 to 5% by weight.

Sulfo-betaine represented by formula (II), which is component (D) of the present invention, possesses the effect of improving the low temperature stability, and in particular, the effect of preventing the composition from becoming turbid or being separated due to liquid crystal formation, when the liquid detergent containing an anionic surfactant and tertiary amine oxide is used in weakly acidic conditions. If the carbon number of R_4 is less than 10, the

compound exhibits only a small effect on preventing the formation of liquid crystals in the composition at low temperature. If the carbon number exceeds 18, the solubility of sulfo-betaine itself decreases remarkably, with the result being that a clear or transparent composition can not be obtained. The number of carbons between 12 and 14 is especially preferable.

It is necessary that component (D) be contained in the detergent composition in an amount of 0.5 to 10% by weight. This is because if the content is less than 0.5% by weight, the effect of improving low temperature stability to obstruct crystal formation in the compositions is small. On the other hand, the content greater than 10% by weight exceeds the maximum amount of the component dissolvable in the composition, resulting in deterioration of the stability of the solution. A preferable range for the content is 1 to 5% by weight.

Weakly acidic liquid detergents using an anionic surfactant together with a tertiary amine oxide readily form liquid crystals due to a strong interaction between the anionic surfactant and the tertiary amine oxide. Since this tendency is particularly strong at a low temperature, the compositions easily become turbid and dissociated by the crystal formation in cold areas.

Conventionally known hydrotropic agents, including lower alcohols such as ethanol, and lower alkyl benzene sulfonates such as p-toluene sulfonate, show virtually no effect on preventing the composition from

becoming turbid and dissociated due to crystal formation. Even though polypropylene oxide adduct of polyhydric alcohol used in the present invention as component (C) also has the effect of increasing low temperature stability, its independent use in the systems in which crystal formation is seen does not have a sufficient effect.

Although sulfo-betaine, component (D) of the present invention, did have the effect of preventing the composition from becoming turbid and dissociated by liquid crystal formation of weakly acidic liquid detergent compositions comprising an anionic surfactant and a tertiary amine oxide, a sufficient result at a temperature of -5°C or below was obtained only by formulating a relatively large amount of this component when used independently. Formulating too much sulfo-betaine results in a drastic increase in the viscosity of the composition. Sometimes the amount to be formulated exceeds the amount of sulfo-betaine soluble in the detergent. These factors very frequently damaged the commercial value of the product.

In the present invention, a polypropylene oxide adduct of polyhydric alcohol works synergistically with sulfo-betaine in a surfactant mixture system containing anionic surfactants, tertiary amine oxides, and sulfo-betaine. The synergistic action reduces the amount of sulfo-betaine necessary to prevent the formation of crystals. In addition, the polypropylene oxide adduct of polyhydric alcohol functions as a very effective solubilizing agent and

viscosity reducing agent, and can produce transparent detergent which possesses a moderate degree of viscosity. Further, a surprising fact is that when the polyvalent alcohol polypropylene oxide adduct is used in conjunction with sulfo-betaine, the foaming ability even in the weakly acidic range increases remarkably, producing abundant foam.

In the liquid detergent compositions of the present invention, anionic surfactant of component (A) and tertiary amine oxide of component (B), as mentioned above, form a strong molecular association complex. The mixing ratio of component (A) to component (B) in the compositions has a great influence on the detergent performance. In the present invention, the molar ratio (B)/(A) of component (A) to component (B) is 0.1 to 1.0, with values from 0.2 to 0.5 being particularly desirable. If the molar ratio is less than 0.1, virtually no detergent capability is obtained in acidic conditions. On the other hand, if the molar ratio is greater than 1.0, the number of molecules of tertiary amine oxide which are free and do not form association complexes with anionic surfactants increases. Such free molecules of tertiary amine oxide are cationized and impart increased irritating feelings to the skin.

A special feature of the liquid detergent compositions of the present invention is that their pH is in an weakly acidic range of 4.0 to 6.0. If the pH is less than 4.0, the stability of the compositions deteriorates remarkably, while over pH 6.0 the detergent power toward oily dirt decreases. Acids that can be used to produce weakly acidic conditions

include organic acids such as citric acid, malic acid, acetic acid, and the like, as well as inorganic acids such as sulfuric acid, hydrochloric acid, and the like.

In the compositions of the present invention, in addition to the essential components described above, it is possible to formulate known surfactants for liquid detergent use inasmuch as they do not bring about a loss of the desired performance. Given as preferable examples of surfactants are nonionic surfactants such as polyoxyethylene (average added molar number: 4 to 20) alkyl ($C_8 - C_{18}$ linear or branched) ether, higher fatty acids ($C_8 - C_{18}$) alkanol amide, and the like; and anionic surfactants such as α -sulfo-fatty acid esters, N-acyl glutamate, monoalkyl phosphate, and the like.

Furthermore, other components commonly used for liquid detergent compositions can also be used, for example, lower alcohols such as ethanol; lower alkylbenzene sulfonates such as p-toluene sulfonate; glycols such as ethylene glycol, propylene glycol; hydrotropic agents such as urea; organic and inorganic builders, natural juices such as lemon and lime, skin protecting agents, enzymes, protein derivatives, pigments, perfumes and aromatics, and preservatives.

Other features of the invention will become apparent in the course of the following description of the exemplary embodiments which are given for illustration of the

invention and are not intended to be limiting thereof.

EXAMPLES

Example 1

The compositions shown in Table 1 were prepared and the detergent power, foaming capability, viscosity and low temperature stability were examined for each composition. Each test was carried out as follows.

<Detergent power>

Sudan III (red color) as an indicator was added to beef tallow in an amount of 0.1% by weight of the beef tallow. Five (5) grams of this mixture was applied to a porcelain dish (diameter: 25 cm) and 30 g of a detergent solution a 10% by weight concentration soaked into a sponge was used to scour and wash the dish. Detergent power was determined by counting the number of dishes washed until the beef tallow could no longer be removed.

<Foaming ability>

Commonly available butter was used as the dirty component. Foaming capability was determined when butter at 0.1% by weight was added to a detergent solution with a detergent concentration of 0.5% by weight. The measurement method consisted of placing the detergent solution described above, to which butter had been added in a 5 cm diameter glass cylinder, and then agitating with rotation for 5 minutes. After stopping the agitating/rotating, the height of the lather was measured.

<Stability at low temperature>

Stability at a low temperature was evaluated by storing the liquid detergent at -5°C for 10 days in a thermostat:

Evaluation

AAA : no change in outward appearance

BBB : somewhat cloudy

CCC : dissociation or precipitation

<Viscosity>

The viscosity of each composition was determined by placing a composition in a viscosity beaker which was maintained at 20°C and then measuring using a B-type viscosimeter [rotor No.3, (rotor No. 4 when the viscosity is more than 2000 cp); 60 rpm)].

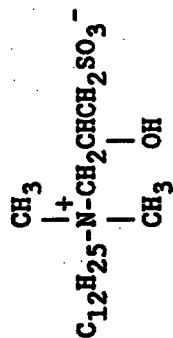
Table 1

Component	Inventive composition				5	Comparative composition					
	1	2	3	4		6	7	8	9	10	
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	
Sodium polyoxyethylene(3) dodecylether sulfate	20.0	10.0	10.0	10.0	-	20.0	10.0	10.0	10.0	-	
Sodium dodecylbenzene sulfonate	-	10.0	-	-	-	-	10.0	-	-	-	
Sodium α -olefin sulfonate (MW = 326)	-	-	10.0	-	-	-	-	10.0	-	-	
Sodium octadecane sulfonate (MW = 356)	-	-	-	10.0	-	-	-	-	10.0	-	
Sodium polyoxyethylene(3) dodecylether Carboxyrate	-	-	-	-	20.0	-	-	-	-	20.0	
Dodecyl dimethyl amine oxide	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
PPG-2000 (triol type) #1	2.0	2.0	2.0	2.0	2.0	-	-	2.0	-	-	
Dodecyl hydroxy sulfo-betaine #2	2.0	2.0	2.0	2.0	2.0	-	2.0	-	-	-	
Ethanol	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
Tap water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	
Viscosity (raw solution/20°C)	200	180	150	120	200	2,500	1,950	80	840	2,180	
pH (raw solution/25°C)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	
Foaming capability (mm)	95	98	95	95	98	55	85	65	95	98	
Low temperature stability	AAA	AAA	AAA	AAA	AAA	CCC	BBB	CCC	CCC	CCC	

Note: Unit of the value in Table is % by weight

#1: Propylene oxide adduct of glycerin (MW = 2000)

#2 Formula:

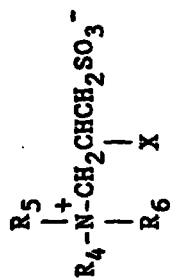


Example 2

Compositions comprising basic detergent components shown below plus sulfo-betaines or polypropylene oxide adducts of polyvalent alcohol listed in Table 2 were prepared, and the viscosity, foaming capability and low temperature stability were examined. The results of the tests are shown in Table 2.

components combined	combination ratio (% by weight)
Sodium polyoxyethylene (4) dodecyl ether sulfate	18.0
Dodecyldimethyl amine oxide	4.0
Sulfo-betaine (see Table 2)	0 or 2.0
Propylene oxide adduct of polyvalent alcohol (see Table 2)	0 or 2.0
Ethanol	4.0
Tap water	Balance
pH (raw solution/25°C)	5.5

Table 2



		Inventive composition				Comparative composition				
		11	12	13	14	15	16	17	18	19
R ₄	C ₁₀ H ₂₁	C ₁₂ H ₂₅	C ₁₄ H ₂₉	C ₁₈ H ₃₄	C ₈ H ₁₇	C ₂₀ H ₄₁	C ₁₂ H ₂₅	C ₁₂ H ₂₅	-	-
R ₅	C ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅	CH ₃	CH ₃	CH ₃	-
R ₆	C ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅	CH ₃	CH ₃	CH ₃	-
X	H	OH	H	OH	OH	H	OH	OH	OH	-
Molecular weight	*1	1,000	1,000	1,000	1,000	1,000	1,000	10,000	250	-
Viscosity of raw solution at 20°C		100	140	180	250	100	450	1,800	980	1,450
Foaming capability (mm)	90	98	92	90	75	70	70	70	75	68
Low temperature stability	AAA	AAA	AAA	AAA	CCC	CCC	CCC	BBB	BBB	CCC

*1: Molecular weight of polypropylene oxide adduct of ethylene glycol

Example 3

The compositions shown in Table 3 were prepared and the detergent power, foaming capability, viscosity and low temperature stability were examined.

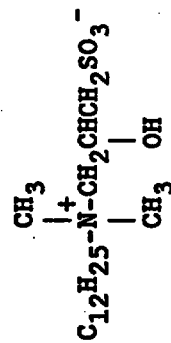
Table 3

Component	inventive composition			Comparative composition		
	20	21	22	23	24	25
	WtZ	WtZ	WtZ	WtZ	WtZ	WtZ
(A) Sodium polyoxyethylene(3) tetradecylether sulfate (MW=448)	18.0	18.0	18.0	18.0	18.0	18.0
(B) Dodecyltrimethylamine oxide (MW=229)	2.0	4.0	6.0	0.4	11.0	2.0
PPG-2000 (triol type) *1	2.0	2.0	3.0	2.0	2.0	2.0
Dodecylhydroxy sulfo-betaine *2	2.0	2.0	3.0	2.0	2.0	0.2
Ethanol	4.0	4.0	4.0	4.0	4.0	4.0
Tap water	Balance	Balance	Balance	Balance	Balance	Balance
pH (raw solution/25°C)	5.5	5.5	5.5	5.5	5.5	5.5
(B)/(A) (molar ratio)	0.22	0.43	0.65	0.04	1.20	0.22
Viscosity (raw solution/20°C)	150	250	300	50	400	150
Detergent power (numbers of sheet)	6	7	8	1	8	6
Foam height (mm)	95	98	100	21	1,200	95
Low temperature stability	AAA	AAA	AAA	AAA	CCC	CCC

Note: Unit of the value in Table is % by weight

*1: Propylene oxide adduct of glycerin (MW = 2,000)

*2 Formula:



The liquid detergent compositions of the present invention possess excellent detergent power and abundant foaming capability. They are very stable at a low temperature. Therefore, they are useful as a kitchen cleanser, particularly as a dish-washing detergent.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.



CLAIMS:

1. A liquid detergent composition having a pH of 4.0 to 6.0 and comprising:

(A) 10 to 40% by weight of at least one anionic surfactant selected from polyoxyethylene alkyl ether sulfate, alkylbenzene sulfonate, α -olefin sulfonate, alkane sulfonate, and polyoxyethylene alkyl ether carboxylate,

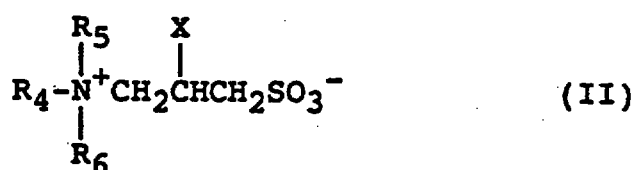
(B) 0.5 to 10% by weight of tertiary amine oxide represented by the following formula (I),



wherein R_1 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, and R_2 and R_3 independently represent an alkyl group having 1 to 2 carbon atoms,

(C) 0.5 to 10% by weight of a propylene oxide adduct of polyhydric alcohol having an average molecular weight of 300 to 4000, and

(D) 0.5 to 10% by weight of sulfo-betaine represented by the following formula (II),





wherein R_4 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, R_5 and R_6 independently represent an alkyl group having 1 to 2 carbon atoms, and X represents a hydroxide group or a hydrogen atom, and in which the molar ratio of component (B) to component (A) $[(B)/(A)]$ is in the range of 0.1 to 1.0.

2. The liquid detergent composition according to Claim 1, wherein component (A) is a polyoxyethylene alkyl ether sulfate having the following formula (III),



wherein R_7 represents an alkyl or alkenyl group having 10 to 18 carbon atoms, M is an alkali metal, ammonium, or alkanolamine, and n has an average value of 1 to 7.

3. The liquid detergent composition according to Claim 1, wherein component (A) is an alkylbenzene sulfonate having the following formula (IV),



wherein R_8 represents an alkyl group having 10 to 16 carbon atoms and M has the same meaning as defined above.

4. The liquid detergent composition according to Claim 1, wherein said polypropylene oxide adduct of polyvalent alcohol which is component (C), is polypropylene oxide adduct of ethylene glycol or glycerin.



5. A composition as claimed in Claim 1 and substantially as described in the Examples.
