

LIQUID DETERGENT COMPOSITION

The present invention relates to a liquid detergent composition, and more particularly, to an improvement of the liquid detergent composition containing an ethoxylated alkyl sulfate as an surface active ingredient. The improved liquid detergent composition forms neither film nor gel, keeping its fluidity, even when it is left exposed to the air.

A variety of anionic surfactants are presently used as an active ingredient of liquid detergent compositions. Among such anionic surfactants, an alkali metal salt or alkaline earth metal salt of ethoxylated alkyl sulfate is generally used because it has good detergency and does not discolor unlike alkanolamine salts.

However, above mentioned ethoxylated alkyl sulfate salt has a disadvantage that where it is used as

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an active ingredient of a liquid detergent composition, it forms film on the liquid surface and moreover forms gel in the liquid as water evaporates when the liquid detergent composition is left in contact with air. The
5 film formation and gelation lose the commercial value of the liquid detergent during use by consumers because they occur when the liquid detergent composition is left in an unclosed container or a measuring cup. They also interfere with quality control in the manufacturing
10 process.

These disadvantages are noticeable particularly in the case of liquid detergent composition which comprises 15 to 70 wt% of surface active ingredients in total and 5 wt% or more of alkali metal
15 salt or alkaline earth metal salt of ethoxylated alkyl sulfate.

In order to overcome these disadvantages, there have been proposed a variety of improvements. For example, Japanese Patent Application Laid-open No.
20 92809/1978 discloses a liquid detergent composition incorporated with polyethylene glycol and a water-soluble inorganic salt for the prevention of film formation. Japanese Patent Application Laid-open No. 36596/1981 discloses a liquid detergent composition

incorporated with polyalkylene ether glycol and a water-soluble salt of mono- and/or disulfate of polyalkylene ether glycol for the improvement in fluidity of concentrated aqueous solutions of surfactant.

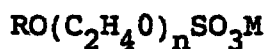
Whereas the incorporation of additional components is successful to some extent in achieving the object, it has a drawback of deteriorating the foaming performance and rinsing performance which are important factors of detergents.

It is an object of the present invention to provide a liquid detergent composition which solves the above-mentioned problems which does not form film nor gel, keeping a good fluidity, and yet has a superior foaming and rinsing performance and an improved stability.

According to the present invention there is provided a liquid detergent composition which comprises an ethoxylated alkyl sulfate of the following formula (I)

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(I)

5 wherein R represents a straight-chain or branched-chain alkyl group having 7 to 18 carbon atoms, n represents a numeral of 1 to 5 on average, and M represents an alkali metal or alkaline earth metal, and 0.3 to 10 wt% of a sulfate of an adduct (having an average molecular weight of 300 to 5000) of polyalkylene oxide with neopentyl glycol or a polyhydric alcohol having three or more hydroxyl groups.

10 This compound of formula I decreases in solubility toward water as a number of carbon atoms in the alkyl group (R) increases, and it also becomes poor in foaming performance as the ~~average~~ number (n) of moles of ethylene oxide added increases. Therefore
15 in accordance with the invention the ethoxylated alkyl sulfates have an alkyl group of 7 to 18 carbon atoms and have an average addition number of ethylene oxide of 1 to 5.

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The ethoxylated alkyl sulfate represented by the formula (I) may be incorporated in an amount of 5 to 60 wt% in the composition.

5 In the liquid detergent composition of this invention, the ethoxylated alkyl sulfate is used in combination with a sulfate of an adduct of polyalkylene oxide with neopentyl glycol or a polyhydric alcohol having three or more hydroxyl groups (these alcohols may be collectively called a polyhydric alcohol

10 hereinafter). The adduct of polyalkylene oxide with a polyhydric alcohol has an average molecular weight of 300 to 5000. Outside this range, the adduct does not produce the effect of this invention. Preferred

15 examples of the polyhydric alcohol having three or more hydroxyl groups include glycerin, polyglycerin, trimethylolpropane, pentaerythritol, and sorbitol. The polyalkylene oxide may preferably be one which is formed by the addition polymerization of ethylene oxide (EO) or propylene oxide (PO) or both. The addition of PO and EO

20 may be performed randomly or in blocks.

The sulfate of an adduct of polyalkylene oxide with a polyhydric alcohol can be produced by conventional method (as disclosed in, for example, Japanese Patent Application Laid-open No. 5796/1982).

Preferred examples of the sulfate include alkali metal salts, alkaline earth metal salts, alkanolamine salts, and ammonium salts thereof. Particularly preferable among them are alkali metal salts and alkaline earth metal salts. These salts may be used individually or in combination with one another. For the sulfate to produce the intended effect, the number of sulfate groups are preferably 4 or less in one molecule, although the sulfate can have as many sulfate groups as the number of hydroxyl groups in the polyhydric alcohol.

The sulfate of an adduct of polyalkylene oxide with a polyhydric alcohol ^{is} ~~may~~ be incorporated in an amount of 0.3 to 10 wt% in the composition. Less than 0.3 wt%, it does not produce the effect of this invention. On the other hand, the composition containing more than 10 wt% is poor in foaming performance.

The liquid detergent composition of this invention may be incorporated, in addition to the above-mentioned essential ingredients, with any known surfactants according to need for the improvement of detergency and foaming performance. The surfactants include nonionic surfactants such as polyoxyethylene (average number of moles added: 4 to 20) alkyl (C₇-C₁₈

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straight-chain or branched chain) ether, mono- or dialkanol (C₂-C₃) amide, and alkyl (C₈-C₂₀) dimethylamine oxide; anionic surfactants such as α-olefin (C₈-C₂₀) sulfonate [Na, K, Mg, triethanolamine (TEA), NH₄], α-sulfofatty acid ester (R₁-CHOO₃M, R₁: C₈-C₁₈, R₂: C₁-C₄, M: alkali metal), N-acyl (C₈-C₁₈) glutamate (Na, K, TEA), monoalkyl (C₈-C₁₈) phosphate (Na, K, TEA, arginine), and straight-chain alkyl (C₁₀-C₁₈) benzenesulfonate (Na, K, Mg); and amphoteric surfactants such as alkyl betaines.

These additional surfactants may be incorporated in such an amount that the total amount of the ethoxylated alkyl sulfate which is an essential ingredient of the invention and the additional surfactant(s) is 15 to 70 wt% in the composition.

The liquid detergent composition of this invention may be incorporated further with a lower alcohol (C₁-C₃) and lower arylsulfonate as a viscosity depressant and low-temperature stabilizer, a benzoate as an antifungal substance, EDTA as a chelating agent, an alkali metal citrate as an antidiscoloration agent, a dye, and a perfume, according to need.

As detailed above, the present invention is designed to prevent an ethoxylated alkyl sulfate ester from forming film and gel by adding a sulfate of an adduct of polyalkylene oxide with a polyhydric alcohol.

5 This effect is not yet theoretically elucidated; however, the following inference is made. Upon evaporation of water, the liquid detergent composition becomes concentrated, forming film on the liquid surface. This film is considered to be an ethoxylated
10 alkyl ester salt of higher order structure (so-called lamellar type liquid crystal). As the concentration proceeds further, the liquid detergent composition becomes less fluid as a whole, and finally gelation takes place. The sulfate of an adduct of polyalkylene
15 oxide with a polyhydric alcohol has a molecular structure that permits the sulfate molecule to enter the body of high order structure. Thus the sulfate molecule destroys the high order structure on account of its high affinity for water.

20 According to this invention, it is possible to prevent liquid detergent compositions containing an ethoxylated alkyl sulfate as an active ingredient from forming film and gel, without deteriorating the detergent's performance such as foaming, rinsing, and
25 stability.

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The invention is now illustrated by examples.

The following test methods were used for the evaluation of performance in the examples.

(1) Film formation

5 20 ml of the liquid detergent composition is placed in a 30-ml sample beaker, and it is allowed to stand at 20°C, 60 %RH for 3 days. The film formation is evaluated according to the following criteria.

- A: No film is formed on the liquid surface.
- 10 B: Film is formed partly on the liquid surface.
- C: Thin film is formed entirely on the liquid surface.
- D: Thick film is formed entirely on the liquid surface.

(2) Gelation

15 The sample used for the film formation test is allowed to stand for additional 7 days under the same conditions. The fluidity of the composition is visually observed and the degree of gelation is rated according to the following criteria.

- 20 A: Extremely fluid without gelation taking place at all.
- B: Considerably fluid despite slight gelation.
- C: Slightly fluid with considerable gelation.
- D: Not fluid at all due to almost entire gelation.

(3) Foaming

A 0.5% detergent solution containing 0.1% of commercial butter as an artificial soil is examined for foaming as follows: 40 ml of the sample solution is placed in a glass cylinder, 5 cm in diameter. The sample solution is stirred for 10 minutes. The foam height is measured without delay.

(4) Low-temperature stability

The sample is stored in a constant temperature room at -5°C for 10 days, and the appearance is evaluated according to the following criteria.

<u>Rating</u>	<u>Criteria</u>
o	: No change
Δ	: Slightly opaque
x	: Separation or precipitation

Example 1

Detergent compositions were prepared each containing a different sulfate of an adduct of EO or PO with a polyhydric alcohol as shown in Table 1. The liquid detergent compositions were examined for film formation, gelation, and foaming. The results are shown in Table 1.

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The symbols used in Table 1 and subsequent tables stand for the following compounds. The parenthesized number that follows the symbol denotes the average molecular weight of the adduct of EO or PO with a polyhydric alcohol.

	PEG-DS (Na)	: Disulfate of polyethylene glycol (Na salt)
	PPG-DS (Na)	: Disulfate of polypropylene glycol (Na salt)
10	GLY-EO-MS (Na):	Monosulfate of the adduct of EO with glycerin (Na salt)
	GLY-EO-DS (Na):	Disulfate of the adduct of EO with glycerin (Na salt)
15	GLY-EO-TS (Na):	Trisulfate of the adduct of EO with glycerin (Na salt)
	GLY-PO-TS (K) :	Trisulfate of the adduct of PO with glycerin (K salt)
	TGL-EO-TS (Na):	Trisulfate of the adduct of EO with triglycerin (Na salt)
20	TMP-EO-TS (Na):	Trisulfate of the adduct of EO with trimethylolpropane (Na salt)
	PET-EO-TeS (Na):	Tetrasulfate of the adduct of EO with pentaerythritol (Na salt)
25	SOB-EO-TS (Na):	Trisulfate of the adduct of EO with sorbitol (Na salt)
	NPG-EO-DS (Na):	Disulfate of the adduct of EO with neopentyl glycol (Na salt)

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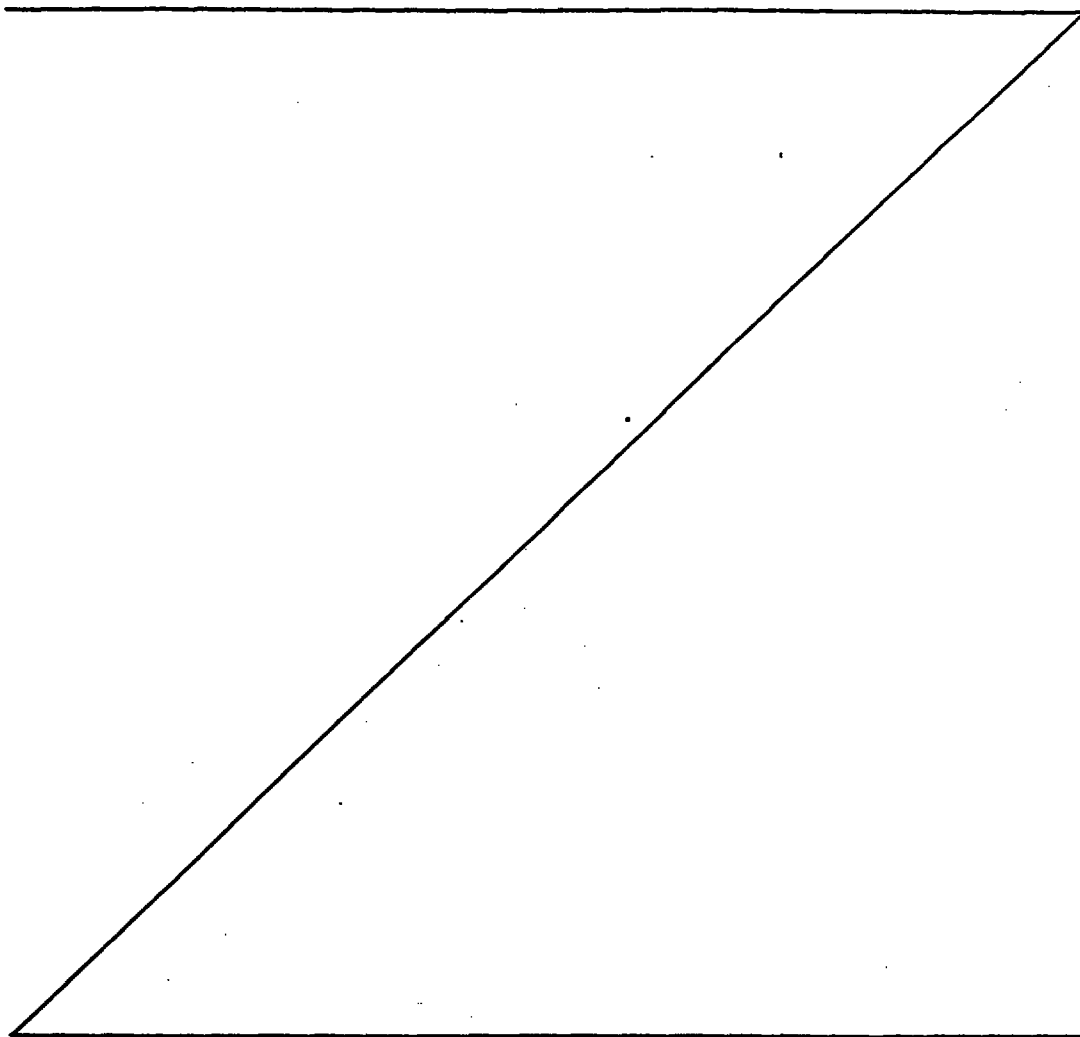
Table 1

Composition No. Components	Inventive Products										Comparative Products				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sodium polyoxyethylene (3 mol) dodecyl sulfate	25	25	25	25	25	25	25	25	25	25	15	20	25	25	25
PEG-DS (Na) (1500)													2		
PPG-DS (Na) (1500)															
GLY-EO-MS (Na) (1500)	0.5	2			1										
GLY-EO-DS (Na) (1500)			2												12
GLY-EO-TS (Na) (1500)				2	1										
GLY-PO-TS (K) (1500)						2									
TGL-EO-TS (Na) (1500)							2								
TMP-EO-TS (Na) (1500)								2							
PET-EO-TeS (Na) (1500)									1						
SOB-EO-TS (Na) (1500)									1	2					
NPG-EO-DS (Na) (1500)															
Water	balance	→	→	→	→	→	→	→	→	→	→	→	→	→	→
Film formation	A	A	A	A	A	A	A	A	A	A	B	D	B	B	A
Gelation	A	A	A	A	A	A	A	A	A	A	C	D	B	B	A
Foaming (mm)	85	90	87	90	85	85	87	85	85	90	56	65	75	73	47

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Example 2

Detergent compositions were prepared each containing a different sulfate of the adduct of EO with trimethylolpropane as shown in Table 2. The liquid
5 detergent compositions were examined for film formation, gelation, foaming, and low temperature stability. The results are shown in Table 2.



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Table 2

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Components	Composition No.		Inventive Products				Comparative Products	
	1 5	1 6	1 7	1 8	1 9	2 0		
Sodium polyoxyethylene (4 mol) dodecyl sulfate	2 5	2 5	2 5	2 5	2 5	2 5	2 5	2 5
TMP-EO-TS (Na) (250)	2	2	2	2	2	2	2	2
TMP-EO-TS (Na) (500)								
TMP-EO-TS (Na) (1000)								
TMP-EO-TS (Na) (3000)								
TMP-EO-TS (Na) (5000)								
TMP-EO-TS (Na) (7000)								
Water	balance	balance	balance	balance	balance	balance	balance	balance
Film formation	A	A	A	A	C	C		
Gelation	A	A	A	A	D	D		
Foaming (mm)	8 8	9 2	8 5	8 2	8 0	7 0		
Low-temperature stability	○	○	○	○	○	△		

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Example 3

Detergent compositions were prepared each containing a different sulfate of an adduct of PO/EO with a polyhydric alcohol as shown in Table 3. The liquid detergent compositions were examined for film formation, gelation, foaming, and low-temperature stability. The results are shown Table 3.

The symbols in Table 3 and subsequent tables stand for the following compounds. The parenthesized number that follows the symbol denotes the average molecular weight of the adduct of PO/EO with a polyhydric alcohol.

- GLY-PE-TS (Na): Trisulfate of the adduct of PO/EO with glycerin (Na salt)
- 15 TMP-PE-TS (Na): Trisulfate of the adduct of PO/EO with trimethylolpropane (Na salt)
- PET-PE-TS (Na): Trisulfate of the adduct of PO/EO with pentaerythritol (Na salt)
- 20 SOB-PE-TS (Na): Trisulfate of the adduct of PO/EO with sorbitol (Na salt)

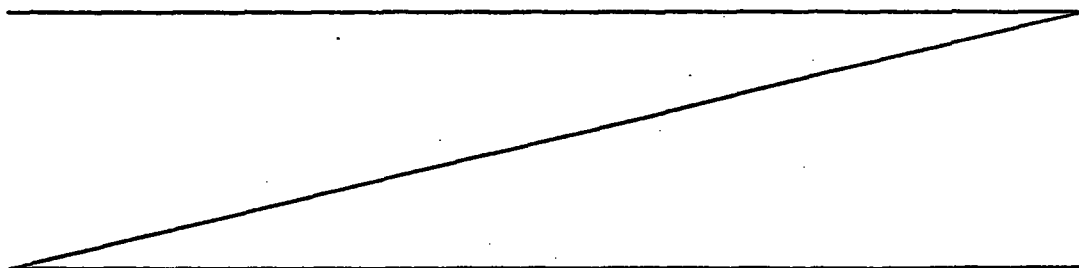


Table 3

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Composition No.		Inventive Products								Comparative Products	
Components		2 1	2 2	2 3	2 4	2 5	2 6	2 7	2 8		
Sodium polyoxyethylene (2 mol) dodecyl sulfate GLY-PE[0.5/0.5]-TS (Na) (200) GLY-PE[0.5/0.5]-TS (Na) (2000) GLY-PE[0.5/0.5]-TS (Na) (6000) GLY-PE[0.8/0.2]-TS (Na) (2000) GLY-PE[0.2/0.8]-TS (Na) (1500) TMP-PE[0.5/0.5]-TS (Na) (1000) PET-PE[0.5/0.5]-TS (Na) (500) SOB-PE[0.5/0.5]-TS (Na) (2000) Water		2 5	2 5	2 5	2 5	2 5	2 5	2 5	2 5		
		2						2			
			2						2		
				2							
					2						
						2					
							2				
	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	
Film formation		A	A	A	A	A	A	C	C		
Gelation		A	A	A	A	A	A	D	D		
Foaming (mm)		8 0	8 3	8 0	9 0	8 0	8 2	8 0	7 0		
Low-temperature stability		○	○	○	○	○	○	○	△		

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Example 4

Detergent compositions were prepared according to the formulation shown in Table 4. The liquid detergent compositions were examined for film formation, gelation, foaming, and low temperature stability. The results are shown Table 4.

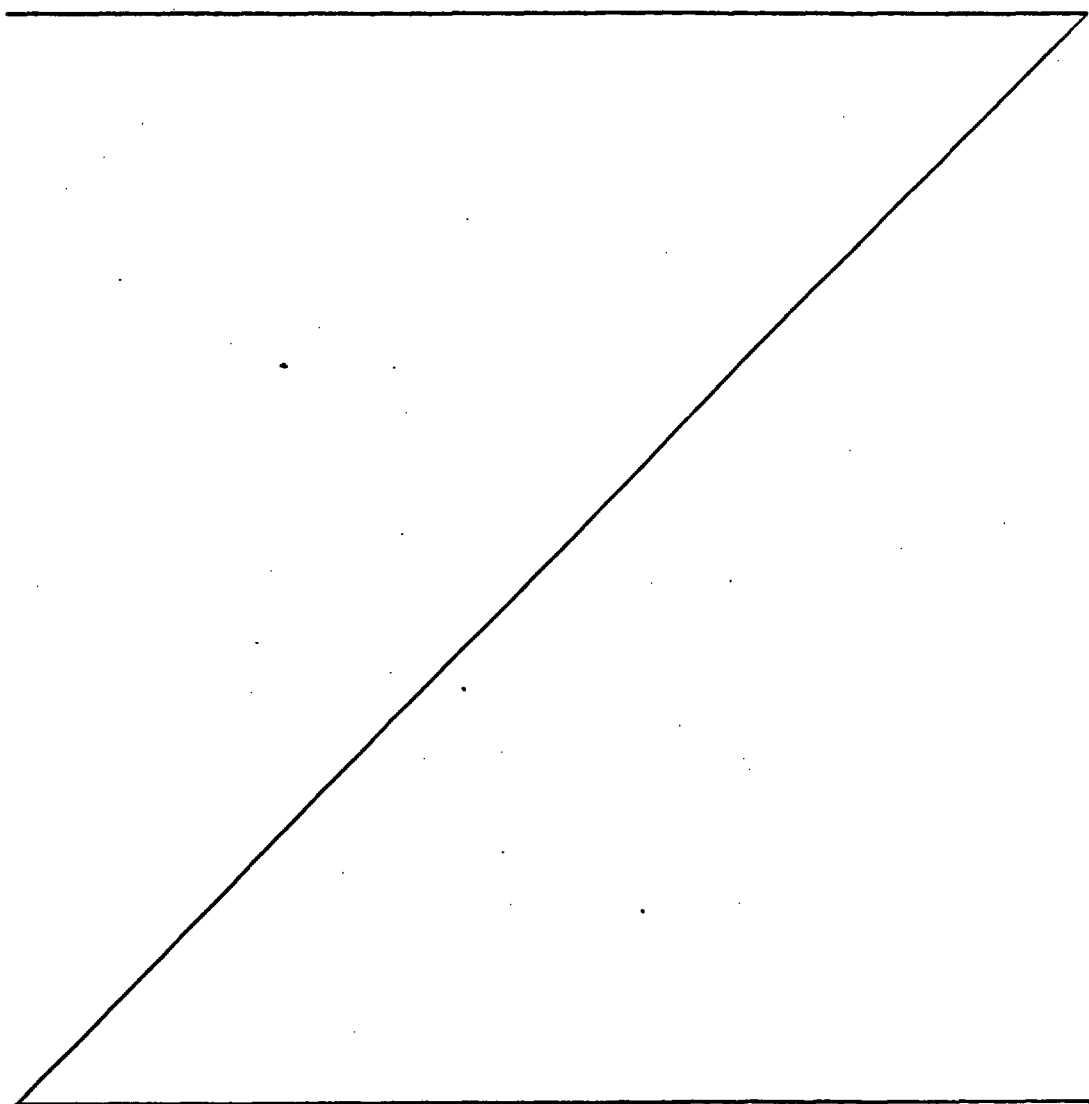


Table 4

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Components	Composition No.	Inventive Products									
		29	30	31	32	33	34	35	36		
Sodium polyoxyethylene (3 mol) alkylsulfate (C ₁₂ -C ₁₃ , ratio of straight chain: about 50%)			20	20	20	20	30	25	25		
Magnesium polyoxyethylene (4 mol) alkylsulfate (C ₁₂ -C ₁₃ , ratio of straight chain: about 75%)		15	5								
Sodium α -olefinsulfonate (average number of carbon atoms: 14)				5				5			
Sodium dodecyl benzenesulfonate					5						5
Sodium salt of methyl ester of α -sulfofatty acid (fatty acid: coconut oil fatty acid)						5					
Dodecyl dimethylamine oxide		0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2		0.2
Coconut oil fatty acid diethanolamide							3	3	3		3
Ethanol							3	3	3		3
GLY-PE[0.5/0.5]-TS(Na) (1500)		1	1	1	1	1					
TMP-EO-TS(Na) (1500)							2	2	2		2
Water		balance	balance	balance	balance	balance	balance	balance	balance	balance	balance
Film formation		A	A	A	A	A	A	A	A	A	A
Gelation		A	A	A	A	A	A	A	A	A	A
Foaming (mm)		74	87	92	93	85	100	100	100	100	100
Low-temperature stability		○	○	○	○	○	○	○	○	○	○

Concluded

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CLAIMS

1. A liquid detergent composition which comprises an ethoxylated alkyl sulfate of the following the formula (I)



5 wherein R represents a straight-chain or branched-chain alkyl group having 7 to 18 carbon atoms, n represents a numeral of 1 to 5 on average, and M represents an alkali metal or alkaline earth metal, and 0.3 to 10 wt% of a sulfate of an adduct (having an average molecular weight
10 of 300 to 5000) of polyalkylene oxide with neopentyl glycol or a polyhydric alcohol having three or more hydroxyl groups.

2. A liquid detergent composition according to Claim 1, wherein the polyhydric alcohol having three
15 or more hydroxyl groups is selected from the group consisting of glycerin, polyglycerin, trimethylolpropane, pentaerythritol, and sorbitol.

3. A liquid detergent composition according to Claim 1, wherein the number of sulfate groups in
20 one molecule of the sulphate of an adduct of polyalkylene oxide with a



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polyhydric alcohol having three or more hydroxyl groups is 4 or less.

4. A liquid detergent composition according
5 to Claim 1, wherein the total amount of the
ethoxylated alkyl sulfate of formula (I) is 5 to 60
wt%.

5. A liquid detergent composition according
10 to Claim 1, wherein the total amount of all the
surface active ingredients is 15 to 70 wt%.

6. A liquid detergent composition according
to Claim 1 wherein the polyalkylene oxide is formed by
15 addition polymerization of ethylene oxide or propylene
oxide, either alone or in admixture.

7. A liquid detergent composition as claimed
in Claim 1 and substantially as described in the
20 Examples.
