(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 439 019 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91100209.5**

(51) Int. Cl.[5]: **C11D 1/66**, C11D 3/37

(22) Date of filing: **08.01.91**

(30) Priority: **10.01.90 JP 4224/90**

(43) Date of publication of application:
31.07.91 Bulletin 91/31

(84) Designated Contracting States:
DE ES FR GB

(71) Applicant: **KAO CORPORATION**
14-10, Nihonbashi Kayabacho 1-chome
Chuo-ku Tokyo(JP)

(72) Inventor: **Tagata, Shuji**
2834-119, Kamitomatsuricho
Utsunomiya-shi, Tochigi(JP)
Inventor: **Tajima, Tomoto**
2-6-23, Maruyama 1-chome
Tagajo-shi, Miyagi(JP)
Inventor: **Sai, Fumio**
4-39, Tenjin 2-chome
Utsunomiya-shi, Tochigi(JP)
Inventor: **Iwamoto, Yoshihiro**
1707, Ohaza Marusu, Kishigawacho
Naga-gun, Wakayama(JP)
Inventor: **Yanagisawa, Atsuko**
1754, Ohaza Shimotakanezawa, Hagamachi
Haga-gun, Tochigi(JP)

(74) Representative: **Patentanwälte Dr. Solf & Zapf**
Zeppelinstrasse 53
W-8000 München 80(DE)

(54) liquid detergent composition for clothes.

(57) The liquid detergent composition is effective to prevent felt from shrinking and is well rinsed. It comprises:
(a) 5 to 70% by weight of an alkyl glycoside and
(b) 0.05 to 5% by weight of an amino-modified silicone or a derivative thereof.

EP 0 439 019 A1

LIQUID DETERGENT COMPOSITION FOR CLOTHES

The present invention relates to a liquid detergent composition. In particular, the present invention relates to a light-duty liquid detergent composition having an excellent effect of preventing the shrinkage of clothes (effect of preventing felting shrinkage) and also a good rinsability.

[Prior Art]

Delicate clothes made of wool or silk are usually washed by hands or a weak mechanical power with a light-duty detergent so as to prevent the damage to them.

However, one often experiences that wool clothes particularly among these clothes are apt to be shrunk (or cause felting shrinkage) even when they are mildly rubbed or pressed in tepid water with meticulous care.

Conventional light-duty detergents of this type contain a polyoxyethylene alkyl ether, polyoxyethylene alkyl ether sulfate, alkylbenzenesulfonate, etc., as the main detergent base.

Recently, alkyl saccharide surfactants attract attention, since they little irritate the skin and have lathering properties and, therefore, are usable as the light-duty detergent base.

For example, Japanese Patent Laid-Open No. 501641/1988 discloses a detergent composition for delicate cloths which contains an alkyl glycoside and an antistatic quaternary ammonium surfactant, and Japanese Patent Laid-Open No. 501642/1988 describes that a detergent composition for delicate cloths which contains an alkyl glycoside and an antistatic amine oxide is capable of imparting antistatic properties superior to those imparted when an ordinary polyoxyethylene alkyl ether is used. Japanese Patent Laid-Open No. 69695/1989 discloses a detergent composition containing both of an alkyl glycoside and an amphoteric surfactant and Japanese Patent Publication No. 168613/1989 discloses another detergent composition containing both of an alkyl glycoside and a phosphoric ester surfactant, each composition having a good detergency, frothing or lathering power and foam release property. JP-A No. 25896/1984 describes that a detergent composition containing a nonionic surfactant having an HLB of 5 to 14, an alkyl glycoside and a di-(long-chain alkyl) quaternary ammonium salt is quite effective in removing stains in granular form and is capable of imparting softness and antistatic properties to the clothes.

However, the shrinkage of wool products cannot be suppressed even by using these detergents.

It is known that a light-duty detergent containing fine particles of a polymer latex having a cationic or tertiary amino group and a particle diameter of 0.005 to 0.2 μm had a remarkable effect of inhibiting the felting shrinkage (see Japanese Patent Laid-Open Nos. 8492/1988 and 89596/1988).

However, it is difficult to incorporate such a polymer latex into an alkyl glycoside detergent composition stably.

(Summary of the invention)

After intensive investigations made for the purpose of solving the above-described problems, the inventors have found that a detergent composition containing an alkyl glycoside and a specified silicone compound has an excellent effect of inhibiting the felting shrinkage, good frothing properties and improved rinsability. The present invention has been completed on the basis of this finding.

Thus the present invention provides a liquid detergent composition for clothes comprising:

(a) 5 to 70% by weight of an alkyl glycoside and

(b) 0.05 to 5% by weight of an amino-modified silicone or a derivative thereof.

The alkyl glycosides used as the component (a) in the present invention are preferably those represented by the following general formula (I):

$$R_1 (OR_2)_x G_y \quad (I)$$

in which R_1 represents a straight-chain or branched alkyl, alkenyl or alkylphenyl group having 8 to 18 carbon atoms, R_2 represents an alkylene group having 2 to 4 carbon atoms, G represents a residue of a reducing sugar having 5 or 6 carbon atoms, and $\underline{x}$ and $\underline{y}$ each represent an average number, $\underline{x}$ being 0 to 5 and $\underline{y}$ being 1 to 10.

From the viewpoints of the solubility, frothing properties and detergency, R_1 in the general formula (I) preferably has 9 to 14 carbon atoms. From the viewpoint of water solubility, R_2 has preferably 2 or 3 carbon atoms. The water solubility and crystallizability vary depending on the value of $\underline{x}$. The higher the value of x,

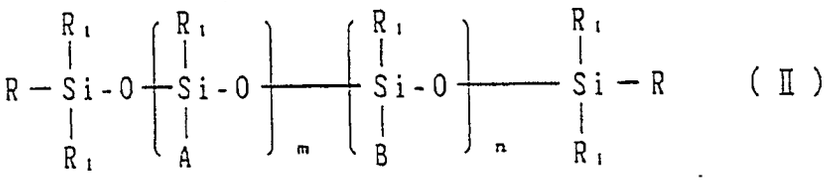
the higher the water solubility and the lower the crystallizability. x is preferably in the range of 0 to 2, particularly 0. y is preferably in the range of 1 to 4. y is desirably selected in consideration of the properties ascribable to the hydrophobic group R_1. For example, when R_1 is a hydrophobic group having 9 to 11 carbon atoms on the average, y is preferably 1 to 1.4, while when R_1 is a hydrophobic group having 12 to 14 carbon atoms, y is preferably 1.5 to 4.0. The average degree of polymerization, y, of the reducing sugar can be determined by proton NMR.

The bonds in the sugar chain may be 1-2, 1-3, 1-4 or 1-6 bond, α- or β-pyranoside bond or furanoside bond, or a combination of them.

The structure of G varies depending on the starting monosaccharide or polysaccharide. The monosaccharides include glucose, fructose, galactose, xylose, mannose, lyxose and arabinose. The polysaccharides include maltose, xylobiose, isomaltose, cellobiose, gentiobiose, lactose, sucrose, nigerose, turanose, raffinose, gentianose and melezitose. They can be used either alone or in combination of two or more of them. Glucose and fructose are preferred among the monosaccharides and maltose and sucrose are preferred among the polysaccharides, because they are easily available and inexpensive.

The amount of the component (a) is 5 to 70% by weight, preferably 10 to 40% by weight, based on the composition.

Examples of the preferred amino-modified silicone or derivative thereof used as the component (b) in the present invention are compounds of the following general formula (II):



(II)

wherein:

R represents an alkyl group having 1 to 4 carbon atoms, a hydroxyl group or an alkoxy group,

R_1 groups may be the same or different from one another and each represent an alkyl group having 1 to 4 carbon atoms,

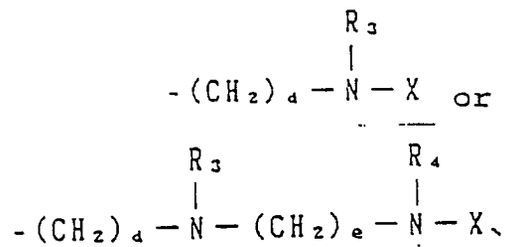
A represents R_1 or $-(CH_2)_a-(OC_2H_4)_b-(OC_3H_6)_c-OR_2$ in which:

a represents 2 or 3,

b and c each represent 0 or 1 to 30 with the proviso that both of them do not represent 0 at the same time, and

R_2 represents an alkyl group having 1 to 24 carbon atoms;

B represents

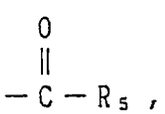


in which:

d and e each represent 2 to 6,

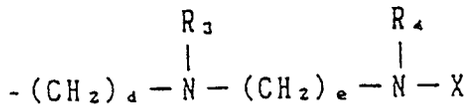
R_3 and R_4 each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms,

X represents a hydrogen atom, an alkyl group having 1 to 24 carbon atoms or

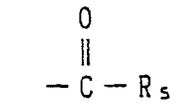


R_5 being an alkyl group having 1 to 18 carbon atoms or $-(CH_2)_f-(C_2H_4O)_g(C_3H_6O)_h-R_6$,
f being 1 to 6, g and h each being 0 or 1 to 30 with the proviso that both of them do not represent 0 at the same time, and R_6 being an alkyl group having 1 to 18 carbon atoms,
and
when X represents H or an alkyl group having 1 to 4 carbon atoms, one or two nitrogen atoms may be quaternized.

Among the silicone compounds represented by the above general formula (II), those wherein B represents



and X represents an alkyl group having 1 to 24 carbon atoms or



are preferred.

In the silicone compounds of the above general formula (II), those having a molecular weight of 2,000 to 150,000 and amine equivalent in the range of 1,000 to 20,000 are preferred and m and n are numbers variable depending on the molecular weight.

The amount of the component (b) is 0.05 to 5% by weight, preferably 0.1 to 3% by weight, based on the composition.

It is well known that silicone compounds such as dimethylpolysiloxane can be incorporated into detergents in a very small amount as a lathering regulator. Japanese Patent Laid-Open No. 215099/1985 describes that when a small amount of an amino-modified silicone or its derivative is incorporated into a detergent in a small amount, the clothes washed therewith can be softened. However, these techniques neither teach nor suggest the construction or effect of the present invention wherein an alkyl glycoside is used.

The balance of the composition of the present invention comprises water. When not more than 50% by weight, preferably 10 to 50% by weight, based on the alkyl glycoside, of another nonionic surfactant, particularly, a polyoxyethylene (having an average molar number of addition of 5 to 20) alkyl (C_9 to C_{14}) ether is incorporated into the composition, the deterging effect thereof is further improved without impairing the effect of the present invention. Incorporation of a cationic surfactant is undesirable, since its adsorbability on the clothes is higher than that of the modified silicone and, therefore, the adsorption of the amino-modified silicone would be inhibited. An anionic or amphoteric surfactant can be incorporated thereinto in only a small amount (not more than 5% by weight, preferably not more than 1% by weight, based on the composition).

The composition of the present invention may contain other components ordinarily incorporated into such a light-duty detergent. They include antiredeposition agents such as polyacrylic acid, polyvinylpyrrolidone, polyethylene glycol and carboxymethylcellulose; enzymes such as protease, amylase, lipase and cellulase; enzyme stabilizers such as calcium chloride; a solubilizing agent such as lower alcohols such as ethanol, benzenesulfonates and lower alkylbenzenesulfonates such as p-toluenesulfonates, glycols such as propylene glycol, benzoic acid salts and urea; antioxidants such as t-butylhydroxytoluene and distyrenated cresol; as well as fluorescent dyes, bluing agents, perfumes and antibacterial agents.

Up to 15 wt.%, preferably up to 10 wt.%, of the solubilizer may be used here to prevent the phase separation. It is not needed when a small amount of a surfactant is only used.

Although the composition of the present invention is desirably substantially free from ordinary builders for detergents, not more than 2 or 3% by weight of a builder component such as a diglycolic acid salt, phosphoric acid salt or carbonic acid salt can be incorporated thereinto.

[Examples]

The following Examples will further illustrate the present invention, which by no means limit the invention.

Example 1

[I] Determination of felting shrinkage rate and area shrinkage rate:

(1) Preparation of sample cloth:

A wool cloth, not yet treated for prevention of shrinking, having a size of 10 x 10 cm, three sides of which had been hemstitched with a lockstitch machine was immersed in city water at ambient temperature for 30 min, then dewatered in a dewatering tank of a washing machine for 30 sec, dried on a net and kept at 20 °C and 65% RH for at least 4 h. The cloth was marked at four points with an oil-base felt pen and numbers were given to the marks. The distances between the marks (a_1^0 and a_2^0 in the direction of the length and b_1^0 and b_2^0 in the direction of the width) were measured. The distances will be called the "original length".

(2) Washing method:

Three sample cloths prepared in the above step (1) were placed in a pot and washed with a Terg-O-Tometer (mfd. by Ueshima Seisakusho Co., Ltd.) at a rate of 120 r.p.m. for 10 min. The detergent concentration was 0.25% by weight and the water temperature was 20 °C. They were then rinsed with running water in a pot and then with running water in a washbasin. Thereafter, the cloths were pressed on the walls of the dewatering tank of the washing machine and dewatered for 30 sec, dried on the net, and kept at 20 °C and 65% RH for at least 4 h.

Then the distances between the marks marked in the above-described step (1) (a_1^w and a_2^w in the direction of the length and b_1^w and b_1^w in the direction of the width) were measured. The felting shrinkage rate and area shrinkage rate were calculated according to the following equations, respectively. The results are given in Table 1.

<Calculation of felting shrinkage rate (according to IWS TM 9)>

$$\text{felting shrinkage rate (\%)} = \frac{\text{R.M.} - \text{W.M.}}{\text{R.M.}} \times 100$$

wherein R.M. represents the distances measured before washing (original length) and W.M. represents the distance measured after washing.

<Calculation of area shrinkage rate>

$$\text{area shrinkage rate (\%)} = \text{W.S.} + \text{L.S.} - \frac{\text{W.S.} \times \text{L.S.}}{100}$$

wherein W.S. represents the felting shrinkage in the direction of the width and L.S. represents the felt shrinkage in the direction of the length.

[II] Evaluation of latheriness and rinsability:

5 ℓ of city water at 30 °C was placed in a 10-ℓ basin. 100 g of a piece of the untreated wool cloth and 100 g of an acrylic jersey cloth (200 g in total) and 12.5 mℓ of a detergent were placed therein. After washing for 5 min, the cloths were dewatered with a dewatering machine for 30 sec. 5 ℓ of city water at 30 °C was added thereto and the cloths were rinsed by repeatedly pressing them in water for 1 min.

The height (cm) of the lather 5 min after the washing and that 1 min after the press rinsing were macroscopically observed and evaluated according to the following criteria:

rinse index:

5: lather remained on the whole water surface,
4: lather remained on 1/2 of the water surface,
3: lather remained on 1/4 of the water surface,
2: fine lather remained on the water surface, and
1: no lather remained on the water surface.

Table 1

Composition (% by weight)	1*	2	3	4	5*	6*	7	8*	9	10
alkyl glycoside (1)	20	20	20	20	20	20			17	14
alkyl glycoside (2)							20			
polyoxyethylene ($\bar{p}$ = 10) alkyl (C_{12} to C_{13}) ether								20	3	6
silicone (1)		0.5					0.5		1.0	0.5
silicone (2)			0.5							
silicone (3)				1.5				0.5		
silicone (4)					0.5	2.0				
ethanol	5	5	5	5	5	5	5	5	5	5
water	B**	B	B	B	B	B	B	B	B	B
area shrinkage rate (%)	12.5	7.5	8.0	7.5	12.0	11.0	7.5	10.0	7.5	8.0
latheriness (cm)	5	4	5	4	2	1	5	3	4	4
rinsability	1	1	1	1	1	1	2	4	1	1∿2

Notes)

*: Comparative Example,

**: the balance

Alkyl glycoside (1):
general formula (I) wherein:
R_1 = C_9 to C_{11}, x = 0, y = 1.35,
G: glucose residue,
Alkyl glycoside (2):

general formula (I) wherein:
R_1 = C_{12}, x = 0, y = 1.7,
G: glucose residue,
Silicone (1):
general formula (II) wherein:
R, R_1 and A: CH_3,

B: $-(CH_2)_3-NH-(CH_2)_2-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_3-(C_2H_4O)_4-C_8H_{17}$

having a molecular weight of 14,000 and an amine equivalent of 4,500,

Silicone (2):
general formula (II) wherein:
A, R_1 and A: CH_3,

B: $-(CH_2)_3-NH-(CH_2)_2-NH-\overset{\overset{O}{\|}}{C}-C_{11}H_{23}$

having a molecular weight of 20,000 and an amine equivalent of 1,000,

Silicone (3):
general formula (II) wherein:
R, R_1 and A: CH_3,
B: $-(CH_2)_3-NH-(CH_2)-NH-C_{12}H_{25}$
having a molecular weight of 7,000 and an amine equivalent of 2,300,

Silicone (4):
dimethylpolysiloxane having a molecular weight of 10,000 and an amine equivalent of 0.

Example 2

Detergent compositions listed in Table 2 were prepared to evaluate the detergency by the following method wherein the alkyl glycoside (1) and silicone (1) were the same as those used in Example 1:

preparation of artificially stained cloth:

* Composition of stain:

carbon black	15%
cotton seed oil	60%
cholesterol	5%
oleic acid	5%
palmitic acid	5%
liquid paraffin	10%

1 kg of the above-described composition was dissolved or dispersed in 80 ℓ of Perclene and a shirting 2023 cloth was immersed therein to adhere the stain to the cloth. Then Perclene was dried and removed. Perclene is the tradename of perchloroethylene.

Washing conditions and evaluation method:

Five cotton cloths (artificially stained cloth) having a size of 10 cm x 10 cm which had been stained with sebum/carbon were placed in 1 ℓ of an aqueous detergent solution prepared for the evaluation and washed with a Terg-O-Tometer at 100 r.p.m. under the following washing conditions:

<washing conditions>

washing time:	3 min
detergent concentration:	0.25%
hardness of water:	4°
water temperature:	30°C
rinse:	city water, 5 min.

The detergency was determined by measuring the reflectivity of the original cloth before staining and those of the stained cloth before and after washing with an autographic colorimeter (mfd. by Shimadzu Corp. to calculate the deterging rate (%) according to the following equation (the average of the five samples is given in the Table):

$$\text{deterging rate (\%)} = \frac{(\text{reflectivity after washing}) - (\text{reflectivity before washing})}{(\text{reflectivity of original cloth}) - (\text{reflectivity before washing})} \times 100$$

The results are given in Table 2.

Table 2

Composition (% by weight)	1	2
alkyl glycoside (1)	20	14
polyoxyethylene ($\overline{p}$ = 10) alkyl (C_{12} to C_{13}) ether		6
silicone (1)	0.5	0.5
ethanol	5	5
water	B*	B
deterging rate (%)	42	48

Note)

*: the balance.

Claims

1. A liquid detergent composition for clothes comprising:
   (a) 5 to 70% by weight of an alkyl glycoside and
   (b) 0.05 to 5% by weight of an amino-modified silicone or a derivative thereof.

2. A liquid detergent composition for clothes according to Claim 1, wherein the alkyl glycoside is one represented by the following general formula (I):

$$R_1(OR_2)_xG_y \quad (I)$$

in which R_1 represents a straight-chain or branched alkyl, alkenyl or alkylphenyl group having 8 to 18 carbon atoms, R_2 represents an alkylene group having 2 to 4 carbon atoms, G represents a residue of a reducing sugar having 5 or 6 carbon atoms, and $\underline{x}$ and $\underline{y}$ each represent an average number, $\underline{x}$ being 0 to 5 and $\underline{y}$ being 1 to 10.

3. A liquid detergent composition for clothes according to Claim 1 or 2, which further contains 10 to 50% by weight, based on the alkyl glycoside, of a polyoxyethylene (having an average molar number of addition of 5 to 20) alkyl (having 9 to 14 carbon atoms) ether.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 0209

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 363 346 (PROCTER AND GAMBLE) * Page 5, line 50 - page 6, line 20; claims 1,2,9-12 *	1-2	C 11 D 1/66 C 11 D 3/37
A	EP-A-0 230 565 (HOFFMANN'S STÄRKEFABRIKEN) * Page 4, lines 15-30; page 5, lines 10-30; page 7, lines 15-30 *	1,2	
A	EP-A-0 094 118 (PROCTER AND GAMBLE) * Claims *	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	07 May 91	GRITTERN A.G.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document