



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 341 071 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the opposition decision:  
**13.11.2002 Bulletin 2002/46**

(51) Int Cl.7: **C11D 1/83**, C11D 1/94,  
C11D 3/32

(45) Mention of the grant of the patent:  
**03.08.1994 Bulletin 1994/31**

(21) Application number: **89304522.9**

(22) Date of filing: **05.05.1989**

(54) **Detergent compositions**

Waschmittelzusammensetzungen

Compositions détergentes

(84) Designated Contracting States:  
**CH DE ES FR GB IT LI NL SE**

(30) Priority: **06.05.1988 GB 8810820**

(43) Date of publication of application:  
**08.11.1989 Bulletin 1989/45**

(73) Proprietors:

- **UNILEVER PLC**  
London EC4P 4BQ (GB)  
Designated Contracting States:  
**GB**
- **UNILEVER N.V.**  
3013 AL Rotterdam (NL)  
Designated Contracting States:  
**CH DE ES FR IT LI NL SE**

(72) Inventor: **Naik, Appaya Raghunath**  
Birkenhead Merseyside, L43 9QT (GB)

(74) Representative: **Dekker, Enno E.J. et al**  
**Unilever N.V.**  
Patents Division  
P.O. Box 137  
3130 AC Vlaardingen (NL)

(56) References cited:

<b>EP-A- 0 070 076</b>	<b>EP-A- 0 155 737</b>
<b>EP-A- 0 216 301</b>	<b>US-A- 4 483 779</b>
<b>US-A- 4 595 526</b>	<b>US-A- 4 668 422</b>
<b>US-A- 4 732 704</b>	

- Falbe, "Surfactants in Consumer Products", Springer-Verlag, 1987, pp. 99-106
- M. and I. Ash, "The condensed encyclopedia of surfactants", Chemical Publishing Co. Inc., 1989, p. 132
- Matissek, "Parfuemerie und Kosmetik", Huethig Publikation, 64. Jahrg., Nr. 2/83, pp. 59-64
- Blake-Haskin et al., "Predicting surfactant irritation from the swelling response of a collagen film", J. Soc. Cosmet. Chem., No. 37, 1986, pp. 199-210
- Technical Bulletin on "Triton CG 110" of Rohm & Haas Company
- Putnik, Borys, "Alkyl Polyglycosides", Soaps/Cosmetics/Chem.Special for June 1986, pp. 34-37,74

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

**EP 0 341 071 B2**

**Description**TECHNICAL FIELD

5 **[0001]** The present invention relates to novel detergent compositions and especially, but not exclusively, to foaming liquid compositions useful for light-duty applications such as manual dishwashing. The compositions may also have use for fabric washing, cleaning carpets and as shampoos.

DESCRIPTION OF THE PRIOR ART

10 **[0002]** Light-duty liquid detergent compositions such as are suitable for use in washing dishes are well known. Many commercially-available formulations are based on a sulphate - or sulphonate-type anionic detergent, especially alkyl sulphate, alkyl benzene sulphonate and alkane sulphonate, in conjunction with an alkyl polyethoxy sulphate (alkyl ether sulphate). The sulphonate-type detergent generally predominates.

15 **[0003]** The use of conventional dishwashing liquids based on alkyl benzene sulphonate/alkyl ether sulphate, or alkyl sulphate alkyl ether sulphate has been found to have a deleterious effect on the hand condition of users. Mildness in detergent products, particularly in washing-up liquids, has hence become a desirable quality.

20 **[0004]** Alkyl mono- and poly-glycosides are known and have been disclosed in a number of prior art patents and literature publications. For example, Boettner (US3219656) discusses the utility of alkyl mono-glycosides as foam stabilisers for anionic and nonionic surfactants. Lew (US 3772269) discloses that decyl glucoside containing less than 1.6 glucose units acts as a good foamer. Several Procter and Gamble disclosures (eg EP 0 070 074, EP 0 070 075 and EP 0 070 076) discuss the utility of alkylpolyglucosides having greater than 1.5 glucose units in detergent compositions. Henkel (EP 216 301 A) disclose the beneficial use of alkyl glycosides having from 1 to 1.4 glucose units which are incorporated in dishwashing liquids comprising ether sulphate and ethanolamide.

SUMMARY OF THE INVENTION

25 **[0005]** The present invention relates to safe, mild liquid detergents with a good foam stability and a good cleansing ability based upon alkyl polyglycosides. The invention aims to provide novel, high-foaming nonionic based liquid detergents comprising an alkyl polyglycoside. It is a further aim to provide a mild, ecologically safe liquid detergent.

30 **[0006]** Accordingly, the present invention relates to an aqueous liquid detergent composition comprising:

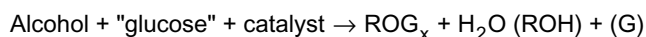
- (a) a C<sub>8</sub>-C<sub>18</sub> alkyl polyglycoside surfactant having an average degree of polymerisation of from 1 to 1.4
- (b) a primary alkyl sulphate surfactant;
- 35 (c) a surface- active betaine and/or amine oxide; and optionally
- (d) an ethanolamide.

40 wherein the amount of anionic surfactant is not greater than 1.5 times (on a molar basis) the level of betaine and/or amine oxide and wherein the level of betaine and/or amine oxide and, if present, ethanolamide is from 12 to 30 wt% of the total active.

DESCRIPTION OF PREFERRED EMBODIMENTSAlkyl Polyglycoside

45 **[0007]** Alkyl polyglycosides, though nonionic in nature, differ from conventional ethoxylated nonionics such as alkyl ethoxylates or alkylphenol ethoxylates in having a different type of hydrophilic group and in consequence exhibit different physical, chemical and hence functional properties compared to conventional ethoxylated nonionics. For example, ethoxylates are low melting solids or liquids at room temperature, are completely miscible in non-polar solvents and their aqueous solutions have cloud points. In comparison, alkyl polyglycosides are high melting solids, sparingly soluble in non-polar solvents and their aqueous solutions do not show cloud points. Alkyl polyglycosides also generally give lower surface tensions and give a more stable foam compared to comparable, conventional nonionics. Alkyl polyglycosides are also prepared by different routes and can be produced entirely based on natural raw materials. Hence the compounds and compositions made therewith can be expected to be biologically safer and more acceptable than conventional nonionics and compositions containing them. Impurities present will also differ from conventional nonionics.

55 **[0008]** Alkyl polyglycosides may be manufactured by the Fischer glycoxidation of a detergent alcohol, eg C<sub>8</sub>-C<sub>18</sub>



**[0009]** Specification of the  $\text{ROG}_x$  product depends on control of the ratios of the reactants. A product will be a ratio of, eg  $\text{ROG}_1:\text{ROG}_2:\text{ROG}_3$ .

**[0010]** The alkyl polyglycosides used in the present invention have a hydrophobic group containing 8 to 20 carbon atoms, preferably about 10 to about 16, most preferably from 12 to 14, and a polysaccharide hydrophilic group containing from 1 to 1.4 preferably 1.2 to 1.4 saccharide units on average. The saccharide unit may be, for example, a galactoside, glucoside, fructoside or glycosyl. Mixtures thereof may be used.

**[0011]** Preferred alkyl polyglycosides are APG 500 from Horizon (APG is a trademark). APG 500 has an average degree of polymerisation of 1.4.

**[0012]** The alkyl polyglycoside is preferably the major active component and may, for example, be present at from 30 to 60 wt% of the total active.

#### Anionic Active

**[0013]** The co-active anionic surfactant used according to the present invention is a primary alkyl sulphate surfactant. The sulphates may be conventional anionic synthetic detergents, and are sulphuric acid half esters of alkanols. Suitable sulphates are from the linear, or branched, primary alcohols. Preferred alcohols are:

- (i) the linear primary alcohols having 10-14 carbon atoms,
- (ii) the mainly straight-chain primary alcohols having 10-15 carbon atoms and about 25% 2-methyl branching.

**[0014]** Primary alcohols with substantial branching may be used.

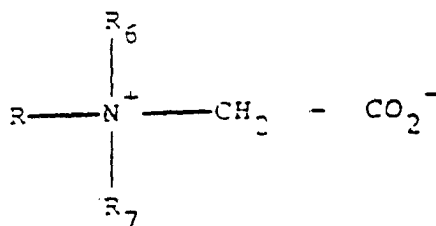
**[0015]** The preferred cations which neutralise the anionic surfactant are sodium and ammonium, and the latter sulphates can be an aid to hydrotropic of the liquid compositions of the invention.

#### Amine Oxide/Betaine

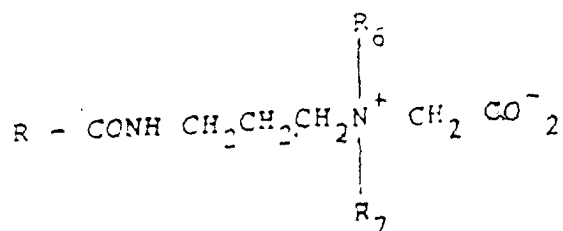
**[0016]** The third essential feature of the present invention is the presence of an amine oxide or a betaine as a lather booster.

**[0017]** It is preferred to avoid using substantial amounts of these, especially amine oxides, for the sake of economy and consequent cost effectiveness. Preferably then the amount of amine oxide is not more than 10% by weight of the active detergent mixture. Preferably the amount of betaine is not more than 30% by weight of this mixture. The total amount of amine oxide and betaine, and, if present, ethanolamide is from 12 to 30% by weight of the active detergent mixture. The lather booster is preferably present at from 2 to 6% by weight of the total composition. It is preferred to use betaines alone.

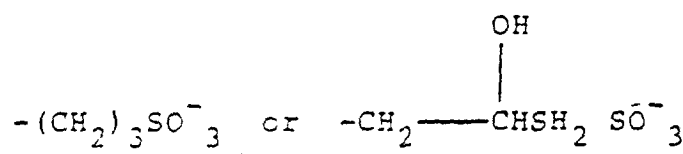
**[0018]** Suitable betaines include simple betaines of formula:



and amido betaines of formula:

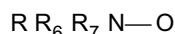


**[0019]** In both formulae R is a C<sub>8</sub> to C<sub>18</sub> straight or branched alkyl group. It may be a lauryl group or a middle cut coconut alkyl group. R<sub>6</sub> and R<sub>7</sub> are each C<sub>1</sub> to C<sub>3</sub> alkyl or C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl. Examples of sulphobetaines have the above formulae with -CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> replaced by:



**[0020]** A suitable simple betaine is Empigen BB from Albright & Wilson. It has the formula quoted above in which R is C<sub>12</sub> to C<sub>14</sub> alkyl, derived from coconut, and R<sub>6</sub> and R<sub>7</sub> are both methyl. Also preferred is Tego L7 from Goldschmidt, which has a whole coconut alkyl group.

**[0021]** Suitable amine oxides have the formula:



wherein R is a straight- or branched-chain C<sub>8</sub> to C<sub>18</sub> alkyl group and R<sub>6</sub> and R<sub>7</sub> are each C<sub>1</sub> to C<sub>3</sub> alkyl, or C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl. A suitable amine oxide is Empigen OB from Albright & Wilson. In it R is middle-cut coconut alkyl and R<sub>6</sub> and R<sub>7</sub> are both methyl.

#### Additional Ingredients

**[0022]** The compositions according to the present invention may include other conventional ingredients such as minor amounts of builders, urea, sodium or ammonium chloride, corrosion inhibitors, colourings and perfumes. Conventional foam boosters such as ethanolamides may be included.

**[0023]** The presence of ethanolamide is optional. If present, the total level of betaine and/or amine oxide and ethanolamide is from 12 to 30 wt% of the total active. A preferred ethanolamide is Empilan LME (Albright & Wilson).

**[0024]** The compositions according to the present invention are of particular use as light duty liquid detergent compositions for manual dishwashing.

**[0025]** The term "dishes" as used herein means any utensils involved in food preparation or consumption which may be required to be washed to free them from food particles and other food residues, greases, proteins, starches, gums dyes, oils and burnt organic residues.

**[0026]** Typical compositions for manual dishwashing comprise from about 5 to about 60 wt%, preferably about 10 to about 40 wt% of the mixture of active components hereinbefore described, the balance comprising water and solvents.

**[0027]** The compositions according to the present invention are mild and environmentally safe. They exhibit good foam characteristics.

**[0028]** The invention will now be described in more detail by the following Examples.

#### EXAMPLES

**[0029]** The foaming performance and mildness of various aqueous formulations were compared. Those formulations falling within the scope of the present application were compared with comparable compositions outside the scope.

**[0030]** Foaming performance was assessed by means of a modified Schlachter-Dierkes test based on the principle

described in Fette und Seifen 1951, 53, 207. A 100 ml aqueous solution of each material tested, having a concentration of 0.04% active detergent in 24°H water (French hardness) at 45°C was rapidly oscillated using a vertically oscillating perforated disc within a graduated cylinder. After the initial generation of foam, increments (0.2 g) of soil (9.5 parts commercial cooking fat, 0.25 parts oleic acid, 0.25 parts stearic acid and 10 parts wheat starch in 120 parts water) were added at 15 second intervals (10 seconds' mild agitation and 5 seconds' rest) until the foam collapsed. The result was recorded as the number of soil increments (NSI score): a score difference of 6 or less is generally regarded as insignificant. Each result was typically the average of 3 or 4 runs.

**[0031]** Several in-vitro and in-vivo methods for evaluating protein denaturation potency of surfactants and their mixtures have been reported (see Miyazowa et al. Int J Cos Sci 6 33-46 1984, and the references cited therein). One such method is the study of interaction of detergents with acid phosphatase enzyme either from skin (Prottey et al. Int J Cos Sci 6 263-273 1984) or from Wheatgerm (Tanaka et al, Anal Biochem 66 489-498 1975).

**[0032]** In vivo mildness of formulations can be assessed using a flex wash test. In this test neat products were rubbed on the forearm of panellists and rinsed. The process was repeated four times a day for five days and the level or erythema developed was assessed by trained assessors.

**[0033]** A comparison of wheatgerm acid phosphatase (WGAP) test and flex wash test results indicated that formulations giving less than 50% enzyme inhibition under the test conditions are substantially mild; any mildness differences between products giving <40% inhibition do not show any detectable mildness differences in flex wash test, indicating that the enzyme test is very sensitive and that in a real life situation there is a threshold level of protein denaturation below which all actives and products are indistinguishably mild. The results of the WGAP test are expressed as percentage inhibition (ie, 100% minus percentage activity remaining). Water gave no inhibition at all, ie 100% of activity remained.

Materials Used

**[0034]**

APG : APG 500 or APG 550 from Horizon Chemicals. Both have C<sub>12</sub>-C<sub>14</sub> alkyl groups. Average degree of polymerisation of 1.4 and 1.8 respectively.

PAS : Dobanol 23-S (Shell)

Betaine : Empigen BB (Albright & Wilson)

Amine Oxide : Empigen OB (Albright & Wilson)

LME : Emplilan LME (Albright & Wilson)

**[0035]** The varying amounts of ingredients used in the compositions tested are shown below as a percentage of the total weight of the composition.

<u>Example Number</u>	<u>Product</u>	<u>Plunger Test</u> 24°H, 45°C, 0.04% AD
1	19/6/4/5	40
2	22/6/6	35
3	22/6/6	37
4	18/8/8	37
5	18/8/8	39
6	22/8/6/4	39
8	9/9/8/8	35
9 (comparative)	18/8/8	29
A	22/12	15
B	18/8/8	31
C	22/8/4	29
D	22/12	27

**[0036]** The foam tests show that compositions falling within the scope of the invention perform better than those outside (A, B and D). Furthermore, APG 500 performs better than APG 550.

**[0037]** The following enzyme inhibition tests were performed:

## EP 0 341 071 B2

	Product	% Enzyme Inhibition
19 6 4 5	Dobanol 91-8EO PAS Betaine LME	4
19 6 4 5	APG 500 PAS Betaine LME	4

**[0038]** In the WGAP test, APG and nonionic formulations give similar low enzyme inhibition, and hence both have similar mildness.

### Claims

1. A aqueous, liquid, detergent, composition comprising:

- (a) a C8-C18 alkyl polyglycoside surfactant having an average degree of polymerisation of from 1 to 1.4,
- (b) a primary alkyl sulphate surfactant,
- (c) a surface active betaine and/or amine oxide; and optionally;
- (d) an ethanolamide,

wherein:

- the amount of anionic surfactant is not greater than 1.5 times (on a molar basis) the level of betaine and/or amine oxide, and,
- the level of betaine and/or amine oxide and, if present, ethanolamide is from 12 to 30%wt of the total active.

2. A composition as claimed in claim 1 wherein a betaine alone is used as a lather booster.

3. A composition according to any one of claims 1 or 2 wherein a nonionic active is also present.

4. An aqueous liquid detergent composition as claimed in claim 1 comprising, based on the total amount of active material,

- (a) from 50-60 wt% of an alkyl polyglycoside surfactant having an average degree of polymerisation of from 1 to 1.4,
- (b) from 15-20 wt% of a primary alkyl sulphate surfactant,
- (c) from 10-15 wt% of a surface active betaine, and,
- (d) from 10-15 wt% of an ethanolamide.

### Patentansprüche

1. Wäßrige flüssige Waschmittelzusammensetzung, umfassend:

- (a) ein C8-C18-Alkylpolyglycosidensid mit einem durchschnittlichen Polymerisationsgrad von 1 bis 1,4,
- (b) ein primäres Alkylsulfattensid,
- (c) ein oberflächenaktives Betain und/oder Aminoxid; und gegebenenfalls;
- (d) ein Ethanolamid;

wobei:

- die Menge an anionischem Tensid nicht größer als das 1,5-fache (auf molarer Basis) des Anteils an Betain und/oder Aminoxid ist, und
- der Anteil an Betain und/oder Aminoxid und, falls vorliegend, Ethanolamid 12 bis 30 Gew.-% des gesamten Aktivstoffs ausmacht.

## EP 0 341 071 B2

2. Mittel nach Anspruch 1, wobei nur ein Betain als Schaumverstärker verwendet wird.
3. Mittel nach einem der Ansprüche 1 oder 2, wobei ebenfalls ein nichtionischer Aktivstoff vorliegt.
- 5 4. Wäßrige flüssige Waschmittelzusammensetzung nach Anspruch 1, umfassend auf der Grundlage der Gesamtmenge an aktivem Stoff:
- 10 (a) 50 bis 60 Gew.-% eines Alkylpolyglycosidens mit einem durchschnittlichen Polymerisationsgrad von 1 bis 1,4;
- (b) 15 bis 20 Gew.-% eines primären Alkylsulfatens;
- (c) 10 bis 15 Gew.-% eines oberflächenaktiven Betains, und,
- 15 (d) 10 bis 15 Gew.-% eines Ethanolamids.

### Revendications

- 20 1. Composition détergente liquide aqueuse comprenant:
- (a) un tensioactif alkyl(en C<sub>8-18</sub>) polyglycoside ayant un degré moyen de polymérisation de 1 à 1,4,
- (b) un tensioactif alkylsulfate primaire,
- 25 (c) une bétaine et/ou un oxyde d'amine agent de surface; et éventuellement,
- (d) un éthanolamide,
- dans laquelle :
- 30 - la quantité de tensioactif anionique n'est pas supérieure à 1,5 fois (sur une base molaire) le niveau de bétaine et/ou d'oxyde d'amine, et
- le niveau de bétaine et/ou d'oxyde d'amine et, le cas échéant, d'éthanolamide, représente de 12 à 30% en poids du total des ingrédients actifs.
- 35 2. Composition selon la revendication 1 dans laquelle on utilise une bétaine seule comme agent renforçateur de mousse.
3. Composition selon l'une quelconque des revendications 1 ou 2 dans laquelle un ingrédient actif non ionique est aussi présent.
- 40 4. Composition détergente liquide aqueuse selon la revendication 1 comprenant, par rapport à la quantité totale des ingrédients actifs,
- (a) de 50 à 60% en poids d'un tensioactif d'alkylpolyglycoside ayant un degré moyen de polymérisation de 1 à 1,4,
- 45 (b) de 15 à 20% en poids d'un tensioactif alkylsulfate primaire,
- (c) de 10 à 15% en poids d'une bétaine agent de surface, et
- (d) de 10 à 15% en poids d'un éthanolamide.
- 50
- 55