



(11) **EP 2 607 469 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.06.2013 Bulletin 2013/26

(51) Int Cl.:
C11D 17/00 (2006.01) **C11D 3/386** (2006.01)
C11D 1/94 (2006.01) **C11D 3/37** (2006.01)
C11D 11/00 (2006.01)

(21) Application number: **11194459.1**

(22) Date of filing: **20.12.2011**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME

- **Green, Andrew David**
Bebington, Wirral
Merseyside CH63 3JW (GB)
- **Stevenson, Paul Simon**
Bebington, Wirral
Merseyside CH63 3JW (GB)

(71) Applicant: **Unilever PLC**
London, Greater London EC4Y 0DY (GB)

(74) Representative: **Bristow, Stephen Robert et al**
Unilever Patent Group
Colworth House
Sharnbrook
Bedford, MK44 1LQ (GB)

(72) Inventors:
• **Cook, Andrew Thomas**
Bebington, Wirral
Merseyside CH63 3JW (GB)

(54) **Liquid detergent with protease and lipase**

(57) An aqueous concentrated isotropic liquid detergent comprising 15 to 60 wt% of a surfactant system comprising at least one anionic surfactant, at least one non-ionic surfactant and at least one surfactant from the group comprising carbobetaine and amine oxide, wherein the anionic surfactant comprises a minimum of 5 wt%, based on the total composition, linear alkyl benzene sulphonate

(LAS), the composition further comprising, EPEI and at least two enzymes; which enzymes comprise a cleaning effective amount of at least one protease and a cleaning effective amount of at least one lipase, characterised in that the in-bottle pH of the composition is buffered to 6.0 to less than 7, preferably 6.3 to 6.7.

EP 2 607 469 A1

DescriptionTECHNICAL FIELD

5 **[0001]** This invention relates to aqueous liquid detergents comprising surfactants, at least one polymer and protease and lipase enzymes.

BACKGROUND

10 **[0002]** Aqueous liquid detergents are typically formulated to have an in-bottle pH of about 8 to 8.5. The stability of enzymes in these liquids may not be good. This is especially so for proteases in the presence of TEA and lipases in the presence of protease.

[0003] W02009/153184 (Unilever) proposes a detergent liquid comprising polymers, enzymes and surfactants. The low in wash surfactant level is compensated by the polymers and enzymes. Combinations of protease and lipase enzymes are proposed. We have now found that these enzymes have poor stability at an in-bottle pH of about 8.3 when using the preferred surfactant system in W02009/153184 comprising: neutralised linear alkyl benzene sulphonic acid (LAS), neutralised fatty acid, ethoxylated fatty alcohol nonionic and carbobetaine amphoteric. The amphoteric is desirable because of its synergy with ethoxylated polyethyleneimine polymers when that type of polymer is also used.

[0004] There are many prior art disclosures of liquid detergent compositions comprising protease and lipase. Most of them are non-specific about the performance of these compositions when they have been stored for a reasonable length of time to simulate actual supply and use of the composition in a domestic environment. A few of the disclosures claim some stability benefit for the protease. The stability of the lipase is not normally disclosed. We have determined that lipase stability is not good enough for a commercial composition that also comprises protease if the in-bottle pH is above 7.0 and the composition comprises LAS.

25 **[0005]** The use of certain alcohol ethoxylates to maintain protease stability in the presence of anionic surfactants is the subject of an article published in the Journal of surfactants and detergents. 2002, vol. 5, no. 1, p. 5-10.

[0006] US2007032395 (Fornana et al) explains that the incorporation of one or more enzymes in aqueous liquid detergent compositions can represent considerable technical problems due to the fact that enzymes can be rapidly inactivated in an aqueous environment in the presence of anionic surfactants, which are a fundamental component of detergents. Such problems of compatibility between enzymes and surfactants occur to a less extent with nonionic surfactants, as their inactivation effect on enzymes is lower. This patent disclosure proposes to use anionic esters of alkylpolyglycosides that exhibit a low inactivating effect on enzymes, in comparison with the normally used anionic surfactants. This surfactant system that is not weight efficient enough to be utilised in the types of concentrated liquid compositions suggested in W02009/153184.

35 **[0007]** Many patent publications teach to avoid anionic surfactants, LAS in particular, if sufficient enzyme stability is to be achieved in a detergent liquid. If LAS is proposed it is typically at less than 10% of the composition.

[0008] US2010240562A (Ecolab) discloses an enzyme stabilization system. Lipase is shown to be more stable in nonionic surfactant based systems containing amines if they are formulated at acidic pH. Surprisingly, preferred ratios of acid to amine are effective at stabilizing enzymes. Nonionic surfactants and solvents also positively contribute to enzyme stability. The amine may be an antimicrobial amine. Cleaning systems based on nonionic are very expensive and have poor performance against some types of common laundry soils and stains. US2002019326 (Unilever) relates to a concentrated and physically stable isotropic liquid detergent composition with good protease stability suitable for cleaning textile articles. Comparative Example A shows that the system at pH 8 (with NaOH) leads to very unstable protease. Examples 5 & 6 have both protease and Lipase at pH 8. The activity is not measured. Sulphite and borate render the liquids non isotropic.

45 **[0009]** US2006234895A (P&G) discloses a liquid laundry detergent for improved grease and oil cleaning having a first wash lipase enzyme, a modified polyethyleneimine polymer and a liquid carrier. Additional enzymes can be included in effective amounts. Their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. The detergent compositions may also optionally contain low levels of materials which serve to adjust or maintain the pH of the detergent compositions at optimum levels. The pH of the compositions herein should range from about 7.8 to 8.5, more preferably from about 8.0 to 8.5. Materials such as NaOH can be added to alter composition pH, if necessary.

50 **[0010]** US2008221008A (Novozymes) discloses detergent compositions with enhanced stability of non protease enzymes present in the compositions. Table 3 of example 1 shows that the stability of the inventive mixture of subtilisin KL protease and lipase is similar to that we find at alkaline pH (the commercial liquid used in Example 1 is almost certainly alkaline and most likely contains LAS as virtually all commercial liquids are based on LAS). The test at elevated temperature in table 7 seems to suggest that the lipase benefit has gone after 4 weeks storage at elevated temperature.

[0011] US2010095987A and US2009111161A (Danisco) disclose a streptomyces protease and its use in cleaning

compositions. It is contemplated that liquid fabric cleaning composition of particular utility under Japanese machine wash conditions be prepared in accordance with the invention. Those compositions may comprise lipase or protease. In one example in Table 11-1 (V) a composition is given which has both lipase and protease. It has a low level of LAS (6 wt%), SLES, AO, PAS a low level of nonionic, sequestrant, MEA and sodium hydroxide and some soil release polymer. This composition V is believed to be alkaline.

[0012] In certain embodiments, the cleaning composition comprises a sufficient amount of a pH modifier to provide said composition with a neat pH of from about 3 to about 5. These embodiments do not comprise protease.

[0013] There remains a need for a stable alkaline detergent liquid comprising protease and lipase whereby those enzymes do not lose so much activity over storage that the contribution to cleaning of the enzyme system in the presence of the polymer cleaning system and the LAS based surfactant system designed to function at low in wash surfactant levels is not unduly compromised.

SUMMARY OF THE INVENTION

[0014] According to the present invention there is provided An aqueous concentrated isotropic laundry liquid comprising 15 to 60 wt% of a surfactant system comprising at least one anionic surfactant, at least one nonionic surfactant and at least one surfactant from the group comprising carbobetaine and amine oxide, wherein the anionic surfactant comprises a minimum of 5 wt%, based on the total composition, linear alkyl benzene sulphonate (LAS), the composition further comprising, EPEI and at least two enzymes; which enzymes comprise a cleaning effective amount of at least one protease and a cleaning effective amount of at least one lipase, characterised in that the in-bottle pH of the composition is buffered to 6.0 to less than 7, preferably 6.3 to 6.7.

[0015] By in-bottle we mean in whatever container or pack the liquid is stored. It could be a plastic pack in the form of a bottle, squeezable or rigid, stored upright or inverted, or a unit dose format such as a soluble pouch, or a sachet.

[0016] We were surprised to find that simply by reducing the in-bottle pH from 8.3 to about 6.5 (by using less sodium hydroxide to neutralise the LAS acid) the enzymatic stability was significantly improved. This acid pH range has the additional benefit that it reduces the hydrolysis of any polyester soil release polymers in the liquid which gives an improved multi-wash benefit in combination with the lipase (and the protease). Surprisingly the wash performance of the liquid is not compromised by the reduction of pH. On the contrary it is improved. This is because the low level of in-wash surfactant used in the liquid is compensated by the polymers, which are not pH dependent. Also the lower amount of surfactant means that the effect of having some LAS acid on both wash performance and in-wash pH is much reduced compared to the effect that would be observed in a conventional liquid that delivers a more conventional level of surfactant to the wash. This, taken together with the improved performance resulting from the better enzyme stability, makes the overall wash performance improve.

[0017] Preferably the liquid further comprises HEDP as sequestrant. The amount of HEDP in the composition is preferably at least 1 wt%, more preferably at least 1.5 wt%, and most preferably at least 2 wt%.

DETAILED DESCRIPTION OF THE INVENTION

[0018] If the in-product pH of the specific detergent liquids is reduced from 8.3 to about 6.5 the enzymatic stability or the protease and lipase enzyme system is significantly improved without compromising the cleaning performance of the liquid.

[0019] Other ingredients of the liquid may be as discussed in W009153184.

[0020] The invention will now be further described with reference to the following nonlimiting examples.

EXAMPLES

[0021]

MPG is mono propylene glycol.

TEA is triethanolamine.

NI 7EO is C12-15 alcohol ethoxylate 7EO nonionic Neodol® 25-7 (ex Shell Chemicals).

LAS acid is C12-14 linear alkylbenzene sulphonic acid.

Prifac® 5908 is saturated lauric fatty acid ex Croda.

EP 2 607 469 A1

SLES 3EO is sodium lauryl ether sulphate with 3 moles EO.

Empigen® BB is an alkyl betaine ex Huntsman (Coco dimethyl carbobetaine).

5 EPEI is Sokalan HP20 - ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.

SRP is soil release polymer.

10 Perfume is free oil perfume.

MEA is Monoethanolamine.

NaOH is 47% sodium hydroxide solution.

15 Lipase is Lipoclean™ 100L, ex Novozymes.

Protease is Relase™ Ultra XL ex Novozymes

20 Table 1 - Liquid detergent compositions

	Composition A	Composition 1
Component	Ingredient (as 100% active) %	
water and minors	to 100	to 100
25 MPG	20.00	20.00
TEA	3.50	3.50
NI 7EO	12.74	12.74
30 LAS acid	8.49	8.49
Prifac® 5908	1.50	1.50
SLES 3EO	4.24	4.24
35 Empigen® BB	1.50	1.50
EPEI	5.50	5.50
SRP	3.75	3.75
Protease**	1.0	1.0
40 Lipase**	0.2	0.2
Perfume	2.43	2.43
pH adjustment hole*	10.00	10.00
45 Composition pH	8.2	6.6
TOTAL	100.00	100.00
* comprising NaOH to required pH, and demineralised water balance. ** as mg/L enzyme.		

50 **[0022]** Remaining enzyme activity (%) after 4-weeks at 37°C was determined for four replicates of the liquid detergent compositions given in Table 1. The results were averaged.

55 Table 2

	% Protease activity	% Lipase activity
Initial (A and 1)	100.00	100.00

(continued)

	% Protease activity	% Lipase activity
A (4 weeks @ 37°C)	52.75	21.00
1 (4 weeks @ 37°C)	100.00	41.50

Claims

1. An aqueous concentrated isotropic liquid detergent comprising 15 to 60 wt% of a surfactant system comprising at least one anionic surfactant, at least one nonionic surfactant and at least one surfactant from the group comprising carbobetaine and amine oxide, wherein the anionic surfactant comprises a minimum of 5 wt%, based on the total composition, linear alkyl benzene sulphonate (LAS), the composition further comprising, EPEI and at least two enzymes; which enzymes comprise a cleaning effective amount of at least one protease and a cleaning effective amount of at least one lipase, **characterised in that** the in-bottle pH of the composition is buffered to 6.0 to less than 7, preferably 6.3 to 6.7.
2. A composition according to claim 1 comprising at least 1.5 wt% triethanolamine.
3. A composition according to any preceding claim comprising at least 4 wt% EPEI.
4. A composition according to any preceding claim further comprising at least 2 wt% polyester based soil release polymer.
5. A composition according to any preceding claim further comprising at least 1% HEDP sequestrant.
6. A composition according to any preceding claim comprising at least 7 wt% nonionic surfactant.
7. A composition according to any preceding claim comprising as an additional anionic surfactant at least 3 wt% alkyl ether sulphate.
8. A composition according to any preceding claim comprising at least 1 wt% carbobetaine.
9. A composition according to any one of claims 1 to 7 comprising at least 1 wt% amine oxide.
10. A washing process comprising the steps of adding to a front loading automatic washing machine 25 ml or less, preferably 20 ml, of a composition according to any preceding claim, diluting it with at least 800 times as much tap water, washing clothes with the wash liquor formed by the dilution step and then rinsing the clothes.



EUROPEAN SEARCH REPORT

Application Number
EP 11 19 4459

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y,D	WO 2009/153184 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; BENNETT) 23 December 2009 (2009-12-23) * page 4, lines 4-31 * * page 14, lines 6-12; claims 2-8 * * page 33 * * page 38, line 22 - page 39, line 6 * * page 40, line 27 - page 42, line 2 * * page 55, lines 9-12; examples 2, 10-31; tables 2a, 2b, 7 *	1-10	INV. C11D17/00 C11D3/386 C11D1/94 C11D3/37 C11D11/00
Y	GB 2 346 153 A (YPLON S A [BE]) 2 August 2000 (2000-08-02) * page 6, line 12 - page 7, line 7; claims 1, 2, 15-18; example 1 *	1-10	
T	WO 99/33946 A1 (COLGATE PALMOLIVE CO [US]) 8 July 1999 (1999-07-08) * page 12, lines 18-29; claims 1, 3, 4 *		
A	WO 2008/114171 A1 (PROCTER & GAMBLE [US]; PANANDIKER RAJAN KESHAV [US]; VETTER KERRY ANDR) 25 September 2008 (2008-09-25) * page 20, paragraph c.; claims 1, 2, 5; examples 17-20, 22 *	1-10	TECHNICAL FIELDS SEARCHED (IPC) C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 16 May 2012	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category 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	

1
EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 11 19 4459

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-05-2012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009153184 A1	23-12-2009	AU 2009259498 A1	23-12-2009
		CA 2728378 A1	23-12-2009
		EP 2300586 A1	30-03-2011
		WO 2009153184 A1	23-12-2009

GB 2346153 A	02-08-2000	EP 1038947 A2	27-09-2000
		GB 2346153 A	02-08-2000

WO 9933946 A1	08-07-1999	AU 2006299 A	19-07-1999
		WO 9933946 A1	08-07-1999

WO 2008114171 A1	25-09-2008	AR 067228 A1	07-10-2009
		CA 2680151 A1	25-09-2008
		EP 2126017 A1	02-12-2009
		JP 2010520350 A	10-06-2010
		US 2008234165 A1	25-09-2008
		WO 2008114171 A1	25-09-2008
		ZA 200906152 A	26-05-2010

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2009153184 A [0003] [0006]
- US 2007032395 A, Fornana [0006]
- US 2010240562 A, Ecolab [0008]
- US 2002019326 A [0008]
- US 2006234895 A [0009]
- US 2008221008 A [0010]
- US 2010095987 A [0011]
- US 2009111161 A, Danisco [0011]
- WO 09153184 A [0019]

Non-patent literature cited in the description

- *Journal of surfactants and detergents*, 2002, vol. 5 (1), 5-10 [0005]