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(54) Detergent compositions

(57) The use of an alkylpolyglycoside in an amount of from 0.5 to 5 wt% in a built particulate laundry detergent composition containing an anionic sulphonate or sulphate detergent to increase mildness to skin.

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Description

TECHNICAL FIELD

[0001] The present invention relates to built laundry detergent compositions containing anionic sulphonate or sulphate surfactants and exhibiting increased mildness to the skin.

BACKGROUND

[0002] Heavy duty laundry detergent compositions have for many years contained an anionic sulphonate or sulphate surfactant, for example, linear alkylbenzene sulphonate (LAS) or primary alcohol sulphate (PAS), as the principal detergent-active ingredient. These anionic surfactants are frequently used in conjunction with ethoxylated alcohol nonionic surfactants which give improved detergency on hydrophobic soils. The nonionic surfactants generally have alkyl chain lengths of C_{12}-C_{18} and degrees of ethoxylation of 1 to 10.

[0003] These anionic and anionic/nonionic surfactant systems are robust and highly efficient on a wide range of soils and under a wide range of conditions, for example, temperature and water hardness. However, they are not noted for mildness to skin. These materials are designed to interact with fatty materials like body soil and protein residues on soiled laundry, and can therefore interact with the skin to give reactions such as dryness and erythema (redness). The milder surfactants used to formulate products intended for prolonged skin contact, for example, shampoos and shower gels, would not perform adequately in heavy duty laundry detergent compositions because of insufficient interaction with fatty materials occurring as soil.

[0004] It has now been surprisingly discovered that the mildness to skin of a laundry detergent composition containing an anionic sulphonate or sulphate detergent and a conventional detergent ethoxylated nonionic surfactant can be significantly improved, without detriment to detergency performance, by the incorporation of a low level of alkylpolyglycoside.

PRIOR ART

[0005] Alkylpolyglycosides (APGs) have been widely disclosed in the art as environmentally friendly carbohydrate-derived nonionic surfactants, and are used in various detergent and personal care products. Disclosures in the prior art include EP 75 994A, EP 75 995A and EP 75 996A (Procter & Gamble), EP 238 638B (Staley/Henkel), EP 487 262A (Unilever), EP 495 176 (Huels), EP 374 702A (Kao), WO 92 06150 (P&G), WO 94 26861A (Henkel), WO 94 24242 (P&G) and WO 96 29977 (Henkel). The use of APGs as detergency builders has been disclosed in EP 976 817A (Henkel).

[0006] WO 00 08129A (Unilever) discloses mild particulate laundry detergent compositions based on high-foaming anionic surfactant (for example linear alkylbenzene sulphonate) plus one or more milder cosurfactants, for example, amine oxide or cocoamidopropyl betaine.

DEFINITION OF THE INVENTION

[0007] The present invention provides the use of a an alkylpolyglycoside in an amount of from 0.5 to 5 wt% to increase the mildness to skin of a built particulate laundry detergent composition containing an anionic sulphonate or sulphate detergent.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The invention is based on the observation that use of alkylpolyglycoside (APG) at low levels to replace part of a conventional anionic/nonionic surfactant system results in a measurable increase in mildness to skin.

[0009] It is well known and intuitively obvious that the mildness to skin of a formulation can be increased simply by reducing the amount of surfactant. However, cleaning efficiency is then reduced. Surprisingly, it has now been found that addition of low levels of APG will increase mildness when the total surfactant level is kept constant, ie the APG replaces a small proportion of the other surfactants. For example, in a formulation containing 15 wt% surfactant (LAS and ethoxylated nonionic) replacement of as little as 5 wt% of that surfactant is beneficial with respect to mildness, and there is no loss of cleaning efficiency. It is surprising that such a small addition has a significant effect.

The built particulate laundry detergent composition

[0010] Preferred detergent compositions utilising the invention contain a conventional anionic sulphonate or sulphate

surfactant and a conventional nonionic surfactant, and also contain as an essential ingredient a low level of alkylpolyglycoside.

[0011] According to a preferred embodiment of the invention the built particulate laundry detergent composition comprises:

(i) from 5 to 25 wt% of an anionic sulphonate or sulphate surfactant,

(ii) from 1 to 10 wt% of an ethoxylated alcohol nonionic surfactant,

(iii) from 0.5 to 5 wt% of alkylpolyglycoside,

(iv) from 10 to 80 wt% of detergency builder and

(v) optionally other detergent ingredients to 100 wt%.

[0012] According to an especially preferred embodiment of the invention, the skin-mild detergent compositions of the invention are free of enzymes, since enzymes can also cause skin irritation to sensitive individuals. However, enzymatic compositions are also within the scope of the invention.

The anionic sulphonate or sulphate surfactant (i)

[0013] Anionic sulphonate and sulphate surfactants are well-known to those skilled in the art. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0014] Examples include alkylbenzene sulphonates, primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Sodium salts are generally preferred.

[0015] Preferably the anionic surfactant is linear alkylbenzene sulphonate or primary alcohol sulphate. More preferably the anionic surfactant is linear alkylbenzene sulphonate.

The nonionic surfactant (ii)

[0016] Conventional nonionic detergent surfactants are ethoxylated alcohols of the formula

$$R_1 - (- O - CH_2 - CH_2)_m - OH$$

wherein R_1 is a C_8-C_{20} hydrocarbyl chain, and the average degree of ethoxylation *m* is generally from 1 to 10, preferably from 3 to 8. The alkyl chain length is preferably in the C_{12} to C_{15} range.

The alkylpolyglycoside

[0017] Alkylpolyglycosides may be represented by the general formula I

$$RO(R'O)_t\,(G)_x \qquad (I)$$

in which R is a hydrocarbyl group containing from 10 to 20 carbon atoms, R' is an alkylene group containing from 2 to 4 carbon atoms, G is a saccharide residue containing 5 or 6 carbon atoms, *t* is in the range of from 0 to 25 and *x* is in the range of from 1 to 10.

[0018] The hydrophobic group R may be aliphatic, either saturated or unsaturated, notably linear or branched alkyl, alkenyl, hydroxyalkyl or hydroxyalkenyl. However, it may include an aryl group for example alkyl-aryl, alkenyl-aryl and hydroxyalkyl-aryl. The preferred R group is an alkyl or alkenyl group having from 8 to 20 carbon atoms, more preferably from 8 to 16 carbon atoms. The most preferred R group is an alkyl group having from 12 to 14 carbon atoms.

[0019] The value of t in the general formula above is preferably zero, so that the $-(RO)_t-$ unit of the general formula is absent. In that case the general formula becomes

$$RO(G)_x \quad \text{(II)}$$

[0020] If t is non-zero it is preferred that R'O is an ethylene oxide residue. Other likely possibilities are propylene oxide and glycerol residues. If the parameter t is non-zero so that R'O is present, the value of t (which may be an average value) will preferably lie in the range of from 0.5 to 10.

[0021] The group G is typically derived from fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and/or ribose. Preferably, the group G is provided substantially exclusively by glucose units.

[0022] The value x, which is an average, is usually termed the degree of polymerisation (dp). Desirably x is within the range of from 1 to 8. Preferred values of x lie within the range of from 1 to 3, especially from 1 to 1.8 and more especially from 1 to 1.6.

[0023] When x lies in the range 1 to 1.6 it is preferred that R is C_8 to C_{14} alkyl or alkenyl. In especially preferred materials, R is C_8 to C_{14} alkyl or alkenyl, *t* is zero, and *x* is within the range of from 1 to 1.6. Most preferably R is C_{12}-C_{14}, t is zero, and x is 1.4.

Commercially available products suitable for use in the compositions of the invention include the Plantacare (Trade Mark) and Glucopon (Trade Mark) ranges ex Cognis Deutschland; Lutensol (Trade Mark) GD 70 ex BASF; Marlosan (Trade Mark) 24 ex Hüls; and Atlas (Trade Mark) G73500 ex ICI.

The detergency builder

[0024] The compositions of the invention also contain from 10 to 80%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

[0025] Preferably the builder is selected from zeolite, sodium tripolyphosphate, sodium carbonate, sodium citrate, layered silicate, and combinations of these.

[0026] The zeolite used as a builder may be the commercially available zeolite A (zeolite 4A) now widely used in laundry detergent powders. Alternatively, the zeolite may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070B (Unilever), and commercially available as Doucil (Trade Mark) A24 from Ineos Silicas Ltd, UK.

[0027] Zeolite MAP is defined as an alkali metal aluminosilicate of zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, preferably within the range of from 0.90 to 1.20. Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The particle size of the zeolite is not critical. Zeolite A or zeolite MAP of any suitable particle size may be used.

[0028] Also preferred according to the present invention are phosphate builders, especially sodium tripolyphosphate.

[0029] This may be used in combination with sodium orthophosphate, and/or sodium pyrophosphate.

[0030] Other inorganic builders that may be present additionally or alternatively include sodium carbonate, layered silicate, amorphous aluminosilicates.

[0031] Organic builders that may be present include polycarboxylate polymers such as polyacrylates and acrylic/maleic copolymers; polyaspartates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-di- and trisuccinates, carboxymethyloxysuccinates, carboxy-methyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

[0032] Organic builders may be used in minor amounts as supplements to inorganic builders such as phosphates and zeolites. Especially preferred supplementary organic builders are citrates, suitably used in amounts of from 5 to 30 wt %, preferably from 10 to 25 wt %; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt %, preferably from 1 to 10 wt%. Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Other detergent ingredients

[0033] As well as the surfactants and builders discussed above, the compositions may optionally contain bleaching components and other active ingredients to enhance performance and properties.

[0034] These optional ingredients may include, but are not limited to, any one or more of the following: soap, peroxyacid and persalt bleaches, bleach activators, sequestrants, cellulose ethers and esters, other antiredeposition agents, sodium sulphate, sodium silicate, sodium chloride, calcium chloride, sodium bicarbonate, other inorganic salts, proteases, lipases, cellulases, amylases, other detergent enzymes, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam controllers, foam boosters, acrylic and acrylic/maleic polymers, citric acid, soil release polymers, fabric conditioning compounds, coloured speckles, and perfume.

[0035] Detergent compositions according to the invention may suitably contain a bleach system. The bleach system is preferably based on peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

[0036] The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

[0037] The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%.

[0038] Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxycarbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED). Also of interest are peroxybenzoic acid precursors, in particular, N,N,N-trimethylammonium toluoyloxy benzene sulphonate.

[0039] A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (Trade Mark), EDTMP.

Although, as previously indicated, in one preferred embodiment of the invention enzymes are preferably absent, in other embodiments detergent enzymes may be present. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

[0040] In particulate detergent compositions, detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used in any effective amount.

[0041] Antiredeposition agents, for example cellulose esters and ethers, for example sodium carboxymethyl cellulose, may also be present.

[0042] The compositions may also contain soil release polymers, for example sulphonated and unsulphonated PET/POET polymers, both end-capped and non-end-capped, and polyethylene glycol/polyvinyl alcohol graft copolymers such as Sokolan (Trade Mark) HP22. Especially preferred soil release polymers are the sulphonated non-end-capped polyesters described and claimed in WO 95 32997A (Rhodia Chimie).

Product form and preparation

[0043] Powders of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally postdosing (dry-mixing) further ingredients. "Concentrated" or "compact" powders may be prepared by mixing and granulating processes, for example, using a high-speed mixer/granulator, or other non-tower processes.

[0044] Tablets may be prepared by compacting powders, especially "concentrated" powders.

EXAMPLES

[0045] The invention is illustrated in further detail by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Examples according to the invention are designated by numbers, and comparative examples by letters.

Examples 1 and 2, Comparative Examples A to E: skin mildness tests

[0046] Skin mildness was determined using the corneosurfametry (CSM) method as described by G Pierard et al, Dermatology 189 (1994) pages 152-156, on pigskin.

[0047] Model formulation solutions were prepared containing the ingredients shown in the table below. The solutions were buffered to a pH of 10.5 which is typical for wash liquors.

	weight %
Total surfactant	0, 0.7, 1.0 or 2.0
Zeolite MAP	0.18
Sodium carbonate	0.11

(continued)

	weight %
Sodium citrate	0.03
Water	to 100%

[0048] The tables below show the surfactant systems tested and the CSM values of the solutions measured on pigskin and human skin. The higher the CSM value, the milder the formulation. The abbreviations used for the surfactants are as follows:

LAS: sodium linear alkylbenzene sulphonate
NI7EO: nonionic surfactant, C_{12}-C_{15} alcohol 7EO.
APG: Glucopon (Trade Mark) ex Cognis:
R = C_{12}-C_{14}, dp = 1.4

	Surfactant system	Total surfactant	CSM value
A	Water only	0	74.1
B	LAS only	1	14.4
C	LAS/NI7EO, ratio 8:7	1	41.8
D	LAS/NI7EO, ratio 8:7	0.7	49.1
1	LAS/NI7EO/APG, ratio 1.3:1:1.15	1	57.8
E	LAS/NI7EO, ratio 8:7	2	38.6
2	LAS/NI7EO/APG, ratio 1.3:1:1.15	2	43.7

Example 3, Comparative Example F: laundry detergent powder formulations

[0049] High bulk density non-enzymatic laundry detergent powders were prepared to the formulations given below.

	3	F
Base powder		
Linear alkylbenzene sulphonate	8.90	7.50
Nonionic surfactant C_{12}-C_{15} 7EO	6.95	5.85
Soap	1.72	1.48
Acrylic/maleic copolymer	1.22	1.08
Zeolite MAP	21.01	17.67
Sodium carbonate (light)	13.71	13.60
Sodium sulphate	11.30	10.05
Sodium silicate	1.17	1.04
Moisture, salts etc	5.38	4.57
Total base powder	71.36	60.98
Postdosed		
APG granule 50%*	-	2.00
PAS granule**	-	2.50

* granule containing 50 wt% APG (C_{12}-C_{14}, dp 1.4) on a sodium sulphate carrier
** primary C_{12}-C_{14} alcohol sulphate granules

(continued)

	3	F
Postdosed		
Antifoam granule	1.30	1.30
Fluorescer granule	0.85	0.85
Sodium carbonate (dense)	3.61	4.00
Sodium sulphate (granular)	-	5.49
Citric acid	2.56	2.56
Na carbonate/silicate granules	3.15	3.15
TAED*** granules (83%)	2.75	2.75
Sodium percarbonate	13.20	13.20
EDTMP****, EHDP*****	1.10	1.10
Perfume	0.12	0.12
Total	100.00	100.00

*** tetraacetyl ethylenediamine

**** ethylenediamine pentamethylene phosphonate, Ca/Na salt

***** 1-hydroxyethane-1,1-diphosphonate, Na salt

[0050] A typical wash liquor based on the formulation of Example 3 (prepared by dissolving 115 g of formulation in 14.5 litres of water) is significantly milder than one based on the formulation of Comparative Example F.

Claims

1. Use of an alkylpolyglycoside in an amount of from 0.5 to 5 wt% to increase the mildness to skin of a built particulate laundry detergent composition containing an anionic sulphonate or sulphate detergent.

2. Use as claimed in claim 1, **characterised in that** the built particulate laundry detergent composition comprises:

   (i) from 5 to 25 wt% of an anionic sulphonate or sulphate surfactant,
   (ii) from 1 to 10 wt% of an ethoxylated alcohol nonionic surfactant,
   (iii) from 0.5 to 5 wt% of the alkylpolyglycoside,
   (iv) from 10 to 80 wt% of detergency builder and
   (v) optionally other detergent ingredients to 100 wt%.

3. Use as claimed in any preceding claim, **characterised in that** the alkylpolyglycoside has the general formula I

$$RO(R'O)_t\,(G)_x \qquad (I)$$

   in which R is a hydrocarbyl group containing from 10 to 20 carbon atoms, R' is an alkylene group containing from 2 to 4 carbon atoms, G is a saccharide residue containing 5 or 6 carbon atoms, *t* is in the range of from 0 to 25 and *x* is in the range of from 1 to 10.

4. Use as claimed in claim 3, **characterised in that** the alkylpolyglycoside has the general formula I wherein R is C_8 to C_{14} alkyl or alkenyl, t is zero and *x* lies within the range of from 1 to 1.6.

5. Use as claimed in claim 4, **characterised in that** the alkylpolyglycoside has the general formula I wherein R is C_{12} to C_{14} alkyl, *t* is zero and *x* is 1.4.

6. Use as claimed in any preceding claim, **characterised in that** the alkylpolyglycoside is present in an amount of

from 1 to 3 wt%.

7. Use as claimed in any preceding claim, **characterised in that** the alkylpolyglycoside is present in the form of separately admixed granules.

8. Use as claimed in any preceding claim, **characterised in that** the detergent composition is free of enzymes.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 25 6296

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.7)
X	DE 199 44 544 A (COGNIS DEUTSCHLAND GMBH) 29 March 2001 (2001-03-29) * page 9, line 59 - page 10, line 56; claims 1-10 *	1-8	C11D1/83 C11D17/06 //C11D1/66, C11D1/14,
X	EP 1 114 640 A (BEIERSDORF AG) 11 July 2001 (2001-07-11) * examples 4-6 *	1,3-6,8	
X	US 5 929 024 A (GORLIN PHILIP ET AL) 27 July 1999 (1999-07-27) * column 16, line 38 - line 56 * * example 5 * * claim 1 *	1,3-6,8	
X	DATABASE WPI Section Ch, Week 199952 Derwent Publications Ltd., London, GB; Class A97, AN 1999-602135 XP002226957 & CN 1 226 595 A (LI Y), 25 August 1999 (1999-08-25) * abstract *	1,6-8	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D
A	CA 2 308 834 A (HENKEL KGAA) 21 August 2000 (2000-08-21) * table 1 *	1-8	
A	US 5 780 417 A (GORLIN PHILIP A) 14 July 1998 (1998-07-14) * column 3, line 63 - column 4, line 14; claim 1 *	1-8	
A	US 5 834 417 A (ZYZYCK LEN ET AL) 10 November 1998 (1998-11-10) * column 1, line 4 - line 8 * * column 8, line 15 - line 21; claim 1 *	1-8	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 January 2003	Richards, M

CATEGORY OF CITED DOCUMENTS

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EP 02 25 6296

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.7)
A	WO 98 46713 A (BELLEMO CORREA DARINO ;UNILEVER PLC (GB); UNILEVER NV (NL)) 22 October 1998 (1998-10-22) * claims 1-8 *	1-8	
A	WO 00 58436 A (ECOLAB INC) 5 October 2000 (2000-10-05) * claims 1-24 *	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 January 2003	Richards, M

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13-01-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19944544 A	29-03-2001	DE 19944544 A1	29-03-2001
EP 1114640 A	11-07-2001	DE 19960766 A1	21-06-2001
		EP 1114640 A2	11-07-2001
		US 2002028188 A1	07-03-2002
US 5929024 A	27-07-1999	US 6156712 A	05-12-2000
CN 1226595 A	25-08-1999	NONE	
CA 2308834 A	21-08-2000	CA 2308834 A1	21-08-2000
US 5780417 A	14-07-1998	AU 8762298 A	22-02-1999
		WO 9906508 A1	11-02-1999
US 5834417 A	10-11-1998	AU 3388497 A	07-01-1998
		CA 2257250 A1	18-12-1997
		WO 9747717 A2	18-12-1997
WO 9846713 A	22-10-1998	AU 7643498 A	11-11-1998
		WO 9846713 A1	22-10-1998
		ZA 9803156 A	15-10-1999
WO 0058436 A	05-10-2000	US 6387870 B1	14-05-2002
		AU 1121500 A	16-10-2000
		US 2002107164 A1	08-08-2002
		WO 0058436 A1	05-10-2000

EPO FORM P0459

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