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(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

(84) **CH GB GR LI SE AT**

(71) Applicant: **Procter & Gamble European Technical Center (Naamloze Vennootschap)**
Temselaan 100
B-1820 Strombeek-Bever(BE)

(84) **BE DE FR IT LU NL**

(72) Inventor: **Barrat, Christian Roland**
avenue Wannecouter 38
B-1020 Bruxelles(BE)

(74) Representative: **Suslic, Lydia et al**
Procter & Gamble European Technical Center N.V. Temselaan 100
B-1820 Strombeek-Bever(BE)

(54) **Softening detergent compositions containing cellulase.**

(57) The compositions disclosed herein clean well and at the same time act as textile softeners. They contain a cellulase enzyme and are formulated at a mild alkaline pH range.

EP 0 269 168 A2

SOFTENING DETERGENT COMPOSITIONS CONTAINING CELLULASE

Technical Field

The present invention relates to detergent compositions which clean well and at the same time act as textile softeners.

Background

Numerous attempts have been made to formulate laundry detergent compositions which provide the good cleaning performance expected of them and which also have textile softening properties. Thus, attempts have been made to incorporate cationic textile softeners in anionic surfactant-based built detergent compositions employing various means of overcoming the natural antagonism between the anionic and cationic surfactant species. For instance, in British Patent specification 1.518.529, detergent compositions are described comprising organic surfactant, builders, and, in particulate form, a quaternary ammonium softener combined with a poorly water-soluble dispersion inhibitor which inhibits premature dispersion of the cationic in the wash liquor. Even in these compositions some compromise between cleaning and softening effectiveness has to be accepted. Another approach to providing built detergent compositions with softening ability has been to employ nonionic surfactants, instead of anionic, with cationic softeners, and compositions of this type have been described in, for example, British patent specification 1,079,388, German Auslegeschrift 12 20 956 and US patent 3,607,763. However, it is found that if enough nonionic surfactant is employed to provide good cleaning, it impairs the softening effect of the cationic softener, so that, once again, a compromise between cleaning and softening effectiveness must be accepted.

Recently it has been disclosed in British patent specification 1,514,276 that certain tertiary amines with two long chain alkyl or alkenyl groups and one short chain alkyl group are effective fabric softeners in detergent compositions.

Another approach to providing detergent compositions with textile softening ability has been the use of smectite-type clays, as described in British patent specification 1,400,898.

European Patent Application 0 026 528 describes the use of water-insoluble long chain tertiary amines in conjunction with a water-soluble cationic quarternary ammonium compound and/or a water-soluble aliphatic amine, optionally with clays, in alkaline detergent compositions to provide fabric softening properties.

Another approach has been to use cellulolytic enzymes, i.e. cellulase, as a harshness reducing agent in fabric softening compositions, as taught in British Patent 1,368,599.

The use of cellulase in detergent compositions has been further disclosed in GB-A-2,075,028 ; GB-A-2,095,275; GB-A-2,094,826 and Jap. Patent 57108-199.

EP-A 0 120 528 teaches alkaline softening detergent compositions comprising a synergistic mixture of a water-insoluble C_{10}-C_{26} tertiary amine and cellulase.

EP-A 0 177 165 discloses alkaline softening detergent compositions containing a mixture of smectite clay and cellulase.

To date however detergent cellulases have not found wide acceptance in the detergent industry in particular in softening-through-the-wash executions. One reason is that the interaction of cellulase and other, more conventional detergent ingredients is poorly understood. Another reason is that compositions formulated according to art-disclosed recipes do not use cellulase at their optimum PH-range.

To date as well, the tendency in the formulation of softening-through-the-wash detergent compositions has been to increase the pH of the compositions (clearly above 10) in order to boost cleaning performance, especially on cotton fabrics, which otherwise would be impaired by depositing softening ingredients.

However, at such alkaline pH ranges, fabric care prblems such as, e.g., fabric harshening, fabric damage, or dye fading are encountered ; there is, consequently, a standing need for compositions formulated at pH below 10, which show good fabric-care performance, excellent softeness, while having good cleaning properties.

The present invention answers the above need, and provides efficient mild-alkaline softening detergent compositions, which exhibit good fabric-care performance and softeness, and good cleaning properties, especially on cottom fabrics.

The present invention also addresses standing prior-art issues by using a cellulase enzyme at a pH

range where its activity is optimum, and by the surprising discovery that water-insoluble long chain amines such as described in EPA 0 026 528 or EPA 0 120 528, give softeness negatives in presence of cellulase, upon cumulative washes, under the mild alkaline conditions of the invention.

It has also been found that a high level of anionic surfactant is necessary in order to get the benefits of the compositions herein.

It is therefore an object of the present invention to provide anionic-rich, cellulase-containing softening detergent compositions which are formulated at mild-alkaline pH (below 10).

It is another object of the present invention to provide cellulase-containing softening detergent compositions which are essentially free of water-insoluble long-chain amine softening agents or derivatives.

It is a further object of the present invention to provide softening detergent compositions which provide good softness and cleaning benefits and exhibit good fabric-car performance.

SUMMARY OF THE INVENTION

The present invention relates to detergent compositions for the cleaning and softening of fabrics, comprising a surface-active agent, of which at least 50% by weight is an anionic surface active agent, and a cellulase ;

The compositions herein have a pH, 1% solution in distilled water, of from 6.5 to 9.5, and are essentially free of water-insoluble long-chain alkyl amine softening agents, or derivatives thereof.

Preferred compositions include in addition a clay softening material.

DETAILED DESCRIPTION OF THE INVENTION

The surface-active agent

The surface-active agent useful herein contains at least 50% by weight, preferably 60% to 100% by weight of an anionic surface-active agent (salt form). In the present context, anionic surface-active agents do not encompass soaps. A wide range of anionic surfactants can be used in the compositions of the present invention.

Suitable anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulphocarboxylates and their esters, alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy-alkane-1-sulphonates, and beta-alkyloxy alkane sulphonates.

Especially preferred alkyl benzene sulphonates have 9 to 15 carbon atoms in a linear or branched alkyl chain, especially from 11 to 13 carbon atoms. Suitable alkyl sulphates have from 10 to 22 carbon atoms in the alkyl chain, more especially from 12 to 18 carbon atoms. Suitable alkyl polyethoxy ether sulphates have from 10 to 18 carbon atoms in the alkyl chain and have an average of from 1 to 23 - CH_2CH_2O-groups per molecule, especially from 10 to 16 carbon atoms in the alkyl chain and an average of from 1 to 6 -CH_2-CH_2O-groups per molecule.

Suitable paraffin sulphonates are essentially linear and contain from 8 to 24 carbon atoms, more especially from 14 to 18 carbon atoms. Suitable alpha-olefin sulphonates have from 10 to 24 carbon atoms, more especially from 14 to 16 carbon atoms; alpha-olefin sulphonates can be made by reaction with sulphur trioxide, followed by neutralization under conditions such that any sultones present are hydrolyzed to the corresponding hydroxy alkane sulphonates. Suitable alpha-sulphocarboxylates contain from 6 to 20 carbon atoms; included herein are not only the salts of alpha-sulphonated fatty acids but also their esters made from alcohols containing 1 to 14 carbon atoms.

Suitable alkyl glycerly ether sulphates are ethers of alcohols having from 10 to 18 carbon atoms, more especially those derived from coconut oil and tallow. Suitable alkyl phenol polyethoxy ether sulphates have from 8 to 12 carbon atoms in the alkyl chain and an average of from 1 to 6 -CH_2CH_2O-groups per molecule. Suitable 2-acyloxyalkane-1-sulphonates contain from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety. Suitable beta-alkyloxy alkane sulphonates contain from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

The alkyl chains of the foregoing anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example by using the Ziegler or Oxo processes. Water-solubility can be achieved by using alkali metal, ammonium, or alkanol-ammonium cations; sodium is preferred. Mixtures of anionic surfactants are contemplated by this invention; a satisfactory mixture contains

alkyl benzene sulphonate having 11-13 carbon atoms in the alkyl group and alkyl sulphate having 12 to 18 carbon atoms in the alkyl group.

Nonionic surfactants may be incorporated in the compositions herein, in limited amounts (less than 50%). Suitable nonionics are water-soluble ethoxylated materials of HLB 11.5-17.0 and include (but are not limited to) C_{10}-C_{20} primary and secondary alcohol ethoxylates and C_6-C_{10} alkylphenol ethoxylates. C_{14}-C_{18} linear primary alcohols condensed with from seven to thirty moles of ethylene oxide per mole of alcohol are preferred, examples being C_{14}-C_{15} $(EO)_7$, C_{16}-C_{18} $(EO)_{25}$ and especially C_{16}-C_{18} $(EO)_{11}$.

Other types of surfactants can be used in limited amounts, in combination with the anionic surface-active agent. They include zwitterionic amphoteric, as well as cationic surfactants.

Cationic co-surfactants which can be used herein, include water-soluble quaternary ammonium compounds of the form $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and R_5, R_6 and R_7 are each C_1 to C_7 alkyl preferably methyl; X^- is an anion, e.g. chloride. Examples of such trimethyl ammonium compounds include C_{12}-C_{14} alkyl trimethyl ammonium chloride and cocalkyl trimethyl ammonium methosulfate.

The Cellulase

The cellulase usable in the present invention may be any bacterial or fungal cellulase having a pH optimum of between 5 and 9.5.

Suitable cellulase are disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly by the Humicola strain DSM 1800, and cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mullosc (Dolabella Auricula Solander).

The cellulase added to the composition of the invention may be in the form of a non-dusting granulate, e.g. "marumes" or "prills", or in the form of a liquid in which the cellulase is provided as a cellulase concentrate suspended in e.g. a nonionic surfactant or dissolved in an aqueous medium.

Activity determination for the cellulase herein is based on the hydrolysis of carboxymethyl cellulose. Generated low molecular reducing carbohydrates are colorimetrically determined by the ferrocyanide reaction as described by W.S. Hoffman "J. Biol. Chem." 120.51 (1973). Key conditions of incubation are pH = 7.0, temperature of 40°C and incubation time of 20 minutes.

One CMCase unit is defined as the amount of enzyme which forms per minute an amount of reducing carbohydrate equivalent to 10^{-6} mole of glucose, in the above-described conditions.

A highly preferred range of cellulase activity in the present context is from 5 to 100 CMCase activity units/gram of composition.

The compositions of the invention are essentially free of water-insoluble long-chain alkyl amine softening agents, and derivatives thereof, since it has surprisingly been discovered that they interact negatively with cellulase, in the pH conditions of the present invention. Derivatives of the amine softening agents include the corresponding amide compounds. Such amine softening agents are disclosed in e.g. EP.A 0.026.528 and EP.A 0.120.528. and include in particular amines of the formula $R_1R_2R_3N$ where R_1 and R_2 are C_6 to C_{20} alkyl chains, and R_3 is C_1 to C_{10} alkyl chain or hydrogen.

The compositions herein are formulated at a pH in the range of from 6.5 to 9.5, measured as a 1% solution of the composition in distilled water.

At this pH-range, the cellulases for use herein have their optimum performance.

Optional ingredients

The compositions herein may contain, in addition to the essential ingredients, optional ingredients, which can be highly desirable.

For example, it is preferred that the compositions herein contain a clay softening agent, in combination with the cellulase. Such clay softening agents ae well-known in the detergency patent literature and are in broad commercial use, both in Europe and in the United States. Included among such clay softeners are various heat-treated kaolins and various multi-layer smectites. Preferred clay softeners are smectite softener clays that are described in German patent document 23 34 899 and in U.K. patent 1,400,898, which can be referred to for details.

The most perferred clay fabric softening materials include those materials of bentonitic origin, ben-

tonites being primarly montmorillonite type clays together with various impurities, the level and nature of which depends on the source of the clay material. Softener clays are used in the preferred compositions at levels of at least 1%, generally 1-20%, preferably 2-10%.

It is preferred as well that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds clasifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, water-soluble phosphates such as tri-polyphosphate and sodium ortho-and pyro-phosphates, and mixtures thereof Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polyphosphonates and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3.579.454 for typical examples of the use of such materials in various cleaning compositions. Preferred polyfunctional organic acids species for use herein are citric acid, ethylene diamine tetramethylenephosphonic acid, and diethylene triaminepentamethylenephosphonic acid.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates. The 1-10 micron size zeolite (e.g., zeolite A) builders disclosed in German Parent 24.22.655 are especially preferred for use in low-phosphate or non-phosphate compositions. In general, the builder/sequestrant will comprise from 0.5% to 45% of the composition.

The compositions herein can also contain fatty acids, saturated or unsaturated, and the corresponding soaps. Suitable fatty acids, saturated or unsaturated, have from 10 to 18 carbon atoms in the alkyl chain. Preferred are unsaturated species having from 14 to 18 carbon atoms in the alkyl chain, most preferably oleic acid. The corresponding soaps can also be used. The optional fatty acid/soaps are used in levels up to 20%.

The compositions herein can also contain compounds of the general formula R-CH(COOH)CH_2(COOH) i.e. derivatives of succinic acid, wherein R is C_{10}-C_{20} alkyl or alkenyl, preferalby C_{12}-C_{16}, or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include : lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenyl succinate (preferred), 2-pentadecenyl succinate, and the like.

Also useful as builders in the present context are the compounds described in US patent 4.663.071, i.e. mixtures of tartrate monosuccinic acid and tartrate disuccinic acid in a weight ratio of monosuccinic to disuccinic of from 97:3 to 20:80, preferably 95:5 to 40:6.

Another optional ingredient is a bleaching agent. Preferred are peroxygen bleaching agents such as sodium perborate, commercially available in the form of mono-and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate perosyhydrate and urea peroxyhydrate.

Bleach activators may be used in combination with the above peroxygen bleaching agents. Classes of bleach activators include esters, imides, imidazoles, oximes, and carbonates. In those classes, preferred materials include methyl o-acetoxy benzoates; sodium-p-acetoxy benzene sulfonates such as sodium 4-octanoyloxybenzene sulfonate; sodium-4-octanoyloxybenzen sulfonat, and sodium-4-decanoylloxybenzenesulfonate : biophenol diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

Other highly preferred peroxygen bleach activators which are disclosed in U.S. Patents 4,483,778 and 4,539,130, are alpho-substituted alkyl or alkenyl esters, such as sodium-4(2-chlorooctanoyloxy) benzene sulfonate, sodium 4-(3,5,5-trimethyl hexanoyloxy)benzene sulfonate. Suitable peroxyacids are also peroxygen bleach activators such as described in published European Patent Application 0 166 571, i.e., compounds of the general type RXAOOH and RXAL, wherein R is a hydroxycarbyl group, X is a hetero-atom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

Enzymes other than cellulases, such as proteolytic, amylolytic, or lipolytic enzymes can be used in combination with the cellulase herein. All generally known enzyme stabilizing systems can be used in the liquid executions of the compositions herein, at the art established level. Examples of suitable stabilizing systems inlcude short C_{1-4} chain carboxylic acid, particularly formic acid in combination with a low level of calcium, boric acid and the water-soluble salts thereof possibly in combination with polyols.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach stabilizing agents.

Form and Preparation of the compositions -The detergent compositions of this invention can be present in any suitable physical state inclusive of granular, liquid, pasty, or sheet-like form. They may be prepared

in any way, as appropriate to their physical form, by mixing the components, co-agglomerating them, micro-encapsulating them, dispersing them in a liquid carrier, and releasably adsorbing or coating them onto a non-particulate substrate, such as a non-woven or paper sheet.
The following examples illustrate the present invention, but are not intended to limit its scope.

Example I

A granular detergent composition was prepared, by using the following ingredients in the stated proportions :

ingredients	% by weight
Sodium Linear C_{12} alkyl benzene sulfonate	11.0
Sodium Tallow alkyl sulfate	5.0
Tallow alcohol ethoxylate (EO11)	0.3
Sodium tripolyphosphate	24.0
Bentonite clay	8.5
Cellulase	3.0*
Proteolytic enzyme	0.9
Sodium Sulfate	40.0
minors and water	up to 100
pH, 1% concentration in distilled water	8.7

* represents 40 CMCase units per g of composition

The above composition showed good cleaning performance as well as good softeness benefits, while exhibiting good fabric-car properties (no fabric damage dye fading, or fabric harshening observed)
The following granular compositions were also prepared :

ingredient	% by weight	
	Example II	Example I
Sodium Linear C_{12} alkyl benzene sulfonate	7.0	6.5
C_{13-15} fatty alcohol/11 ethylene oxide condensate	1.0	0.5
Sodium sulfate	15.0	15.0
Sodium tripolyphosphate	24.	-
Zeolite A	-	26.0
Sodium nitrilotriacetate	-	5.0
Bentonite clay	6.5	6.5
Cellulase	3.5**	3.5**
Proteolytic enzyme	0.5	0.5
Sodium Perborate tetrahydrate	20.0	20.0
TAED*	1.2	3.0
Boric acid	4.0	4.0
Optical brightener	0.3	0.5
minors and water	- up to 100 -	
pH, 1% concentration in distilled water	9.0	9.0

*tetra acetyl ethylene diamine

**represents 47CMCase units per g of composition

The compositions of Example II and II showed good cleaning, softening, and fabric-care performance.

Example IV

The following liquid detergent composition was also prepared :

ingredient	% by weight
Linear C_{12} alkyl benzene sulphonic acid	11.0
Coconut alkyl sulphate (TEA salt)	4.0
Tallow C_{12-15} alcohol ethoxylate (EO7)	10.0
Coconut fatty acid	10.0
Oleic acid	5.0
Citric acid	1.0
Trethanolamine	4.0
Ethanol	6.0
Propanediol	1.5
Sodium hydroxide	3.0
Sodium formate	1.0
Cellulase	2.5*
Proteolytic enzyme	0.6
minors, water	up to 100
pH, 1% concentration in distilled water	7.5

*represents 34CMCase units per g of composition

Claims

1. A detergent composition for the cleaning and softening of fabric containing, a surface-active agent and a detergent cellulase, characterized in that :
-the surface acitve agent contains at least 50% by weight of anionic surface-active agent;
-the composition is essentially free of water-insoluble long-chain-alkyl amines, softening agents, or derivatives thereof;
-the pH of a 1% solution of the detergent composition in distilled water is from 6.5 to 9.5.

2. A composition in accordance with claim 1, wherein the cellulase is baterial or fungal cellulase having a pH optimum of between 5 and 11.5.

3. A composition in accordance with claim 1 or 2, wherein the cellulase is an alkali cellulase having an optimum pH from 6.5 to 9.5.

4. A composition in accordance with any of the preceding claims, wherein the composition has a cellulase activity of from 5 to 100 CMCase activity unit/gram of composition.

5. A composition in accordance with any of the preceeding claims, wherein the surface-acitive agent contains from 60% to 100% by weight of anionic surface-active agent.

6. A composition in accordance with any of the preceeding claims, which further contains a fabric-softening clay material.

7. A composition in accordance with claim 6 wherein the fabric-softening clay material is a bentonite clay.