



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 286 342
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **88302989.4**

(51) Int. Cl. 4: **C11D 3/22 , C11D 3/37**

(22) Date of filing: **05.04.88**

(30) Priority: **07.04.87 GB 8708312**

(43) Date of publication of application:
12.10.88 Bulletin 88/41

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

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

(84) **GB**

(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(84) **BE CH DE ES FR IT LI NL SE**

(72) Inventor: **Pilidis, Aquillis Panagiotis**
70 Rue de Verdun
F-59249 Aubers(FR)
Inventor: **Tai, Ho Tan**
19 Rue G. Tell
F-59000 Lille(FR)

(74) Representative: **Gambell, Derek et al**
UNILEVER PLC Patents Division P.O. Box 68
Unilever House
London EC4P 4BQ(GB)

(54) **Light duty detergent powder composition.**

(57) A powdered detergent composition suitable for washing fine garments and synthetic and coloured fabrics is free of bleach and sodium silicate. In addition to conventional surfactants and builders it contains a polymer mixture of sodium carboxymethyl cellulose, an alkyl hydroxyalkyl cellulose ether derivative and a polycarboxylate polymer such as a polyacrylate or a maleic/acrylic copolymer. The powders have a low bulk density with an appealing appearance and a soft feel to the hands. They exhibit good solubility and detergency properties.

EP 0 286 342 A2

LIGHT DUTY DETERGENT POWDER COMPOSITION

This invention relates to a light duty detergent powder composition designed especially for washing fine garments and synthetic fabrics.

Fine garments and synthetic and coloured fabrics require careful treatment and yet need to be cleansed and washed like any other wash goods. The washing process, and therefore any composition used in such a process, should not damage the fabric fibres, should not bleach any dyes or pigments in the fabrics and should not cause loss of brightness by the deposition of insoluble material onto the fabric surface. At the same time effective soil removal is required. Furthermore a detergent powder that feels soft and non-gritty in the hands would likely have a better consumer appeal for being identified with mildness to fine garments.

French patent specification 2 237 960 (Unilever NV) describes a detergent composition which in addition to a detergent active material contains an alkyl hydroxyalkyl cellulose and a maleic acid copolymer. Compositions are disclosed therein which contain no bleach and are thus suitable for the treatment of fine garments. European patent specification EP 54 325-B (Unilever NV et al) describes compositions which contain a mixture of sodium carboxymethyl cellulose, a linear polymer polycarboxylate and a cellulose ether. The specifically exemplified compositions recommend the presence of 5% sodium silicate.

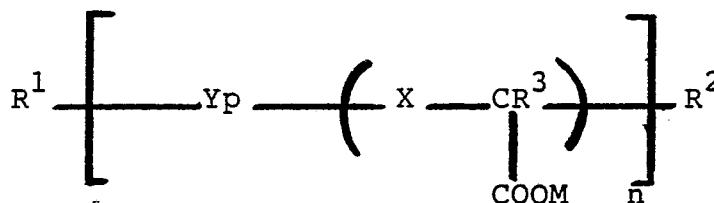
It is an object of this invention to provide a non-gritty, soft-feeling light duty detergent powder composition especially designed for effective washing of fine garments and synthetic fabrics and yet is exceptionally mild to colour and fabric caring.

According to the invention there is provided a bleach-free powdered detergent composition for washing fine garments and synthetic and coloured fabrics, comprising:

(i) from 10% to 35% by weight of an organic surface active agent selected from anionic surfactants, nonionic surfactants and mixtures thereof;

(ii) from 5% to 60% of a detergency builder; and

(iii) from 1% to 15% of a polymer mixture containing (a) an alkali metal carboxymethyl cellulose having from 0.5 to 0.9 carboxymethyl ether groups per anhydrose unit and (b) an alkylhydroxyalkyl cellulose derivative having a total number of substituent groups per glucose unit of between 1.5 and 3.0; characterised in that the composition contains no sodium silicate and the polymer mixture additionally contains (c) a polycarboxylate polymer selected from compounds having the empirical formula:



wherein X is O or $-\text{CH}_2-$, Y is a comonomer or mixture of co-monomers, R^1 and R^2 are bleach stable polymer end groups, R^3 is H, OH or C_1 to C_4 alkyl, M is a water-soluble cation, p is from 0 to 2 and n is at least 10, and mixtures thereof.

The compositions of the present invention are essentially free of bleach and sodium silicate. Impurities in other ingredients may accidentally introduce these materials, especially the sodium silicate. Such impurities will generally only be present in small amounts in the overall composition, up to about 0.5% by weight.

The individual components of the polymer mixture system are known in the art. However the use of this particular mixture in a high active, non-bleaching and sodium silicate-free detergent composition provides for the desired beneficial properties of an attractive light duty detergent powder composition destined for the fine wash.

Polymer (a) - A well-known representative of this polymer is sodium carboxymethylcellulose as available on the market, which has been used as soil-suspending and anti-redeposition agent in fabric washing detergent compositions.

Polymer (b) - To be of use in accordance with the invention, the total number of substituent groups per glucose unit of the cellulose derivative should be between about 1.5 and about 3.0, preferably between about 2.0 and about 3.0. There should be at least about 1.0, preferably from about 1.0 to about 2.5, and particularly preferably from about 1.5 to about 2.1, alkyl groups per glucose unit; and at least about 0.1,

preferably from about 0.2 to about 1.5, and particularly preferably from about 0.5 to 1.5, hydroxyalkyl groups per glucose unit. The alkyl groups should contain from 1 to 4, and preferably from 1 to 3, carbon atoms, and the hydroxyalkyl groups should contain from 2 to 4, preferably from 2 to 3, carbon atoms. Particularly preferred alkyl groups are methyl and ethyl, and the preferred hydroxyalkyl groups are hydroxyethyl and hydroxypropyl. Propyl, butyl and hydroxybutyl groups may also be used. When the alkyl group is methyl it is preferred that the hydroxyalkyl group be hydroxypropyl, and when the alkyl group is ethyl it is preferred that the hydroxyalkyl group be hydroxyethyl, although it will be appreciated that other combinations of alkyl and hydroxyalkyl groups may be used if desired. Particularly preferred cellulose derivatives for use in accordance with the invention are methyl hydroxypropyl celluloses having from 1.7 to 2.1 methyl groups per glucose unit and from 0.8 to 1.0 hydroxypropyl groups per glucose unit, and ethyl hydroxyethyl celluloses having from 1.5 to 1.6 ethyl groups per glucose unit and from 0.5 to 0.6 hydroxyethyl groups per glucose unit.

Many of these cellulose derivatives are available commercially, for example under the Trade name of Modocoll®, supplied by the Mo och Domsjö Company, and others may readily be prepared by simple chemical procedures. For instance, a methyl hydroxypropyl cellulose derivative may be prepared by reacting the cellulose with dimethylsulphate and then with propylene oxide (or vice versa: if one substituent is to be present in a greater amount than the other, it is preferable that the major substituent is applied first), and an ethyl hydroxyethyl cellulose may be prepared by reacting the cellulose with ethylene oxide and then with ethyl chloride.

The polycarboxylate polymers (c) are disclosed and further characterised in EP-A-137 669, the most important members of which are:

(i) those belonging to the class of copolymeric polycarboxylates which, formally at least, are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid and metaconic acid as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an α -C₁-C₄-alkyl acrylic acid as second monomer.

Preferred copolymers of this class are copolymers of maleic acid (anhydride) and (meth)acrylic acid, as disclosed in EP-B-25 551 and GB Patent 1 596 756.

(ii) those belonging to the class of poly (α -hydroxyacrylates);

(iii) those belonging to the class of polyacetal carboxylates or acetal polycarboxylates; and

(iv) those belonging to the class of homopolymeric polyacrylates.

Any polymer of these classes can be chosen as polymer (c) in the polymer mixture, either alone or as mixture, though preference is given to polymers of the classes (i) and (iv).

These polymers should preferably be present in the composition at a total level of from 1.5% to 10% by weight in proportions of about 0.2-2% by weight of polymer (a), about 0.1-3% by weight of polymer (b) and about 0.5-10%, most preferably about 1-5% by weight of polymer (c).

The detergent composition of the invention contains at least one detergent-active material, preferably at a level of 15% to 25% by weight. This material may be anionic or nonionic in nature, but mixtures of anionic and nonionic materials are preferred.

The anionic detergent-active material can be a soap or a non-soap (synthetic) anionic material. Anionic detergent-active materials are commercially 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.

Synthetic anionic detergent-active materials useful in the present invention are water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C₈-C₁₈) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amines of methyl taurine; alkane monosulphonates such as those derived by reacting α -olefins ((C₈-C₂₀)) with sodium bisulphite and those derived from reacting paraffins with SO₂ and Cl₂ and then hydrolysing with a base to produce a random sulphonate; sodium and potassium salts of fatty acid ester sulphonates; water-soluble salts of dialkyl esters of sulphosuccinic acid; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀-C₂₀ α -olefins, with SO₃ and then neutralising and hydrolysing the reaction product. The preferred

anionic detergent compounds are sodium (C₁₁-C₁₅) alkyl benzene sulphonates and sodium (C₁₅-C₁₈) alkyl sulphates.

Mixtures of anionic compounds may also be used, preferably mixtures of synthetic anionic surfactants and alkalimetal soaps.

5 Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 3 to 30, preferably 5 to 14 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such
10 compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and diisooctylphenol condensed with 13 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon
15 atoms, in either straight chain or branched chain configuration, with from 2 to about 40 moles, preferably 2 to about 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or prepared by the Ziegler process from
20 ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols, Dobanols and Neodols which have about 25% 2-methyl branching (Lutensol being a Trade Name of BASF, Dobanol and Neodol being Trade Names of Shell), or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a Trade Name of ICI) or the primary alcohols having more than 50% branched structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling
25 within the scope of the invention include Dobanol 45-4, Eobanol 45-7, Dobanol 45-9, Dobanol 91-2.5, Dobanol 91-3, Dobanol 91-4, Dobanol 91-6, Dobanol 91-8, Dobanol 23-6.5, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of
30 alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the
35 condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic", supplied by Wyandotte Chemicals Corporation.

The mixing ratio of anionic to nonionic materials is not very critical and can be varied as desired by the skilled artisan. However, preference here is given to ratios within the range of 6:1 to 1:2, preferably from 5:1
40 to 1:1.

The detergent compositions according to the invention also contain a detergency builder, which can be an inorganic builder or an organic builder, in an amount generally within the range of from about 5% to about 60%, preferably from 15% to 50% by weight.

45 Examples of phosphorus-containing inorganic detergency builders include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates and polyphosphates. Specific examples of inorganic phosphate builders include sodium and potassium triphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonate, bicarbonates, and crystalline and amorphous aluminosilicates. Specific
50 examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates.

Examples of organic detergency builders, when present, include the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetal carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted
55 ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acid and citric acid.

Sodium silicate is usually relied upon in detergent compositions to provide alkalinity. In the compositions of this invention the desired alkalinity can be obtained by the use of water-soluble alkaline builder

materials. Alkali metal carbonates and their mixtures with alkali metal phosphates are especially suitable.

In use, the detergent compositions according to the invention will preferably show a pH of between 9.0 and 10.5.

It should be appreciated that the detergent composition according to the invention may further contain
5 any of the conventional additives in amounts in which such materials are normally employed in fabric-washing detergent compositions and which serve to further improve the laundering characteristics and/or add aesthetic appeal to the compositions. Examples of these additives include lather boosters, anti-foaming agents, non-silicate alkaline materials fabric-softening agents, corrosion inhibitors, inorganic salts, sequestering agents, colouring agents and perfumes, so long as these additives do not adversely influence the basic
10 objective of the invention. Enzymes such as proteolytic, lipolytic and amylolytic enzymes are preferably incorporated to effect stain removal by bioaction.

Though in a preferred embodiment, the invention omits the use of fluorescent agents or optical bleaching agents, as these additives could change the hue of the original fabric colours, their presence in very small amounts up to about 0.02% by weight is generally desirable for aesthetic reasons in giving
15 brightness to the powder appearance.

The detergent composition of the invention is generally manufactured and presented in the form of a particulate powder, which includes the form of granules. Detergent powder compositions according to the invention can be prepared using any of the conventional manufacturing techniques commonly used or proposed for the preparation of fabric-washing detergent powder compositions. These include slurry-making
20 of the basic ingredients followed by spray-drying or spray-cooling and subsequent dry-dosing of sensitive ingredients not suitable for incorporation prior to the drying or heating step. Other conventional techniques, such as noodling, granulation, dry-mixing, and mixing by fluidisation in a fluidised bed, may be utilised as and when necessary and desired. Such techniques are familiar to those skilled in the art of detergent powder composition manufacture and require no further explanation as being essential to the invention.

25 The absence of silicate gives a snowy aspect of the powder and favours quick solubility of the product without insolubles.

Whereas polymer (c), such as polyacrylates or acrylic acid/maleic acid copolymers, aids in giving structure to the powder, the combined use thereof with polymer (a) e.g. sodium carboxymethyl cellulose, and polymer (b) e.g. ethyl hydroxyethyl cellulose, results in a further enhancement of the anti-redeposition
30 properties of the composition; with improved wettability of synthetic fibres being observed.

The invention will now be further described with reference to the following non-limiting examples.

35

40

45

50

55

Example 1

The following detergent composition was prepared by spray-drying the basic ingredients and dry-mixing the enzyme and anti-foaming agent.

5

	<u>% by weight</u>
10 C ₁₂ -alkyl benzene sulphonate	12.5
Nonionic fatty alcohol/7 ethoxylate	3.5
Sodium soap	2.0
Sodium triphosphate	25.0
15 Sodium carbonate	5.0
Sodium carboxymethylcellulose	0.35
Ethylhydroxyethylcellulose (Modocoll ^R)	0.35
20 Acrylic/maleic acid copolymer (Sokalan CP5 ^R)	1.5
Fluorescer	0.01
Sodium sulphate	39.0
25 Anti foaming agent	1.5
Proteolytic enzyme (Savinase 4.OT)	0.65
Water	up to 100%

30

- * Modocoll is a register Trade Mark (Mo och Domsjö)
Sokalan CP5 is a registered Trade Mark (BASF).

35

The product obtained was a light powder of bulk density 0.40 g/cc having an appealing white snowy appearance and a soft feel in the hands with very good solubility and detergency properties.

When two similar products are compared, one containing 6.0% sodium silicate and one in which the silicate was absent (the balance being made up by sodium sulphate), it was found that the composition containing the silicate left a residue of insoluble material when dissolved in water at 20°C, which residue was 3 times greater than that left by the silicate-free composition.

40

Claims

45

1. A bleach-free powdered detergent composition for washing fine garments and synthetic and coloured fabrics, comprising:

(i) from 10% to 35% by weight of an organic surface active agent selected from anionic surfactants, nonionic surfactants and mixtures thereof;

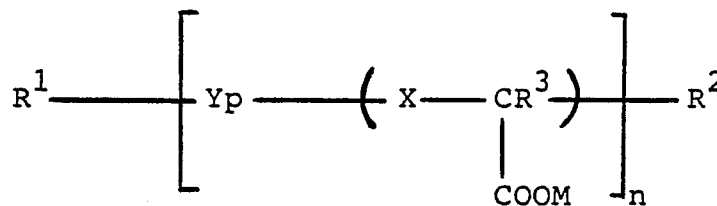
50

(ii) from 5% to 60% of a detergency builder; and

(iii) from 1% to 15% of a polymer mixture containing (a) an alkali metal carboxymethyl cellulose having from 0.5 to 0.9 carboxymethyl ether groups per anhydrose unit and (b) an alkylhydroxyalkyl cellulose derivative having a total number of substituent groups per glucose unit of between 1.5 and 3.0;

55

characterised in that the composition contains no sodium silicate and the polymer mixture additionally contains (c) a polycarboxylate polymer selected from compounds having the empirical formula:



wherein X is O or -CH₂-, Y is a comonomer or mixture of co-monomers, R¹ and R² are bleach stable polymer end groups, R³ is H, OH or C₁ to C₄ alkyl, M is a water-soluble cation, p is from 0 to 2 and n is at least 10, and mixtures thereof.

2. A composition according to Claim 1 in which polymer (c) is a copolymer of an unsaturated polycarboxylic acid and an unsaturated monocarboxylic acid.

3. A composition according to Claim 1, in which the polymer (c) is a homopolymeric polyacrylate.

4. A composition according to Claim 1, in which the polymer mixture contains from 0.2 to 2% by weight of polymer (a), from 0.1 to 3% of polymer (b) and from 0.5 to 10% of polymer (c).

5. A composition according to Claim 1, in which the detergency builder comprises an alkali metal carbonate or a mixture thereof with an alkali metal phosphate.

6. A composition according to Claim 1, which is free of fluorescent agents and optical bleaching agents.