(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 246 896
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 87304524.9

(22) Date of filing: 21.05.87

(51) Int. Cl.4: C 11 D 3/12

(30) Priority: 23.05.86 GB 8612705

(43) Date of publication of application:
25.11.87 Bulletin 87/48

(84) Designated Contracting States:
AT 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) Designated Contracting States: GB

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

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

(72) Inventor: Van Kralingen, Cornelis Gerhard
Verzetsstraat 67
NL-2912 CT Nieuwerkerk a/d Ijssel (NL)

Niemantsverdriet, Robert Ernst
Racinelaan 4
NL-3533 VM Utrecht (NL)

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

(54) **Detergent compositions.**

(57) A zero or low phosphate built detergent composition comprises a detergent active material and, as builders, an alkali metal carbonate such as sodium carbonate, and an aluminosilicate material, such as a zeolite. A calcium carbonate crystallisation seed, such as calcite, is also present in the composition to reduce hardness of the water. The calcite preferably has a surface area of at least $2m^2/g$ and is present at a level from about 1% to about 10% by weight of the composition. The composition may also contain optional additives such as perfume.

EP 0 246 896 A1

Description

DETERGENT COMPOSITIONS

This invention relates to detergent compositions, in particular built detergent compositions with low or zero levels of phosphate. Detergent compositions conventionally include, in addition to a detergent active material, a phosphate detergency builder, such as sodium tripolyphosphate. However, in view of the environmental problems which may occur in some cases with the discharge of phosphates into waste waters, it is desirable to reduce the level of phosphorous in detergent compositions.

It has been proposed to use both alkali metal carbonates and aluminosilicate material as alternatives to phosphate builder materials. Belgium Patent 861 435 (Colgate) discloses a phosphate-free particulate detergent composition comprising both an alkali metal carbonate and bicarbonate, zeolite and a nonionic detergent.

We have now discovered that improved detergency can be achieved with a detergent composition which is substantially free of phosphate builders, and which includes an alkali metal carbonate and an aluminosilicate material, by the addition of a seed crystal. Thus, according to the invention there is provided a detergent composition comprising at least one synthetic detergent active material, an alkali metal carbonate and a water-insoluble aluminosilicate material, characterised in that it further comprises a calcium carbonate seed crystal.

The detergent composition according to the invention necessarily includes a synthetic detergent active material otherwise referred to herein simply as a detergent compound. The detergent compound may be selected from anionic, nonionic, zwitterionic and amphoteric synthetic detergent active materials and mixtures thereof. Many suitable detergent compounds 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.

The level of the detergent compound in the composition is from about 5% to about 40%, preferably from about 10% to about 25% by weight.

The preferred detergent compounds which can be used are synthetic anionic and nonionic compounds. The former are usually 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 (C_8-C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) 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 (C_8-C_{18}) 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 amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, generally up to 25 EO, ie up to 25 units of ethylene oxide per molecule, the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally up to 40 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent compounds, for example mixed anionic or mixed anionic and nonionic compounds may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines.

Amounts of amphoteric or zwitterionic detergent compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and/or nonionic detergent compounds.

For example, mixtures of amine oxides and ethoxylated nonionic detergent compounds can be used.

Soaps may also be present in the detergent compositions of the invention. The soaps are particularly useful at low levels in binary and ternary mixtures, together with nonionic or mixed synthetic anionic and nonionic detergent compounds, which have low sudsing properties. The soaps which are used are the water-soluble salts of C_{10}-C_{20} fatty acids in particular with inorganic cations such as sodium and potassium. It is particularly preferred that the soaps should be based mainly on the longer chain fatty acids within this range, that is with at least half of the soaps having a carbon chain length of 16 or over. This is most conveniently accomplished by using soaps from natural sources such as tallow, palm oil or rapeseed oil, which can be hardened if desired, with lesser amounts of other shorter chain soaps, prepared from nut oils such as coconut oil or palm kernel oil. The amount of such soaps can be up to about 20% by weight, with lower amounts of 0.5% to about 5% being generally sufficient for lather control. Amounts of soap between about 2% and about 20%, especially between about 5% and about 15%, can advantageously be used to give a beneficial effect on detergency and reduced levels of incrustation.

The alkali metal carbonate and water insoluble aluminosilicate are used as detergency builder materials in the present invention. The alkali metal carbonate is preferably selected from carbonates and sesquicarbonates of sodium and potassium and is most preferably sodium carbonate.

The alkali metal carbonate is preferably present in the detergent composition at a level of about 5% to about 50% by weight, most preferably from about 10% to about 40% by weight of the composition.

The aluminosilicate material is preferably crystalline or amorphous material having the general formula:

$Na_Z (AlO_2)_Z (SiO_2)_Y \ x\ H_2O$

wherein Z and Y are integers of at least 6, the molar ratio of Z to Y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264 such that the moisture content is from 10% to 28% by weight. The alumino-silicate preferably has a particle size of from 0.1 to 100 microns, ideally between 0.1 and 10 microns and a calcium ion exchange capacity of at least 200 mg.calcium carbonate/g. In a preferred embodiment, the water-insoluble aluminosilicate ion exchange material has the formula

$Na_{12}(AlO_2SiO_2)_{12}xH_2O$

wherein x is an integer of from 20 to 30, preferably about 27. This material is available commercially as Zeolite A.

The aluminosilicate material is preferably present in the detergent composition at a level within the range from about 1% to about 40%, based on the anhydrous material, by weight of the composition.

In addition to the essential alkali metal carbonate and aluminosilicate material it is possible to include minor amounts of other precipitating builder materials, other ion-exchange builder materials and sequestering builder materials. Preferably the further builder material is a non-phosphate material.

Preferably the calcium carbonate seed crystal is any crystalline form of calcium carbonate, such as calcite, aragonite or travertine or a mixture thereof. Most preferably the seed crystal is calcite. The calcium carbonate seed crystal preferably has a surface area of at least $2m^2/g$, most preferably at least $30m^2/g$. A level from about 1% to about 10% by weight of the seed crystal in the detergent composition is preferred. Below a level of 1% the addition of calcite has no effect on the detergency of the detergent composition. No further improvement in detergency is found if more than 10% by weight of calcite is added to the detergent composition.

Apart from the essential detergent active compounds, alkali metal carbonate, aluminosilicate builder and crystallisation seed, a detergent composition according to the invention may contain any of the conventional additives in the amounts in which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, antiredeposition agents, such as sodium carboxymethyl cellulose and cellulose ethers, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents, fabric softening agents, inorganic salts, such as sodium sulphate, and usually present in very minor amounts fluorescent agents, perfumes, germicides and colourants.

It is also desirable to include in the compositions an amount of an alkali metal silicate, particularly sodium ortho-, meta- or preferably neutral or alkaline silicate. The presence of such alkali metal silicates at levels of at least about 1%, and preferably from about 3% to about 15%, by weight of the composition, is advantageous in decreasing the corrosion of metal parts in washing machines, besides giving processing benefits and generally improved powder properties. The more highly alkaline ortho- and metasilicates would normally only be used at lower amounts within this range, in admixture with the neutral or alkaline silicates.

It is generally also desirable to include a structurant material, such as succinic acid, and/or other dicarboxylic acids, sucrose and polymers, in detergent compositions of the invention, to provide a powder having excellent physical properties. When the detergent compositions contain succinic acid this can react with the alkali metal carbonate present to give an alkali-metal bicarbonate, or sesquicarbonate.

Detergent compositions according to the invention may be produced by any of the techniques commonly employed in the manufacture of fabric washing detergent compositions, including particularly slurry-making and spray-drying processes. The calcium carbonate seed crystal and the following optional components, the silicate material, enzyme, bleach and perfume, may be post-dosed to a spray-dried powder comprising the detergent active, the detergency builders and any other optional materials.

The invention is further illustrated by the following non-limiting examples.

Example 1

The water softening capacity of a number of co-builders when added to zeolite A (Wessalith, P, ex Degussa) was examined. Two grams of zeolite were added to a litre of 40°FH water. (The water hardness was adjusted using stock solutions of calcium chloride). After one minute, 1g (occasionally 2g) of a co-builder was added. Experiments were carried out at ambient temperature and at 40°C. Values of pCa for each solution were determined using conventional methods.

Co-builder	pCa (after 20 minutes) ambient	40°C
Na_2CO_3 (+0.1g calcite*)	5.19	6.01
Na_2CO_3	-	5.59
zeolite	5.60	5.60
No co-builder (control)	4.20	4.42

* calcite (Omyalite 90, ex Omya).

These results demonstrate that the addition of calcite to a solution comprising zeolite and carbonate has a positive effect on the softness of the water when compared with the control.

Example 2

The influence of the amount, and type, of calcite on the water softening performance of a detergent composition was investigated in this example.

Varying amounts of two forms of calcite, Omyalite 90 and Socal U3 (ex Solvay), which have surface areas of $10.8m^2/g$ and $80m^2/g$ respectively, were added to a solution of a detergent composition in 40°FH water, at a temperature of 22°C. The detergent composition comprised 20% zeolite A, 20% sodium carbonate, 9% alkyl benzene sulphonate (DOBS JN) and 4% of an alkoxylated alcohol (Synperonic A7) and was present at a level of 5g/l.

After 15 minutes a value of pCa for each detergent composition was measured. Figure 1 shows graphically the variation of pCa with the concentration of calcite, where the level of calcite is based on the weight of sodium carbonate present in the composition.

Clearly, at a level of calcite of greater than 15%, based on the weight of sodium carbonate, the replacement of low surface area calcite by high surface area calcite gives a significant improvement in the water softening capacity of the detergent composition.

Example 3

Calcite (Socal U3), sodium perborate monohydrate and alkaline sodium silicate were post-dosed to a spray-dried powder detergent composition comprising 8.1% alkyl benzene sulphonate (Sirene X12L, ex SIR), 3.6% of an alkoxylated alcohol (Lutensol AO-7, ex BASF), 3.7% soap, 27.7% sodium carbonate, 18% zeolite A, 6.5% sodium sulphate, 2% succinic acid, and minor quantities of other conventional detergent additives. The sodium perborate monohydrate and alkaline sodium silicate were present at levels of 9% and 5% respectively in the detergent composition. For comparison purposes a composition was prepared in which the calcite was replaced by an equivalent amount of sodium sulphate. The compositions were added to water of varying hardness and pCa values were measured. The following results were obtained.

Dosage	Water hardness	pCa No Socal U3	pCa 4% Socal U3
5g/l	40°FH (all Ca)	3.85	5.28
5g/l	27°FH (Ca:Mg of 4:1)	4.25	5.25
2g/l	10°FH (all Ca)	4.40	5.26
5g/l	27°FH (all Ca)	3.74	4.10

Clearly the presence of calcite in the composition has a positive effect on the softness of the water.

Example 4

Six different test cloths were washed in a laboratory apparatus with a detergent composition (X) comprising 9% alkyl benzene sulphonate (DOBS JN), 4% of an alkoxylated alcohol (Synperonic A7), 20% zeolite A, 20% sodium carbonate, 2% calcite (Socal U3), 10% sodium sulphate, 5% alkaline sodium silicate and 0.5% sodium carboxylmethyl cellulose. For comparison purposes test cloths were also washed in the same detergent composition except that it contained no calcite (Detergent composition Y). These experiments were carried out in 40°FH water at a temperature of 40°C with a concentration of the detergent composition of either 4 or 8g/l; the duration of the wash cycle was 20 minutes. The test cloths were then dried and the value of ΔR at 460 nm was determined using a "Zeiss Elrepho" reflectometer fitted with a UV filter (ΔR represents the difference in the value of the reflectance of the test cloth compared to the untreated cloth). Triplicate experiments were performed and the following results were obtained.

Test cloths were washed at 40°C with the detergent composition present at a level of 4g/l.

ΔR_{460}

Test Cloths	Detergent composition X	Detergent composition Y
a	13.1	9.2
b	15.8	15.2
c	12.2	11.1
d	17.5	9.4
e	16.8	13.3
f	9.8	5.4

Test cloths were washed at 40°C with the detergent composition present at a level of 8g/l.

	ΔR_{460}	
	Detergent composition	
	X	Y
Test Cloths		
a	17.7	14.6
b	24.7	21.0
c	16.6	15.6
d	21.7	20.5
e	25.3	22.4
f	21.6	14.9

These results demonstrate the significant effect including calcite in a detergent composition, comprising carbonate and zeolite as co-builders, has on reflectance values.

Example 5

Calcite, sodium perborate monohydrate and alkaline sodium silicate were as post-dosed to a spray-dried powder detergent composition comprising 8.1% alkyl benzene sulphonate (Sirene X12L, ex SIR), 3.6% of an alkoxylated alcohol (Lutensol AO-7, ex BASF), 3.7% soap, 27.7% sodium carbonate, 18% zeolite A, 6.5% sodium sulphate, 2% succinic acid, and minor quantities of other conventional detergent additives. The sodium perborate monhydrate and alkaline sodium silicate were present at levels of 9% and 5% respectively in the detergent composition.

A range of different calcite materials (defined in terms of surface area m^2/g) were tested. The following table gives the levels of calcite used.

Example	Surface Area Calcite (m^2/g)	% Calcite	ΔR_{460}
5A		0	23.9
5B	0.75	10	28.4
5C	10.8	10	28.7
5D	23	10	30.4
5E	80	3	31.8
5F	80	6	31.3
5G	80	10	31.8
5H	80	20	28.5

Test cloths were washed in a laboratory apparatus with each of the above detergent compositions. The experiments were carried out in 40°FH water at a temperature of 60°C with a concentration of the detergent composition of 5g/l, the duration of the wash cycle was 20 minutes. The test cloths were then dried and the value of ΔR at 460nm was determined using a "Zeiss Elrepho" reflectometer fitted with a UV filter. (ΔR is defined as in Example 4).

The results clearly demonstrate that replacement of low surface area calcite by high surface area calcite gives a detergent composition with improved detergency. The results further show that increasing the level of calcite above 10% by weight gives no further improvement in detergency.

As used herein, "°FH" with respect to water hardness is the molar concentration of free hard water ions x 10^{-4}.

As used herein, "pCa" is the negative logarithm of the free calcium ion concentration.

All percentage weights are based on the anhydrous material.

The words "Zeiss Elrepho" used herein is a registered Trade Mark.

Claims

1. A detergent composition comprising at least one synthetic detergent active material, an alkali metal carbonate and a water-insoluble aluminosilicate material, characterised in that it further comprises a calcium carbonate seed crystal.

2. A detergent composition according to Claim 1, further characterised in that it comprises from about 5 to about 40% by weight of synthetic detergent active material, from about 1 to about 40% by weight of a water-insoluble aluminosilicate based on the anhydrous material, from 5% to 50% by weight of an alkali metal carbonate and from 1% to 10% by weight of a calcium carbonate seed crystal.

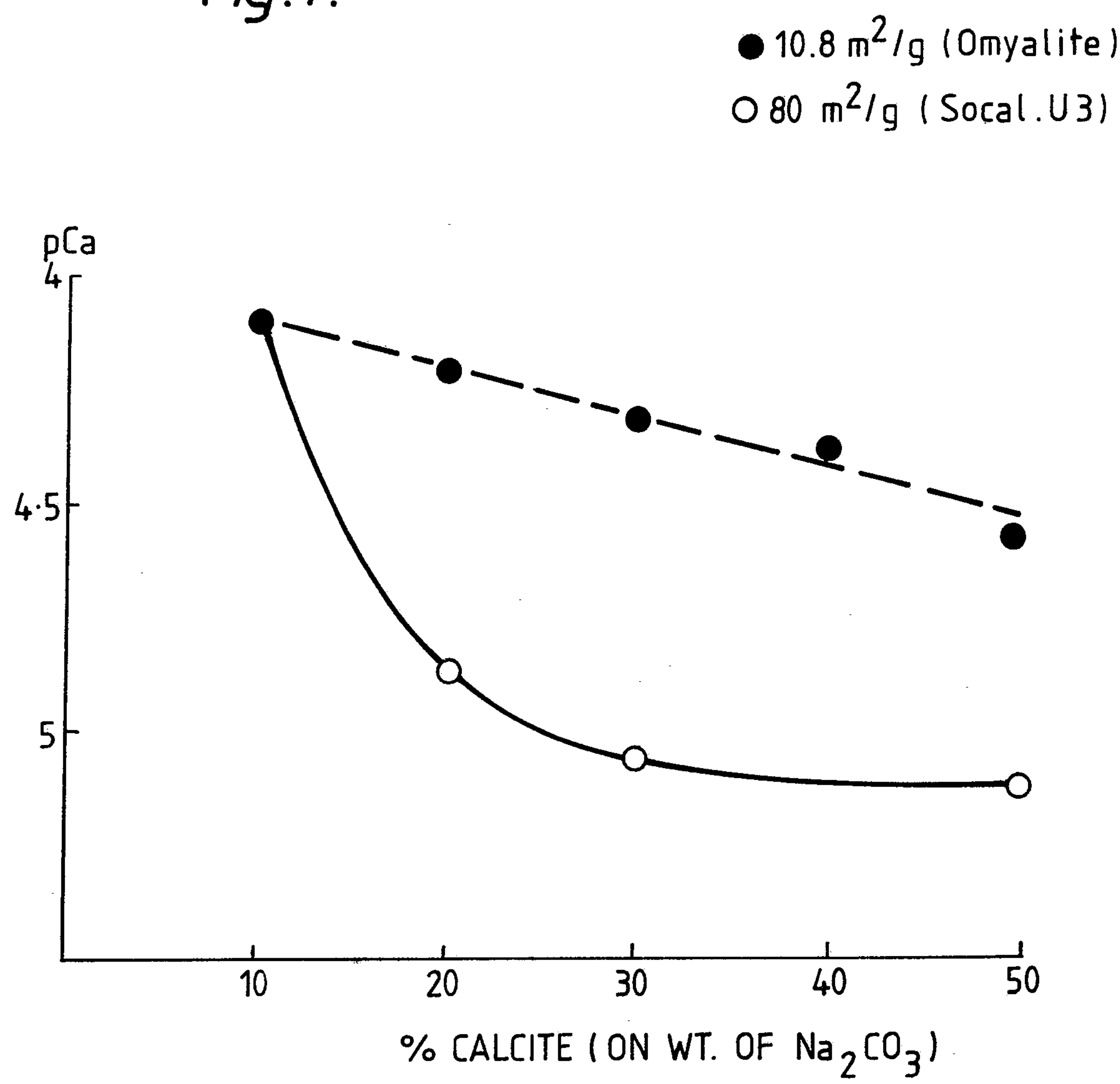
3. A detergent composition according to Claims 1 or 2, further characterised in that the synthetic detergent active material is selected from synthetic anionic, nonionic, amphoteric or zwitteronic detergent compounds or mixtures thereof.

4. A detergent composition according to any one of the preceding claims, further characterised in that the calcium carbonate seed crystal is calcite.

5. A detergent composition according to any one of the preceding claims, further characterised in that the calcium carbonate seed crystal has a surface area of at least $2m^2/g$.

6. A detergent composition according to any one of the preceding claims, further characterised in that the water insoluble aluminosilicate material is a zeolite.

Fig.1.



10.8 m²/g (Omyalite)
80 m²/g (Socal.U3)
pCa
4
4·5
5
10
20
30
40
50
% CALCITE (ON WT. OF Na₂CO₃)

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 30 4524

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.4)
Y	US-A-4 347 152 (H.E. WIXON) * claims 1-7 * ---	1-3,6	C 11 D 3/12
Y	DE-A-3 534 888 (TOYO SODA MANUFACTURING CO.) * claims 1-4 * ---	1-3,6	
Y	US-A-4 399 048 (W.J. GANGWISCH et al.) * claims 1-4 * ---	1-3,6	
Y	GB-A-2 060 676 (UNILEVER LTD.) * page 3, examples, table 1 * ---	1-4	
Y	US-A-3 966 432 (G.G. RAYNER) * claims 1-3 * -----	1-4	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)** C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	31-07-1987	SCHULTZE D

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

EPO Form 1503 03.82