

12

EUROPEAN PATENT APPLICATION

21 Application number: **87301227.2**

51 Int. Cl.4: **C 11 D 1/83**
C 11 D 3/12

22 Date of filing: **12.02.87**

30 Priority: **14.02.86 GB 8603667**

43 Date of publication of application:
02.09.87 Bulletin 87/36

84 Designated Contracting States:
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

72 Inventor: **Niven, Ian Eric**
a 16 Childwall Park Avenue
Liverpool L16 OJG (GB)

74 Representative: **Waldren, Robin Michael et al**
Unilever PLC Patent Division P.O. Box 68 Unilever House
Blackfriars
London EC4P 4BQ (GB)

54 **Detergent compositions.**

57 A detergent composition having improved dispensibility in automatic washing machines and based on a builder mixture of a water-soluble alkali metal carbonate such as sodium carbonate and a water-insoluble particulate carbonate seed crystal for calcium carbonate, e.g. calcite. The composition comprises a ternary active system containing 30-70% anionic active such as an alkyl benzene sulphonate, 20-27% of a nonionic active such as an ethoxylated alcohol and at least 10% soap. However, the soap must not exceed 10% of the composition as a whole. The composition leaves lower levels of residue in the machine dispenser.

Description

DETERGENT COMPOSITION

This invention relates to detergent compositions, in particular to detergent compositions intended to be used for washing fabrics in an automatic washing machine, and more especially to such compositions which contain little or no phosphorus containing materials.

Detergent compositions usually contain, in addition to a detergent active material, a detergency builder whose role, *inter alia*, is to remove hardness ions from the wash liquor which would otherwise reduce the efficiency of the detergent active material. Water-soluble phosphate materials have been extensively used as detergency builders. However for a number of reasons, including eutrofication allegedly caused by phosphates and cost, there has been a desire to use alkali metal carbonates especially sodium carbonate instead. Alkali metal carbonate detergency builders suffer however from a number of disadvantages. Firstly, the reaction between the alkali metal carbonate and calcium ions which are present in hard water results in the formation of water-insoluble calcium carbonate which, depending on the conditions, may be in such a form as to become deposited on the washed fabrics. Secondly, the reaction between the alkali metal carbonate and the calcium ions of the water is slow, especially at low temperatures and is readily inhibited by materials which act as calcium carbonate precipitate growth inhibitors, referred to herein as poisons. The result of this is that the concentration of calcium ions in the wash liquor is not reduced as far or as fast as desired, so that some free calcium ions are still available to reduce the efficiency of the detergent active material.

As a possible solution to this problem it has been proposed to include in the detergent composition, a water-insoluble material which would act as a seed crystal for the precipitated calcium carbonate and would adsorb the poisons from the wash liquor. Among other materials, finely divided calcite has been proposed as such a material - see GB 1 437 950.

The detergent active material may be chosen from a number of classes of materials but it is preferred to use a mixture of an anionic non-soap detergent active, a nonionic detergent active and soap.

However, it has been found that detergent compositions containing such a ternary active system together with an alkali metal carbonate and calcite, in comparison with equivalent compositions containing phosphates as detergency builders, suffer from poor dispensibility from automatic washing machines. In such machines the user places an appropriate amount of detergent powder in a dispenser where it is retained until needed by the machine. At an appropriate moment in the washing cycle, water enters the dispenser and washes the powder into a feed pipe leading to the washing compartment of the machine. If the powder is not substantially washed out of the dispenser by the process, not only is it wasted but after repeated use it will build up and eventually block the dispenser and/or the feed pipe. Alternatively, it requires the user to clean out the dispenser after each wash cycle.

The reason for the poor dispensibility of carbonate/calcite based powders in some machines is not fully understood, but we have surprisingly discovered that relatively good dispensibility can be obtained with selected ternary active systems.

Thus, according to the invention there is provided a detergent composition containing

- (i) a detergent active system comprising a mixture of
 - (a) an anionic non-soap detergent active;
 - (b) a nonionic detergent active; and
 - (c) soap;
 - (ii) a water-soluble alkali metal carbonate; and
 - (iii) a water-insoluble particulate carbonate material which is a seed crystal for calcium carbonate;
- wherein based on the total weight of components (a), (b) and (c), the level of (a) is from 30% to 70%; the level of (b) is from 20% to 27%; and the level of (c) is at least 10%, but no more than 10% by weight of the total composition.

UK Patent Specification GB 2 104 912 A describes at Example 8, a calcite/carbonate built composition having a ternary active system wherein the proportions of anionic, nonionic and soap within that system, fall within the ranges specified above. However, the composition does not fall within the above definition as a whole because the soap content is stated to be 12%. Moreover, the prior UK Specification contains no teaching, explicit or implicit, as to how one may obtain improved dispensing properties with calcite/carbonate built ternary systems.

Although our invention requires the soap content not to exceed 10% by weight of the total composition, it is preferred for this figure to be no more than 8%.

Preferably the composition contains from 5% to 40% by weight of the detergent active system, preferably not more than 25%.

We have found particularly beneficial results when the detergent active mixture contains

- from about 35% to about 60% anionic active;
- from about 21% to about 26% nonionic active; and
- from about 15% to about 35% soap.

The non-soap (synthetic) anionic detergent active compound is usually the water-soluble alkali metal salt of an organic sulphate and sulphonate 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 amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-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; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀-C₂₀ alpha-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 C₁₆-C₁₈) alkyl sulphates.

Suitable nonionic detergent compounds 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 (C₆-C₂₂) phenols-ethylene oxide condensates, generally 5 to 25 EO, ie 5 to 25 units of ethylene oxide per molecule, the condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, generally 5 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.

As used herein, the term "soap" includes not only the usual alkali metal and alkaline earth metal salts of fatty acids, but also the organic salts which can be formed by complexing fatty acids with organic nitrogen-containing materials such as amines and derivatives thereof. Usually, the soap comprises salts of higher fatty acids containing from 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms in the molecule, or mixtures thereof.

Preferred examples of soaps include sodium stearate, sodium palmitate, sodium salts of tallow, coconut oil and palm oil fatty acids and complexes between stearic and/or palmitic fatty acid and/or tallow and/or coconut oil and/or palm oil fatty acids with water-soluble alkanolamines such as ethanolamine, di- or triethanolamine, N-methylethanol- amine, N-ethylethanolamine, 2-methylethanolamine and 2,2-dimethyl ethanolamine and N-containing ring compounds such as morpholine, 2'-pyrrolidone and their methyl derivatives.

Mixtures of soaps can also be employed.

Particularly preferred are the sodium and potassium salts of the mixed fatty acids derived from coconut oil and tallow, that is sodium and potassium tallow and coconut soap.

An essential ingredient of the composition is a water-soluble carbonate material as a builder. This is preferably sodium or potassium carbonate or a mixture thereof, for reasons of cost and efficiency. The carbonate salt is preferably fully neutralised but it may be partially neutralised, for example a sesquicarbonate may be used in partial replacement of the normal carbonate salt; the partial salts tend to be less alkaline and therefore less efficient. The amount of water-soluble carbonate material in the detergent composition can be varied widely, but the amount should be at least 5% by weight, such as from 10% to 40%, preferably 10% to 35% by weight, though an amount of up to 75% could possibly be used if desired in special products. The amount of the water-soluble carbonate material is determined on an anhydrous basis, though the salts may be hydrated either before or when incorporated into the detergent composition. It should be noted that it may also be desirable to limit the carbonate content to a lower level within the range mentioned, so as to decrease the risk of internal damage following any accidental ingestion, for example by children.

The composition necessarily contains a water-insoluble particulate carbonate material. This material must be capable of acting as a seed crystal for the precipitate which results from the reaction between the calcium hardness ions of the water and the water-soluble carbonate. Thus this water-insoluble particulate material is a seed crystal for calcium carbonate, such as calcium carbonate itself.

The water-insoluble particulate carbonate material should be finely divided, and should have a surface area of at least 10 m²/g, and preferably at least 15 m²/g. The particularly preferred material has surface area from 30-100 m²/g. Insoluble carbonate material with surface areas in excess of 100 m²/g may be used, if such materials are economically available.

Surface area is measured by nitrogen absorption using the standard Bruauer, Emmet & Teller (BET) method. A suitable machine for carrying out this method is a Carlo Erba Sorpty 1750 instrument operated according to the manufacturer's instructions.

It is most preferred that the high surface area material be prepared in the absence of poisons, so as to retain its seed activity.

The insoluble carbonate material will usually have an average particle size of less than 10 microns, as measured by sieve analysis, but may be granulated for ease of handling.

When the insoluble carbonate material is calcium carbonate, any crystalline form thereof may be used or a mixture thereof, but calcite is preferred as aragonite and vaterite are less readily available commercially, and calcite is a little less soluble than aragonite or vaterite at most usual wash temperatures. When any aragonite or vaterite is used it is generally in admixture with calcite. In the following general description, the term 'calcite' is used to mean either calcite itself or any other suitable water-insoluble calcium carbonate seed material.

The selected level of calcite in the overall composition depends on the specific surface area as described above. The amount of calcite used in the compositions should be from 50% to 60%, more preferably from 50% to 30%.

In addition to the water-insoluble carbonate material, the detergent active material and the water-soluble carbonate material it is possible to include minor amounts of other detergency builders, provided that the total amount of the detergency builders does not exceed 85% by weight, so as to leave room in the detergent composition for other desirable ingredients.

Apart from the calcite, the detergent active compounds and detergency builders, the detergent composition can optionally contain any of the conventional ingredients in the amounts in which such ingredients are normally employed in fabric washing detergent compositions.

One such optional ingredient is an alkali metal silicate, particularly sodium neutral, alkaline, meta- or orthosilicate. A low level of silicate, for example 5-10% by weight, is usually advantageous in decreasing the corrosion of metal parts in fabric washing machines, and it may give processing benefits. If higher levels of silicate are used up to a practical maximum of 30%, for example from 10% to 20% by weight, there can be a more noticeable improvement in detergency, which may permit some decrease in the water-soluble carbonate material content. This effect appears to be particularly beneficial when the wash liquor are used in water with appreciable levels of magnesium hardness. The amount of silicate can also be used to some extent to control the equilibrium pH of the wash liquor, which is generally within the range of 9-11, preferably 10-11 for an aqueous solution of the composition at the recommended concentration. It should be noted that a higher pH (ie over pH 10.5) tends to be more efficient as regards detergency, but it may be less desirable for domestic safety. Sodium silicate is commonly supplied in concentrated aqueous solution, but the amounts are calculated on an anhydrous basis.

Examples of other optional ingredients include the lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, fabric softening agents, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants.

The detergent compositions 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 for the manufacture of detergent powders.

The invention will now be illustrated by the following non-limiting examples.

EXAMPLES 1 TO 7

Compositions were prepared according to the following formulations. Each composition was made in the form of a powder by spray drying a slurry of the stated components, with the exception of the sodium silicate, sodium perborate and TAED (when used), which were added separately to the spray dried base powder. The powders were sprayed to a target moisture content of 3-4%.

| Example No | 1 | 2 | 3 | 4 | 5 | 6 | 7 | A | B | C | D |
|---|-------------------|------|-----|-----|----|-----|-----|----|-----|----|----|
| <u>Ingredients (%)</u> | | | | | | | | | | | |
| Anionic detergent active ¹ | 6.5 | 6.2 | 7.7 | 7 | 9 | 8.2 | 9 | 11 | 9 | 9 | 4 |
| Nonionic detergent active ² | 3 | 2.8 | 3.4 | 3.5 | 4 | 3.6 | 4 | 4 | 4 | 4 | 9 |
| Soap ³ | 5 | 4 | 3.4 | 4 | 4 | 2.7 | 2.5 | - | 1.5 | - | - |
| Sodium carbonate ⁴ | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Calcite ⁵ | 20 | 15 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Sodium silicate (Na ₂ O/SiO ₂ =1:3.3) ⁶ | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| Sucrose | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| Sodium perborate ⁶ | 10 | 12.3 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Sodium sulphate, water and minors | -----balance----- | | | | | | | | | | |

Notes

1 - Dobane 113 (ex Shell Chemicals) which is sulphonated to form approximately a sodium benzene sulphonate in which the alkyl group contains from 10 to 15 carbon atoms.

5 2 - Synperonic A7 (ex ICI - an alcohol having an alkyl chain length of 13 - 15 carbon atoms ethoxylated with an average of 7 ethylene oxide groups per molecule)

3 - hardened tallow sodium soap except Examples 1 and 4, which used a 50:50 mixture of hardened tallow and hardened rape seed sodium soaps

4 - measured as anhydrous

10 5 - Socal U3 (ex Solvay) having a nominal surface area of 100 m²/g

6 - as the monohydrate.

15 In each example 150g of powder was placed in the dispenser of a HOOVER (Trade Mark) automatic washing machine. Cold water was allowed to enter the dispenser at a rate of 2 litres per minute for 2 minutes. The water had a hardness of 24° FH (ie a free calcium ion concentration of 24×10^{-4} molar). The water pressure was 5 psi. After allowing the water to drain naturally out of the dispenser the weight of the powder residue therein was measured.

The results were as follows. A residue weight of less than 20g in this test is considered to be acceptable. The following table also shows the percentage of anionic active, nonionic active and soap in each formulation.

20

25

30

35

40

45

50

55

60

65

| Example No: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | A | B | C | D |
|-------------|----|----|-----|----|----|----|----|----|----|----|-----|
| % anionic | 45 | 48 | 53 | 48 | 53 | 57 | 58 | 73 | 62 | 69 | 31 |
| % nonionic | 21 | 22 | 23 | 24 | 24 | 25 | 26 | 27 | 28 | 31 | 69 |
| % soap | 34 | 31 | 23 | 28 | 24 | 19 | 16 | -- | 10 | -- | -- |
| residue (g) | 9 | 2 | 10* | 8 | 3 | 8 | 11 | 69 | 63 | 67 | 134 |

* The residue in Example 3 was 7g when the 30% sodium carbonate was replaced by 35% sodium carbonate, and the 10% sodium perborate was replaced by 5.3% sodium perborate together with 2.3% TAED as a bleach activator.

These results demonstrate that the compositions according to the invention (Examples 1 to 7) leave significantly less residue in the residue than the comparison compositions A to D.

5
10
15
20
25
30
35
40
45
50
55
60
65

Claims

5

1. A detergent composition containing
 (i) a detergent active system comprising a mixture of
 (a) an anionic non-soap detergent active;
 (b) a nonionic detergent active; and

10

(c) soap;

- (ii) a water-soluble alkali metal carbonate; and

(iii) a water-insoluble particulate carbonate material which is a seed crystal for calcium carbonate;
 wherein based on the total weight of components (a), (b) and (c), the level of (a) is from 30% to 70%;
 the level of (b) is from 20% to 27%; and the level of (c) is at least 10%, but no more than 10% by
 weight of the total composition

15

2. A composition according to claim 1, wherein the soap content of the total composition does not
 exceed 8% by weight

3. A composition according to either preceding claim, wherein the detergent active system is from 5 to
 40% by weight of the total composition

20

4. A composition according to claim 3, wherein the detergent active system does not exceed 25% by
 weight of the total composition.

5. A composition according to any preceding claim wherein the anionic non-soap detergent active is a
 water-soluble alkali metal salt of an organic sulphate or sulphonate having an alkyl radical containing from
 about 8 to about 22 carbon atoms.

25

6. A composition according to any preceding claim, wherein the nonionic detergent active is selected
 from

C₆-C₂₂ alkyl phenol-ethylene oxide condensates having from 5 to 25 units of ethylene oxide per molecule,

30

the condensation products of C₈-C₁₅ primary and secondary linear or branched alkylene alcohols having
 from 5 to 40 units of ethylene oxide per molecule, and

products made by condensation of ethylene oxide with the reaction products of propylene oxide and
 ethylenediamine.

35

7. A composition according to any preceding claim, wherein the soap is a fatty acid salt with an alkali
 metal, alkali earth metal or a nitrogen containing organic moiety complexed therewith.

8. A composition according to any preceding claim, wherein the amount of water-soluble carbonate
 material in the total composition is at least 5% by weight.

40

9. A composition according to any preceding claim, wherein the water-soluble particulate carbonate
 material is calcite.

10. A composition according to claim 9, wherein the calcite comprises from 5% to 60% of the total
 composition.

11. A composition according to any preceding claim, which also contains an alkali metal silicate.

45

50

55

60

65