(12) UK Patent Application (19) GB (11) 2 238 315 (13) A

(43) Date of A publication 29.05.1991

(21) Application No 8926641.5

(22) Date of filing 24.11.1989

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(51) INT CL^5
C11D 3/12

(52) UK CL (Edition K)
C5D DHC D107 D108 D111 D113 D118 D129 D149
D152 D153 D157 D159 D183

(56) Documents cited
GB 2138439 A **GB 1504878 A** **GB 1481516 A**
GB 1437950 A **EP 0267043 A2** **EP 0267042 A2**
EP 0246896 A1

(58) Field of search
UK CL (Edition K) **C5D**
INT CL^5 **C11D**
Online databases: WPI

(54) Detergent composition

(57) A built non-soap detergent composition in a form for direct application to fabrics or hard surfaces comprises:

5% to 60% by weight of a non-soap detergent active,
5% to 50% by weight of alkali metal carbonate
2% to 40% by weight of water insoluble carbonate with a free surface area greater than 10m^2/g

the composition being substantially free of inorganic phosphate.

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1990.

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Detergent Bar Composition

The present invention relates to a built, non-soap detergent composition in a form for direct application to fabric or hard surfaces comprising a non-phosphate detergency builder.

Detergent manufacturers have long recognised the need to control water hardness to ensure adequate cleaning by detergents. Detergent builders are commonly used to prevent the precipitation onto fabrics of the insoluble salts of water hardness ions.

The detergency builders employed in the past have been of two main types, sequestering builders and precipitating builders. Sequestering builders are true chelating agents which complex calcium and magnesium ions to reduce their interference with the detergency process. Examples of sequestering builders are the water soluble salts of pyrophosphates and tripolyphosphates. The use of water soluble phosphates as builders has been under criticism since phosphates are believed to accelerate eutrophication. In certain countries phosphates are expensive and there is a need for a lower cost alternative.

Alternative builders are precipitating builders such as alkali metal carbonates and silicates. A disadvantage of alkali metal carbonate is that it tends to be slow acting. From GB 1 437 950 it is known that the rate of calcium carbonate precipitation and hence the speed with which carbonate builds can be accelerated by the presence of calcium carbonate particles of high surface area which act as crystallisation seeds. Various other prior patents disclose the use of calcite seeded carbonate builder systems in detergent powder compositions.

Although the calcite seeded carbonate system may be effective in removing soluble calcium, the presence of alkali metal silicate is needed to remove magnesium ions from solution. From US 4 040 988 it is known that the effectiveness of such crystallisation seeds can be destroyed or poisoned by the presence of sequestering builders or alkali metal silicates. In the case of silicate the poisoning is thought to occur by the adsorption of silicate onto the calcite particles rendering the latter ineffective as crystallisation seeds.

The poisoning of the calcite seeds gives rise to the disadvantage that the rate of removal of calcium from the wash solution is slow.

For direct application products this rate is very important since the detergent composition is in contact with the fabric and wash solution for a relatively shorter time compared with the contact time, for example, in machine washing.

In general, products for direct application have relied on phosphates as detergency builders. Furthermore, it would not be expected that an insoluble carbonate seeded carbonate building system would be effective in a detergent composition for direct application also comprising silicate.

We have now found that insoluble carbonate seeded carbonate builder systems are effective in detergent compositions for direct application in the presence of alkali silicate and that the removal of calcium ions from the wash solution occurs at the required speed. We have also found that surprisingly the carbonate seed crystals survive the often high shear processes encountered in the manufacture of an extruded bar or of a detergent cream.

According to the present invention there is provided a built non-soap detergent composition in a form for direct application to fabrics or hard surfaces which composition comprises:

5% to 60% by weight of a non-soap detergent active,
5% to 50% by weight of alkali metal carbonate,
2% to 40% by weight of water insoluble carbonate with a free surface area greater than 10 m^2/g
the composition being substantially free of inorganic phosphate.

The composition has the advantage that a built non-soap detergent composition in a form for direct application is provided which contains an alternative builder system to phosphates.

It is well known to incorporate calcite as a filler in detergent bars and it may be used as such in compositions according to the invention. However, the aforementioned insoluble carbonate in the form of calcite seeds required for the present invention is distinctly different from calcite used as a filler.

The insoluble carbonate used as seeds in the present invention may be calcite but must have a free surface area of more than $10m^2/g$. In contrast calcite used as a filler has a surface area of much less than this, typically less than $5m^2/g$. The insoluble carbonate of high free surface area acts as seeds for precipitating carbonate which results from the reaction between the calcium hardness ions of water and the water soluble alkali metal carbonate.

The water-insoluble carbonate used as seeds in the present invention preferably has a free surface area of at least $10m^2/g$ and more preferably in the range $30-100m^2/g$, most preferably $70m^2/g$. Insoluble carbonate material with surface area in excess of $100m^2/g$ may be used, if such materials are economic.

Surface areas as quoted herein are measured by nitrogen adsorption using the standard Brunauer, Emmet and Teller (BET) method on a Quantisorb Sorption System.

The insoluble carbonate material will usually have an average particle size of less than 10 microns, as measured by conventional techniques more preferably 4 microns with not more than 3% of the particles greater in size than 10 microns.

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 aragonite or vaterite are used it is generally in admixture with calcite. The amount of water insoluble carbonate in the detergent composition is at least 2%, preferably from 2% to 40% by weight.

The non-soap detergent active of the present invention can be anionic, nonionic or ampholytic in nature or can be mixtures thereof. It is present at levels of at least 5% and preferably between 5% and 60% most preferably between 15% and 35% by weight.

Preferred anionic surfactants of the present invention are water-soluble salts of branched or linear chain alkyl benzene sulfonate with an average alkyl chain length between 11 and 13, preferably 11.8 carbon atoms; either alone or in admixture with other actives. Specific examples of detergent actives useable as alternatives or in admixture are primary alcohol sulphates with saturated alkyl chain group containing C_{12} average, fatty acid ester sulphonates with saturated alkyl chain group containing C_{12} average and alcohol radical derived from a straight chain saturated alcohol having C_1-C_6 average, alpha olefin sulphonate with a carbon chain length distribution C_{14}-C_{16}.

Water-soluble nonionic surfactants are also useful in the instant composition. Many nonionic surfactants can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Also utilisable herein are water-soluble condensation products with ethylene oxide of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched configuration; e.g. a coconut alcohol-ethylene oxide condensate having from 10 to 14 carbon atoms. Other useful nonionics are the condensation product of tallow fatty alcohol with about 11 mols of ethylene oxide and the condensation produce of tallow fatty alcohol with about 11 mols of ethylene oxide and the condensation product of a C_{13} (avg.) secondary alcohol with 9 mols of ethylene oxide.

The alkali metal carbonate of the present invention is sodium or potassium carbonate or a mixture thereof. The carbonate salt is preferably fully neutralised, but it may be partially neutralised, for example a sesquicarbonate may be used, the partial salts tend to be less alkaline and therefore less efficient. The amount of alkali metal carbonate in the detergent composition is at least 5% by weight, preferably from about 5% to 50% by weight, more preferably 15% to 25% by weight.

The amount of the alkali metal carbonate is determined on an anhydrous basis, though the salts may be hydrated.

Silicates which may be used in compositions according to the invention are sodium neutral silicates or alkaline silicates with a weight ration of SiO_2 to Na_2O in the range from 1.6:1 to 3.4:1. When silicate is present the amount is generally at least 1% by weight of the composition preferably from 1% to 15% by weight and more preferably 2% to 5%

Many materials common in the detergency arts can be optional ingredients in the compositions of this invention. Among these optional ingredients are antiredeposition agents such as sodium carboxymethyl cellulose, inorganic salts such as sodium sulphate, fillers such as talc, kaolin, colouring material fluorescers, germicides, opacifiers, perfumes and bleaching agents. Also among these optional ingredients are structuring agents such as aluminosilicate formed in-situ during mixing of the composition and described in GB 2 099 013, amorphous aluminosilicates and crystalline zeolites also commonly used as a detergency builders.

Preparation of detergent bars can be carried out by the conventional procedure of mixing the bar ingredients under conditions of shear, milling the resulting dough and plodding to extrude bars.

Preparation of detergent creams can be carried out by the conventional procedure of mixing ingredients at 70°C using a conventional paddle mixer.

The following Examples illustrate the invention but are not intended to be limiting thereof.

Example 1

The following detergent formulations were prepared by mixing all of the ingredients of the formulations in a Z blade mixer at a temperature of 65°C. The alkyl benzene sulphonic acid was first neutralised with soda ash and then the other ingredients were added and mixed. The resulting dough was milled and plodded to form bars in a single or twin screw extruder.

	Formulation (% by weight)				
	A	B	C	D	E
Branched alkyl benzene Sulphonate with an average chain length of 11 carbon atoms	29	29	29	29	29
Soda Ash	17	17	17	25	25
Calcite of mean particle diameter 40 microns	28	21	18	22	12
Kaolin	14	14	14	9	9
Calcium carbonate seed material of surface area greater than $20m^2/g$, average particle size 4μ .	-	7	7	-	7
Sodium silicate having $Na_2O: SiO_2$ of 1:2	-	-	3	-	3
Sodium sulphate	2.0	2.0	2.0	4.0	4.0
Alumino-silicate	1.0	1.0	1.0	1.0	1.0
Sodium carboxy methyl cellulose	2.0	2.0	2.0	2.0	2.0
Water, minors etc.	7.0	7.0	7.0	8.0	8.0
Depletion of water hardness ions (Ca/Mg) %	75.5	84.0	88.5	79	88.5
R	14.8	15.8	21	26.5	28.8

Test cloths of polyester-cotton soiled with clay/sebum soil mixture are washed with the product and compared to standard cloths by means of an Elrepho reflectormeter. The value R represents the difference between the reflectance of the washed cloth and the reflectance of the unwashed cloth. The greater the value of R the cleaner the test cloth. The washing procedure was as follows, a bar of formulation A, B, C, D or E is applied directly to the wet fabric until the equivalent of 13g of bar per kg of cloth has been rubbed onto the fabric. The test cloth is then washed in 12 deg FH water at 30°C (Ca: Mg was 3:1).

The depletion of water hardness was determined by measuring the soluble water hardness ion level remaining in the wash water. This is done titremetrically using EDTA after filtration of the insoluble matter.

These results show the greater depletion of water hardness obtained when a calcite seeded carbonate builder system is used in the formulation bar. (comparison of A with B or D with E). Comparison of A or B with C, or D with E shows the surprising advantage obtained when silicate is incorporated in a composition according to the invention.

Example 2

The advantage of adding silicate to direct application products contrasts with the situation normally experienced with granular detergent compositions where silicate decreases the depletion of water hardness ions.

	Powder Formulations (% by weight)	
	F	G
ABS	28	28
Sodium sulphate	6	-
calcium carbonate	20	20
sodium carbonate	36	36
silicate	-	6
Water	10	10
Depletion of water hardness ions (Ca/Mg)%	97	80

The depletion of water hardness ions was determined as described above.

Comparison of F with G shows the decrease in depletion obtained when silicate is added to the composition, this contrasts with the increase seen in C when silicate is added.

<u>Example 3</u>

	C	H
branched alkyl benzene sulphonate, C_{11} average	29	29
Soda ash	17	17
Sodium pyrophosphate	--	8
Calcite of mean particle diameter 40 microns	18	18

Kaolin	14	13
Calcium carbonate seed material as in Example 1.	7	--
Sodium silicate having $Na_2O:SiO2$ ratio of 1:2	3	3
Water, minors	12	12

A washing test as described above Example 1 was carried out and used to determine the effectiveness of detergent bars made from formulations C and H at various stages during the wash.

	R	
	C	H
Wash Time (mins)		
2.5	64.3	67.2
4.5	67.4	69.2
15.0	69.5	70.0

Comparison of C and H shows that the invention provides an equal alternative builder system to phosphate for direct application products. This contrasts with the situation in granular detergents.

Example 4

Particularly preferred compositions according to the invention are as follows. The cleaning performance of these bars was equal to equivalent phosphate containing bars.

Composition % by weight

	I	J	K	L
Branched alkyl benzene sulphonate with an average chain length of 11 carbon atoms	-	19	12	12.5
(1) PAS	30	-	18	-
(2) AOS	-	6	-	-
(3) FAES	-	-	-	12.5
Calcium carbonate seed material	7	10	7	10
Soda Ash	25	11	17	17.5
Kaolin	10	8	-	-
Talc	-	-	-	10.0
Alkaline silicate having $Na_2O:SiO_2$ of -:-	5	5	5	5
Aluminosilicate	4	-	4	-
Calcite of mean diameter 40 microns	10	30	27	21
Water/minors	balance	balance	balance	balance

(1) Primary alcohol sulphate comprising an average chain length of 12 carbon atoms. Escane F ex Exxon.

(2) Sulphonated alpha olefin with C_{12}-C_{16} distribution. Alphanox 46 ex Molins-kao.

(3) Fatty acid ester sulphonate with C_{12} alkyl chain. Alphastep ML 40 ex Stepan.

Claims

1. A built non-soap detergent composition in a form for direct application to fabrics or hard surfaces which composition comprises:

5% to 60% by weight of a non-soap detergent active,
5% to 50% by weight of alkali metal carbonate
2% to 40% by weight of water insoluble carbonate with a free surface area greater than $10m^2/g$

the composition being substantially free of inorganic phosphate.

2. A composition as claimed in claim 1 wherein the water insoluble carbonate has a free surface area in the range 30 to $100m^2/g$.

3. A composition as claimed in claim 1 or 2 wherein the alkali metal carbonate is present at a level between 15% and 25% by weight.

4. A composition as claimed in any preceding claim wherein the composition comprises from 15% to 35% by weight of non-soap detergent active.

5. A composition as claimed in any preceding claim wherein the composition further comprises from 1% to 15% by weight of silicate.

Published 1991 at The Patent Office, State House, 66/71 High Holborn, London WC1R 4TP. Further copies may be obtained from Sales Branch, Unit 6, Nine Mile Point, Cwmfelinfach, Cross Keys, Newport, NP1 7HZ. Printed by Multiplex techniques ltd, St Mary Cray, Kent.