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WO 01/04246 A1

(54) Title: FABRIC CLEANING COMPOSITION CONTAINING ZEOLITE

(57) Abstract: The present invention relates to a composition containing zeolite, ethoxylated nonionic surfactant and an alkali metal carbonate.

Fabric Cleaning Composition Containing Zeolite

Field of the Invention

The present invention relates to a free flowing granular cleaning composition for use in fabric care, wherein the composition contains a nonionic surfactant and a zeolite MAP.

Background of the Invention

In recent years the use of zeolite in fabric cleaning compositions as a replacement for phosphate as a detergent builder has increased because of the ability of the zeolite (crystalline alkali metal aluminosilicate) to sequester calcium ions from the aqueous wash solution.

More recently the use of the traditional Zeolite A has been replaced by the use of zeolite MAP (maximum aluminum zeolite P which has a silicon to aluminum ratio of less than 1.33).

Zeolite MAP has been previously disclosed in the literature. EP384070A discloses the use of zeolite MAP in a cleaning composition. EP0448297A, EP0502675A, EP0533392B1 and EP0695341B1 teaches the use of zeolite MAP in combination with a bleach system for use in cleaning compositions. PCT WO97/34979 also teaches the use of zeolite MAP in combination with a bleaching system. U.S. Patents 5,238,594; 5,259,981; 5,259,982 and 5,498,342 are also directed to cleaning compositions containing Zeolite MAP.

Summary of the Invention

The present invention relates to a free flowing granular, low foaming fabric cleaning composition which comprises a zeolite MAP builder, a nonionic surfactant, less than 2.5 wt. % of an anionic surfactant, a polyacrylate polymer, at least one nonphosphate supplemental builder, which is not a zeolite and enzymes.

An object of the instant invention is to provide a free flowing granular, low foaming fabric cleaning composition which has a foam height at the end of the wash cycle in a top load washing machine at a dose level of 92 ml of less than 3 inches.

PCT Wo94/28109, EP0714432B1 and U.S. Patents 5,490,954 and 5,518,649 teach cleaning compositions using zeolite MAP in combination with high levels of anionic surfactant as well as salts of fatty acids.

The aforementioned patents fail to provide a bleach free cleaning composition which has a low foam profile of less than 3 inches such that the cleaning composition can be used in either a front or top load washing machine.

Description of the Preferred Embodiment

The present invention relates to a free flowing granular, low foaming fabric cleaning composition having a bulk density of 0.4 to 0.85, more preferably 0.60 to 0.65 grams/cc which comprises approximately by weight:

(a) 5% to 20%, more preferably 7% to 11% of an ethoxylated nonionic surfactant;

(b) 2.5% to 30%, more preferably 12% to 18% of a zeolite on active basis or express as anhydrosis zeolite having a silicon to aluminum weight ratio of less than 1.33;

(c) 20% to 40%, preferably 32% to 38% of a supplemental detergent builder salt such as an alkali metal carbonate such as sodium carbonate;

(d) 0 to 2.5%, more preferably 0.5% to 2% of a sulfate or sulfonate anionic surfactant;

(e) 0.5% to 5.0%, more preferably 1.0% to 3.0% of a polyacrylate type polymer which functions as an agglomerating aid as well as a chelating agent for calcium and/or magnesium ions as well as an antiredeposition agent;

(f) 0.5% to 35%, more preferably 15% to 25% of sodium sulfate;

(g) 0.5% to 7%, more preferably 1% to 6% of an alkali metal silicate such as sodium silicate or potassium silicate; and

(h) 0 to 3%, more preferably 0.05% to 1.5% of at least one enzyme, wherein the composition does not contain an alkali metal salt of a fatty acid or a bleach compound.

The present invention also relates to a composition having a bulk density of 0.75 to 0.85 grams/cc comprising approximately by weight:

(a) 5% to 60%, more preferably 10% to 45% of a zeolite having a silicon to aluminum ratio of less than 1.33;

(b) 0 to 55%, more preferably 5% to 50% of an alkali metal carbonate;

(c) 0 to 10%, more preferably 0.1% to 6% of a polyacrylate type polymer;

(d) 0 to 2%, more preferably 0.1% to 1% of a brightener; and

(e) 10% to 40% of an ethoxylated nonionic surfactant, wherein said ethoxylated nonionic surfactant is adsorbed on said zeolite and said alkali metal carbonate, wherein the composition does not contain a bleach compound or an alkali metal salt of a fatty acid or more than 6 wt. % of a sulfate or sulfonated surfactant.

Suitable anionic surfactants used in the instant compositions at less than 6 wt. % include the water-soluble alkali metal salts 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 sulfonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulfonates; sodium alkyl glycerol ether sulfates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulfates and sulfonates; sodium and potassium salts of sulfuric 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 neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulfonates such as those derived from reacting alpha-olefins (C_8-C_{20}) with sodium bisulfite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulfonate; and olefin sulfonates which term is used to describe the material made by reacting olefins,

particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. The preferred anionic surfactants are (C_{10}-C_{18}) alkyl polyethoxy (1-11 Eo) sulfates and mixtures thereof having differing water solubilities.

Suitable nonionic surfactants used in the instant compositions include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides and alkyl phenols with alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic surfactant compounds are alkyl (C_6-C_{18}) primary or secondary linear or branched alcohols condensed with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. [Other so-called nonionic surfactant compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides, dialkyl sulfoxides, fatty (C_8-C_{18}) esters of glycerol, sorbitan and the like, alkyl polyglycosides, ethoxylated glycerol esters, ethyoxylated sorbitans and ethoxylated phosphate esters.]

The preferred non-ionic surfactant compounds are those of the ethoxylated and mixed ethyoxylated-propyloxylated (C_{12}-C_{15}), (C12-C14) (C14-C16) fatty alcohol or synthetic alcohol, containing 6 to 11 ethylene oxide (EO) groups.

The Zeolite MAP used in the instant compositions is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminum ratio not greater than 1.33, preferably within the range of from 0.9 to 1.33, and more preferably within the range of 0.9 to 1.2. Of especial interest is zeolite MAP having a silicon to aluminum ratio not greater than 1.15; and zeolite MAP having a silicon to aluminum ratio not greater than 1.07 is especially preferred. Although zeolite MAP like other zeolites contains water of hydration, for the purposes of the present invention amounts and percentages of zeolite are generally expressed in terms of the notional anhydrous material. The amount of water present in hydrated zeolite MAP at ambient temperature and humidity is normally about 20 wt. %. Zeolite MAP generally has a calcium binding capacity of at least 150 mg CaO per g of anhydrous aluminosilicate, as measured by the standard method described in GB1473201 (Henkel) and also

described, as "Method I" in EP384070A (Unilever). The calcium binding capacity is normally at least 160 mg CaO/g and may be as high as 170 mg CaO/g. Zeolite MAP also generally has an "effective calcium binding capacity" measured as described under "Method II" in EP384070A (Unilever) of at least 145 mg CaO/g, preferably at least 150 mg CaO/g.

Preferred zeolite MAP for use in the present invention is especially finely divided and has a d_{50} (as defined below) within the range of from 1.0 to 5.0 micrometers, more preferably at least 2.0 micrometer, more preferably at least 2.4 micrometers. The quantity "d_{50}" indicates that 50 wt. % of the particles have a diameter smaller than that figure.

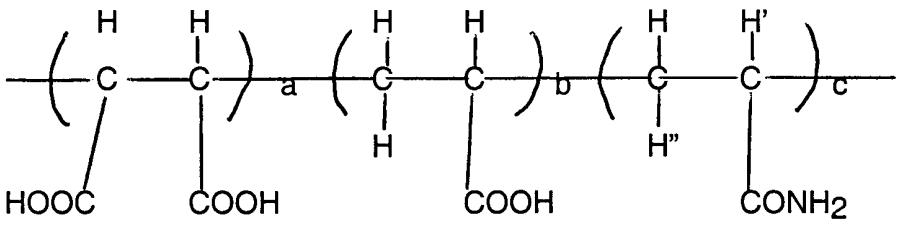
Various methods of measuring particle size are known, and all give slightly different results. In the present specification, the particle size distributions and average values (by weight) quoted were measured by means of a Sedigraph 5100.

Advantageously, but not essentially, the zeolite MAP may have not only a small average particle size, but may also contain a low proportion, or even be substantially free, of large particles. Thus the particle size distribution may advantageously be such that at least 90 wt. % and preferably at least 95 wt. % are smaller than 10 micrometers; at least 85 wt. % and preferably at least 90 wt. % are smaller than 6 micrometers; and at least 80 wt. % and preferably at least 85 wt. % are smaller than 5 micrometers.

The zeolite MAP in the instant composition is used in conjunction with other inorganic or organic builders. Inorganic builders that may be present include the sodium carbonate. Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymmethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive. Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

The alkali metal silicate such as sodium or potassium silicate used in the instant compositions are generally added in the form of an aqueous solution, preferably having $Na_2O:SiO_2$ ratios of about 1:1.3 to about 1.28 and $K_2O:SiO_2$ ratios of about 1:2.0 to about 1:2.6.

The polyacrylate type polymer used in the instant compositions as a calcium sequestering agent is selected from the group consisting of a sodium or potassium salt of a copolymer of polyacrylic acid and maleic anhydride having a molecular weight of about 1,000 to about 5,000 such as Alco™ AR978 sold by Alco Chemical and Alcosperse™ 412 sold by Alco Chemical which is a terpolymer of polyacrylic acid, maleic anhydride and polyacrylamide. This terpolymer which has a molecular weight of about 1,000 to about 6,000 is characterized by the formula:



wherein a+b+c=1; a≥b+c; and c≤0.1

The detergent composition may also contain one or more enzymes which are active against biodegradable stains, e.g., starches, vegetable and blood, and which are also active at a pH of about 5 to about 12. Preferred enzymes which may be used include amylolytic enzymes (alpha amylases), alkaline and neutral proteases, lipolases, cellulases and the like, and mixtures thereof.

Alkaline or neutral proteolytic enzymes suitable for the present composition include the various commercial liquid enzyme preparations which have been adapted for use in detergent compositions. Enzyme preparations in powdered form are also useful although, as a general rule, less convenient for incorporation into a built liquid detergent composition. Thus, suitable liquid enzyme preparations include "Alcalase" and "Savinase", trademarked products sold by Novo Industries, Copenhagen, Denmark, and "Purafect" and "Properase" sold by Genencor, Rochester, New York.

Other suitable alpha-amylase liquid enzyme preparations are those sold by Novo

Industries and Genencor under the tradenames "Termamyl" and "Purastar", respectively. Another enzyme preparation which may be used is a powdered enzyme preparation containing alpha-amylase and a mixture of alkaline and neutral proteases available as CRD-Protease from the Monsanto Co of St. Louis, Missouri.

The enzymes are normally present in the detergent composition at a level of from about 0 up to about 3 wt. %, more preferably from about 0.05 to 1.5 wt. %.

The detergent composition may also contain one or more softening components known in the art. Suitable softeners include swelling bentonite clays such as sodium and calcium montmorillonites, sodium saponites and sodium hectorites. These may be present in the detergent composition at levels of from about 0.5 to 20 wt. %, more preferably from about 5 to 15 wt. %.

Other conventional materials may also be present in the liquid detergent compositions of the invention, for example, soil-suspending agent, silicon antifoaming agents and cationic antifoaming agents. Typical cationic antifoaming agents are dimethyl dialkyl (C_{8-22}) ammonium chloride, methyl benzyl dialkyl (C_{12-18}) ammonium chloride and C_{12}-C_{22} alkyl trimethyl ammonium chloride and mixtures thereof. Typical silicon antifoaming agents are sold by Dow Corning are Q2-3302, 2-3485, 2-4248S and 2200. The composition can also contain sequesterants such as salts of ethylene diamine tetraacetic acid or analogous phosphonic acid salts, hydrotropes, corrosion inhibitors, dyes, perfumes, germicides, e.g., preservatives, e.g., quaternium 15, anti-tarnishing agents, buffers and the like. Such other conventional materials may be used in the amounts they are normally used generally up to about 5% by weight, more preferably up to about 3% by weight.

As necessary, pH modifiers, such as water soluble bases, e.g., NaOH, KOH, amines, or ammonia, will be added to obtain the desired pH level. The preferred pH will range from about 8 up to 11, more preferably from about 9 up to less than 11.

The instant compositions are made by an agglomeration process. In the agglomeration process, liquid components can be added to the powder components in several ways. In some cases, the entire liquid portion of the formulation can be added

to the powder components in the agglomerator itself (Method 1). In other cases, some of the liquids can be pre-loaded on to a portion or all of the powder components before the final liquid constituents are added in the agglomerator device (Method 2). For this invention, both methods have been employed successfully. Method 2 is preferred.

Using the preferred methods, all or part of the nonionic surfactant mix is loaded onto either zeolite or a combination zeolite and sodium carbonate mix in a suitable liquid/solids mixing device. Examples of such mixing equipment are Ross mixers, Lodige, ribbon or paddle mixers, and Schugi contactors, etc. Surfactant loading can range from 0.1 to 60% of the powder weight. This step allows the surfactant material to be adsorbed by the powder material. Adsorption is a function of time, temperature, porosity, pore size, surfactant size, surface area, mixing energy and capillary action. After application of the surfactant, additional powder materials such as zeolite, sodium carbonate, or other type materials can be added to the mix. In addition, if the entire surfactant component was not initially added, part or all of the remaining surfactant component or other liquid compotents can be added at this time. The powder/surfactant mix is then mechanically or pneumatically conveyed to a small holding bin or directly into an agglomerator.

In the preferred method, the material is conveyed into a small bin. From this bin, the surfactant/zeolite/carbonate mix is metered and fed into a Schugi type agglomerator, In addition to the surfactant/zeolite/carbonate mix additional powder components can be added to the Schugi other suitable agglomerator. Examples of such materials are: brighteners and polymers. In the Schugi agglomerator, liquid polymers, of potentially differing types, and water are added as binders. These materials are added in the appropriate amount to generate the chemical composition and physical properties, i.e., particle size, desired.

From the Schugi agglormerator, the material is conveyed via mechanical device or by gravity to a fluid bed dryer. In this dryer, a combination of hot and cold air is used to dry and condition the material. From the fluid bed dryer, the free flowing material can be used as is or mixed with a variety of materials to form detergents of any

composition. Examples of such materials are: detergent or detergent components made via the conventional spray dry process, enzymes, flow aids, perfumes or brighteners.

The detergent compositions of this invention are suitable for use as laundry detergents, dishwasher detergents, shampoos, body lotions and the like and may be modified by inclusion of specific known ingredients to accommodate these applications, e.g., dispersing agents, skin conditioning agents, antidandruff agents and the like.

The detergents of the invention are generally added to wash water at levels in the range of about 0.05 to 0.30 wt. %. For conventional washing machines; powder detergents are preferably used at levels of about 60 to 300 grams per load.

The following examples are illustrative of the invention.

Example I

The following compositions in wt. % were prepared by the previously defined process.

	A	B	Reference
Sodium linear alkyl benzene sulfonate	1.4	1.4	8.9
Nonionic surfactant 24-7	9.9	10.5	7.0
Sodium carbonate	35	35	31.3
Zeolite A (dry basis)	--	--	18.7
Zeolite high absorbent (dry basis) MAP	15.0	16.0	--
Sodium sulfate	20.7	20.3	15.2
Sodium polyacrylate	2.5	2.5	2.5
Sodium silicate	5.0	5.0	4.4
Protease Enzyme	0.5	0.3	0.3
Optical brightener	0.3	0.3	0.3
Fragrance	0.4	0.4	0.4
Moisture	Bal.	Bal.	Bal.
Density grams/cc	0.61	0.61	0.61

Detergency Test
12 Stain Multistain Test
Average Total L *(Hunter Scale)

	Top Loader 10 min. Wash		Front Loader 18 min. Wash		
	60°F	90°F	60°F	90°F	Dose in ml.
New	1045	1056	1039	1055	120
Current	1041	1053	1042	1054	92

Foam Study #1 at 90°F

Front Loader

Product	Dose ml.	Foam Height End of Wash	Foam Height End of Rinse	Average Total L*	
New	92	None detected	None detected	1049	foam height was
Current	92	3 inches	None detected	1080	measured with
New	220	2.5 inches	None detected	1081	ruler attached to
Current	220	6+ inches	6+ inches	1074	door window of washer.

Top Loader

Product	Dose ml.	Foam Height End of Wash	Foam Height End of Rinse	Average Total L*	
New	92	Trace	None detected	1049	foam height was
Current	92	5 inches	Trace	1061	measured with
New	220	5 inches	Trace	1084	ruler hand held
Current	220	6 inches	Trace	1082	from surface of water in the washer.

All washes for the foam study contained four pound ballast loads which included a set of the Twelve Stain Multistain Test swatches as a standard soil load. All wash cycles were run for eighteen minutes. The 92 ml. Level represents the lowest marked volume used with the Regular Ultra scoop. The 220 ml. Level represents the proposed full scoop volume used with the Bleach Alternative Ultra (representing a best and worst

case foam generation of the respective formulas in the different washers currently available to the consumer). All washes were duplicated.

Foam Study #2 at 60°F

Front Loader (18 min. wash)

Product	Dose ml.	Foam Height End of Wash	Foam Height End of Rinse	Average Total L*
New 24-7	160	3 inches	0.5 inches	1069
New 46-7	160	0.5 inches	None detected	1068
Current	160	6+ inches	6+ inches	1062

foam height was measured with ruler attached to door window of washer.

Top Loader (10 min. wash)

Product	Dose ml.	Foam Height End of Wash	Foam Height End of Rinse	Average Total L*	
New 24-7	160	3 inches	Trace	1036	foam height was
New 46-7	160	0.13 inches	None detected	1031	measured with
Current	160	4 inches	Trace	1041	ruler handheld from surface of water in the washer.

All washes for foam study contained four pound ballast loads which included a set of the Twelve Stain Multistain Test Swatches as a standard soil load. The 160 ml. represents the Large level used with the Regular Ultra Scoop.

What Is Claimed:

1. A cleaning composition comprising approximately by weight:

(a) 5% to 20% of an ethoxylated nonionic surfactant;

(b) 25% to 30% of a zeolite having a silicone to aluminum weight ratio of less than 1.33;

(c) 20% to 40% of a supplemental detergent builder salt;

(d) 0.5% to 5% of a polyacrylate type polymer; and;

(e) 0.5% to 35% of a sodium sulfate.

2. The composition of Claim 1 further including an anionic surfactant.

3. The composition of Claim 1 further including at least one enzyme.

4. The composition of Claim 3 wherein at least one of said enzymers is a protoelytic enzyme.

5. The composition of Claim 4 wherein said supplemental detergent builder salt is sodium carbonate.

6. The composition of Claim 5 wherein said ethoxylated nonionic surfactant contains 6 to 11 ethylene oxide groups.

7. The composition of Claim 6 wherein said anionic surfactant is a sulfonate surfactant.

8. The composition of Claim 7 wherein said polyacrylate polymer is a terpolymer of polyacrylamide, polyacrylic acid and maleic anhydride.

9. The composition of Claim 1 wherein the zeolite has a particle size of at least 2.4 micrometer.

10. A composition comprising approximately by weight:

(a) 5% to 60% of a zeolite;

(b) 0 to 55% of an alkali metal carbonate; and

(c) 10% to 40% of an ethoxylated nonionic surfactant.

11. The composition of Claim 1 wherein said zeolite has a silicone to aluminum weight ratio of less than 1.33.

12. The composition of Claim 11 wherein said alkali metal carbonate is sodium carbonate at a concentration level of 5 wt. % to 40 wt. %.

13. The composition of Claim 12 wherein said ethoxylated nonionic surfactant has 6 to 11 ethylene oxide groups.

14. The composition of Claim 10 further including a polyacrylate type polymer.

INTERNATIONAL SEARCH REPORT

Int. ational Application No
PCT/US 00/18651

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D1/72 C11D3/12 C11D3/37 C11D3/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 518 649 A (CHAPPLE ANDREW P ET AL) 21 May 1996 (1996-05-21) cited in the application	10-14
A	claims 1,5; examples 2,5-7	1-9

X	WO 95 05445 A (UNILEVER) 23 February 1995 (1995-02-23) page 10, line 24 -page 11, line 22	10-14
A	page 14, line 16 - line 37; examples 1-3,8-11 & EP 0 714 432 A 5 June 1996 (1996-06-05) cited in the application	1-9

X	EP 0 502 675 A (UNILEVER) 9 September 1992 (1992-09-09) cited in the application	10-14
A	claim 1; examples 1,2	1-8

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 October 2000	26/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Saunders, T

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INTERNATIONAL SEARCH REPORT

In. ational Application No
PCT/US 00/18651

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 34979 A (UNILEVER) 25 September 1997 (1997-09-25) cited in the application	10,11, 13,14
A	claim 6; example 9	1-8,12
X	WO 94 24251 A (UNILEVER) 27 October 1994 (1994-10-27)	10,11,13
A	example M & EP 0 695 341 A 7 February 1996 (1996-02-07) cited in the application	1,2,5-9, 12,14
A	EP 0 384 070 A (UNILEVER) 29 August 1990 (1990-08-29) cited in the application claims 1,9; example 14	1-14
A	WO 96 21705 A (PROCTER & GAMBLE) 18 July 1996 (1996-07-18) example D	1-8, 10-14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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