

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 694 608 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
31.01.1996 Bulletin 1996/05

(51) Int. Cl.⁶: **C11D 17/06**, C11D 3/20

(21) Application number: **94305619.2**

(22) Date of filing: **28.07.1994**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

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(54) **Process for making granular detergents and detergent compositions comprising nonionic surfactant**

(57) The present invention provides a process for making a granular laundry detergent component or composition having a bulk density of at least 650 g/l comprising the steps of ;

- a) dissolving a structuring agent in a nonionic surfactant to form a pumpable premix, wherein the structuring agent comprises a glyceride, and wherein the nonionic surfactant comprises polyhydroxy fatty acid amide at a level of at least 3% (by weight of the component or composition);
- b) granulating said premix

Granular laundry compositions and components comprising polyhydroxy fatty acid amide and glyceride fats are also disclosed.

EP 0 694 608 A1

Description

The present invention relates to improving storage stability and physical properties of granular detergents which are rich in nonionic surfactant. In particular the invention relates to a process for incorporating a certain class of nonionic surfactants, namely polyhydroxy fatty acid amides, into granular detergent compositions.

The use of nonionic surfactants in granular detergents has been widely discussed in the prior art. In particular, detergent compositions comprising ethoxylated nonionic surfactants and polyhydroxy fatty acid amides have been described in WO9206160, published on 16th April 1992.

WO9206160 discloses compositions which comprise ethoxylated nonionic surfactant and polyhydroxy fatty acid amides, and granulation processes for making them (Examples 14, 15, 20). The mixed nonionic systems are granulated with zeolite, carbonate and, optionally, citrate. Water may also be present during the granulation step, but there is no suggestion of the use of an organic structuring agent.

The Applicants co-pending application EP93870075.4, filed on 30th April 1993, describes a process for granulating nonionic surfactants wherein a polymer is premixed with nonionic surfactant to increase its viscosity prior to granulation. Organic polymers such as PVP are preferred. Polyhydroxy fatty acid amides are also disclosed as optional components which may also have a structuring effect.

The previous applications have been concerned with providing excellent stain removal performance, especially on greasy / oily stains. Particles which retain good handling properties during storage and which dissolve rapidly upon contact with water in order to release their active ingredients to the site of the stains are required for commercial purposes. It has been found that the need for good handling properties and rapid rates of dissolution tend to impose conflicting requirements upon the formulator.

The present invention deals with the problem of these conflicting requirements by incorporating an organic structuring agent, selected from the family of glyceride fats, which provides sufficient structure to the nonionic surfactant granules to give the required handling properties, and which still permits rapid rates of dissolution.

The present invention provides a process for making nonionic surfactant particles having excellent stain removal performance by providing high bulk density detergent particles which have a high activity of nonionic surfactants which are efficient stain removers.

The present invention also provides a process for making nonionic surfactant particles which are stable upon storage, and which in particular do not "leak" liquid nonionic surfactant into the container when stored. Nonionic surfactant "leakage", if not prevented, leads to cardboard containers being stained and also to product caking. Both of these undesirable consequences are avoided by the present invention.

The present invention also provides a means for structuring a nonionic surfactant system with an organic structuring agent which is both weight- and cost-efficient.

Summary of the Invention

The present invention provides a process for making a granular laundry detergent component or composition having a bulk density of at least 650 g/l comprising the steps of ;

- a) dissolving a structuring agent in a nonionic surfactant to form a pumpable premix, wherein the nonionic surfactant comprises polyhydroxy fatty acid amide at a level of at least 3% (by weight of the component or composition), and wherein the structuring agent comprises a glyceride; and
- b) granulating said premix.

It is preferred that the glyceride structuring agent is a triglyceride, especially glycerol tristearate.

The nonionic surfactant comprises polyhydroxy fatty acid amide and optionally also comprises ethoxylated nonionic surfactant, the ratio of polyhydroxy fatty acid amide to ethoxylated nonionic surfactant being at least 1:4, and preferably from 1:4 to 4:1.

The preferred pumpable premix comprises:

- a) from 10% to 70% by weight of ethoxylated nonionic surfactant;
- b) from 10% to 70% by weight of polyhydroxy fatty acid amide;
- c) from 0.1% to 20% by weight of glyceride;
- d) from 0% to 20% by weight of fatty acid; and optionally water.

The premix may subsequently be granulated with a powder, said powder preferably being selected from the group consisting of aluminosilicate, carbonate, bicarbonate, silicate, sulphate, citrate and mixtures thereof, and ratio of the premix to the powder being at least 1:4, preferably between 1:4 and 4:1.

The granular laundry detergent composition or component of the present invention typically comprise:

- a) up to 35% (preferably from 10% to 35%, and more preferably 15% to 25%) by weight of ethoxylated nonionic surfactant;
- b) from 3% to 80% (preferably 3% to 35%, and more preferably 5% to 15%) by weight of polyhydroxy fatty acid amide;
- c) from 0.01% to 10% (preferably 0.5% to 8%) by weight of glyceride;
- d) up to 10% (preferably 0.1% to 5%) by weight of fatty acid; and
- e) from 10% to 90% (preferably 25% to 86.99%, and more preferably 50% to 79.4%) by weight of a powder, said powder being selected from the group consisting of aluminosilicate, carbonate, bicarbonate, silicate, sulphate, citrate and mixtures thereof.

Detailed Description of the Invention

The process aspect of the present invention comprises two essential steps. The first process step is the formation of a nonionic surfactant premix which comprises a structuring agent. The second process step is the processing of the surfactant premix into the form of a granular detergent having the desired physical properties of bulk density, flow properties and storage characteristics.

The first process step of the invention is the preparation of a structured nonionic surfactant premix. This premix comprises two essential components which will be described in more detail below. These components are the nonionic surfactant (comprising polyhydroxy fatty acid amide) and the glyceride structuring agent. In the first process step the glyceride structuring agent is dissolved or slurried in the nonionic surfactant.

The second process step may be based upon any of the techniques of forming granules which are known to the man skilled in the art. However, the most preferred granulation techniques for use in the present invention are fine dispersion of the structured nonionic surfactant paste premix in the presence of powders. One example of such a process is to pump or spray the surfactant paste premix into a high shear mixer. The high shear conditions in the mixer break up the surfactant paste premix into small droplets and distribute those droplets onto and around the powder. The process is often described as "agglomeration". Another example of such a process is to spray the surfactant paste premix onto a powder under low shear conditions (such as a rotating drum). In this case the energy to break the paste into fine droplets comes at the spray nozzle, and in the low shear mixer the droplets are absorbed on to the surface, or into the pores of the powder. Preferred granulation processes are described in more detail below.

Nonionic Surfactant

Polyhydroxy fatty acid amides.

Polyhydroxy fatty acid amides may be prepared by reacting a fatty acid ester and an N-alkyl polyhydroxy amine. The preferred amine for use in the present invention is N-(R1)-CH₂(CH₂OH)₄-CH₂-OH and the preferred ester is a C12-C20 fatty acid methyl ester. Most preferred is the reaction product of N-methyl glucamine (which may be derived from glucose) with C12-C20 fatty acid methyl ester.

Methods of manufacturing polyhydroxy fatty acid amides have been described in WO 9206073, published on 16th April, 1992. This application describes the preparation of polyhydroxy fatty acid amides in the presence of solvents. In a highly preferred embodiment of the invention N-methyl glucamine is reacted with a C12-C20 methyl ester. It also says that the formulator of granular detergent compositions may find it convenient to run the amidation reaction in the presence of solvents which comprise alkoxyated, especially ethoxylated (EO 3-8) C12-C14 alcohols (page 15, lines 22-27). This directly yields nonionic surfactant systems which are preferred in the present invention, such as those comprising N-methyl glucamide and C12-C14 alcohols with an average of 3 ethoxylate groups per molecule.

Other Nonionic Surfactants

Suitable nonionic surfactants include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. 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.

Particularly preferred for use in the present invention are nonionic surfactants such as the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 1 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 20 carbon atoms, in either straight chain or branched configuration, with an average of from 1 to 25 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 2 to 10 moles of ethylene oxide per mole of alcohol; and condensation

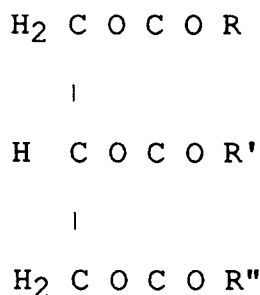
products of propylene glycol with ethylene oxide. Most preferred are condensation products of alcohols having an alkyl group containing from about 12 to 15 carbon atoms with an average of about 3 moles of ethylene oxide per mole of alcohol.

Many of the nonionic surfactants which fall within the definitions given above have are liquid at temperatures below 40°C (that is to say the solidification temperature is below 40°C). The present invention has been found to be particularly useful for such nonionic surfactants.

Structuring Agent

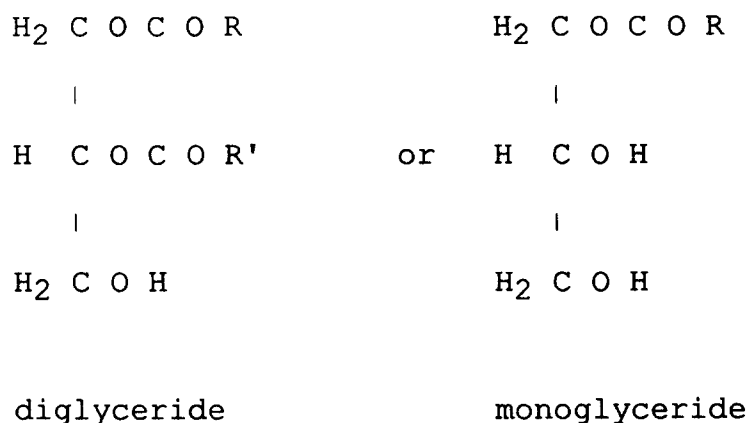
The structuring agents of the present invention should preferably having a melting point of at least 40°C, and more preferably at least 60°C. Glycerides suitable for use as structuring agents in the present invention include tri-, di- and mono-glycerides.

Triglycerides are described in Kirk-Othmer, Encyclopedia of Chemical technology, 3rd Edition, Wiley, Volume 9, page 795 onwards. Triglycerides are fats which may be derived from vegetable, animal and marine sources. A generalised triglyceride has the structure:



Preferably R, R' and R'' are alkyl chains having between 1 and 26 carbon atoms, more preferably between 12 and 22 carbon atoms. For example when R = R' = R'' = C₁₇ H₃₅ the triglyceride is called tristearin or glycerol tristearate. When R = R' = R'' = CH₃ the triglyceride is glycerol triacetate. Hardened tallow triglyceride is particularly preferred for use as a structuring agent for use in the present invention. Preferably the glyceride has an iodine value of less than 1.

Diglycerides and monoglycerides may be derived from triglycerides by hydrolysis to give :



Processing the Structured Paste Premix

The paste premix including the structuring agent may be prepared in any suitable manner, but will typically be a simple mixing process. Any type of mixer may be used to prepare the premix, especially a dynamic mixer. The mixing equipment will need to be selected to handle the relatively high viscosities that the structured paste premix will reach. The exact viscosity will depend on the composition of the structured paste premix, and on the processing temperature.

Preferably the processing temperature is greater than 50°C, more preferably greater than 60°C and most preferably greater than 70°C.

In a particularly preferred embodiment of the present invention the temperature of the paste premix is controlled to the required processing temperature (and viscosity) by passing it through a scraped surface heat exchanger, such as a Chemetator[®], before the subsequent granulation step.

The structured paste premix may be subsequently granulated by various process means. Preferred means are described in more detail below.

Fine Dispersion Mixing and Granulation

Suitable pieces of equipment in which to carry out the fine dispersion mixing or granulation of the present invention are mixers of the Fukae[®] FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another and at separately variable speeds. The vessel can be fitted with a cooling jacket or, if necessary, a cryogenic unit.

Other similar mixers found to be suitable for use in the process of the invention include Diosna[®] V series ex Dierks & Söhne, Germany; and the Pharma Matrix[®] ex T K Fielder Ltd., England. Other mixers believed to be suitable for use in the process of the invention are the Fuji[®] VG-C series ex Fuji Sangyo Co., Japan; and the Roto[®] ex Zanchetta & Co srl, Italy.

Other preferred suitable equipment can include Eirich[®], series RV, manufactured by Gustav Eirich Hardheim, Germany; Lödige[®], series FM for batch mixing, or series CB and KM, either separately or in series for continuous mixing/agglomeration, manufactured by Lödige Maschinenbau GmbH, Paderborn Germany; Drais[®] T160 series, manufactured by Drais Werke GmbH, Mannheim Germany; and Winkworth[®] RT 25 series, manufactured by Winkworth Machinery Ltd., Berkshire, England.

The Littleford Mixer, Model #FM-130-D-12, with internal chopping blades and the Cuisinart Food Processor, Model #DCX-Plus, with 7.75 inch (19.7 cm) blades are two examples of suitable mixers. Any other mixer with fine dispersion mixing and granulation capability and having a residence time in the order of 0.1 to 10 minutes can be used. The "turbine-type" impeller mixer, having several blades on an axis of rotation, is preferred. The invention can be practiced as a batch or a continuous process.

Further Processing Steps

The granular components or compositions obtained by the process described herein may be suitable for use directly, or they may be treated by additional process steps. Commonly used process steps include drying, cooling and/or dusting the granules with a finely divided flow aid. In addition the granules may be blended with other components in order to provide a composition suitable for the desired end use.

Any type of mixer or dryer (such as fluid bed dryers) may be found to be suitable for this purpose.

The finely divided flow aid, if used, may be chosen from a wide variety of suitable ingredients such as zeolite, silica, talc, clay or mixtures of these.

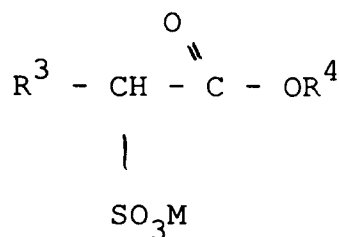
Normally the detergent compositions made according to the present invention may include a wide range of other ingredients and components which are known to the man skilled in the art to have a function in the washing process. Typical examples of such ingredients which may be used in detergent compositions are given below. These optional ingredients may be co-granulated with the nonionic surfactant by the process of the present invention, or, alternatively, they may be granulated by separate means and subsequently combined with the nonionic surfactant granulates of the present invention by dry mixing, spraying-on etc.

Anionic Surfactants

Alkyl Ester Sulfonate Surfactant

Alkyl Ester sulfonate surfactants hereof include linear esters of C₈-C₂₀ carboxylic acids (i.e. fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society" 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprises alkyl ester sulfonate surfactants of the structural formula:



wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₄-C₁₆ alkyl.

Alkyl Sulfate Surfactant

Alkyl sulfate surfactants hereof are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g., below about 50°C) and C₁₆-C₁₈ alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl Alkoxyated Sulfate Surfactant

Alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethylammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate, C₁₂-C₁₈E(1.0)M, C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate, C₁₂-C₁₈E(2.25)M, C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate C₁₂-C₁₈E(3.0), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate C₁₂-C₁₈E(4.0)M, wherein M is conveniently selected from sodium and potassium.

Other Anionic Surfactants

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₉-C₂₀ linear alkylbenzenesulphonates, C₈-C₂₂ primary or secondary alkanesulphonates, C₈-C₂₄ olefin sulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycol ethersulfates (containing up to 10 moles of ethylene oxide); acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside, branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_kCH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin

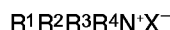
acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

- 5 When included therein, the laundry detergent compositions of the present invention typically comprise from about 1 % to about 40 %, preferably from about 3 % to about 20 % by weight of such anionic surfactants.

Other Surfactants

- 10 The laundry detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as nonionic surfactants other than those already described herein, including the semi-polar nonionic amine oxides described below.

- Cationic detergent surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants
15 such as alkyldimethylammonium halogenides, and those surfactants having the formula :



- wherein R¹ is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each of
20 R², R³, R⁴ is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄)_xH where x has a value from 2 to 5, and X⁻ is an anion. Not more than one of R₂, R₃, R₄ should be benzyl.

- The preferred alkyl chain length for R¹ is C₁₂-C₁₅, particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat, or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R₂, R₃, R₄ are methyl and hydroxyethyl groups, and the anion X may be selected from halide, methosulphate, acetate
25 and phosphate ions.

Examples of suitable quaternary ammonium compounds for use herein are:

- coconut trimethyl ammonium chloride or bromide coconut methyl dihydroxyethyl ammonium chloride or bromide
decyl triethyl ammonium chloride or bromide decyl dimethyl hydroxyethyl ammonium chloride or bromide
C12-14 dimethyl hydroxyethyl ammonium chloride or bromide
30 myristyl trimethyl ammonium methyl sulphate lauryl dimethyl benzyl ammonium chloride or bromide lauryl methyl
(ethenoxy)₄ ammonium chloride or bromide

The above water-soluble cationic components of the compositions of the present invention, are capable of existing in cationic form in a 0.1% aqueous solution at pH10.

- Other cationic surfactants useful herein are also described in US Patent 4,228,044, Cambre, issued October 14,
35 1980, incorporated herein by reference.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 25 %, preferably from about 3 % to about 15 % by weight of such cationic surfactants.

- Ampholytic surfactants are also suitable for use in the laundry detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic deriv-
40 atives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched chain. One of the aliphatic substituents contains at least 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 (herein incorporated by reference) for examples of ampholytic surfactants.

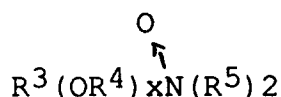
- 45 When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 15 %, preferably from about 1 % to about 10 % by weight of such ampholytic surfactants.

- Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No.
50 3,929,678 to Laughlin et al., issued December 30, 1975 at columns 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 15 %, preferably from about 1 % to about 10 % by weight of such zwitterionic surfactants.

- Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine
55 oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula :



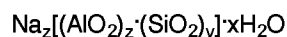
wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

There amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

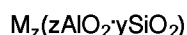
When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 15 %, preferably from about 1 % to about 10 % by weight of such semi-polar nonionic surfactants.

Builders

Sodium aluminosilicate may take many forms. One example is crystalline aluminosilicate ion exchange material of the formula



wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.4 and z is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula



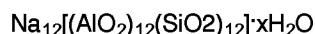
wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 1 to 10 microns is preferred.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca^{++} /gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

The amorphous aluminosilicate ion exchange materials usually have a Mg^{++} exchange of at least about 50 mg eq. $CaCO_3$ /g (12 mg Mg^{++} /g) and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite

MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula



wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

Other ingredients which are known for use in the components and compositions may also be used as optional ingredients in the present invention.

The granular detergents of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Citric acid and, in general, any other organic or inorganic acid may be incorporated into the granular detergents of the present invention as long as it is chemically compatible with the rest of the agglomerate composition.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, and polyhydroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium triphosphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Layered, crystalline silicates such as those supplied by Hoechst under the name SKS-6® may also be used.

As mentioned above powders normally used in detergents such as zeolite, carbonate, bicarbonate, silica, silicate, citrate, phosphate, perborate, etc. and process acids such as starch, can be used in preferred embodiments of the present invention.

Polymers

Also useful are various organic polymers, some of which also may function as builders to improve detergency. Included among such polymers may be mentioned sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols (which often also include some polyvinyl acetate), polyvinylpyrrolidone, polyacrylamides, polyacrylates and various copolymers, such as those of maleic and acrylic acids. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other Optionals Ingredients

Other ingredients commonly used in detergent compositions can be included in the components and compositions of the present invention. These include color speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, nonbuilder alkalinity sources, hydrotropes, enzymes, enzyme-stabilizing agents, and perfumes.

Examples

In these examples the following abbreviations have been used :

- 5 Glucose Amide Polyhydroxy fatty acid amide (C16-C18 alkyl N-methyl glucose amide)
 C25E5 : C12-C15 alcohol ethoxylated with an average of 5 ethoxy groups per molecule
 Glyceride : glycerol tristearate
 Hyfac : hydrogenated C16-C18 fatty acid
 Zeolite : Zeolite A (hydrated)

10 Examples 1 to 7

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	1	2	3	4
a) Glucose Amide	8.9	5.1	41.65	8.9
b) C25E5	20.8	11.9	17.85	20.8
c) Glyceride	1.8	1	3.5	5.3
d) Hyfac	3.5	2	7	-
e) Zeolite	62	77	27	62

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	5	6	7	8
a) Glucose Amide	9.5	14.9	20.8	8.9
b) C25E5	22	14.9	8.9	20.8
c) Glyceride	0.1	1.8	1.8	1.8
d) Hyfac	3.4	3.4	3.5	3.5
e) Zeolite	62	62	62	60

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40 In each of examples 1 to 7 a mixture of polyhydroxy fatty acid amide and ethoxylated nonionic surfactant was prepared in the proportions required. Glyceride and hyfac were then added successively and mixed to form the structured premix maintained at 75°C.

The structured premix was then pumped into a high shear batch mixer (Eirich ®) together with the zeolite in the proportions required. Granulation occurred within the high shear mixer.

45 The granulates were subsequently processed through a low shear mixer (rotating drum) to which an additional 3 parts zeolite (by weight of the finished product) was added and then cooled.

Example 8

50 The composition of example 1 was prepared in a continuous process. The structured premix (35 parts by weight) was sprayed into a high shear mixer (Loedige CB ®) at a temperature of 55°C with 60 parts of zeolite A, and the product from the exit of the high shear mixer was subsequently fed into a low shear mixer (Loedige KM ®). Finally, 5 parts zeolite (by weight of the finished product) was added in the low shear mixer.

55 Example 9

The continuous process of example 8 was repeated replacing 60 parts of zeolite A by a mixture comprising 6.5 parts of sodium carbonate and 53.5 parts of zeolite A. The granular product formed was again treated by dusting with 5 parts of zeolite A (by weight of the finished product).

Examples 10 to 16

Examples 1 to 7 were repeated, in each case component (e), the zeolite A, was replaced by a mixture of zeolite A and sodium carbonate in a ratio of 1:2.

Claims

1. A process for making a granular laundry detergent component or composition having a bulk density of at least 650 g/l comprising the steps of ;

- a) dissolving a structuring agent in a nonionic surfactant to form a pumpable premix, said nonionic surfactant comprising polyhydroxy fatty acid amide at a level of at least 3% by weight of the component or composition; and
- b) granulating said premix characterised in that said structuring agent comprises a glyceride.

2. A process according to claim 1 wherein the glyceride is a triglyceride

3. A process according to claim 2 wherein the triglyceride is glycerol tristearate.

4. A process according to claim 1 wherein the nonionic surfactant further comprises ethoxylated nonionic surfactant, the ratio of polyhydroxy fatty acid amide to ethoxylated nonionic surfactant being at least 1:4, and preferably from 1:4 to 4:1.

5. A process according to claim 4 wherein the premix comprises:

- a) from 10% to 70% by weight of ethoxylated nonionic surfactant;
- b) from 10% to 70% by weight of polyhydroxy fatty acid amide;
- c) from 0.1% to 20% by weight of glyceride;
- d) from 0% to 20% by weight of fatty acid; and optionally water.

6. A process according to claim 5 wherein said premix is granulated with a powder by finely dispersing said premix and granulating in the presence of said powder, said powder being selected from the group consisting of aluminosilicate, carbonate, bicarbonate, silicate, sulphate, citrate and mixtures thereof, and ratio of the premix to the powder being at least 1:4.

7. A granular laundry detergent composition or component comprising:

- a) from 0% to 35% by weight of ethoxylated nonionic surfactant;
- b) from 3% to 80% by weight of polyhydroxy fatty acid amide;
- c) from 0.01% to 10% by weight of glyceride; and
- e) from 10% to 90% by weight of a powder, said powder being selected from the group consisting of aluminosilicate, carbonate, bicarbonate, silicate, sulphate, citrate and mixtures thereof.

8. A granular laundry detergent composition or component according to claim 7 comprising:

- a) from 10% to 35% by weight of ethoxylated nonionic surfactant;
- b) from 3% to 35% by weight of polyhydroxy fatty acid amide;
- c) from 0.01% to 10% by weight of glyceride;
- d) from 0% to 10% by weight of fatty acid; and
- e) from 25% to 86.99% by weight of a powder, said powder being selected from the group consisting of aluminosilicate, carbonate, bicarbonate, silicate, sulphate, citrate and mixtures thereof.

9. A granular laundry detergent composition or component according to claim 8 comprising:

- a) from 15% to 25% by weight of ethoxylated nonionic surfactant;
- b) from 5% to 15% by weight of polyhydroxy fatty acid amide;
- c) from 0.5% to 8% by weight of glyceride;
- d) from 0.1% to 5% by weight of fatty acid; and

EP 0 694 608 A1

e) from 50% to 79.4% by weight of a powder, said powder being selected from the group consisting of aluminosilicate, carbonate, bicarbonate, silicate, sulphate, citrate and mixtures thereof.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5619

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.6)
Y	EP-A-0 492 679 (UNILEVER NV ET AL.) * page 3, line 39 - line 52 * * page 4, line 7 - line 11 * * page 4, line 17 - line 18 * * page 4, line 43 - line 45 * * page 5; examples 1-4 * ---	1-9	C11D17/06 C11D3/20
Y	EP-A-0 364 881 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) * page 3, line 3 - line 12 * * page 3, line 43 - line 45; claims * ---	1-9	
A	EP-A-0 513 824 (KAO CORP) * page 11, line 14 - line 25 * * page 11, line 28 - line 30 * * claims 1,13 * ---	1	
A	FR-A-795 664 (LEVER BROTHERS LTD) * the whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 21 December 1994	Examiner Pelli Wablat, B
CATEGORY OF CITED DOCUMENTS		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	
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