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(54) Fabric washing process and detergent composition for use therein.

(57) Particulate detergent compositions, especially for use in cold water, contain a detergent active material, optionally an alkaline material and builder particles comprising a dispersant in solid solution with a salt of a saturated fatty acid having at least 16 carbon atoms. The dispersant is an alkyl benzene sulphonate. The particles may further contain a water-soluble or water-dispersible carrier to aid release of the fatty acid when the composition is added to a wash liquor. The builder particles have a size of 100 to 1500 μm. Suitable carrier materials include starch, clay, silica and inorganic salts. When the alkaline material is carbonate, the addition of the builder particles to the wash liquor may be delayed until after a critical state is reached.

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FABRIC WASHING PROCESS AND DETERGENT COMPOSITION FOR USE THEREIN

TECHNICAL FIELD

This invention relates to a method of washing fabrics and to a composition useful in carrying out such a process.

BACKGROUND ART

Detergent manufacturers have long recognised the need to control water hardness to ensure adequate cleaning by detergents. The detergency builders used in the past have been of three main types, namely water-soluble sequestering builders, water-insoluble ion exchange builders and water-soluble precipitating builders. A typical precipitating builder is an alkali metal carbonate, especially sodium carbonate. Other water-soluble precipitating builders include sodium silicate (particularly effective against magnesium hardness), sodium orthophosphate and water-soluble alkali

metal soaps. While from a cost point of view sodium carbonate is an attractive builder, it has at least two significant disadvantages. Firstly, sodium carbonate alone is not usually capable of reducing the calcium ion concentration in calcium hard water to sufficiently low levels to achieve good detergency under practical washing conditions. This is because crystal growth is inhibited by materials, in particular condensed phosphates, which can arise from the soiled laundry load, or be present as contamination in the detergent composition. Secondly, the use of carbonate ions to precipitate the calcium hardness from the water can result in the deposition of calcium carbonate on the washed fabrics. It is known that the calcium carbonate precipitate is produced in such a crystal type and such a particle size that deposition on the fabrics is favoured. The presence of certain crystal growth poisons in the wash liquor can encourage this deposition. Typical such poisons are inorganic phosphates carried into the wash liquor from the soiled fabrics in cases where the fabrics have previously been washed in a composition containing tripolyphosphate.

The calcium ion concentration in a wash liquor can be reduced to sufficiently low levels by the use of, for example, a sequestering builder material such as sodium tripolyphosphate, and considerable commercial success has been achieved with phosphate-built formulations. However, it has now become apparent that, under some conditions, the discharge of significant quantities of phosphates into waste waters may produce environmental problems. There is therefore an increasing desire in some countries to reduce the level of phosphorus in detergent compositions.

It has previously been thought that it was essential for precipitating builders to be substantially soluble at

the temperature of use to achieve efficient water softening. With the present trend towards washing fabrics at lower temperatures with a view to saving energy costs, it has not previously been thought possible to use, as a precipitating builder material, materials which themselves are not substantially soluble in water at low temperatures. Thus, the fatty acid salts which are not substantially soluble in water at room temperature, have not previously been proposed for use as precipitating builder materials at low temperatures.

We have now surprisingly found that particular fatty acid salts can be incorporated together with particular dispersant materials into a builder particle and by including these particles in detergent compositions which contain an alkaline material, efficient building of calcium-hard water can be achieved, even at low temperatures.

Thus, according to the invention, there is provided a particulate solid detergent composition comprising: builder particles having a particle size of between 100 microns and 1500 microns and comprising an alkyl benzene sulphonate as a dispersant in solid solution with a builder material selected from salts of saturated fatty acids, the which contain at least 16 carbon atoms, said salts being the salts of said fatty acids with alkali metals or organic nitrogen containing cations, optionally together with a non-soap detergent active material separate from the builder particles.

DISCLOSURE OF THE INVENTION

The builder particles essentially consist of an alkyl benzene sulphonate (ABS) and a fatty acid salt. It

is essential that the ABS is soluble in the fatty acid salt.

The alkyl benzene sulphonate may be selected from sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates. As an alternative to the alkali metal alkyl benzene sulphonates, the corresponding ammonium salts or the complexes of alkyl benzene sulphonic acids with organic nitrogen containing basic materials may be used. In addition to ABS one or more further dispersant materials may be present in the particles.

Examples of further dispersants which may be used to form builder particles include organic long chain (>C_4) compounds with a straight or branched chain, an optional aromatic ring or cycloaliphatic group and one or more hydrophilic groups, eg hydroxyl, amino, amine oxide, sulphate, sulphonate, phosphate, phosphonate, carboxy or sulphobetaine groups. These compounds may be soluble or insoluble in water. Examples of such compounds are other surfactants (anionic, nonionic, amine oxide, carboxy or sulphobetaine), alkanols, alkanediols, alkanedioic acids, alkanoic acid mono- or diethanolamides, and alkyl amines.

An optional feature of the builder particles of the present invention is the presence of a carrier material in which the fatty acid salt is insoluble, to effectively increase and maintain the surface area of the fatty acid salt in the composition.

Examples of carrier materials which may be used include: inorganic water-soluble salts such as sodium perborate (monohydrate, correctly designated anhydrate and tetrahydrate, correctly designated hexahydrate), mono-, di- and trivalent metal sulphates, especially alkali metal

sulphates and more especially the alums, alkali metal phosphates, especially sodium tripoly-phosphate, pyrophosphate and orthophosphate, alkali metal carbonates, especially sodium carbonate, sodium hydrogen carbonate and sodium sesquicarbonate, and their mixed carbonates, and also mixtures of any of these inorganic water soluble salts; inorganic water insoluble materials such as naturally occurring silicas, precipitated silicas and silica gels, alumina and aluminosilicate minerals including zeolites and clays; water-soluble organic materials such as carbohydrates, especially crystalline sugars such as sucrose, solid, preferably crystalline, polyhydric alcohols, such as pentaerythritol, sorbitol and mannitol; water-soluble film forming materials such as poly- saccharides especially derivatives of starch and cellulose; synthetic polymers such as polyacrylates and proteins such as gelatin.

The builder particles may further contain a material for improving the structure thereof. Such materials may be water-soluble inorganic salts such as sodium silicate.

The preferred level of fatty acid salt in the builder particles depends inter alia on the nature of the dispersant and the carrier material, if any, and on whether the composition contains further builder materials. Thus, where the dispersant and the carrier material, if any, serve little or no purpose in the composition other than to disperse and carry the fatty acid salt it is clearly desirable that the level of dispersant and carrier material, if any, should be as low as possible. In this case, the level of fatty acid salt may be up to 95%. However, where the dispersant and the carrier material, if any, serve some other useful purpose in the composition, the level of fatty acid salt in the builder particles can be less, say up to 80%. A further

consideration is that the efficiency of building, all other factors remaining the same, depends on size of fatty acid salt particles which are released into the wash liquor, smaller sizes resulting in faster building. Thus, for example when the builder particles include a carrier material, a lower level of fatty acid salt in the builder particles may lead to smaller particles of fatty acid salt being released into the wash liquor, which in turn leads to more efficient building.

In practice however, it is preferred for the level of fatty acid salt in the builder particles to be between 20% and 95%. Preferably the ratio by weight of the fatty acid salt to the dispersant in the builder particles is from 0.5:1 to 5:1, most preferably from 0.8:1 to 3:1.

The builder particle may be made by a variety of techniques. The fatty acid salt/ABS builder particles described herein may be processed by conventional spray-drying, by spray-cooling or granulation techniques.

Where the fatty acid salt and/or the alkyl benzene sulphonate are salts with organic N-containing cations and are meltable at convenient temperatures, a molten mixture of ABS and the fatty acid salt may be transformed into builder particles by spray-cooling.

Where the particles contain a carrier material, they may also be processed by melting the solid solution which is then sprayed as fine droplets by means of suitable atomising equipment on a moving bed of carrier material, or mixture of carrier materials, by any convenient granulation technique, eg rotating drum, inclined pan granulator, fluidised bed and solid mixer. An even distribution of solidified fatty acid salt/ABS solution through the carrier material can thus be obtained. The

carrier material can be milled to smaller particle sizes (eg using a swing-hammer mill) before the fatty acid salt/ABS solution is applied so as to increase the weight of fatty acid salt/ABS that can be carried by a given weight of said carrier material.

The particle size of the builder particles, as measured by sieve analysis, should be such that the majority of the particles have a size between 100 microns and 1500 microns, preferably between 200 microns and 1200 microns.

The fatty acid salt which can be used in the present invention should be saturated and contains at least 16 carbon atoms, preferably not more than 18 carbon atoms. Fatty acid salts containing less than 16 carbon atoms are unsuitable for present purposes, their corresponding calcium salts having a solubility product which is not sufficiently low for acceptable building to be possible. Salts of fatty acids derived from natural sources will normally contain a mixture of alkyl chain lengths, and may often contain unsaturated and/or hydroxy-substituted alkyl chains. In such circumstances it is essential that at least 30%, preferably at least 40% of the fatty acid consists of acids which are saturated and contain at least 16 carbon atoms, preferably from 16 to 18 carbon atoms. Suitable fatty acid salts for use in the present invention include the salts of palmitic acid, stearic acid and fatty acid derived from tallow fat or palm oil.

The fatty acid salts, as with the ABS referred to above, which can be used in the present invention include not only the alkali metal salts of the above 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.

Suitable fatty acid salts include sodium stearate, sodium palmitate, and complexes between stearic and/or palmitic fatty acid with water-soluble alkanolamides such as ethanolamine, di- or tri- ethanolamine, N-methyl-ethanolamine, 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 fatty acid salts, and mixtures of fatty acids with fatty acid salts may also be used.

The level of builder particles in the detergent composition should be such that the composition contains the equivalent of more than 10% up to 70%, preferably up to 50%, most preferably up to 40% of fatty acid or up to 15% when sodium carbonate is present as a further builder material. These levels render the compositions capable of softening water of typical calcium hardness under typical dosage conditions.

A desired feature of the compositions of the present invention is the presence of an alkaline material.

The compositions of the invention are required to be alkaline, but not too strongly alkaline as this could result in fabric damage and also be hazardous for domestic usage. In practice the compositions should give a pH of more than 8.0, preferably from 9.5 to 11 in use in aqueous wash solution. The pH measured at the lowest normal usage concentration of 0.1% w/v of the product in water of 12° FH (Ca) (French permanent hardness, calcium only) at 25°C so that a satisfactory degree of alkalinity can be assured in use at all normal product concentrations.

The alkaline material may be selected from alkali metal and ammonium salts of weak acids such as alkali metal and ammonium carbonates including sodium carbonate and sodium sesquicarbonate, alkali metal and ammonium silicates including sodium alkaline silicate, alkali metal and ammonium phosphates including sodium orthophosphate, alkali metal hydroxides including sodium hydroxides, alkali metal borates and the alkali metal and ammonium water-soluble salts of weak organic acids including sodium citrate, sodium acetate, and the cold water soluble soaps such as sodium oleate, and mixtures of such materials.

In some cases the alkaline material will itself also act as a builder. Thus, for example, sodium carbonate will contribute to building by precipitation of calcium carbonate while sodium citrate will contribute to building by sequestering calcium ions. In this case it may be beneficial to further include, as an alkaline material, a material which is relatively calcium insensitive, such as sodium silicate, so as to maintain a high pH throughout the wash. The other ingredients in the alkaline detergent compositions of the invention should of course be chosen for alkaline stability, especially the pH sensitive materials such as enzymes.

The detergent compositions are particularly suitable for washing fabrics at low temperatures ie below 50°C, even below 35°C. Successful results can also be achieved at temperatures above 50°C.

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

compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

As ABS is itself a detergent active material, this may constitute the whole of the detergent active material in the composition, but more usually further detergent active material may be included as a further dispersant in the builder particles and/or separate from the builder particles.

The preferred detergent compounds which can be used are synthetic anionic and nonionic compounds. The former are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting

alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Suitable nonionic detergent compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, generally 5 to 25 EO, ie 5 to 25 units of ethylene oxide per molecule, the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 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.

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

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

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

Cold water-soluble soaps may also be present in the detergent compositions of the invention. The soaps are particularly useful at low levels in binary and ternary mixtures, together with nonionic or mixed synthetic anionic and nonionic detergent compounds, which have low sudsing properties. The soaps which are used are the water-soluble salts of unsaturated fatty acids in particular with inorganic cations such as sodium and potassium. The amount of such soaps can be between 2% and 20%, especially between 5% and 15%, can advantageously be used to give a beneficial effect on detergency.

The compositions of the invention may contain a further builder material other than the fatty acid salt.

Where the further builder material is other than sodium or potassium carbonate this may be present at levels less than the level of the fatty acid salt. Where the composition contains sodium or potassium carbonate as the alkaline material and as a further builder, this may be present at a level more than the level of the fatty acid salt.

Any such further builder material may be selected from other precipitating builder materials, optionally together with a precipitation seed material, or from sequestering builder materials and ion-exchange builder materials and materials capable of forming such builder materials in situ.

Where the further builder material is a water-soluble precipitating material, it may be selected from soaps, alkyl malonates, alkyl or alkenyl succinates, sodium fatty acid sulphonates, orthophosphates of sodium, potassium and ammonium, or in their water-soluble partially or fully acidified forms. Particularly where the hard water contains magnesium ions, the silicates of sodium and potassium may be included in the compositions.

The further builder may also be constituted by a sequestering builder material, particularly those selected from water-soluble pyro-phosphates, poly- phosphates, phosphonates, polyhydroxy-sulfonates, poly- acetates, carboxylates, polycarboxylates, and succinates.

Specified examples of inorganic phosphate sequestering builders include sodium and potassium tri-polyphosphates, pyro-phosphates, and polymerphosphates such as hexameta- phosphate or glassy phosphates. The polyphosphonates specifically include, for example, the sodium and potassium salts of ethane 1-hydroxy-1,1-di-phosphonic acid and the sodium and potassium salts of ethane-1,1,2-tri- phosphonic acid.

In some embodiments of this invention, the compositions will not contain more than about 5% by weight phosphate builder materials or phosphorus containing materials of any kind.

Water-soluble, organic sequestering builders are also useful herein as further builder materials. For example, the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetylcarboxylates and polyhydroxysulfonates are useful sequestering builders in the present compositions. Specific examples of the polyacetate and polycarboxylate builder salts include sodium, potassium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitriloacetic acid, dipicolinic acid, oxydisuccinic acid, benzene polycarboxylic acids eg mellitic acid, citric acid and the polyacetalcarboxylates disclosed in US 4 144 226 and 4 146 495. The acid forms of these materials may also be used.

Highly preferred organic sequestering builder materials herein include sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetates, and sodium ethylene diamine tetraacetate and mixtures thereof.

Other highly preferred sequestering builders are the polycarboxylate builders. Examples of such materials include the water-soluble salts of the homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid, methylenemalonic acid, 1,1,2,2-ethane tetracarboxylic acid, dihydroxy tartaric acid, and ketomalonic acid.

Additional preferred sequestering builders herein include the water-soluble salts, especially the sodium and potassium salts of carboxy methyloxymalonate, carboxy methyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate, and phloroglucinol trisulfonate.

The further builder material may also be constituted by an ion-exchange material. Suitable ion-exchange materials include the smorphous or crystalline alumino-silicates such as disclosed in GB 1 473 201/2 (HENKEL).

When the further builder material is an ion-exchange material, it may be present at a level which is more than the level of the fatty acid salt.

A preferred composition of this invention comprises

(i) from 2.0% to 30% of at least one non-soap detergent active material;

(ii) at least 3% of an alkaline material; and

(iii) the builder particles in such an amount as to be equivalent to at least 15% fatty acid salt.

The non-soap detergent active material and the alkaline material can be incorporated in the builder particle and/or can be separate therefrom.

In a wash liquor containing sodium carbonate as an alkaline material, the precipitation of calcium carbonate by reaction between the calcium hardness and the sodium carbonate takes place via a series of steps which are transient in the absence of crystal growth poisons, but can be isolated in their presence. If the builder particles are added after the system has reached a particular state referred to herein as the "critical state", the free calcium ion concentration in the wash liquor is reduced to about 10^{-5} molar or lower. If, on the other hand, the builder particles are added prior to the system reaching the critical state, this reduction in

free calcium ion concentration may not be achieved at all or not within a reasonable time.

The time period required for a system to reach the critical state after the addition of sodium carbonate to the hard water is thought to depend on a number of factors among which are the initial water hardness, the quantity of sodium carbonate added, the quantity of crystal growth poisons present either from the wash load, from the added composition or in the liquor itself, the pH of the liquor, the temperature or temperature profile of the liquor and the nature of other materials which may be present.

According to a preferred feature of the invention there is provided a method of washing fabrics in water containing calcium hardness, comprising contacting the fabrics with a wash liquor to which has been added at least a synthetic detergent active material and an alkali metal carbonate and bringing into effective contact with the wash liquor the fatty acid builder particles, the latter being brought into effective contact with the wash liquor at or after the wash liquor has reached the critical state as hereinbefore defined, and being added in such an amount as to reduce the free calcium ion concentration in the wash liquor to 10^{-5} or less within at most 60 minutes preferably within 30 minutes from the addition of the alkali metal carbonate to the hard water.

The term "effective contact" between builder particles and the wash liquor as used herein is intended to mean the reaction between the fatty acid salt and the calcium hardness of the water.

The time at which the critical state is reached for a given composition and wash condition may be determined by a series of experiments as follows. A substantially

similar load of fabrics is washed in an identical wash liquor under identical conditions and the builder particles are added at various times between 1 minute and 30 minutes from the addition of the alkali metal carbonate to the liquor. After 60 minutes the free calcium ion concentration is measured. The critical state has been achieved when this final free calcium ion concentration is not more than 10^{-5} molar. Alternatively, or where a similar load of soiled fabrics is not available, this series of experiments may be carried out with a clean load of similar fabrics while an appropriate level of crystal growth poison is included in the hard water.

It is also possible to determine whether the system has reached the critical state by determining one or more of a number of alternative or additional criteria. Thus, when the system has reached its critical state the form of the calcium carbonate precipitate changes from an X-ray amorphous form to an X-ray crystalline form. Still further, the calcium carbonate precipitate is colloidally suspended. When the critical state is reached the precipitate settles rapidly.

When the builder particles are added, some of the already precipitated calcium carbonate may pass back into the solution, for the calcium ions to be precipitated as calcium soap. It is found that, after the system has reached the critical state, at least 40% of the initial calcium hardness remains as the solid calcium carbonate form when the builder particles are added.

When the conditions are such that the precipitation of calcium carbonate occurs in such a manner that calcium carbonate hexahydrate is formed, it is found that this form of calcium carbonate has disappeared when the system reaches its critical state. The transient formation of

the hexahydrate may occur in conditions of high water hardness, high poison levels, low temperatures and in the absence of seed crystals.

One may take steps to promote occurrence of the critical state. Such promotion may be achieved for example by

(a) adding to the wash liquor up to 1.5 g/l, preferably up to 1.0 g/l of a seed crystal such as fine particulate calcium carbonate (eg calcite vaterite and aragonite);

(b) increasing the initial hardness of the water by adding to the wash liquor a source of calcium ions such as calcium chloride; or

(c) adding to the wash liquor a calcium carbonate growth poison suppressing agent such as a source of aluminium ions (eg aluminium sulphate).

Alternative calcium carbonate growth poison suppressing agents include the soluble salts of lanthanum ion, cobalt, manganese and copper.

Where the promotion of the critical state is achieved by the addition of a seed crystal, this material is preferably calcite having a surface area of from 2 to 80 m^2/g. Suitable materials are Calofort U, available from Sturge Chemicals having a surface area of about 16 m^2/g and calcite having a larger surface area (such as for example 80 m^2/g) as available from Solvay. In the latter case less of the material would be necessary. A level of up to 15% by weight of calcite in the composition is suitable.

Particularly where the composition contains a material to promote the critical state, the builder particles are added to the wash liquor or the fatty acid content thereof is released into the wash liquor between about one and about ten minutes after the addition of the sodium carbonate.

A composition according to the embodiment of the present invention may comprise at least

(i) from 2.0% to 30% of at least one non-soap detergent active material;

(ii) at least 10% of an alkali metal carbonate as an alkaline material; and

(iii) the builder particles in such an amount as to be equivalent to at least 10% fatty acid,

the builder particles being adapted to delay the reaction between the fatty acid and the calcium hardness of the water until the critical state is reached. Such delay may be achieved by suitable choice of the dispersant and the carrier material and the level of fatty acid salt therein, or by coating or encapsulating the builder particles with a water-soluble or water-dispersible material in any convenient apparatus suitable for coating or encapsulating powders, eg an inclined pan granulator, fluidised bed, solid mixer, extruder, rotating drum. Examples of such coating materials include sodium silicate, polyethyleneglycol, polyvinyl- alcohol, fatty acids C_{12}-C_{22}, long chain aliphatic alcohols, paraffin waxes, nonionic surface active agents, starch and cellulose derivatives, gelatin and sugars.

Particularly preferred compositions according to the invention contain, based on the weight of the total composition:

from 5% to 30%, such as between 8% and 25% of at least one non-soap detergent active material;

from 10% to 80%, preferably from 15%, more preferably from 20% to 40% of an alkali metal carbonate;

up to 15%, preferably from 6% to 12% calcite; and

up to 20%, preferably up to 15% of fatty acid salt in the form of builder particles.

The balance of the composition, if any, will be water and other conventional additives as referred to below.

As an alternative to the above described method of washing fabrics in which the fabric washing composition contains sodium carbonate as a further builder material and in which effective contact between the wash liquor and the fatty acid salt is delayed until the system reaches the critical state, it may also be beneficial to arrange that the fatty acid salt comes into effective contact with the wash liquor relatively rapidly, and the reaction between the sodium carbonate and the free calcium ions in the wash liquor is retarded by including in the composition a calcium-carbonate crystal growth inhibitor, such as a phosphate material.

Apart from the essential detergent active compounds and detergency builders, the detergent compositions used in the process of the invention can contain any of the

conventional additives in the amounts in which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include lather boosters such as alkanolamines, particularly the mono-ethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants such as alkyl phosphate, long-chain fatty acids or soaps thereof, waxes and silicones, anti-redeposition agents such as sodium carboxymethyl-cellulose and cellulose ethers, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, per-acid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, fabric softening agents, inorganic salts, such as sodium sulphate, and magnesium silicate, and usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants.

It is particularly beneficial to include in the detergent compositions an amount of sodium perborate or percarbonate, preferably between 10% and 40%, for example 15% to 30% by weight.

It is desirable to include one or more anti-deposition agents in the detergent compositions of the invention, to further decrease the tendency to form inorganic deposits on washed fabrics. The most effective antideposition agents are anionic poly electrolytes, especially polymeric aliphatic carboxylates. The amount of any such antideposition agent can be from 0.01% to 5% by weight, preferably from 0.2% to 2% by weight of the compositions.

Specific preferred antideposition agents are the alkali metal or ammonium, preferably the sodium, salts or homo- and co-polymers of acrylic acid or substituted

acrylic acids, such as sodium polyacrylate, the sodium salt of copolymethacrylamide/acrylic acid and sodium poly-alphahydroxyacrylate, salts of copolymers of maleic anhydride with ethylene, acrylic acids, vinylmethylether allyl acetate or styrene, especially 1:1 copolymers, and optionally with partial esterification of the carboxyl groups. Such copolymers preferably have relatively low molecular weights, eg in the range of 1,000 to 50,000. Other antideposition agents include the sodium salts of polyitaconic acid and polyaspartic acid, phosphate esters of ethoxylated aliphatic alcohols, polyethylene glycol phosphate esters, and certain phosphonates such as sodium ethane-1-hydroxy-1,1- diphosphonate, sodium ethylene-diamine tetramethylene phosphonate, and sodium 2-phosphonobutane tri carboxylate. Mixtures of organic phosphonic acids or substituted acids or their salts with protective colloids such as gelatin may also be used. The most preferred antideposition agent is sodium polyacrylate having a MW of 10,000 to 50,000, for example 20,000 to 30,000. Where the antideposition agent is itself a calcium carbonate crystal growth poison, or in any case, and the composition contains sodium carbonate as a further builder material, it may be desirable to delay contact between this agent and the wash liquor until after the critical state is reached.

Even if the alkaline material other than an alkali metal silicate is included in the composition, it is generally also desirable to include an amount of an alkali metal silicate, to decrease the corrosion of metal parts in washing machines and provide processing benefits and generally improved powder properties. The presence of such alkali metal silicates, particularly sodium ortho-, meta- or preferably neutral or alkaline silicate, at levels of at least about 1%, and preferably from 5% to 15%, by weight of the composition, is advantageous. The

more highly alkaline ortho- and meta- silicates would normally only be used at lower amounts within this range, in admixture with the neutral or alkaline silicates.

The washing process of the invention can be accomplished manually, if desired, but is normally accomplished in a domestic or commercial laundry washing machine. The latter permits the use of higher alkalinity, and more effective agitation, all of which contribute generally to better detergency. The type of washing machine used, if any, is not significant.

The detergent compositions of the invention should be solid particulate compositions. Dry-mixing and granulation of all components may be used or alternatively the fatty acid salt containing particles may be post-dosed to a spray-dried base powder.

The invention will now be further illustrated with reference to the following Examples.

EXAMPLE 1

The following particles were added at room temperature (about 20°C) to hard water, having a hardness of 20° FH (Ca). The particles consisted of 2 parts of the sodium salt of a mixture of C_{16} and C_{18} saturated fatty acids to 1 part of DOBS 055, an anionic detergent active material which approximates to sodium dodeconyl benzene sulphonate acting as both dispersant for the soap and detergent active material. The particles had sizes between 355 and 1000µm. The particles were added at 3.0 g/l.

By use of a calcium sensitive electrode, the concentration of free calcium ions after 5 minutes was measured and was 0.2°FH.

When the experiment was repeated replacing the DOBS 055 by DOBANOL 45 11 EO, which is an ethoxylated linear primary alcohol (ex SHELL), a nonionic surface active material, the free calcium ion concentration after 5 minutes was about 4.2°FH.

When the experiment was repeated replacing the DOBS 055 by DOBANOL 25 sulphate, an anionic surface active material constituted by the sodium salt of a linear primary alcohol ethoxysulphate (ex SHELL), the free calcium ion concentration after 5 minutes was about 0.5°FH.

The soap control containing no dispersant showed very little calcium ion lowering. A final free calcium concentration of 15° FH was achieved.

These experiments demonstrate the benefit of using an alkyl benzene sulphonate as a dispersant in comparison with other anionic or nonionic dispersants.

EXAMPLE 2

The following particles were added at room temperature (about 20°C) to hard water, having a hardness of 20°FH (Ca). The particles consisted of 2 parts by weight sodium oleate, 1 part by weight sodium stearate, 1 part by weight sodium palmitate, 2 parts by weight DOBS 055 (as in Example 1) and 1 part by weight sodium silicate (as a structurant). The particles were dosed at the level of 1.3 g/l to the water together with 0.5 g/l calcite, 1.5 g/l sodium carbonate (measured as anhydrous)

and 10 ppm sodium tripolyphosphate as a crystal growth poison.

After 5 minutes the free calcium ion concentration was found to be 0.072° FH, showing that even in the presence of the crystal growth poison, effective water softening can be achieved.

When the experiment was repeated with similar builder particles, but which contained no sodium silicate, the free calcium ion concentration after 5 minutes was about 0.2° FH, indicating the benefit of delaying the effective contact between the fatty acid salt and the liquor until after the critical state had been reached, by including sodium silicate in the builder particles.

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CLAIMS

1. A particulate solid detergent composition which includes builder particles comprising a water-soluble or water-dispersible dispersant material in solid solution with builder material selected from salts of saturated fatty acids, which contain at least 16 carbon atoms, said salts being the salts of said fatty acids with alkali metals or organic nitrogen-containing cations, characterised in that the dispersant is constituted by an alkyl benzene sulphonate and the particles have a particle size of between 100 and 1500 microns.

2. A composition according to Claim 1, characterised in that it further contains a non-soap detergent active material separate from the builder particles and/or incorporated in said builder particles as a further dispersant material.

3. A composition according to Claim 1, characterised in that it comprises an alkaline material capable of providing the composition with a pH of more than 8.0, when added to water of 12° French hardness (Ca) at 25°C and at a concentration of 1.0 g/l.

4. A composition according to Claim 3, characterised in that the alkaline material is selected from alkali metal carbonates, alkali metal silicates and mixtures thereof.

5. A composition according to Claim 1, characterised in that the dispersant material is selected from sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates.

6. A composition according to Claim 1, characterised in that the builder particles include a carrier material in which the fatty acid salt is insoluble.

7. A composition according to Claim 6, characterised in that the carrier material is selected from inorganic water-soluble salts, inorganic water-insoluble materials, water-soluble organic materials, water-soluble film forming materials, synthetic polymers and proteins.

8. A composition according to Claim 1, characterised in that the builder material is selected from salts of palmitic acid, stearic acid, tallow fatty acid and palm oil fatty acid.

9. A composition according to Claim 1, characterised in that it comprises

(i) from 2% to 30% of at least one non-soap detergent active material;

(ii) at least 3% of an alkaline material; and

(iii) said builder particles in such an amount as to be equivalent to at least 15% fatty acid salt.

10. A composition according to Claim 1, characterised in that it comprises

(i) from 5% to 30% of a detergent active material selected from synthetic anionic detergent active materials, nonionic detergent active materials and mixtures thereof;

(ii) from 10% to 80% of sodium carbonate;

(iii) up to 15% calcite; and

(iv) from 10% to 20% fatty acid salt in the form of builder particles comprising, based on the weight of the particles, from 5% to 80% of said dispersant and from 20% to 95% of said fatty acid salt.

11. A method of washing fabrics in water containing calcium hardness ions, characterised by contacting the fabrics at a temperature below 50°C with a wash liquor obtained by adding to water a particulate solid detergent composition according to any one of claims 1 to 9.

European Patent Office

EUROPEAN SEARCH REPORT

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Application number

EP 83 30 7640

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. ³)
A	DE-A-3 004 140 (KUREHA KAGAKU KOGYO K.K.) * Claims 1, 3 *		C 11 D 3/20
A	US-A-4 196 095 (F.R. CALA et al.) * Claim 1 *		
A	GB-A-2 047 264 (MIRA LANZA S.p.A.) * Claim 1 *		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	07-03-1984	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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