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(54) Solid bleach activator compositions

(57) Solid bleach activator compositions are disclosed which comprise a particulate bleach activator material, wherein said bleach activator is co-agglomerated with a secondary (2,3) alkyl sulfate and may be further coated with such a secondary (2,3) alkyl sulfate surfactant. The present invention also encompasses a process for manufacturing said particulate bleach activator materials.

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DescriptionTechnical field

5 The present invention relates to the field of detergency, especially laundry detergents. Ingredients commonly used in laundry detergents, especially bleach activators, are formed into particles using secondary (2,3) alkyl sulfate surfactants as an agglomerating agent. The resulting particles exhibit improved bleaching performance in aqueous laundering operations.

10 Background of the invention

Many fully-formulated laundry detergents provide both cleaning and bleaching benefits in a single product. Accordingly, such products will typically comprise one or more deterative surfactants, various builders, one or more types of deterative enzymes, chelants, soil release polymers, and the like, together with effective bleaching agents such as perborate, percarbonate or persulfate compounds. The objective of the detergent formulator is to use ingredients of a type and in the proper proportions that will safely and effectively remove a variety of soils and stains from a variety of fabrics under widely disparate laundering conditions, ranging from cold water to boil washes. As is well known, bleaching agents such as those noted above do not function optimally at washing temperatures below about 60°C. However, many users of laundry detergent compositions now prefer to launder fabrics at somewhat cooler temperatures, both to save energy and to help maintain fabric appearance. Accordingly, conventional bleach-assisted detergents do not provide optimal cleaning benefits to such cool-water users. In a successful attempt to improve cool water bleaching performance, formulators have added the so-called "bleach activators" to laundry detergent compositions. Such activators co-act with bleaching agents such as perborate, percarbonate and the like, by a perhydrolysis mechanism to provide active bleaching species in the aqueous laundry liquor even at cool water temperatures. Bleach activators such as tetraacetyethylene diamine ("TAED"), nonanoyloxybenzene sulfonate ("NOBS") and mixtures thereof, are well-known bleach activators in commercial practice. Unfortunately, many bleach activators such as TAED are solids which are relatively insoluble in aqueous wash liquors during the time span of a typical laundering operation. Hence, the effectiveness of such insoluble bleach activators would be substantially decreased if means were not found to enhance their dispersion in aqueous wash liquors and, correspondingly, their rate of perhydrolysis. Moreover, unsolubilized particles of such activators can deposit onto fabrics from the wash liquor and cause "pin-point" color damage. Merely decreasing the particle size of such solid bleach activators to improve their dispersion is impractical, since extremely small particles tend to be unstable in finished products.

Accordingly a need exists to provide detergent compositions in which the bleach activator is incorporated in a form that minimizes and preferably eliminates damage to fabric colours and materials while enhancing the dispersion in aqueous wash liquors and rate of perhydrolysis of said bleach activators.

The prior art contains numerous examples of bleach activators coated or agglomerated so as to increase their stability on storage in detergent compositions and/or to influence their solution behaviour. Various patents disclose the coating of bleach activators with fatty acids (see for instance GB-A-1507312 or GB-A-1381121). EP-A-0375241 describes stabilized bleach activator extrudates in which C₅-C₁₈ alkyl peroxy carboxylic acid precursors are mixed with a binder selected from anionic and nonionic surfactants, film forming polymers fatty acids or mixtures of such binders. Furthermore, detergent formulators who wish to use relatively insoluble materials such as the TAED bleach activators have also learned to agglomerate particles of said materials with nonionic surfactants, especially the highly ethoxylated alcohols such as ethoxylated (EO25) tallow alcohol. Where coating and/or agglomeration has been proposed with poorly soluble materials such as fatty acids or with nonionic surfactants such as EO25, this has resulted in a rate of perhydrolysis of the bleach activator which is slower than that which would occur if it had not been so protected. Accordingly, improved means for enhancing the performance of bleach activators is of substantial importance in this field. It is thus an object of the present invention to provide a solid bleach activator composition comprising a particulate bleach activator material with a significantly increased rate of perhydrolysis, thereby increasing the effectiveness of the resultant bleach.

Another problem encountered with the compositions of the prior art relates to the storage and handling properties of said compositions, and it is thus an additional object of the present invention to provide a bleach activator composition as a free-flowable powder which remains as such throughout prolonged storage time.

The applicant has now surprisingly found that surfactants which comprise the class of secondary (2,3) alkyl sulfates provide superior means for agglomerating deterative ingredients such as TAED bleach activators and further coating said agglomerated deterative ingredients. The particulate bleach activator materials obtained accordingly allow to enhance the dispersion in aqueous wash liquors of said activators as well as to improve their rate of perhydrolysis as compared to activators-plus-nonionic agglomerating agents, noted above, this without requiring a decreased particle size. Furthermore, solid bleach activator compositions comprising said particulate bleach activator materials result in storage-stable free-flowable powders. Moreover, the secondary (2,3) alkyl sulfates are calcium-insensitive and are thus useful in under-built compositions, including nil-phosphate compositions. The secondary (2,3) alkyl sulfates are solids, and can be used

in the molten state to quickly and easily agglomerate powders such as TAED with less moisture/solvents than other anionic surfactants. Moreover, the secondary (2,3) alkyl sulfates are degradable both aerobically and anaerobically, which assists in their disposal in the environment.

The satisfactorily perhydrolysis rate and dispersion properties associated to the use of a solid bleach activator composition comprising the present particulate bleach activator materials wherein the secondary (2,3) alkyl sulfates are used as an agglomerating agent and optionally as an coating agent are unexpected and beneficial as said secondary (2,3) alkyl sulfates are only known in the art context of laundry compositions as surfactants, see for instance the following patents; US. 2,900,346, Fowkes et al, August 18, 1959; U.S. 3,468,805, Grifo et al, September 23, 1969; U.S. 3,480,556, DeWitt et al, November 25, 1969; U.S. 3,681,424, Bloch et al, August 1, 1972; U.S. 4,052,342, Fernley et al, October 4, 1977; U.S. 4,079,020, Mills et al, March 14, 1978; U.S. 4,235,752, Rossall et al, November 25, 1980; U.S. 4,529,541, Wilms et al, July 16, 1985; U.S. 4,614,612, Reilly et al, September 30, 1986; U.S. 4,880,569, Leng et al, November 14, 1989; U.S. 5,075,041, Lutz, December 24, 1991; U.K. 818,367, Bataafsche Petroleum, August 12, 1959; U.K. 1,585,030, Shell, February 18, 1981; GB 2,179,054A, Leng et al, February 25, 1987 (referring to GB 2,155,031).

Summary of the Invention

The present invention is directed to a solid bleach activator composition comprising a particulate bleach activator material wherein said activator is co-agglomerated with an agglomerating agent, characterized in that said agglomerating agent is selected from the group of secondary (2,3) alkyl sulfate surfactants.

The present invention also encompasses a solid bleach activator composition comprising a co-agglomerated particulate bleach activator material as previously defined which is further coated with a coating agent. Said coating agent may be selected from the group of secondary (2,3) alkyl sulfate surfactants or any others coating agents well known in the art.

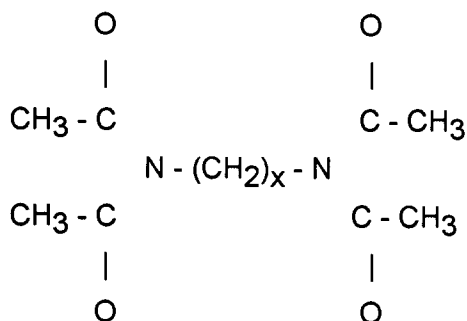
The present invention further encompasses process for manufacturing the particulate bleach activator materials according to the present invention.

Detailed description of the invention

The solid bleach activator compositions of the present invention comprise particulate bleach activator materials wherein said activator is co-agglomerated with a secondary (2,3) alkyl sulfate surfactant.

As a first essential ingredient the compositions of the present invention contain a bleach activator, or mixtures thereof. Said bleach activator leads to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to said bleach activator. Said bleach activators used herein can be any of the bleach activators useful for detergent compositions in textile cleaning, hard surface cleaning or other cleaning purposes that are now known or become known. Various nonlimiting examples of activators are disclosed in U.S. Patent US-4 915 854 and in U.S. Patent US-4 412 934. For instance bleach activators particularly suitable to be used in the present invention contain one or more N- or O- acyl groups, said activators can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836988, 864,798, 1147871 and 2143231 and imides such as are disclosed in GB-A-855735 & 1246338.

Particularly preferred bleach activators are the N-,N',N'' tetra acetylated compounds of formula



wherein x can be O or an integer between 1 & 6.

Examples include tetra acetyl methylene diamine (TAMD) in which $x=1$, tetra acetyl ethylene diamine (TAED) in which $x=2$ and tetraacetyl hexylene diamine (TAHD) in which $x=6$. These and analogous compounds are described in GB-A-907356. The most preferred peroxyacid bleach activator is TAED.

Said solid peroxyacid bleach activators useful in the present invention have a $M_{pt}>30^{\circ}\text{C}$ and preferably $>40^{\circ}\text{C}$. Such activators will normally be in fine powder or crystalline form in which at least 90% by weight of the powder has a particle size < 150 micrometers.

Other particularly suitable bleach activators to be used in the present invention are nonanoyloxybenzene sulfonate (NOBS), isononanoyloxybenzene sulfonate (isoNOBS), benzoyloxybenzene sulfonate (BOBS), benzoxazin-type activators, peroxyacid activators having amide moieties and/or caprolactam derivatives. Also particularly preferred are N-acyl caprolactam selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecanoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam, pentanoyl caprolactam. These and analogous compounds are described in the co-pending US patent applications 08064623, 08064627, 08064562, 08064564, 08064624 and 08064563 and US patent US-4 634 551.

Another essential ingredient of the compositions according to the present invention is a secondary (2,3) alkyl sulfate surfactant. Said secondary (2,3) alkyl sulfate surfactant is used in the compositions according to the present invention as an agglomerating agent to co-agglomerate said bleach activator. In another embodiment of the present invention said secondary (2,3) alkyl sulfate surfactant may also be used as a coating agent to coat said co-agglomerate bleach activator.

For the convenience of the formulator, the following identifies and illustrates the differences between the sulfated surfactants employed herein as an agglomerating and/or coating agent and otherwise conventional alkyl sulfate surfactants.

Conventional primary alkyl sulfate surfactants have the general formula



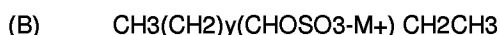
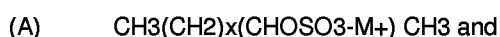
wherein R is typically a linear C10-C20 hydrocarbyl group and M is a water-solubilizing cation. Branched-chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 10-20 carbon atoms are also known; see, for example, European Patent Application EP-439 316.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbon "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of $m + n$ is typically 9 to 15, and M is a water-solubilizing cation.

By contrast with the above, the selected secondary (2,3) alkyl sulfate surfactants used herein comprise structures of formulas A and B



for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas A and B, x and (y-1) are, respectively, integers of at least 6, and can range from 7 to 20, preferably 10 to 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, alkaline earth metal, or the like. Sodium is typical for use as M to prepare the water-soluble (2,3) alkyl sulfates, but ethanolanmonium, diethanolanmonium, triethanolanmonium, potassium, ammonium, and the like, can also be used.

By the present invention it has been determined that the physical/chemical properties of the foregoing types of alkyl sulfate surfactants are unexpectedly different, one from another, in several aspects which are important to formulators of various types of detergent compositions. For example, the primary alkyl sulfates can disadvantageously interact with, and even be precipitated by, metal cations such as calcium and magnesium. Thus, water hardness can negatively affect the primary alkyl sulfates to a greater extent than the secondary (2,3) alkyl sulfates herein. Accordingly, the secondary (2,3) alkyl sulfates have now been found to be preferred for use in the presence of calcium ions and under conditions of high water hardness, or in the so-called "under-built" situation which can occur with nonphosphate builders.

Importantly, when formulating concentrated liquid detergents with calcium or magnesium ions to enhance grease cutting or sudsing performance it has now been found that the primary alkyl sulfates can be problematic due to such interactions with calcium or magnesium cations. Moreover, the solubility of the primary alkyl sulfates is not as great as the secondary (2,3) alkyl sulfates. Hence, the formulation of high-active liquid and gel detergents has now been found to be simpler and more effective with the secondary (2,3) alkyl sulfates than with the primary alkyl sulfates.

With regard to the random secondary alkyl sulfates (i.e., secondary alkyl sulfates with the sulfate group at positions such as the 4, 5, 6, 7, and the like secondary carbon atoms), such materials tend to be tacky solids or pastes, and thus do not afford the processing advantages associated with the secondary (2,3) alkyl sulfates when formulating detergent bars, granules or tablets.

One additional advantage of the secondary (2,3) alkyl sulfate surfactants herein over other positional or "random" alkyl sulfate isomers is in regard to the improved benefits afforded by said secondary (2,3) alkyl sulfates with respect to soil redeposition in the context of fabric laundering operations. As is well-known to users, laundry detergents loosen soils from fabrics being washed and suspend the soils in the aqueous laundry liquor. However, as is well-known to detergent formulators, some portion of the suspended soil can be redeposited back onto the fabrics. Thus, some redistribution and redeposition of the soil onto all fabrics in the load being washed can occur. This, of course, is undesirable and can lead to the phenomenon known as fabric "greying". (As a simple test of the redeposition characteristics of any given laundry detergent formulation, unsoiled white "tracer" cloths can be included with the soiled fabrics being laundered. At the end of the laundering operation the extent that the white tracers deviate from their initial degree of whiteness can be measured photometrically or estimated visually by skilled observers. The more the tracers' whiteness is retained, the less soil redeposition has occurred.)

It has now been determined that the secondary (2,3) alkyl sulfates afford substantial advantages in soil redeposition characteristics over the other positional isomers of secondary alkyl sulfates in laundry detergents, as measured by the cloth tracer method noted above. Thus, the selection of secondary (2,3) alkyl sulfate surfactants according to the practice of this invention which preferably are substantially free of other positional secondary isomers unexpectedly assist in solving the problem of soil redeposition in a manner not heretofore recognized. It is to be noted that the secondary (2,3) alkyl sulfates used herein are quite different in several important properties from the secondary olefin sulfonates (e.g., US-4 064 076); accordingly, the secondary sulfonates are not the focus of the present invention.

The preparation of the secondary (2,3) alkyl sulfates of the type useful herein can be carried out by the addition of H₂SO₄ to olefins. A typical synthesis using α -olefins and sulfuric acid is disclosed in the U.S. patents US-3 234 258 or US-5 075 041. The synthesis, conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the corresponding sulfated nonionics, randomly sulfated materials, unsulfated by-products such as C₁₀ and higher alcohols, secondary olefin sulfonates, and the like, are typically 90+% pure mixtures of 2- and 3-sulfated materials (some sodium sulfate may be present) and are white, non-tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available as under the name "DAN", e.g., "DAN 200" from Shell Oil Company.

If increased solubility or lower melting temperatures of the "crystalline" secondary (2,3) alkyl sulfate surfactants is desired, the formulator may wish to employ mixtures of such surfactants having a mixture of alkyl chain lengths. Thus, a mixture of C₁₂-C₁₈ alkyl chains will provide an increase in solubility over a secondary (2,3) alkyl sulfate wherein the alkyl chain is, say, entirely C₁₆. The solubility of the secondary (2,3) alkyl sulfates can also be enhanced by the addition thereto of other surfactants such as the alkyl ethoxylates or other nonionic surfactants, or by any other material which decreases the crystallinity of the secondary (2,3) alkyl sulfates. Such crystallinity-interrupting materials are typically effective at levels of 20%, or less, of the secondary (2,3) alkyl sulfate.

When formulating liquid and gel compositions, especially clear liquids, it is preferred that the secondary (2,3) alkyl sulfates contain less than 3% sodium sulfate, preferably less than 1% sodium sulfate. In and of itself, sodium sulfate is an innocuous material. However, it dissolves and adds to the ionic "load" in aqueous media, and this can contribute to phase separation in liquid compositions and to gel breaking in the gel compositions. Various means can be used to lower the sodium sulfate content of the secondary (2,3) alkyl sulfates. For example, when the H₂SO₄ addition to the olefin is completed, care can be taken to remove unreacted H₂SO₄ before the acid form of the secondary (2,3) alkyl sulfate is neutralized. In another method, the sodium salt form of the secondary (2,3) alkyl sulfate which contains sodium sulfate can be rinsed with water at a temperature near or below the Krafft temperature of the sodium secondary (2,3) alkyl sulfate. This will remove Na₂SO₄ with only minimal loss of the desired, purified sodium secondary (2,3) alkyl sulfate. Of course, both procedures can be used, the first as a pre-neutralization step and the second as a post-neutralization step. The term "Krafft temperature" as used herein is a term of art which is well-known to workers in the field of surfactant sciences. Krafft temperature is described by K. Shinoda in the text "Principles of Solution and solubility", translation in collaboration with Paul Becher, published by Marcel Dekker, Inc. 1978 at pages 160-161. Stated succinctly, the solubility of a surface active agent in water increases rather slowly with temperature up to that point, i.e., the Krafft temperature, at which the solubility evidences an extremely rapid rise. At a temperature approximately 4°C above the Krafft temperature a solution of almost any composition becomes a homogeneous phase. In general, the Krafft temperature of any given type of surfactant, such as the secondary (2,3) alkyl sulfates herein which comprise an anionic hydrophilic sulfate group and a hydrophobic hydrocarbyl group, will vary with the chain length of the hydrocarbyl group. This is due to the change in water solubility with the variation in the hydrophobic portion of the surfactant molecule.

In the practice of the present invention the formulator may optionally wash the secondary (2,3) alkyl sulfate surfactant which is contaminated with sodium sulfate with water at a temperature that is no higher than the Krafft temperature,

and which is preferably lower than the Krafft temperature, for the particular secondary (2,3) alkyl sulfate being washed. This allows the sodium sulfate to be dissolved and removed with the wash water, while keeping losses of the secondary (2,3) alkyl sulfate into the wash water to a minimum.

Under circumstances where the secondary (2,3) alkyl sulfate surfactant herein comprises a mixture of alkyl chain lengths, it will be appreciated that the Krafft temperature will not be a single point but, rather, will be denoted as a "Krafft boundary". Such matters are well-known to those skilled in the science of surfactant/solution measurements. In any event, for such mixtures of secondary (2,3) alkyl sulfates, it is preferred to conduct the optional sodium sulfate removal operation at a temperature which is below the Krafft boundary, and preferably below the Krafft temperature of the shortest chain-length surfactant present in such mixtures, since this avoids excessive losses of secondary (2,3) alkyl sulfate to the wash solution. For example, for C16 secondary sodium alkyl (2,3) sulfate surfactants, it is preferred to conduct the washing operation at temperatures below 30°C, preferably secondary (2,3) alkyl sulfates below 20°C. It will be appreciated that changes in the cation will change the preferred temperature for washing the secondary (2,3) alkyl sulfates, due to changes in the Krafft temperature.

The washing process can be conducted batchwise by suspending wet or dry secondary (2,3) alkyl sulfates in sufficient water to provide 10-50% solids, typically for a mixing time of at least 10 minutes at 22°C (for a C16 secondary (2,3) alkyl sulfate), followed by pressure filtration. In a preferred mode, the slurry secondary (2,3) alkyl sulfates will comprise somewhat less than 35% solids, inasmuch as such slurries are free-flowing and amenable to agitation during the washing process.

As an additional benefit, the washing process also reduces the levels of organic contaminants which comprise the random secondary alkyl sulfates noted above.

The present invention encompasses a process for manufacturing a particulate bleach activator material according to the present invention, said process includes the steps of:

- co-agglomerating a bleach activator with a secondary (2,3) alkyl sulfate surfactant as the agglomerating agent;
- drying said co-agglomerate.

Any agglomerating technique known to the man skilled in the art is suitable for use herein. For example, particulate materials can be formed by agglomeration, wherein solids (including the secondary (2,3) alkyl sulfates) are forced/hurled together by physical mixing and held together by a binder. Suitable apparatus for agglomeration includes dry powder mixers, fluid beds and turbilizers, available from manufacturers such as Lodge, Eric, Bepex and Aeromatic.

In another mode, particulate materials can be formed by extrusion. In this method, solids (including the secondary (2,3) alkyl sulfates) are forced together by pumping a damp powder at relatively high pressures and high energy inputs through small holes in a die plate. This process results in rod like particles which can be divided into any desired particle size. Apparatus includes axial or radial extruders such as those available from Fuji, Bepex and Teledyne/Readco.

In yet another mode, particulate materials can be formed by prilling. In this method, a liquid mixture containing the desired ingredients (i.e., one of them being secondary (2,3) alkyl sulfates) is pumped under high pressure and sprayed into cool air. As the liquid droplets cool they become more solid and thus the particulate materials are formed. The solidification can occur due to the phase change of a molten binder to a solid or through hydration of free moisture into crystalline bound moisture by some hydratable material in the original liquid mixture.

In still another mode, particulate materials can be formed by compaction. This method is similar to tablet formation processes, wherein solids (including secondary (2,3) alkyl sulfates) are forced together by compressing the powder feed into a die/mold on rollers or flat sheets.

In another mode, particulate materials can be formed by melt/solidification. In this method, particulate materials are formed by melting the secondary (2,3) alkyl sulfates with any desired additional ingredient such as TAED and allowing the melt to cool, e.g., in a mold or as droplets.

Binders can optionally be used in the foregoing methods to enhance particle integrity and strength. Such binders include, for example, starches, polyacrylates, carboxymethylcellulose and the like. Binders are well-known in the particle making literature. If used, binders are typically employed at levels of 0.1%-5% by weight of the finished particulate materials.

Fillers such as hydratable and nonhydratable salts, crystalline and glassy solids, various detergent ingredients such as zeolites and the like, can be incorporated in the particulate materials. If used, such fillers typically comprise up to 20% by weight of the particulate materials.

Chelants can be incorporated in the particle during the agglomeration process. Such chelants include, for example, diethylene triamine penta methyl phosphonates or hydroxy ethyl diphosphonic acid, or ethylene diamino disuccinic acid and the like. If used, chelants are typically employed at levels of from 0.1% to 9% by weight of the finished particulate materials, preferably of from 0.1% to 5% and more preferably from 0.5% to 2%.

Particulate materials prepared in the foregoing manner can be subsequently dried or cooled to adjust their strength, physical properties and final moisture content, according to the desires of the formulator.

One mode for preparing particulate materials comprising either solely secondary (2,3) alkyl sulfates or mixtures

thereof together with the co-surfactants comprises mixing molten secondary (2,3) alkyl sulfates with one or more molten co-surfactants and forming the resulting solidified melt into particles, prills or agglomerates of any desired size. The desired particle size can be achieved, for example, in blenders, such as that marketed under the trademark OSTER or in large-scale mills, such as that available under the trademark WILEY mill.

In an alternate mode, the melt comprising the mixed surfactant can be sprayed through a nozzle to form droplets which, when cooled, provide particles of the desired size.

In another mode, a rotating disc can be used to form droplets of a melt comprising the secondary (2,3) alkyl sulfate and any desired co-surfactants. The droplets are then solidified by cooling and may be passed through appropriate sieves to secure particulate materials of any desired size. In yet another mode, tower prilling can be used to provide particulate materials having a distribution of sizes around a given mean size range.

In yet another mode, a homogeneous melt of the secondary (2,3) alkyl sulfates plus co-surfactants is solidified and comminuted to provide particulate materials. High energy comminution processes such as hammer, rod and ball mills can be used. In a different mode, low energy comminution processes such as grating through sieves of any desired pore size can be employed.

The present invention also encompasses a process for manufacturing a particulate bleach activator material according to the present invention, said process including the steps of:

- co-agglomerating a bleach activator with a secondary (2,3) alkyl sulfate surfactant as the agglomerating agent;
- optionally drying said co-agglomerate;
- coating said dried co-agglomerate with a coating material as hereinbefore defined;
- drying said coated co-agglomerate.

According to the present invention the co-agglomerated bleach activator as hereinbefore described can be coated with either a secondary (2,3) alkyl sulfate surfactant coating agent as hereinbefore defined or with any others coating agents well known in the art. Such coating agents include for instance soluble polymers (i.e. polyacrylates or copolymers of acrylic/maleic units) or low molecular weight polycarboxylic acids (citric acid) or glycolic acid.

The coating of the co-agglomerated material with the coating agent can be carried out in several ways. The coating agent may be sprayed on as a molten material or as a solution or dispersion in a solvent/carrier liquid which is subsequently removed by evaporation. The coating agent can also be applied as a powder coating e.g. by electrostatic techniques although this is less preferred as the adherence of powdered coating agent is more difficult to achieve and can be more expensive.

When used as the bulk surfactant ingredient in the detergent compositions herein, the particles ("base granules") will typically range in size from 50 to 2000 micrometers, preferably from 150 to 2000 micrometers. When used to coat larger particles comprising surfactant, the secondary alkyl sulfate coating particles will typically be in a substantially finer size range, typically from 0.01 to 5 micrometers. In any event, size ranges herein can be established using standard sieves. A sieve size in the range of 425 to 2000 micrometers is typical for base granules. A sieve size in the range of 0.05 to 1 micrometer is typical for coating particles.

The solid bleach activator compositions according to the present invention comprise at least 30 % by weight of the total composition of said bleach activator, preferably at least 50% and most preferably at least 70 %, and from 2 % to 60 % by weight of the total composition of said secondary (2,3) alkyl sulfate, preferably from 4 % to 40 % and most preferably from 4 % to 20 %.

Solid bleach activator compositions in accordance with the invention can be used in a variety of applications. Thus said solid bleach activator compositions according to the present invention may themselves be incorporated into other solid compositions such as tablets, extrudates and agglomerates. The compositions can also be suspended in non aqueous liquid compositions in which the organic acid surface treating material is insoluble and inert. However, the preferred application for the solid bleach activator compositions of the invention is as particulate components of granular detergent compositions, particularly the so-called concentrated detergent compositions that are added to a washing machine by means of a dosing device placed in the machine drum with the soiled fabric load. Concentrated granular detergent compositions dispensed into the wash liquor via a dosing device are more subject to dissolution problems than compositions added via the dispensing compartment of a washing machine because, in the initial stages of a wash cycle, the agitation in the immediate environment of the product is inhibited by the presence of the fabric load. Whilst this can constitute a benefit in permitting the development of high transient concentrations of builder and surfactant, the development of high transient peroxyacid concentrations can, as noted previously, lead to fabric and colour damage. The compositions of the present invention, when incorporated into concentrated detergent products delivered to the wash liquor via a dispensing device, mitigate if not eliminate this problem.

Detergent compositions according to the present invention will normally contain from 0.5% to 20% by weight of the total detergent composition of a solid bleach activator composition, preferably from 1.0% to 15% and more preferably from 1.0% to 10%.

Such detergent compositions will, of course, contain any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents, or mixtures thereof.

Indeed, perborate beaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) as well as percarboxylic acid bleaching agents and salts thereof can be used herein. Suitable examples of percarboxylic acid bleaching agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed for instance in the US patent, US-4 483 781 or in the European patent EP-0 133 354 and in US patent, US-4 412 934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyheptanoic acid as described in US-4 634 551.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxy hydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Mixtures of bleaching agents can also be used.

Bleaching agents other than oxygen bleaching agents include for examples photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al.

The detergent compositions herein comprise typically from 0.5% to 65% by weight of the total composition of a bleaching agent, preferably from 1.0% to 50%.

The detergent compositions herein may typically comprise other optional ingredients such as various deterative and aesthetic adjunct ingredients. Nonlimiting examples of such ingredients are as follows.

Enzymes - can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, for the prevention of refugee dye transfer, and fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1%, by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B.subtilis* and *B.licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification GB-1 243 784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application EP-130 756) and Protease B (see European Patent Application Serial No. 87303761.8, and European Patent Application EP-130 756).

Amylases include, for example, α -amylases described in British Patent Specification GB-1 296 839 (Novo), RAP-IDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent US-4 435 307 which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2 075 028; GB-A-2 095 275 and DE-OS-2 247 832.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent GB-1 372 034. See also lipases in Japanese Patent Application 53-20487, laid open to public inspection in February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341 947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art,

and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT international Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent US-3 553 139. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 4,261,868, issued April 14, 1981 to Horn, et al, U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319, and 3,519,570.

Enzyme Stabilizers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium ions in the finished compositions which provide calcium ions to the enzymes. Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706, cited above. Typical detergents will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium ions. The level of calcium ion should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium salt can be used as the source of calcium ion, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium hydroxide, calcium formate, and calcium acetate. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. Solid detergent compositions according to the present invention may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium ions are sufficient to provide enzyme stability. More calcium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, the compositions herein may comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium ions. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

In addition to enzymes, the compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. Moreover, the secondary (2,3) alkyl sulfate plus enzyme components perform best in the presence of weak, nonphosphate builders which allow free calcium ions to be present.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain alu-

minum. NaSKS-6 has the delta-Na₂SiO₅ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi_xO_{2x+1}·yH₂O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na₂SiO₅ (NaSKS-6 form) is most preferred for use herein.

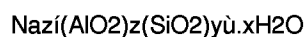
Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are also useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions. Aluminosilicate builders include those having the empirical formula:

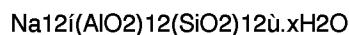


wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO₃ hardness per gram of anhydrous aluminosilicate. Preferred aluminosilicates are zeolite builders which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates 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 disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), 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. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates.

Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxy polycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic

acid builders include the C5-C20 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C12-C18 monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C4-C6 alkylene or oxy C4-C6 alkylene segments, or mixtures therein, (iii) poly(vinyl ester) segments, preferably poly(vinyl acetate), having a degree of polymerization of at least 2, or (iv) C1-C4 alkyl ether or C4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C1-C4 alkyl ether or C4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C1-C4 alkyl ether and/or C4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from 2 to about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C4-C6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $\text{MO}_3\text{S}(\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{O}-$, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C1-C4 alkyl and C4 hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C1-C6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from

about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units containing 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J. J. Scheibel and E. P. Gosselink.

Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfo aryl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethyl-ethylenediaminetetraacetates, nitrilotriacetates, ethylenediaminetetrapropionates, triethylenetetraaminehexaacetates, diethylenetriamine pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylated amines.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal/antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred anti-redeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric

dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal/antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Arctic White CC and Arctic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol(1,2-d)triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the y-aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis-(benzimidazol-2-yl)ethylene; 1,3-diphenylphrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styrylnaphth-(1,2-d)oxazole; and 2-(stilbene-4-yl)-2H-naphtho-(1,2-d)triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance under conditions such as those found in European-style front loading laundry washing machines, or in the concentrated detergency process of U.S. Patents 4,489,455 and 4,489,574, or when the detergent compositions herein optionally include a relatively high sudsing adjunct surfactant.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acids and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters

of monovalent alcohols, aliphatic C18-C40 ketones (e.g. stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g. K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions.

Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S. Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel;

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), and not polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and not linear.

To illustrate this point further, typical laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/poly propylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C6-C16 alkyl alcohols having a C1-C16 chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under

the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount." By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

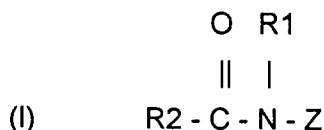
The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners, as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Adjunct Surfactants - The compositions herein can optionally contain various anionic, nonionic, zwitterionic, etc. surfactants. If used, such adjunct surfactants are typically present at levels of from about 5% to about 35% of the compositions. However, it is to be understood that the incorporation of adjunct anionic surfactants is entirely optional herein, inasmuch as the cleaning performance of the secondary (2,3) alkyl sulfates is excellent and these materials can be used to entirely replace such surfactants as the alkyl benzene sulfonates in fully-formulated detergent compositions.

Nonlimiting examples of optional surfactants useful herein include the conventional C11-C18 alkyl benzene sulfonates and primary and random alkyl sulfates (having due regard for the enzyme stability issues noted above), the C10-C18 alkyl alkoxy sulfates (especially EO 1-5 ethoxy sulfates), the C10-C18 alkyl alkoxy carboxylates (especially the EO 1-5 ethoxy carboxylates), the C10-C18 alkyl polyglycosides and their corresponding sulfated polyglycosides, C12-C18 alpha-sulfonated fatty acid esters, C12-C18 alkyl and alkyl phenol alkoxyates (especially ethoxyates and mixed ethoxy/propoxy), C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

One particular class of adjunct nonionic surfactants especially useful herein comprises the polyhydroxy fatty acid amides of the formula:



wherein: R1 is H, C1-C8 hydrocarbyl, 2-hydroxyethyl, 2-hydroxy propyl, or a mixture thereof, preferably C1-C4 alkyl, more preferably C1 or C2 alkyl, most preferably C1 alkyl (i.e., methyl); and R2 is a C5-C32 hydrocarbyl moiety, preferably straight chain C7-C19 alkyl or alkenyl, more preferably straight chain C9-C17 alkyl or alkenyl, most preferably straight chain C11-C19 alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glyceryl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from

the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly-saccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

In Formula (I), R_1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R_1 is preferably methyl or hydroxyalkyl. If low sudsing is desired, R_1 is preferably C2-C8 alkyl, especially n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

$R_2\text{-CO-N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmi-
tamide, tallowamide, etc.

While polyhydroxy fatty acid amides can be made by the process of Schwartz, U.S. 2,703,798, contamination with cyclized by-products and other colored materials can be problematic. As an overall proposition, the preparative methods described in WO-9,206,154 and WO-9,206,984 will afford high quality polyhydroxy fatty acid amides. The methods comprise reacting N-alkylamino polyols with, preferably, fatty acid methyl esters in a solvent using an alkoxide catalyst at temperatures of about 85°C to provide high yields (90-98%) of polyhydroxy fatty acid amides having desirable low levels (typically, less than about 1.0%) of sub-optimally degradable cyclized by-products and also with improved color and improved color stability, e.g., Gardner Colors below about 4, preferably between 0 and 2. (With compounds such as butyl, iso-butyl and n-hexyl, the methanol introduced via the catalyst or generated during the reaction provides sufficient fluidization that the use of additional reaction solvent may be optional.) If desired, any unreacted N-alkylamino polyol remaining in the product can be acylated with an acid anhydride, e.g., acetic anhydride, maleic anhydride, or the like, to minimize the overall level of such residual amines in the product. Residual sources of classical fatty acids, which can suppress suds, can be depleted by reaction with, for example, triethanolamine.

By "cyclized by-products" herein is meant the undesirable reaction by-products of the primary reaction wherein it appears that the multiple hydroxyl groups in the polyhydroxy fatty acid amides can form ring structures which are, in the main, not readily biodegradable. It will be appreciated by those skilled in the chemical arts that the preparation of the polyhydroxy fatty acid amides herein using the di- and higher saccharides such as maltose will result in the formation of polyhydroxy fatty acid amides wherein linear substituent Z (which contains multiple hydroxy substituents) is naturally "capped" by a polyhydroxy ring structure. Such materials are not cyclized by-products, as defined herein.

The foregoing polyhydroxy fatty acid amides can also be sulfated, e.g., by reaction with $\text{SO}_3/\text{pyridine}$, and the resulting sulfated material used as an adjunct anionic surfactant herein.

Such adjunct surfactants can be added separately to the compositions herein or, as noted above, can be combined with the secondary (2,3) alkyl sulfates to provide dense, high-active, mixed detergent particles.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments. If high sudsing is desired, suds boosters such as the C10-C16 alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C10-C14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl_2 , MgSO_4 , and the like, can be added at levels of, typically, 0.1%-2%, to provide additional sudsing.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C13-15 ethoxylated alcohol EO(7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and about 10.5. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Experimental data

The following are typical, nonlimiting examples which illustrate the detergent compositions and uses of the secondary (2,3) alkyl sulfates (SAS) according to this invention.

Tetra Acetyl Ethylene Diamine (TAED) in fine powder form (purity ca 99.0%, particle size 90% by weight less than 150 micrometers) was agglomerated with a secondary (2,3) alkyl sulfate (C16; 2,3 isomer, 91.8% active). The agglomeration was carried out in a small mixer and the resultant, wet, agglomerate was then dried by placing overnight in a vacuum oven at 40°C. Said resultant agglomerate was then sieved using a screen mesh size 1180 um through 425 um.

The TAED/SAS agglomerate obtained contained 85 % of TAED and 15% of SAS.

A reference TAED agglomerate was prepared by agglomerating the same TAED powder with molten TAE25 as an agglomerating agent in the same mixing device as above. However, so drying of said agglomerate is not needed as TAE25 simply solidifies. Said agglomerate was made using a TAED: TAE25 ratio of 85 %: 15 %. Particles were then cooled and sized to the same standards as above.

The rate of perhydrolysis of both these agglomerates were measured.

Beaker perhydrolysis was measured in pots containing 1 liter of distilled water. A percarbonate (PC)/carbonate(C) system was used. In each pot we put 1.75 g percarbonate, 0.89 g of carbonate and 0.6 g of either TAED/SAS agglomerate or TAED/TAE25 agglomerate, 10 ml aliquots were taken after 3 minutes and 5 minutes. Said aliquots were added to 20 ml glacial acetic acid and 5 ml potassium iodide (1%) indicator solution and this was then titrated against 0.01M thiosulphate.

Results

Rate of perhydrolysis in %	TAED/SAS agglomerate	TAED/TAE25 agglomerate
After 3 mins	75	60
After 5 mins	85	70

According to the present invention, the results show that when the bleach activator, i.e. TAED is agglomerated with a secondary (2,3) alkyl sulfate the rate of perhydrolysis is significantly increased compared to particulate wherein the TAED is agglomerated with TAE25. Additionally a satisfactorily perhydrolysis rate is obtained without requiring a decrease in the particle size.

Furthermore, the SAS has been found to be stable during the agglomeration process and during the storage of the resulting agglomerate.

The particulate bleach activator material as for example the TAED/SAS agglomerate can be incorporated in different detergent compositions such as the following detergent matrix (composition in parts by weight):

C12 Linear Alkyl Benzene Sulfonate	9.0
Tallow Alkyl Sulphate	2.8
Dobanol 45E7	3.8
Zeolite A	20
Citrate	6.5
Carbonate	15.0
Silicate (SiO ₂ :Na ₂ O=2:1)	3.5
Perborate monohydrate	16.0
Sokalan ^(R) CP45	4.0
Miscellaneous	up to 100

The amount of agglomerate in the composition was such as to provide an active level of 5% by weight of TAED versus the total composition.

Claims

- 5 1. A solid bleach activator composition comprising a particulate bleach activator material wherein said activator is co-agglomerated with an agglomerating agent, characterized in that said agglomerating agent is selected from the group of secondary (2,3) alkyl sulfate surfactants.
2. A solid bleach activator composition according to claim 1 wherein said particulate bleach activator material is further coated with a coating agent.
- 10 3. A solid bleach activator composition according to claim 2 wherein said coating agent is a secondary (2,3) alkyl sulfate surfactants.
- 15 4. A solid bleach activator composition according to any of the preceding claims which comprises at least 30 % by weight of the total composition of said bleach activator, preferably at least 50 % and most preferably at least 70 % and from 2 % to 60 % by weight of the total composition of said secondary (2,3) alkyl sulfate surfactants, preferably from 4 % to 40 % and most preferably from 4 % to 20 %.
- 20 5. A solid bleach activator composition according to any of the preceding claims wherein said bleach activator is tetraacetyl ethylenediamine.
6. A detergent composition comprising from 0.5 % to 20 % by weight of the total composition of a solid bleach activator composition according to any of the preceding claims and from 0.5 % to 65 % by weight of the total composition of a bleaching agent.
- 25 7. A composition according to claim 6 wherein said bleaching agent is an oxygen bleach, preferably sodium perborate or a peroxygen bleach preferably percarbonate or mixtures thereof.
8. A composition according to claims 6 and 7 which further comprises surfactants and builders.
- 30 9. A process for manufacturing a particulate bleach activator material according to claims 1 and 4 to 8 which comprises the steps of:
 - co-agglomerating said bleach activator with said agglomerating agent;
 - drying said co-agglomerate.
- 35 10. A process according to claim 9 for manufacturing a particulate bleach activator material according to claims 2 and 3 which comprises the additional steps of:
 - coating said dried co-agglomerate with said coating agent;
 - 40 - drying said coated co-agglomerate.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5300

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)
A	US-A-4 087 369 (J,WEVERS) * the whole document * ---	1-9	C11D3/39 C11D17/00
A	SOVIET PATENTS ABSTRACTS Week 9043, Derwent Publications Ltd., London, GB; AN 90-326473 & SU-A-1 532 051 (DONSKOL AGRIC INST) 30 December 1989 * abstract * ---	1	
A	SOVIET PATENTS ABSTRACTS Week 8313, Derwent Publications Ltd., London, GB; AN 83-31717 & SU-A-929 701 (CHEM IND RES DES) 23 May 1982 * abstract * ---	1	
A	EP-A-0 374 867 (HOECHST AKTIENGESELLSCHAFT) * the whole document * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP-A-0 051 987 (PROCTER & GAMBLE CO.) * abstract; claims * ---	1-3,8	C11D
A	EP-A-0 156 977 (MIRA LANZA S.P.A.) * claims * -----	1,9	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 8 December 1994	Examiner PELLI WABLAT, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		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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