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(54) FOAMING SYSTEM AND DETERGENT COMPOSITIONS CONTAINING THE SAME

SCHAUMSYSTEM SOWIE DIESE ENTHALTENDE WASCHMITTEL

SYSTEME MOUSSANT ET COMPOSITIONS DETERGENTES LE CONTENANT

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Description

FIELD

[0001] This invention relates to a novel foaming system useful in a detergent composition. More particularly, the present invention relates to granular detergent compositions intended for cleaning fabrics containing novel foaming components.

BACKGROUND

[0002] Foam or suds formation is desired in various applications, such as during the wash process. In detergent compositions, specific surfactants are known to provide sudsing in the wash water. Not only is the formation of foaming or sudsing desirable, but there is also a desire to readily create foam as well as maintaining the foam for a desired duration. For example, it may be desired that the foam occurs immediately upon contact of a detergent composition with water. Although there are various reasons as to why foam formation is desired, one known reason is that consumers who use detergent compositions directly associate the formation of foam with the cleaning ability of the detergent composition.

[0003] Although the formation of foam is desired, foam may also pose problems during the washing process. For example, drainage of the suds or foam during the washing process may be difficult. Particularly for a machine wash process, the suds or foam may hamper the drainage of the wash solution from the machine before the rinse stage. Therefore, it is desired to gradually suppress the formation of foam over time.

[0004] Accordingly, there is a need to produce foaming or sudsing early in the wash process, such as when the detergent composition first comes into contact with water, as well as a foam suppressing component to control the foam after formation.

[0005] WO 93/01269 describes antifoam particles comprising a porous particulate organic carrier material , a specific silicone antifoam and a coating layer.

[0006] None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

[0007] This need is met by the present invention which is directed to a controlled foaming system especially adapted for use in detergent compositions containing a foaming component capable of providing foaming or sudsing without agitation, and a delayed-release foam suppressing component according to claim 1. The present invention also relates to detergent compositions containing the controlled foaming system.

[0008] These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure and the appended claims.

DETAILED DESCRIPTION

[0009] While this specification concludes with claims distinctly pointing out and particularly claiming that which is regarded as the invention, it is believed that the invention can be better understood through a careful reading of the following detailed description of the invention. In this specification, all percentages, ratios, and proportions are by weight, all temperatures are expressed in degrees Celsius, molecular weights are in weight average, and the decimal is represented by the point (.), unless otherwise indicated. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

[0010] As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of and "consisting essentially of".

[0011] As used herein, the term "alkyl" means a hydrocarbyl moiety which is straight or branched, saturated or unsaturated. Unless otherwise specified, alkyl moieties are preferably saturated or unsaturated with double bonds, preferably with one or two double bonds. Included in the term "alkyl" is the alkyl portion of acyl groups.

[0012] The present invention is directed to a controlled foaming system especially adapted for use in detergent compositions containing a foaming component capable of providing foaming or sudsing without agitation, and a delayed-release foam suppressing component. The delayed-release foam suppressing component is a silicone foam suppressing agent which is releasably incorporated in a carrier, thereby delaying the release of the silicone foam suppressing agent.

[0013] When the controlled foaming system first comes into contact with water, the foaming component generates rapid and stable foaming without agitation. When used herein, the term "foaming" means any form of formation of gas bubbles, including sudsing and effervescing. Agitation is not necessary, but may enhance the generation of foam, and

thus, may be preferred. Preferably, the foaming component produces upon contact with water, gas bubbles having an average bubble particle size of 400 microns or less, preferably 200 microns or less, and more preferably 100 microns or less.

[0014] After the formation of foam, the delayed-release foam suppressing component is released over time and the foaming is suppressed or otherwise controlled by decreasing the amount of foam. Depending on when the foam should be suppressed, the time delay may be adjusted by choosing the appropriate type of foam suppressing component. For example, for some machine wash conditions, the foam suppressing component reduces the water gas bubbles as early as upon agitation, so that preferably after 120 seconds, the bubbles have been reduced at least 30%. Also for example in some other machine wash conditions, after from 360 seconds to 600 seconds, the bubbles have been reduced to from 40 to 70% percentage, or otherwise become substantially suppressed before the rinse stage.

[0015] Preferably for hand wash conditions, the foam suppressing component may not reduce the water gas bubbles at the initial stages in the wash, since it may be preferable to maintain the amount of foam for a longer period of time.

[0016] In one preferred embodiment, the foaming component and the delayed-release foam suppressing component are independent dry particles. The term "dry" is to be understood that the particles of the raw materials are substantially free of water, i.e., that no water has been added other than the moisture of the raw materials themselves. Typically, the level of water is below 5% by weight of the total particle, preferably below 3% and more preferably below 1.5%.

[0017] For example in a detergent composition, such as a granular detergent composition, the final composition contains a mixture of the two types of particles in addition to other conventional detersive components. In another preferred embodiment one of the particles is present as a part of an other conventional detersive component. Having separate particles is particularly useful because one can control the different levels and thus provide controlled delivery of the foaming component and the suppressing component to the washing process, e.g., both a more efficient and a time delivery can be achieved, to provide optimum performance.

[0018] Although not wanting to be limited by theory, it is believed that a detergent composition having a controlled foaming system, especially in the early phases of the wash cycle, has cleaning benefits. For example, it is believed that the foam helps transfer the surfactant in the detergent composition onto the soil to be removed and/or on to the fabric. In addition, it is believed that the foam helps further wetting and dissolution of the detergent composition. Furthermore, the foam is believed to provide an early reservoir of unprecipitated surfactant to wet fabrics and helps suspend the soil in the wash solution.

[0019] The controlled foaming system also is storage stable. For example, the components do not degrade during storage while being exposed to moisture from the air. In addition, because the foaming component contains an effervescent granule, the incorporation of the controlled foaming system in a detergent composition improves the dissolution characteristics of the active ingredients present in the detergent composition.

[0020] Another advantage of the present invention is the improved dispensing characteristics associated to the detergent compositions of the present invention, e.g., the detergent compositions intended for use in a drum-type fabric washing machine. Indeed, a difficulty with conventional high density granular detergent compositions is that they are not easily flushed from the dispenser drawer of a washing machine: i.e. when the granular composition is wetted by the water flowing through the dispenser, the detergent ingredients may become stuck together resulting in considerable residues of wetted and adhering powder left behind the drawer. Similar problems are encountered when using such granular detergent compositions in a dosing device in the washing drum. The presence of the effervescent granule in the granular detergent compositions provides improved dispensing typically when used in a washing machine and good storage stability in respect of the dispensing potential.

[0021] The detergent compositions containing the controlled foaming system are preferably solid laundry or dish washing compositions, preferably in the form of granules, extrudates, or tablets. Preferably, granular detergent compositions have a density of at least 500 g/l, more preferably at least 700 g/l. The detergent compositions as well as the foaming component and the delayed-release foam suppressing component may also comprise additional ingredients, as described herein. The precise nature of these additional ingredients, and levels of incorporation thereof will depend on the application of the component or composition and the physical form of the component and composition.

A. Foaming Component

[0022] The foaming component preferably contains an effervescent granule. Any effervescent granule capable of forming gas upon contact with water, known in the art, can be used. A preferred effervescent granule comprises an acid source, capable of reacting with an alkali source in the presence of water to produce a gas.

[0023] The acid source may be any organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. Preferably the acid source comprises an organic acid. The acid source is preferably substantially anhydrous or non-hydroscopic and the acid is preferably water-soluble. It may be preferred that the acid source is overdried. Suitable acids source components include an acid or salt form of a mono or polycarboxylic acid. Such preferred acids include those selected from the group consisting of citric, malic, maleic, fumaric, aspartic, glutaric, tartaric, malonic, succinic

or adipic acid, monosodium phosphate, boric acid, 3 ketoglutaric acid acid, citramalic acid, and mixtures thereof. Citric acid, maleic or malic acid are especially preferred.

[0024] Also preferably, the acid source provides acidic compounds which have an average particle size in the range of from 75 microns to 1180 microns, more preferably from 150 microns to 710 microns, calculated by sieving a sample of the source of acidity on a series of Tyler sieves.

[0025] The effervescent granule preferably comprises an alkali source. Any alkali source which has the capacity to react with the acid source to produce a gas may be present in the particle, including sources capable of producing nitrogen, oxygen or carbon dioxide gas. Preferred can be perhydrate bleaches and silicate material The alkali source is preferably substantial anhydrous or non-hydroscopic. It may be preferred that the alkali source is overdried.

[0026] Preferably the produced gas is carbon dioxide, and therefore the alkali source is preferably a source of carbonate; and in particular, a carbonate salt. Examples of preferred carbonates are the alkaline earth and alkali metal carbonates, including sodium or potassium carbonate, bicarbonate and sesquicarbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Alkali metal percarbonate salts are also suitable sources of carbonate species, which may be present combined with one or more other carbonate sources.

[0027] The carbonate and bicarbonate preferably have an amorphous structure. The carbonate and/ or bicarbonates may be coated with coating materials. The particles of carbonate and bicarbonate can have a mean particle size of 75 microns or greater, preferably 150μm or greater, more preferably of 250μm or greater, preferably 500μm or greater. It may be preferred that the carbonate salt is such that fewer than 20% (by weight) of the particles have a particle size below 500μm, calculated by sieving a sample of the carbonate or bicarbonate on a series of Tyler sieves. Alternatively or in addition to the previous carbonate salt, it may be preferred that fewer than 60% or even 25% of the particles have a particle size below 150μm, whilst fewer than 5% has a particle size of more than 1.18 mm, more preferably fewer than 20% have a particle size of more than 212 μm, calculated by sieving a sample of the carbonate or bicarbonate on a series of Tyler sieves.

[0028] The molecular ratio of the acid source to the alkali source present in the particle core is preferably from 60;1 to 1:60, more preferably from 20:1 to 1:20, more preferably from 10:1 to 1:10, more preferably from 5:1 to 1:3, more preferably from 3:1 to 1:2, more preferably from 2:1 to 1:2.

[0029] In a preferred embodiment, the effervescent granule optionally contains a binder which binds the acid source with the alkali source. Preferably, the effervescent granule comprises up to 50 % by weight of the total granule of a binder or a mixture thereof, preferably up to 35% and more preferably up to 20%. Suitable binders to use herein are those known to those skilled in the art and include anionic surfactants like C6-C20 alkyl or alkylaryl sulphonates or sulphates, preferably C8-C20 alkylbenzene sulphonates, cellulose derivatives such as carboxymethylcellulose and homo- or co- polymeric polycarboxylic acid or their salts, nonionic surfactants, preferably C10-C20 alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C15-C20 primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Of these tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol (TAE25) or 50 moles of ethylene oxide per mole of alcohol (TAE50) are preferred. Other preferred binders include the polymeric materials like polyvinylpyrrolidones with an average molecular weight of from 12 000 to 700 000 and polyethylene glycols with an average weight of from 600 to 10 000. Copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid are other examples of polymeric binders. Others binders further include C10-C20 mono and diglycerol ethers as well as C10-C20 fatty acids. In the embodiment of the present invention where a binder is desired C8-C20 alkylbenzene sulphonates are particularly preferred.

[0030] In another preferred embodiment, the foaming component may-also contain a surface active component which reduces the water-air surface tension. The preferred surface active component has a melting point above 45°C, and is preferably selected from the group consisting of nonionic alkoxylated amides, alkyl esters of fatty acids, or alkoxylated alcohols. Especially preferred surface active components are selected from the group consisting of polyhydroxy fatty acid amides and condensation products of aliphatic alcohols with from 1 to 15 moles of alkylene oxide. If a surface active component is used, the weight ratio of the surface active component to the effervescent granule is preferably from 20:1 to 1:10.

[0031] In still another preferred embodiment, the foaming component may further include the addition of suds boosters. The suds boosters may enhance the formation of suds in conjunction with the effervescent granule. The suds booster may be part of the same particle or component as the foaming component, or the suds booster may be a separate independent particle or component.

[0032] Preferred suds boosters include amine oxide, polyethylene glycol, monoethanol amine, diethanol amine, fatty alcohol, sugar, protein, betaine, and mixtures thereof.

[0033] Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x

is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

[0034] Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

[0035] The foaming component may be made my conventional methods, including as part of a tabletting process, extrusion process, and/or an agglomeration process. The foaming component, whether in the form of a particle or comprised in a particle, is preferably such that 80% by weight of the particles have a particle size of more than 75 microns (more than 80% by weight of the particles on Tyler sieve mesh 200) and less than 10% by weight of the particles have a particle size of more than 2 cm; preferably 80% by weight of the particles have a particle size of more than 150 microns (80% by weight on Tyler sieve mesh 100) and Less than 10% by weight of the particles have a particle size of more than 1 cm; or more preferably 80% by weight of the particles have a particle size of more than 300 microns (80% by weight on Tyler sieve mesh 48) and less than 10% by weight of the particles have a particle size of more than 0.5 cm; or even more preferably the particles have an average particle size of from 500 microns (on Tyler sieve mesh 32) to 3000 microns, more preferably from 710 microns (on Tyler mesh sieve 24) to 1180 microns (through Tyler mesh sieve 14).

[0036] In a preferred embodiment of the present invention, the foaming component and the delayed-release foam suppressing component are independent dry particles, wherein the foaming component has an average particle size of from 75 microns to 2 cm.

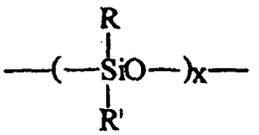
B. Delayed-release Foam Suppressing Component

[0037] A suds suppressing amount of the delayed-release foam suppressing component is used in the present invention. The term "delayed-release foam suppressing component" means that the foam suppressing component begins to suppress foam over time. Depending on when the foam should be suppressed, the time delay may be adjusted by choosing the appropriate type of foam suppressing component. The term "suds suppressing amount" is meant that the formulator of the detergent composition selected an amount of this component which will control the suds to the extent desired. The amount of suppressing component will vary with the detergent component selected.

[0038] The delayed-release foam suppressing component is a silicone foam suppressing component. Said silicone foam suppressing component contains a silicone suds controlling agent having an average droplet diameter of from 1 to 50 microns, releasably incorporated in a water-soluble or water dispersible, substantially non-surface active, detergent-impermeable, and non-hydroscopic carrier, the silicone foam suppressing component being substantially free of water-soluble relatively hydroscopic inorganic salts and in the form of an irregularly shaped particle having a minimum dimension of not less than 0.05 cm and the maximum dimension being at least 20% greater than the minimum dimension.

[0039] The preferred suppressing component contains a silicone suds controlling agent which is substantially isolated from the other detersive components of the detergent composition. This "isolation" is achieved by incorporating the controlling agent in a water-soluble or water-dispersible organic carrier matrix. The matrix is a substantially non-surface active, non-hydroscopic material which does not interact with the controlling agent. Moreover, the carrier must be substantially impenetrable by the detersive components to prevent undesirable silicone/detergent and/or silicone/alkalinity interactions. Moreover the carrier matrix herein preferably does not contain added surface active agents, other than the silicone. The carrier is selected such that, upon admixture with water, the carrier matrix dissolves or disperses to release the silicone suds controlling agent to perform its suds or foam controlling function.

[0040] The silicone materials employed as the preferred silicone suds controlling agents herein can be alkylated polysiloxane materials of several types, either singly or in combination with various solid materials such as silica aerogels and xerogels and hydrophobic silicas of various types. in industrial practice, the term "silicone" has become a generic term which encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl groups of various types. In general terms, the silicone suds controllers can be described as siloxanes having the general structure backbone.



wherein x is from 20 to 2,000 and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl or phenyl. The polydimethylsiloxanes (R and R' are methyl) having a molecular weight within the range of from 200 to 200,000, and higher, are all useful as suds controlling agents. Silicone materials are commercially available from the Dow Coming Corporation under the trade name Silicone 200 Fluids®. Suitable polydimethylsiloxanes have a viscosity of from 2×10^{-5} to 1.5×10^{-3} m^2s^{-1}(20-1500cs), at 25°C when used with silica and/or siloxane resin.

[0041] Additionally, other silicone materials wherein the side chain groups R and R' are alkyl, aryl, or mixed alkyl and aryl hydrocarbyl groups exhibit useful suds controlling properties. These materials are readily prepared by the hydrolysis of the appropriate alkyl, aryl or mixed alkylaryl or aralkyl silicone dichlorides with water in the manner well known in the art. As specific examples of such silicone suds controlling agents useful herein there can be mentioned, for example, diethyl polysiloxanes; dipropyl polysiloxanes; dibutyl polysiloxanes; methylethyl polysiloxanes; phenylmethyl polysiloxanes. The dimethyl polysiloxanes are particularly useful herein due to their low cost and ready availability.

[0042] The silicone "droplets" in the carrier matrix preferably have an average diameter of 1 to 50 μm, preferably from 5 to 40 μm, more preferably from 5 to 30 μm for maximum effectiveness. Droplets below 5 μm in diameter are not very effective and above 30 μm in diameter are increasingly less effective. Similar sizes are required for the other silicone suds controlling agents disclosed hereinafter.

[0043] A second highly preferred type of silicone suds controlling agent useful herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica. Such mixtures of silicone and silica can be prepared by affixing the silicone to the surface of silica (SiO_2), for example by means of the catalytic reaction disclosed in U.S. Pat. No. 3,235,509. Suds controlling agents comprising mixtures of silicone and silica prepared in this manner preferably comprise silicone and silica in a silicone:silica ratio of from 19:1 to 1:2, preferably from 10:1 to 1:1. The silica can be chemically and/or physically bound to the silicone in an amount which is preferably 5% to 20%, preferably from 10 to 15%, by weight, based on the silicone. The particle size of the silica employed in such silica/silicone suds controlling agents should preferably be not more than about 1000, preferably not more than 100 nm, preferably from 5 nm to 50 nm, more preferably from 10 to 20 nm, and the specific surface area of the silica should exceed 5 m^2/g, preferably more than 50 m^2/g.

[0044] Alternatively, suds controlling agents containing silicone and silica can be prepared by admixing a silicone fluid of the type hereinabove disclosed with a hydrophobic silica having a particle size and surface area in the range disclosed above. Any of several known methods may be used for making a hydrophobic silica which can be employed herein in combination with a silicone as the suds controlling agent. For example, a fumed silica can be reacted with a trialkyl chlorosilane (i.e., "silanated") to affix hydrophobic trialkylsilane groups on the surface of the silica. In a preferred and well known process, fumed silica is contacted with trimethylchlorosilane and a preferred hydrophobic silanated silica useful in the present compositions is prepared.

[0045] In an alternate procedure, a hydrophobic silica useful in the present compositions is obtained by contacting silica with any of the following compounds: metal, ammonium and substituted ammonium salts of long chain fatty acids, such as sodium stearate, aluminum stearate; silylhalides, such as ethyltrichlorosilane, butyltrichlorosilane, tricyclohexylchlorosilane; and long chain alkyl amines or ammonium salts, such as cetyl trimethyl amine, cetyl trimethyl ammonium chloride.

[0046] A preferred suds controlling agent herein comprises a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from 10 nm to 20 nm and a specific surface area above 50 m^2 /g intimately admixed with a dimethyl silicone fluid having a molecular weight in the range of from 500 to 200,000, at a weight ratio of silicone to silanated silica of from 10:1 to 1:2. Such suds controlling agents preferably comprise silicone and the silanated silica in a weight ratio of silicone:silanated silica of from 10:1 to 1:1. The mixed hydrophobic silanated (especially trimethylsilanated) silica-silicone suds controlling agents provide suds control over a broad range of temperatures, presumably due to the controlled release of the silicone from the surface of the silanated silica.

[0047] Another type of suds control agent herein comprises a silicone material of the type hereinabove disclosed sorbed onto and into a solid. Such suds controlling agents comprise the silicone and solid in a silicone:solid ratio of from 20:1 to 1:20, preferably from 5:1 to 1:1. Examples of suitable solid sorbents for the silicones herein include clay, starch, kieselguhr, Fuller's Earth. The alkalinity of the solid sorbents is of no consequence to the compositions herein, inasmuch as it has been discovered that the silicones are stable when admixed therewith. As disclosed hereinabove, the sorbent-plus-silicone suds controlling agent must be coated or otherwise incorporated into a carrier material of the type hereinafter disclosed to effectively isolate the silicone from the detergent component of the instant compositions.

[0048] Yet another preferred type of silicone suds controlling agent herein comprises a silicone fluid, a silicone resin and silica. The silicone fluids useful in such suds controlling mixtures are any of the types hereinabove disclosed, but are preferably dimethyl silicones. The silicone "resins" used in such compositions can be any alkylated silicone resins, but are usually those prepared from methylsilanes. Silicone resins are commonly described as "three-dimensional" polymers arising from the hydrolysis of alkyl trichlorosilanes, whereas the silicone fluids are "two-dimensionat" polymers prepared by the hydrolysis of dichlorosilanes. The silica components of such compositions are microporous materials such as the fumed silica aerogels and xerogels having the particle sizes and surface areas hereinabove disclosed.

[0049] The mixed silicone fluid/silicone resin/silica materials useful in the present compositions can be prepared in the manner disclosed in U.S. Pat. No. 3,455,839. These mixed materials are commercially available from the Dow Coming Corporation. According to U.S. Pat. No. 3,455,839, such materials can be described as mixtures consisting essentially of: for each 100 parts by weight of a polydimethylsiloxane fluid having a viscosity in the range from 2×10^{-5} to 1.5×10^{-3} m^2s^{-1}(20cs. to 1500cs.) at 25°C, (a) from 5 to 50, preferably from 5 to 20, parts by weight of a siloxane resin composed of $(CH_3)_3SiO_{1/2}$ units and SiO_2 units in which the ratio of the $(CH_3)_3SiO_{1/2}$ units to the SiO_2 units is within the range of from 0.6/1 to 1.2/1; and (b) from 1 to 10, preferably from 1 to 5, parts by weight of a solid silica gel, preferably an aerogel.

[0050] Again, such mixed silicone/silicone resin/silica suds controlling agents must be combined with a detergent-impermeable carrier material to be useful in the compositions herein.

[0051] The silicone suds controlling agents of the aforementioned type is preferably incorporated within (i.e., coated, encapsulated, covered by, internalized. or otherwise substantially contained within) a substantially water-soluble, or water-dispersible, and non-hydroscopic carrier material which must be impermeable to detergents and alkalinity and which, itself, must be substantially nonsurface active. By substantially nonsurface active is meant that the carrier material, itself, does not interact with the silicone material in such fashion that the silicone material is emulsified or otherwise excessively dispersed prior to its release in the wash water. I.e., the particle size of the silicone droplet should be maintained above 1, more preferably above 5 mm.

[0052] Of course, when preparing a dry powder or granulated detergent composition, it is preferable that the silicone suds controlling component thereof also be substantially dry and nontacky at ambient temperatures. Accordingly, it is preferred herein to use as the carrier material, or vehicle, plastic, organic compounds which can be conveniently melted, admixed with the silicone suds controlling agent, and thereafter cooled to form solid flakes. There are a wide variety of such carrier material useful herein. Since the silicone suds controlling agent is to be releasably incorporated in the carrier, such that the silicone is released into the aqueous bath upon admixture of the composition therewith, it is preferred that the carrier material be water soluble. However, water-dispersible materials are also useful, inasmuch as they will also release the silicone upon addition to an aqueous bath.

[0053] A wide variety of carrier materials having the requisite solubility/dispersibility characteristics and the essential features of being substantially non-surface active, substantially non-hydroscopic and substantially detergent-impermeable are known. However, polyethylene glycol (PEG) which has substantially no surface active characteristics is highly preferred herein. PEG, having molecular weights of from 1,500 to 100,000, preferably from 3,000 to 20,000, more preferably from 5,000 to 10,000 can be used.

[0054] Surprisingly, highly ethoxylated fatty alcohols such as tallow alcohol condensed with at least 25 molar proportions of ethylene oxide are also useful herein. Other alcohol condensates containing extremely high ethoxylate proportions (25 and above) are also useful herein. Such high ethoxylates apparently lack sufficient surface active characteristics to interact or otherwise interfere with the desired suds control properties of the silicone agents herein. A variety of other materials useful as the carrier agents herein can also be used, e.g., gelatin; agar; gum arabic; and various algae-derived gels.

[0055] A very preferred carrier material is a mixture of from 0.2% to 15%, preferably from 0.25% to 5%, more preferably from 0.25% to 2% of fatty acids containing from 12 to 30, preferably from 14 to 20, more preferably from 14 to 16, carbon atoms and the balance PEG. Such a carrier material gives a more desirable suds pattern over the duration of the washing process, providing more suds at the start and less suds at the end than PEG alone. The fatty acid delays the solubility of the suds suppressor particle and thereby delays the release of the silicone. Soap and/or wax may also be used in place of the fatty acid.

[0056] The preferred irregularly shaped particulate silicone suds controlling component can be conveniently prepared in a highly preferred flake form by admixing the silicone suds controlling agent with a molten carrier material, mixing to form the appropriate silicone droplet size, and flaking, e.g., by milling or extruding to form a thin sheet, cooling to solidify the carrier material, and breaking the sheet into particles of the right size. In another preferred process thin films can be formed by cooling molten carrier material with the suds suppressor dispersed therein on, e.g., a chill roll or belt cooler and then breaking said film into appropriate sized flakes. The thickness of the flake should be from 0.05 to 0.15 cm, preferably from 0.05 to 0.1 cm. When this procedure is used, the silicone suds controlling agent is contained within the carrier material so effectively that when this material is eventually admixed with, or incorporated into, a detergent composition, the silicone does not substantially come into contact with the detergent surfactant ingredient.

[0057] In order to provide a granular, nontacky suds controlling component useful in dry granular detergent compositions, the flake of the silicone suds controlling agent and carrier material should be substantially solidified. This can be achieved by use of belt coolers and which quickly cool the sheets or flakes such that the carrier melt is hardened. Extrusion techniques can also be used.

[0058] It is to be recognized that the amount of carrier used to isolate the silicone suds controlling agent herein from the detergent component of the compositions herein is not critical. It is only necessary that enough carrier be used to provide sufficient volume that substantially all the silicone can be incorporated therein. Likewise, it is preferred to have

sufficient carrier material to provide for sufficient strength of the resultant granule to resist premature breakage. Generally, above a 2:1, preferably from 5:1 to 100:1, more preferably from 20:1 to 40:1, weight ratio of carrier to silicone suds controlling agent is employed.

[0059] The size of the particles of the suds controlling component used in the present compositions is selected to be compatible with the remainder of the detergent composition. The suds controlling components herein do not segregate unacceptably within the detergent composition. In general, particles with a maximum dimension of from 600 to 2000, preferably from 800 to 1600 μm are compatible with spray-dried detergent granules. Therefore, the majority of the particles should have these maximum dimensions. The majority of the particles should have a ratio of the maximum to the minimum diameter of from 1.5:1 to 5:1, preferably from 1.5:1 to 4:1.

[0060] Other alternative suds controlling components which can be releasably incorporated in a carrier material besides silicone, include monocarboxylic fatty acids and soluble salts thereof. These typically have hydrocarbyl chains of 10 to 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. Other suitable suds controlling components include high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C18-C40 ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexaalkylmelamines or di- to tetraalkyldiamine 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, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

[0061] In addition to the above-mentioned silicone foam suppressing component, other delayed-release foam suppressing components may be used. For example, an encapsulated antifoam composition having a suds controlling agent and the reaction product of (i) an alkylalkoxysilane; and (ii) a silicone condensation cure catalyst wherein the suds controlling agent is encapsulated by the reaction product may be used. The method of making such preferred encapsulated antifoam compositions are described in GB 2 318 355, published on April 22, 1998, by General Electric Co. In another example, a homogenous rosin/silicone mixture made from a mixture of liquid polydimethyl siloxane with aqueous caustic soda solution and melted rosin can also be used as a delayed-release foam suppressing component. Because the rosin/silicone mixture becomes soluble at higher temperatures, such foam suppressing is especially useful for the delayed-release in washing conditions in which the wash water is heated over time. See also GB 1340043, published December 5, 1978, by Griffiths et. al.

[0062] In another example for a silicone based foam suppressing component, the carrier for the suds controlling agent can be a solid particulate structure of modified cellulose which is soluble in water, but dissolves at a relatively slow rate due to the swelling of the surface of the cellulose. For examples of a preferred process for making such foam suppressing components, please see US 4,894,177, Starch et al., granted January 16, 1990 to Dow Corning Corp. In yet another example, a suds controlling agent can be enclosed in a microcapsule composed of a core and a shell of a polymer, so that there is a controlled release of the core material (suds controlling agent) by destruction of the polymer shell by the action of bases.

[0063] In another example, microcapsules can be used as a delayed-release foam suppressing component. One preferred microcapsule is made by polymerizing (i) more than 40% by weight of maleic anhydride, (ii) 0-99% by weight of at least one monoethylenically unsaturated monomer which is oil-soluble and which is different from the monomers of maleic anhydride, (iii) 0-80% by weight of crosslinking monomers which are oil soluble and different from maleic anhydride which have at least two monoethylenically unsaturated non-conjugated double bonds in the molecule, and (iv) 0-20% by weight of water-soluble monoethylenically unsaturated monomers, the percentages relating to the total amount of monomers (i) to (iv), in the oil phase of a stable oil-in-water emulsion in the presence of polymerization initiators which form free radicals, where the temperature of the polymerizing reaction mixture may be continuously or periodically increased during the polymerization. For a detailed process description, see US 5,596,051, Jahns et. al., granted on January 21, 1997 to BASF.

C. Detersive components

[0064] The detergent composition of the invention can comprise additional detersive components known in the art. In addition, the foaming component and/or the delayed-release foam suppressing component may further contain detersive components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

[0065] The detergent compositions preferably contains one or more additional detersive components selected from the group consisting of surfactants, bleaches, alkali metal salt of silicate, builders, chelating agents, enzymes, fillers, soil suspending agents, optical brighteners, dispersants, soil release agents, photoactivated bleaches, dyes, dye transfer inhibitors, pigments, perfumes, clay softening system, cationic fabric softening agents, and mixtures thereof.

[0066] In particular, it can be preferred that the particles comprises at least one or more anionic surfactants and

preferably one or more cationic surfactants, as described herein. It can also be preferred that the particles also, or alternatively comprise builder material and bleaching species, as described herein

[0067] The detergent compositions may contain one or more surfactants selected from anionic, cationic, ampholytic, amphoteric and zwitterionic surfactants or nonionic surfactants as described above, and mixtures thereof. A typical listing of these surfactants, is given in U.S. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S. 4,259,217 issued to Murphy on March 31, 1981.

Anionic Surfactant

[0068] Any anionic surfactant useful for detersive purposes is suitable. Examples include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

[0069] Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

[0070] The anionic surfactant can be present at a level of 0.5% to 80%, preferably at a level of from 3% to 60%, more preferably of from 5% to 35% by weight of the composition or the particle. The ratio of the stabilising agent to the anionic surfactant is preferably from 1:20 to 20:1, more preferably from 1:6 to 6:1.

Anionic Sulfate Surfactant

[0071] Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

[0072] Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_9-C_{22} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

[0073] Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 50 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

[0074] A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic Sulfonate Surfactant

[0075] Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear or branched alkylbenzene sulfonates, alkyl ester sulfonates, in particular methyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof

Anionic Carboxylate Surfactant

[0076] Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

[0077] Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_20)_x\ CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO\text{-}(CHR_1\text{-}CHR_2\text{-}O)_X\text{-}R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

[0078] Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-no-

nanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali Metal Sarcosinate Surfactant

[0079] Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

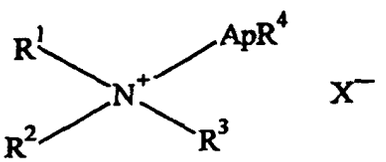
Cationic Surfactant

[0080] Another preferred surfactant is a cationic surfactant, which may preferably be present at a level of from 0.1% to 60% by weight of the composition or particle, more preferably from 0.4% to 20%, most preferably from 0.5% to 5% by weight of the composition. When present, the ratio of the anionic surfactant to the cationic surfactant is preferably from 25:1 to 1:3, more preferably from 15:1 to 1:1. most preferably from 10:1 to 1:1 The ratio of cationic surfactant to the stabilising agent is preferably from 1:30 to 20: 1, more preferably from 1:20 to 10:1.

[0081] Preferably the cationic surfactant is selected from the group consisting of cationic ester surfactants, cationic mono-alkoxylated amine surfactants, cationic bis-alkoxylated amine surfactants and mixtures thereof.

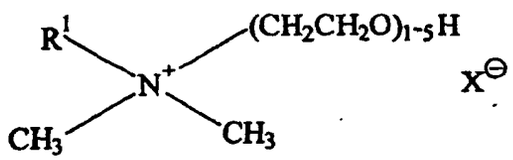
Cationic Mono-Alkoxylated Amine Surfactants

[0082] The optional cationic mono-alkoxylated amine surfactant for use herein, has the general formula:



wherein R^1 is an alkyl or alkenyl moiety containing from 6 to 18 carbon atoms, preferably 6 to 16 carbon atoms, most preferably from 6 to 11 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R^4 is selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, or sulfate, to provide electrical neutrality; A is selected from C_1-C_4 alkoxy, especially ethoxy (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof: and p is from 1 to 30, preferably 1 to 15, most preferably 1 to 8.

[0083] Highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula

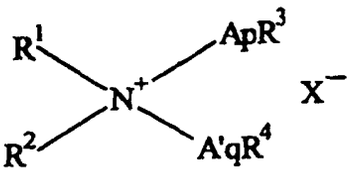


wherein R^1 is C_6-C_{18} hydrocarbyl and mixtures thereof, preferably C_6-C_{14}, especially C_6-C_{11} alkyl, preferably C_8 and C_{10} alkyl, and X^- is any convenient anion to provide charge balance, preferably chloride or bromide.

[0084] As noted, compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy, isopropoxy [$CH(CH_3)CH_2O$] and [$CH_2CH(CH_3O$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

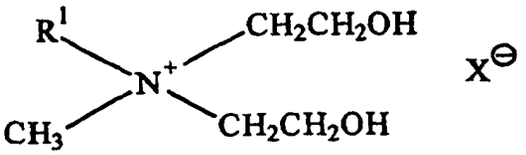
Cationic Bis-Alkoxylated Amine Surfactant

[0085] The cationic bis-alkoxylated amine surfactant for use herein, has the general formula:



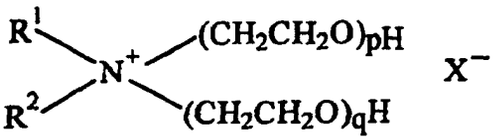
wherein R^1 is an alkyl or alkenyl moiety containing from 6 to 18 carbon atoms, preferably 6 to 16 carbon atoms, more preferably 6 to 11, most preferably from 8 to 10 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, or sulfate, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C_1-C_4 alkoxy, especially ethoxy, (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof; p is from 1 to 30, preferably 1 to 4 and q is from 1 to 30, preferably 1 to 4, and most preferably both p and q are 1.

[0086] Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



wherein R^1 is C_6-C_{18} hydrocarbyl and mixtures thereof, preferably C_6, C_8, C_{10}, C_{12}, C_{14} alkyl and mixtures thereof. X^- is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R^1 is derived from (coconut) C_{12}-C_{14} alkyl fraction fatty acids, R^2 is methyl and ApR^3 and $A'qR^4$ are each monoethoxy.

[0087] Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R^1 is C_6-C_{18} hydrocarbyl, preferably C_6-C_{14} alkyl, independently p is 1 to 3 and q is 1 to 3, R^2 is C_1-C_3 alkyl, preferably methyl, and X^- is an anion, especially chloride or bromide.

[0088] Other compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy (Bu) isopropoxy [$CH(CH_3)CH_2O$] and [$CH_2CH(CH_3O$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

Amphoteric Surfactant

[0089] Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids. Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and $C_{10\text{-}18}$ acylamido alkyl dimethylamine oxide. A suitable example of an alkyl aphodicarboxylic acid is Miranol (TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

[0090] Zwitterionic surfactants can also be incorporated into the particle of the invention or the compositions containing the particle of the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein. Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10^-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Water-Soluble Builder Compound

[0091] The compositions preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition or particle.

[0092] Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

[0093] The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

[0094] Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,24l, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

[0095] Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

[0096] Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

[0097] Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from 6 to 21, and salts of phytic acid.

Partially Soluble or Insoluble Builder Compound

[0098] The composition may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition or particle.

[0099] Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicate zeolites have the unit cell formula $Na_{z[}(AlO_2)_z(SiO_2)y]. xH_2O$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

[0100] The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

$$Na_{12}[AlO_2)_{12}(SiO_2)_{12}].xH_2O$$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$. 276 H_2O.

[0101] Preferred crystalline layered silicates for use herein have the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_20_5$, available from Hoechst AG as NaSKS-6.

Perhydrate Bleaches

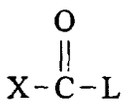
[0102] An preferred additional components of the composition is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. Potassium peroxymonopersulfate is another optional inorganic perhydrate salt of use in the detergent compositions herein.

Organic Peroxyacid Bleaching System

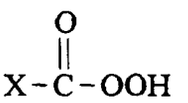
[0103] A preferred feature of compositions is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the claimed invention. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Peroxyacid Bleach Precursor

[0104] Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



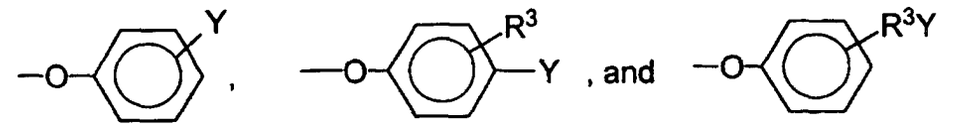
where L is a leaving group and X is essentially any functionality, such that on perhydroloysis the structure of the peroxyacid produced is

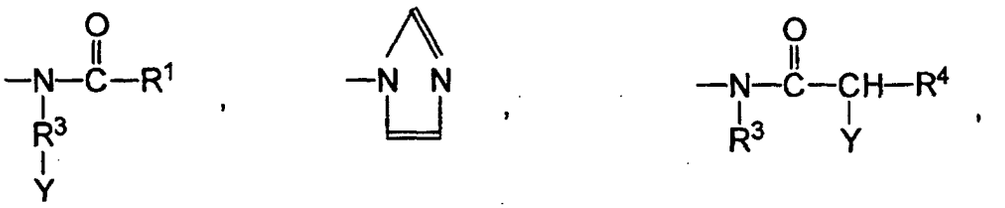


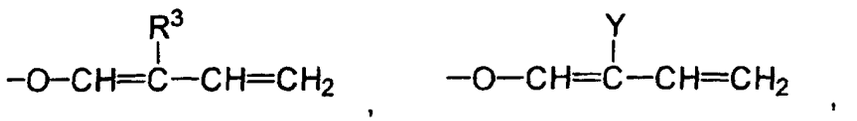
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 80% by weight of the particle, more preferably from 5% to 45% by weight, most preferably from 3% to 15% by weight of the compositions. Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

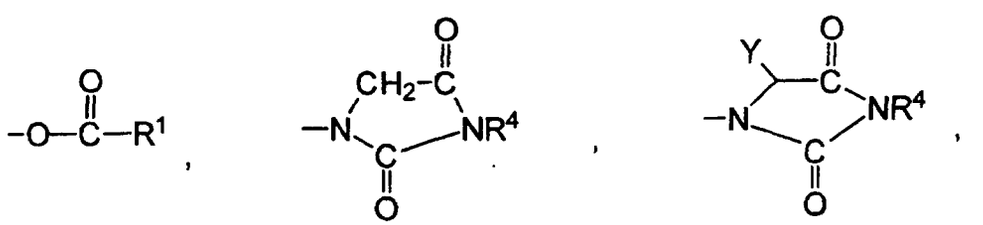
Leaving Groups

[0105] The leaving group, hereinafter L group, must be sufficiency reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.
Preferred L groups are selected from the group consisting of:











and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group. Any of R^1, R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammmonium groups.

[0106] The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4$ X^- and O<--$N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

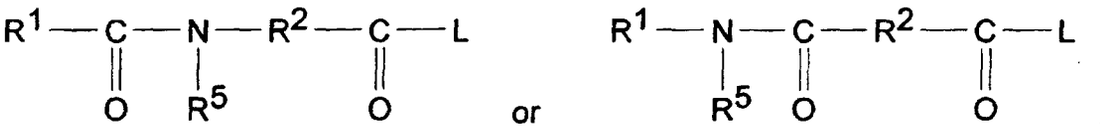
Alkyl Percarboxylic Acid Bleach Precursors

[0107] Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis. Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N^1N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred. The TAED is preferably not present in the agglomerated particle of the present invention, but preferably present in the detergent composition, comprising the particle.

[0108] Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide Substituted Alkyl Peroxyacid Precursors

[0109] Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic Acid Precursor

[0110] Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoytating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyi pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic Peroxyacid Precursors

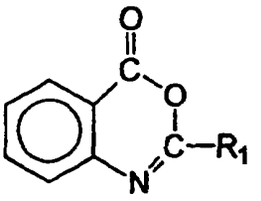
[0111] Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis. Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

[0112] The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter. Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332. Examples of preferred cationic peroxyacid precursors are described in WO95/29160 (claiming priority of UK Patent Application No. 9407944.9) and US Patent Nos. US 5,686,015, US 5,460,747, US 5,578,136 and US 5,584,888.

[0113] Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin Organic Peroxyacid Precursors

[0114] Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

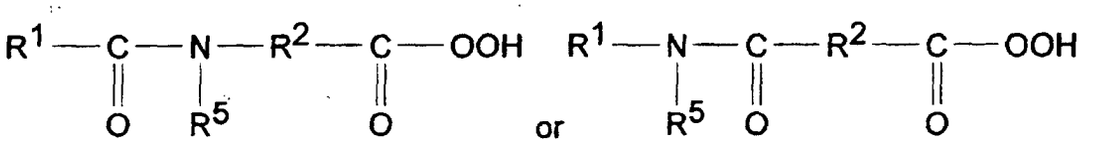


wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed Organic Peroxyacid

[0115] >

[0116] The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid , typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition. A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386. Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach Catatyst

[0117] The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

[0118] Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

[0119] For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least

three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$ and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]\text{-}(ClO_4)_3$.

[0120] Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy Metal Ion Sequestrant

[0121] The composition preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions or particle. Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

[0122] Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate. Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

[0123] Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

[0124] EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are alos suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

[0125] Another preferred ingredient useful in the composition is one or more additional enzymes. Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139. Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

[0126] Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

[0127] Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 10% by weight of the particle, preferably 0.001% to 3% by weight of the composition, most preferably from 0.001% to 0.5% by weight of the

compositions.

[0128] The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

[0129] Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Organic Polymeric Compound

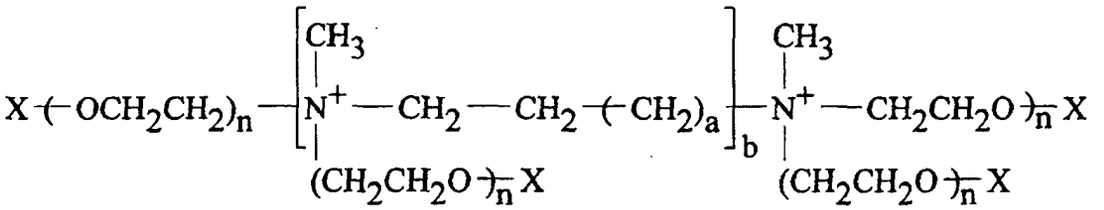
[0130] Organic polymeric compounds are preferred in compositions. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

[0131] Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 50% by weight of the particle, preferably from 0.5% to 25%, most preferably from 1% to 15% by weight of the compositions.

[0132] Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000. The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

[0133] Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein. Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

[0134] Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C_1-C_4 alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical. range of from 20 to 35; for cationic diamines (b=1), n is at least 12 with a typical range of from 12 to 42.

[0135] Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Clay Softening System

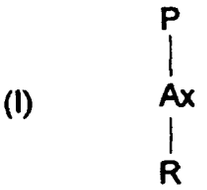
[0136] The compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent. The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

Polymeric Dye Transfer Inhibiting Agents

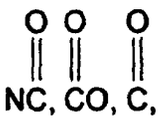
[0137] The particles or compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents. The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

a) Polyamine N-oxide polymers.

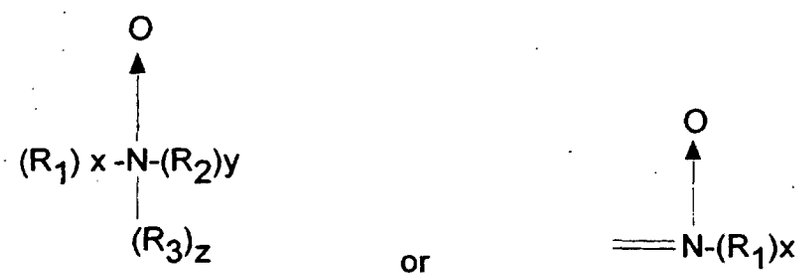
[0138] Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



wherein P is a polymerisable unit, and
A is



- O-, -S-, -N-; x is O or 1;
R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups. The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

[0139] Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

[0140] Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic,heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group

is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

[0141] The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrrolidone and N-vinylimidazole

[0142] Suitable herein are coploymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

[0143] The compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinyloxazolidone

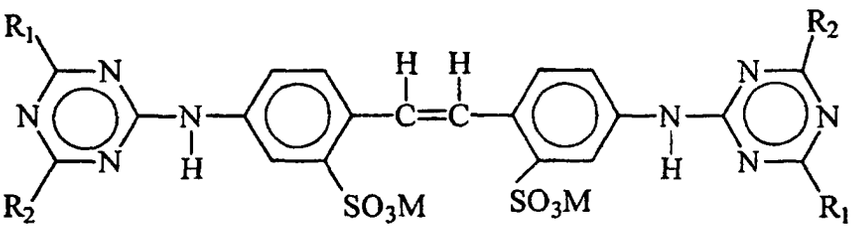
[0144] The compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

e) Polyvinylimidazole

[0145] The compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical Brightener

[0146] The compositions herein also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners. Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

[0147] When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein. When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2 -hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal

5BM-GX by Ciba-Geigy Corporation. When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic Fabric Softening Agents

[0148] Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340. Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

pH of the Compositions

[0149] The detergent compositions preferably can have an acidic or an alkaline pH, depending on the application or the additional ingredients. It may be preferred that the particles or the compositions have a pH, measured as a 1% solution in distilled water, of at least 3.0, preferably from 4.0 to 12.5.

D. Laundry Methods

[0150] In a manual laundry method, the method typically comprises contacting and/or treating soiled fabric with an aqueous wash solution containing detergent composition in a bucket or a container with a solid bar. The consumer contacts the solid bar with the soiled fabric by scrubbing. After all the fabric has been scrubbed, fresh water is added to the container and the fabrics are rinsed. This rinsing process may be repeated. During a typical manual laundry method, a cleaning or scrubbing implement may also be used.

[0151] In a machine laundry method, the method typically comprises treating soiled laundry with an aqueous wash solution having dissolved or dispensed therein an effective amount of detergent composition. Preferably, an effective amount is from 10g to 300 g or product dissolved or dispersed in a wash solution of volume from 5 to 65 litres.

[0152] In a method of soaking fabrics, soiled fabrics are immersed in an aqueous soaking solution containing the detergent composition for an effective period of time. Then, the fabrics are removed from the soaking solution.

EXAMPLES

[0153] The following examples further describe and demonstrate embodiments within the scope of the present invention.

[0154] The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

Abbreviations used in Examples

[0155] In the exemplified foaming systems and cleaning compositions, the abbreviated component identifications have the following meanings:

LAS :	Sodium linear C_{12} alkyl benzene sulfonate
TAS :	Sodium tallow alkyl sulfate
C45AS :	Sodium C_{14}-C_{15} linear alkyl sulfate
MES :	α-sulpho methylester of C_{18} fatty acid
CxyEzS :	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
$MBAS_{x,\,y}$:	Sodium mid-chain branched alkyl sulfate having an average of x carbon atoms, whereof an average of y carbons comprised in (a) branching unit(s)
C_{48} SAS :	Sodium C_{14}-C_{18} secondary alcohol sulfate
SADExS :	Sodium C_{14}-C_{22} alkyl disulfate of formula 2-(R).C_4 H_7-1,4-(SO_4-)$_2$ where R = $C_{10}0C_{18}$, condensed with z moles of ethylene oxide
CxyEz :	A C-)$_{1x\text{-}1y}$ branched primary alcohol condensed with an average of z moles of ethylene oxide
QAS I :	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with R_2 = 50%-60% Cg; 40%-50% C_{11}
QAS II :	$R_1.N^+(CH_3)(C_2H_4OH)_2$ with R_1 = C_{12}-C_{14}
Soap :	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA I :	C_{12}-C_{14} alkyl N-methyl glucamide

TFAA II :	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA :	C_{12}-C_{14} topped whole cut fatty acids
STPP :	Anhydrous sodium tripolyphosphate
Zeolite A I :	Hydrated Sodium Aluminosilicate of formula $Na_{12}(A10_2SiO_2)_{12}$. $27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
Zeolite A II :	overdried Zeolite AI
NaSKS-6 :	Crystalline layered silicate of formula δ -$Na_2Si_2O_5$
Citric acid I :	Anhydrous citric acid
Citric acid II :	Citric acid monohydrate
Malic acid :	Anhydrous malic acid
Maleic acid :	Anhydrous maleic acid
Aspartic acid :	Anhydrous aspartic acid
Carbonate I :	Anhydrous sodium carbonate with an average particle size between 200μm and 900μm
Carbonate II :	Anhydrous sodium carbonate with an average particle size between 100μm and 200μm
Bicarbonate :	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate :	Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
Sodium sulfate :	Anhydrous sodium sulfate
Citrate :	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA :	Copolymer of 1:4 maleic/acrylic acid, average molecular weight 70,000
CMC :	Sodium carboxymethyl cellulose
Protease :	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Alcalase :	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase :	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase :	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase :	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase :	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4 :	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1 :	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate :	Sodium Percarbonate of nominal formula 2Na2CO3.3H2O2
NAC-OBS :	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
NOBS :	Nonanoyl oxybenzene sulfonate in the form of the sodium salt
DPDA :	Diperoxydodecanedioic acid
PAP :	N-phthaloylamidoperoxicaproic acid
NAPAA :	Nonanoylamido peroxo-adipic acid
NACA :	6 nonylamino - 6 oxo - capronic acid.
TAED :	Tetraacetylethylenediamine
DTPMP :	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated :	Sulfonated Zinc or aluminium Phthlocyanine encapsulated
Brightener 1 :	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2 :	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP :	1,1-hydroxyethane diphosphonic acid
PVNO :	Polyvinylpyridine N-oxide
PVPVI :	Copolymer of polyvinylpyrolidone and vinylimidazole
QEA :	bis $((C_2H_5O)(C_2H_4O)_n)$ (CH_3) -N^+-C_6H_{12}-N^+- (CH_3) bis $((C_2H_5O)$-$(C_2H_4O)_n)$, wherein n=from 20 to 30
SRP 1 :	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2 :	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer
Delayed-release foam suppressing comp. 1 :	A flake material containing 10%, by weight, of silicone/silica fluid and 90% by weight, of polyethylene glycol having a molecular weight of 8,000. The flake material has a particle size of 2000 microns to 500 microns (-10/+35 Tyler mesh).
Delayed-release foam suppressing comp. 2 :	A flake material containing 10% by weight of silicone/silica fluid, 0 to 7% by weight of palmitic acid

or Hyfac® fatty acids, and the balance polyethylene glycol having a molecular weight of 8,000. The flake material has a particle size of 2000 microns to 500 microns (-10/+35 Tyler mesh).

Suds Booster: One or a mixture of polyethylene glycol, amine oxide, monoethanol amine, diethanol amine, fatty alcohol, sugar, protein and betaine.

[0156] In the following Examples all levels are quoted as parts per weight of the composition:

Controlled Foaming System Examples

[0157] The following examples exemplify foaming systems in accord with the invention, each of which, or mixtures thereof, can be used in detergent compositions.

[0158] The controlled foaming system of the present invention can be made by any method known in the art for formation of particles, as described above.

[0159] In the foaming system, there are many variations of how the foaming component and the delayed-release foam suppressing component may be combined. For example, the foaming component and the foam suppressing component may be agglomerated or otherwise mixed together with other optional components to form one solid particle. In addition, the foaming component and the foam suppressing component may be two separate particles. Either the one solid particle or the two separate particles making up the foaming system may be used in detergent compositions.

Example 1

Foaming Systems A to J

[0160]

	A	B	C	D	E	F	G	H	I	J
TFAA I/ TFAAII	31.0	28.0	11.0	27.5	13.0	15.0	22.0	15.0	-	10.0
C24E3/C24E5	-	-	28.0	-	25.0	22.0	-	5.0	10.0	10.0
PEG 4000	5.0	5.3	-	5.0	-	-	7.0	5.0	-	5.0
citric acid I	13.5	14.0	20.0	15.5	16.0	15.0	15.0	10.0	-	10.0
Maleic acid	-	-	-	-	-	-	-	-	10.5	10.0
sodium carbonate I	13.5	-	20.0	-	-	-	-		15.0	10.0
sodium carbonate II	-	14.0	-	6.0	14.0	10.0	10.0	10.0	5.0	-
sodium bicarbonate	-	-	-	6.0	-	-	10.0	-	5.5	5.0
Zeolite A II	18.0	35.7	20.0	18.0	-	9.0	10.0	5.0	14.0	17.0
LAS	9.0	-	-	-	12.0	-	-	10.0	-	13.0
QAS I/ QAS II	9.0	-	-	-	-	-	6.0	3.0	-	-
TAED/NOBS/ NACA-OBS	-	-	-	19.0	10.0	-	-	7.0	20.0	-
Perborate/ percarbonate	-	-	-	-	-	19.0	-	10.0	-	-
Foam supp. Component 1	1.0	3.0	-	-	10.0	-	10.0	-	-	5.0
Foam supp. Component 2	-	-	1.0	3.0		10.0	-	10.0	10.0	5.0
Suds Booster	-	-	-	-	-	-	10.0	10.0	10.0	-

[0161] Foaming systems A-J produces upon contact with water gas bubbles having an average bubble particle size of 400 microns or less, and the foam suppressing components reduces the water gas bubbles as soon as the mixture is agitated. The bubbles have been reduced at least 40% to 70% after 6 to 10 minutes after the mixture is first agitated.

[0162] The following examples exemplify cleaning compositions comprising the foaming component of the invention:

Example 2

[0163] The following are high density and bleach-containing detergent formulations according to the present invention (can be for either granular form or tablet form):

		a	b	c
Blown Powder				
	Zeolite A	5.0	5.0	15.0
	Sodium sulfate	0.0	5.0	0.0
	LAS	20.0	30.0	20.0
	C45AS	3.0	5.0	20.0
	QAS	-	-	1.5
	DTPMP	0.4	0.4	0.4
	CMC	0.4	0.4	0.4
	MA/AA	4.0	2.0	2.0
Foaming System A		20.0		
Foaming System B		-	15.0	-
Foaming System G		-	-	10.0
Spray On (on particles)				
Encapsulated Perfume		0.3	0.3	0.3
	C25E3	-	-	2.0
Dry additives				
	QEA	-	-	0.5
	Citrate	5.0	-	2.0
	Bicarbonate	-	3.0	-
	Carbonate	8.0	10.0	5.0
	NAC OBS	6.0	-	-
Manganese catalyst		-	-	0.3
	NOBS	-	2.0	-
	PB1	14.0	7.0	-
Polyethylene oxide of MW 5,000,000		-	-	0.2
	Bentonite clay	-	-	10.0
	Citric acid	-	-	0.5
	Protease	1.0	1.0	1.0
	Lipase	0.4	0.4	0.4
	Amylase	0.6	0.6	0.6
	Cellulase	0.6	0.6	0.6
	Suds Booster	5.0	1.0	5.0
Dry additives				
	Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)		100.0	100.0	100.0

(continued)

		a	b	c
Dry additives				
Density (g/litre)		750	800	700

Example 3

[0164] The following are high density detergent formulations according to the present invention:

		d	e
Foaming System A		45.0	
Foaming System H			60.0
Spray On			
	C25E3	-	1.0
	Perfume	0.5	0.5
Dry Adds			
	HEDP	0.5	0.3
	SKS 6	13.0	10.0
	Citrate	-	1.0
	NAC OBS	4.1	-
	TAED	0.8	-
	Percarbonate	20.0	5.0
	SRP 1	0.3	0.3
	Protease	1.4	1.4
	Lipase	0.4	0.4
	Cellulase	0.6	0.6
	Amylase	0.6	0.6
	QEA	1.0	-
	Suds Booster	5.0	-
	Brightener 1	0.2	0.2
	Brightener 2	0.2	-
Density (g/litre)		700	850

Claims

1. A controlled foaming system especially adapted for use in detergent compositions comprising:

(a) a foaming component capable of providing foaming or sudsing without agitation; and
(b) a delayed-release foam suppressing component,

wherein the delayed-release foam suppressing component is a silicone foam suppressing agent which is releasably incorporated in a carrier, thereby delaying the release of a silicone foam suppressing agent, **characterised in that** the silicone foam suppressing agent has an average droplet diameter of from 1 to 50 microns releasably incorporated in a water-soluble or water dispersible, substantially non-surface active, detergent-impermeable, and non-hydroscopic carrier, the silicone foam suppressing component being substantially free of water-

soluble relatively hydroscopic inorganic salts and in the form of an irregularly shaped particle having a minimum dimension of not less than 0.05 cm and the maximum dimension being at least 20% greater than the minimum dimension.

2. The controlled foaming system of Claim 1, wherein the foaming component comprises an effervescent granule comprising an acid source, and carbonate 2 and/or bicarbonate.

3. The controlled foaming system of Claim 2, wherein the foaming component produces upon contact with water gas bubbles having an average bubble particle size of 400 microns or less, preferably 200 microns or less, and more preferably 100 microns or less.

4. The controlled foaming system of Claim 2, wherein the acid source is selected from acids and hydrated or anhydrous sources of acids and is a mono or polycarboxylic acid selected from the group consisting of citric, malic, maleic, fumaric, aspartic, glutaric, tartaric, malonic succinic or adipic acid, monosodium phosphate, boric acid, 3 ketoglutaric acid, citramalic acid, and mixtures thereof.

5. The controlled foaming. system of Claim 2, wherein the effervescent granule further comprises a binder selected from the group consisting of cellulose derivatives, carboxymethylcellulose and homo- and co- polymeric polycarboxylic acid and their salts, C6-C20 alkyl and alkylaryl sulphonates and sulphates, C10-C20 alcohol ethoxylates containing from 5 to 100 moles of ethylene oxide per mole of alcohol, polyvinylpyrrolidones with an average molecular weight of from 12 000 to 700 000, polyethylene glycols with an average weight of from 600 to 10 000, copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid, C10-C20 mono and diglycerol ethers, C10-C20 fatty acids and mixtures thereof.

6. The controlled foaming system of Claim 1, wherein the non-hydroscopic carrier is a polyethylene glycol carrier, the carrier further comprising from 0.2% to 15% fatty acid or soap having from 12 to 30 carbon atoms, and/or wax.

7. The controlled foaming system of Claim 2, wherein the foaming component further comprises a suds booster selected from the group consisting of amine oxide, polyethylene glycol, monoethanol amine, diethanol amine, fatty alcohol, sugar, protein, betaine, and mixtures thereof.

8. The controlled foaming system of Claim 1, wherein the foaming component and the delayed-release foam suppressing component are independent dry particles, wherein the foaming component has an average particle size of from 75 microns to 2 cm.

9. A granular detergent composition comprising the controlled foaming system of Claim 1, further comprising a detersive component selected from the group consisting of surfactants, bleaches, alkali metal salt of silicate, builders, chelating agents, enzymes, fillers, soil suspending agents, optical brighteners, dispersants, soil release agents, photoactivated bleaches, dyes, dye transfer inhibitors, pigments, perfumes, clay softening system, cationic fabric softening agents, and mixtures thereof.

10. A method of cleaning and soaking fabrics, comprising contacting the fabric in a solution containing water and the granular detergent composition of Claim 9 for an effective period of time for a time sufficient to clean said fabric.

Patentansprüche

1. Reguliertes Schaumsystem, insbesondere angepasst zur Verwendung in Detergenszusammensetzungen, umfassend:

   (a) eine schäumende Komponente, die in der Lage ist, ohne Bewegung ein Aufschäumen oder Schäumen vorzusehen; und
   (b) eine Schaumunterdrückungskomponente mit verzögerter Freisetzung, wobei die Schaumunterdrückungskomponente mit verzögerter Freisetzung ein Silicon-Schaumunterdrückungsmittel ist, das freisetzbar in einem Träger eingebracht ist, wodurch die Freisetzung eines Silicon-Schaumunterdrückungsmittels verzögert wird,

   dadurch gekennzeichnet, dass das Silicon-Schaumunterdrückungsmittel einen durchschnittlichen Tropfendurchmesser von 1 bis 50 μm besitzt und freisetzbar in einem wasserlöslichen oder wasserdispergierbaren, im

Wesentlichen nichtoberflächenaktiven, detergensundurchlässigen und nichthydroskopischen Träger eingebracht ist, wobei die Silicon-Schaumunterdrückungskomponente im Wesentlichen frei ist an wasserlöslichen, relativ hydroskopischen anorganischen Salzen und in Form eines irregulär geformten Teilchens einer minimalen Abmessung von nicht weniger als 0,05 cm vorliegt, und wobei die maximale Abmessung mindestens 20% größer ist als die minimale Abmessung

2. Reguliertes Schaumsystem nach Anspruch 1, wobei die schäumende Komponente eine aufbrausende Granalie umfasst, die eine Säurequelle, ein Carbonat und/oder Bicarbonat umfasst.

3. Reguliertes Schaumsystem nach Anspruch 2, wobei die schäumende Komponente bei Berührung mit Wasser Gasbläschen erzeugt, die eine durchschnittliche Bläschenteilchengröße von 400 μm oder weniger, vorzugsweise 200 μm oder weniger, und weiter vorzugsweise 100 μm oder weniger, besitzen.

4. Reguliertes Schaumsystem nach Anspruch 2, wobei die Säurequelle gewählt ist aus Säuren und hydratisierten oder wasserfreien Quellen von Säuren und eine Mono- oder Polycarbonsäure ist, gewählt aus der Gruppe, bestehend aus Zitronen-, Äpfel-, Malein-, Fumar-, Asparagin-, Glutar-, Wein-, Malon-, Bernstein- oder Adipinsäure, Mononatriumphosphat, Borsäure, 3-Ketoglutarsäure, Citramalsäure und Mischungen hiervon.

5. Reguliertes Schaumsystem nach Anspruch 2, wobei die aufbrausende Granalie weiterhin ein Bindemittel umfasst, gewählt aus der Gruppe, bestehend aus Cellulosederivaten, Carboxymethylcellulose und homo- und copolymeren Polycarbonsäuren und deren Salzen, C_6-C_{20}-Alkyl- und -Alkylarylsulfonaten und -sulfaten, C_{10}-C_{20}-Alkoholethoxylaten, enthaltend 5 bis 100 Mol Ethylenoxid pro Mol Alkohol, Polyvinylpyrrolidonen mit einem Durchschnittsmolekulargewicht von 12.000 bis 700.000, Polyethylenglykolen mit einem Durchschnittsmolekulargewicht von 600 bis 10.000, Copolymeren von Maleinsäureanhydrid mit Ethylen, Methylvinylether, Methacrylsäure oder Acrylsäure, C_{10}-C_{20}-Mono- und Diglycerinethern, C_{10}-C_{20}-Fettsäuren und Mischungen hiervon.

6. Reguliertes Schaumsystem nach Anspruch 1, wobei der nichthydroskopische Träger ein Polyethylenglykolträger ist, der Träger weiterhin 0.2% bis 15% Fettsäure oder Seife mit 12 bis 30 Kohlenstoffatomen und/oder Wachs umfasst.

7. Reguliertes Schaumsystem nach Anspruch 2, wobei die schäumende Komponente weiterhin einen Schaumverstärker umfasst, gewählt aus der Gruppe, bestehend aus Aminoxid, Polyethylenglykol, Monoethanolamin, Diethanolamin, Fettalkohol, Zucker, Protein, Betain und Mischungen hiervon.

8. Reguliertes Schaumsystem nach Anspruch 1, wobei die schäumende Komponente und die Schaumunterdrükkungskomponente mit verzögerter Freisetzung unabhängige trockene Teilchen sind, wobei die schäumende Komponente eine durchschnittliche Teilchengröße von 75 μm bis 2 cm aufweist.

9. Granuläre Detergenszusammensetzung, umfassend das regulierte Schaumsystem nach Anspruch 1, umfassend weiterhin eine Detergenskomponente, gewählt aus der Gruppe, bestehend aus Tensiden, Bleichmitteln, Alkalimetallsalz von Silicat, Buildern, Komplexbildnern, Enzymen, Füllstoffen, Schmutzsuspendiermitteln, optischen Aufhellern, Dispergiermitteln. Schmutzabweisemitteln, fotoaktivierbaren Bleichmitteln. Farbstoffen, Farbstoffübertragungsinhibitoren, Pigmenten, Duftstoffen, Ton-Weichmachungssystem, kationischen Textilweichmachern und Mischungen hiervon.

10. Verfahren zum Reinigen und Einweichen von Textilien, umfassend das Kontaktieren der Textilie in einer Lösung, enthaltend Wasser und die granuläre Detergenszusammensetzung nach Anspruch 9, über einen wirksamen Zeitraum während eines ausreichenden Zeitraums, um die Textilie zu reinigen.

Revendications

1. Système moussant contrôlé spécialement adapté pour un usage dans des compositions détergentes, comprenant :

(a) un composant moussant capable d'effectuer un moussage sans agitation; et
(b) un composant suppresseur de mousse à libération retardée,

dans lequel le composant suppresseur de mousse à libération retardée est un agent suppresseur de mousse

siliconé qui est incorporé de manière libérable à un véhicule, retardant de la sorte la libération de l'agent suppresseur de mousse siliconé,
caractérisé en ce que l'agent suppresseur de mousse siliconé a un diamètre moyen de gouttelettes de 1 à 50 micromètres et est incorporé de manière libérable à un véhicule soluble ou dispersable dans l'eau, sensiblement non tensioactif, imperméable aux détergents et non hygroscopique, le composant suppresseur de mousse siliconé étant sensiblement exempt de sels inorganiques relativement hygroscopiques solubles dans l'eau et se présentant sous la forme d'une particule de forme irrégulière ayant une dimension minimale qui n'est pas inférieure à 0,05 cm et une dimension maximale qui est au moins 20% supérieure à la dimension minimale.

2. Système moussant contrôlé selon la revendication 1, dans lequel le composant moussant comprend un granulé effervescent comprenant une source d'acide et un carbonate et/ou un bicarbonate.

3. Système moussant contrôlé selon la revendication 2, dans lequel le composant moussant produit, par contact avec de l'eau, des bulles de gaz ayant une taille particulaire moyenne de 400 micromètres ou moins, de préférence de 200 micromètres ou moins, mieux encore de 100 micromètres ou moins.

4. Système moussant contrôlé selon la revendication 2, dans lequel la source d'acide est choisie parmi les acides et les sources hydratées ou anhydres d'acides et est un acide mono- ou polycarboxylique choisi dans le groupe constitué des acides citrique, malique, maléique, fumarique, aspartique, glutarique, tartrique, malonique, succinique ou adipique, du phosphate monosodique, de l'acide borique, de l'acide 3-cétoglutarique, de l'acide citramalique et de leurs mélanges.

5. Système moussant contrôlé selon la revendication 2, dans lequel le granulé effervescent comprend en outre un liant choisi dans le groupe constitué des dérivés de la cellulose, de la carboxyméthylcellulose et des acides homo- et copolymères et de leurs sels, des sulfonates et sulfates d'alkyle et d'alkylaryle en C_6-C_{20}, des éthoxylates d'alcools en C_{10}-C_{20} contenant 5 à 100 moles d'oxyde d'éthylène par mole d'alcool, des polyvinylpyrrolidones avec un poids moléculaire moyen de 12 000 à 700 000, des polyéthylèneglycols ayant un poids moyen de 600 à 10 000, des copolymères d'anhydride maléique avec de l'éthylène, du méthylvinyléther, de l'acide méthacrylique ou de l'acide acrylique, des mono- et diglycéroléthers en C_{10}-C_{20}, des acides gras en C_{10}-C_{20} et de leurs mélanges.

6. Système moussant contrôlé selon la revendication 1, dans lequel le véhicule non hygroscopique est un véhicule de polyéthylèneglycol, le véhicule comprenant en outre 0,2% à 15% d'acide gras ou de savon ayant 12 à 30 atomes de carbone et/ou de cire.

7. Système moussant contrôlé selon la revendication 2, dans lequel le composant moussant comprend en outre un accélérateur de mousse choisi dans le groupe constitué d'un oxyde d'amine, du polyéthylèneglycol, de la monoéthanolamine, de la diéthanolamine, d'un alcool gras, de sucre, de protéine, de bétaïne et de leurs mélanges.

8. Système moussant contrôlé selon la revendication 1, dans lequel le composant moussant et le composant suppresseur de mousse à libération retardée sont des particules sèches indépendantes, le composant moussant ayant une taille particulaire moyenne de 75 micromètres à 2 cm.

9. Composition détergente granulaire comprenant le système moussant contrôlé selon la revendication 1, comprenant en outre un composant détersif choisi dans le groupe constitué des agents tensioactifs, des agents de blanchiment, des sels silicates de métaux alcalins, des adjuvants, des agents chélatants, des enzymes, des charges, des agents de suspension de crasses, des azureurs optiques, des dispersants, des agents de libération de crasses, des agents de blanchiment photoactivés, des colorants, des inhibiteurs de transfert de colorants, des pigments, des parfums, des systèmes adoucisseurs argileux, des agents adoucisseurs de tissus cationiques et de leurs mélanges.

10. Procédé de nettoyage et de trempage de tissus, comprenant la mise en contact du tissu dans une solution contenant de l'eau et la composition détergente granulaire selon la revendication 9 pendant une période de temps efficace suffisante pour nettoyer ledit tissu.