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(11) **EP 0 675 978 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
02.02.2000 Bulletin 2000/05

(21) Application number: **93917292.0**

(22) Date of filing: **20.07.1993**

(51) Int. Cl.⁷: **D06L 3/02**, C11D 3/30,
C11D 3/37, C11D 3/39,
C11D 3/395, C11D 11/00,
C11D 17/06

(86) International application number:
PCT/US93/06818

(87) International publication number:
WO 94/15010 (07.07.1994 Gazette 1994/15)

(54) **COATED PEROXYACID BLEACH PRECURSOR COMPOSITIONS**

ZUSAMMENSETZUNGEN AUS BLEICHMITTELVORLÄUFERN ENTHALTEND EINE
BESCHICHTETE PEROXYSÄURE

COMPOSITION DE PRECURSEURS DE PEROXYACIDE ENROBES, SERVANT D'AGENTS DE
BLANCHIMENT

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

(30) Priority: **22.12.1992 EP 92204060**

(43) Date of publication of application:
11.10.1995 Bulletin 1995/41

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Remarks:

The file contains technical information submitted
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EP 0 675 978 B1

DescriptionTechnical Field

5 [0001] This invention relates to solid peroxy acid bleach precursor particles and to particulate bleaching and detergent compositions incorporating inorganic perhydrate bleaches together with N- or O- acyl group - containing peroxycarboxylic acid bleach precursors (so-called bleach activators).

[0002] The invention also pertains to a process for manufacturing said bleach precursor particles.

10 Background of the Invention

[0003] Bleach precursor compositions have come into widespread use in recent years as heavy duty fabric cleaning products, particularly in automatic washing machines. The growth in usage of bleach activators has mirrored a decrease in fabric wash temperatures which itself has accompanied an increase in the proportion of fabrics that are coloured.

15 [0004] One problem that has become more significant as a result of these trends is that of damage to fabric colours and materials caused by the development of localised high concentrations of bleaching species. High bleach concentrations can arise around any particulate bleaching species for several reasons. The bleaching species may itself have an intrinsically low solubility, its solubility may have been hindered by the presence of other materials such as viscous surfactant phases or the agitation regime in the immediate environment of the bleach species may not be high enough to disperse the dissolved bleach. Where a bleach activator forms a component of the composition the potential problem is increased. In addition to the potential for localised high concentrations of perhydroxyl ion arising from dissolution of the inorganic perhydrate normally contained in laundry detergent compositions, the perhydrolysis of the bleach activator to form peroxycarboxyl anions can give rise to significant localised peroxycarboxylate bleach concentrations.

20 [0005] The development of so-called concentrated products and their delivery via dispensing devices placed in the machine drum together with the fabric load has merely served to exacerbate these problems. Accordingly a need exists to provide detergent compositions in which the bleach activator is incorporated in a form that minimises and preferably eliminates damage to fabric colours and materials during its dissolution and perhydrolysis in the wash liquor.

[0006] The prior art contains numerous examples of bleach activators coated or agglomerated so as to increase their stability on storage in detergent compositions and/or to influence their solution behaviour.

30 [0007] EP-A-0070474 discloses granulate bleach activators prepared by spray drying an aqueous pumpable dispersion containing an N-acyl or O-acyl compound together with at least one water soluble cellulose ether, starch or starch derivative in a weight ratio of activator to coating of from 98:2 to 90:10.

[0008] GB-A-1507312 discloses the coating of bleach activators with a mixture of alkali metal C₈ - C₂₂ fatty acid salts in admixture with the corresponding fatty acids. GB-A-1381121 employs a molten coating of inter alia C₁₄ - C₁₈ fatty acid mixtures to protect solid bleach activators. GB-A-1441416 discloses a similar process employing a mixture of C₁₂ - C₁₄ fatty acids and C₁₀ - C₂₀ aliphatic alcohols. EP-A-0375241 describes stabilised bleach activator extrudates in which C₅- C₁₈ alkyl peroxy carboxylic acid precursors are mixed with a binder selected from anionic and nonionic surfactants, film toning polymers fatty acids or mixtures of such binders.

40 [0009] EP-A-0356700 discloses compositions comprising a bleach activator, a water soluble film forming polymer and 2-15% of a C₃-C₆ polyvalent carboxylic acid or hydroxycarboxylic acid for enhanced stability and ease of dispersion/solubility. The carboxylic acid, of which a preferred example is citric acid, is dry mixed with the bleach activator and then granulated with the film forming polymer. The citric acid is asserted to provide an enhanced rate of dissolution of the bleach activator granules.

45 [0010] EP-A-0382464 concerns a process for coating or encapsulation of solid particles including bleaching compounds and bleach activators in which a melt is formed of coating material in which the particles form a disperse phase, the melt is destabilised and then caused to crumble to a particulate material in which the disperse phase particles are embedded in the continuous (coating) phase. A variety of coating materials are disclosed and certain materials such as polyacrylic acid and cellulose acetate phthalate are taught as being useful where release of the coated material is dependent on pH.

50 [0011] The overall emphasis in the prior art has thus been on the protection of the bleach activator against a hostile environment during storage and relatively little attention has been paid to the dissolution characteristics of the coated or agglomerated material in use. Where coating and/or agglomeration has been proposed with poorly soluble materials such as fatty acids, this has resulted in a rate of perhydrolysis of the bleach activator which is slower than that which would occur if it had not been so protected. Any use of more rapidly soluble materials such as citric acid has been in the context of an agglomerate component in which more rapid solution of the bleach activator has been the objective. In both instances, because perhydrolysis commences as soon as the detergent product starts to dissolve and form an alkaline hydrogen peroxide solution the problem of localised peroxy acid bleach concentrations has remained unsolved.

[0012] One solution to this problem would be to delay the start of perhydrolysis in order to avoid the fabric colour damage problems associated with the dissolution behaviour of other detergent product components. However it is important that perhydrolysis of the bleach precursor and subsequent dispersion of the peroxy-carboxylate bleach is as rapid as possible when it commences because of the short wash times of modern automatic washing machines.

[0013] The problem that arises in simultaneously satisfying these two objectives does not appear to have been recognised in the prior art.

[0014] It is known that the rate of perhydrolysis of a percarboxylic acid bleach precursor in an aqueous oxidising medium is progressively reduced as the pH of the medium is reduced, particularly when the pH falls below the pKa of the parent acid of the precursor leaving group. However the fatty acids taught as coating agents in the prior art are not useful as a means of providing a low pH environment in an aqueous wash liquor because of their insolubility. Moreover fatty acids used as coating and/or agglomerating agents for peroxy acid bleach precursors have been found to reduce the rate of perhydrolysis of the latter, thereby reducing the effectiveness of the resultant peroxy-carboxylic acid bleach.

[0015] Another problem encountered within the compositions of the prior art relates to the storage and handling properties of said compositions, and is thus an additional object of the present invention to provide a bleach precursor composition as a free-flowable powder which remains as such throughout prolonged storage time.

[0016] EP 429 108-A₂ describes bleach particles which are granulated with specific polymeric binders. DE 40 40 654-A₁ describes bleach activator particles of particle size around 0.1-0.4 mm, which are coated with specific polymeric materials.

[0017] It has further been found that a coated bleach precursor material can be improved by controlling the level of coating as a function of the particle size. This results in improved bleaching performance whilst maintaining stability, and safety to fabric colours. Alternatively, one can use the finding of the present invention to further reduce fabric damage for a given bleaching performance.

Summary of the Invention

[0018] The present invention is directed to a composition comprising particles of coated peroxyacid bleach precursor, wherein said composition comprises particles of different sizes, wherein said precursor comprises one or more N-, or O- acyl groups and has a M_{pt}>30°C, wherein said precursor is coated with a coating material, wherein said coating material is selected from water-soluble acidic polymers, wherein said polymers have a water solubility greater than 5 g/l at 20°C, a molecular weight of from 1000 to 250,000, wherein a 1% solution of said polymer has a pH of less than 7, preferably less than 5.5, and wherein the level of said coating in said particles is greater in particles of smaller size. Preferably, said precursor is co-agglomerated with a said water-soluble acidic polymer before it is coated.

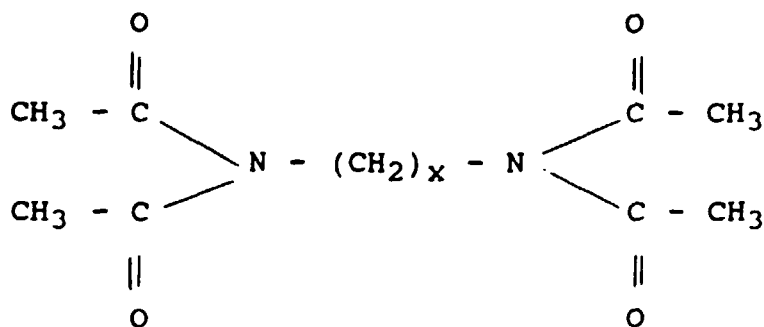
[0019] The invention also comprises a bleaching and a laundry detergent composition as well as a process for manufacturing said bleach precursor.

Detailed Description of the Invention

[0020] The compositions of the present invention comprise particles of coated peroxyacid bleach precursor. The compositions according to the present invention comprise particles of different sizes. All particles, which can be different or, preferably, identical as to the specific ingredients they comprise, comprise a solid peroxyacid bleach precursor, a coating material and, preferably a binder material.

[0021] As a first essential ingredient, the solid peroxyacid bleach precursor compositions of the present invention incorporate precursors containing 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 and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836988, 864,798, 1147871 and 2143231 and imides such as are disclosed in GB-A-855735 & 1246338.

[0022] Particularly preferred precursor compounds are the N-,N,N¹N¹ tetra acetylated compounds of formula



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

[0023] Examples include tetra acetyl methylene diamine (TAMD) in which x=1, tetra acetyl ethylene diamine (TAED) in which x=2 and tetraacetyl hexylene diamine (TAHD) in which x=6. These and analogous compounds are described in GB-A-907356. The most preferred peroxyacid bleach precursor is TAED.

[0024] Solid peroxyacid bleach precursors useful in the present invention have a Mpt>30°C and preferably >40°C. Such precursors will normally be in fine powder or crystalline form in which at least 90% by weight of the powder has a particle size < 150 micrometers.

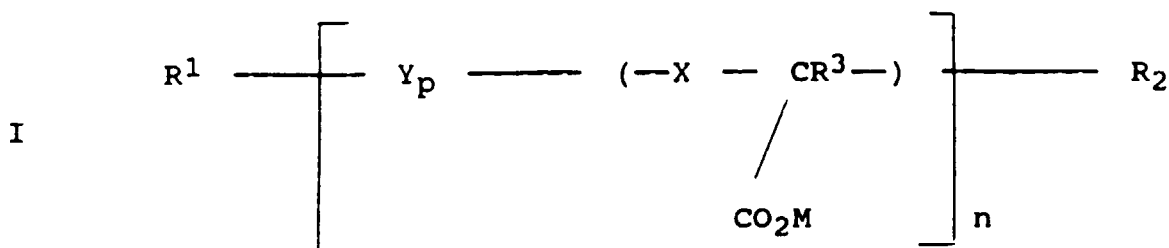
[0025] Another essential ingredient of the compositions according to the present invention is a water-soluble acidic polymer. Said polymer is used in the compositions according to the present invention as the coating material to coat said precursor. In one embodiment of the present invention, said precursor is co-agglomerated with a binder material before it is coated. Said binder material is preferably but not necessarily also a said water-soluble acidic polymer. In a preferred embodiment of the invention the binder material and the coating material are different water-soluble acidic polymers, but in another, most preferred embodiment of the present invention, the binder material and the coating material are the same water-soluble acidic polymer.

[0026] Suitable polymers for use herein are water-soluble. By water-soluble, it is meant herein that the polymers have a solubility greater than 5 g/l at 20°C.

[0027] Suitable polymers for use herein are acidic. By acidic, it is meant herein that a 1% solution of said polymers has a pH of less than 7, preferably less than 5.5.

[0028] Suitable polymers for use herein have a molecular weight in the range of from 1000 to 280,000, preferably from 1500 to 150,000, preferably, suitable polymers for use herein have a melting point superior to 30°C.

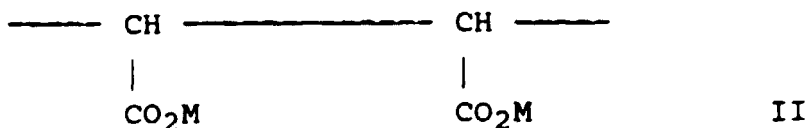
[0029] Suitable polymers which meet the above criteria and are therefore particularly useful in the present invention, include those having the following empirical formula I :



wherein X is O or CH₂; Y is a comonomer or comonomer mixture; R¹ and R² are bleach-stable polymer-end groups; R³ is H, OH or C₁₋₄ alkyl; M is H, and mixtures thereof with alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, and mixtures thereof. the proportion of M being H in such polymers must be such as to ensure that the polymer is sufficiently acidic to meet the acidity criteria as hereinbefore defined.

[0030] Polymers according to formula I are known in the field of laundry detergents, and are typically used as chelating agents, as for instance in GB-A-1,597,756. Preferred polycarboxylate polymers fall into several categories. A first category belongs to the class of copolymeric polycarboxylate polymers which, formally at least, are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid and mesaconic acid as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an alpha -C₁₋₄ alkyl acrylic acid as second monomer. Referring to formula I, therefore, preferred polycarboxylate polymers of this type are those in which X is CH₂, R³ is H or C₁₋₄ alkyl, especially methyl, p is from about 0.1 to about 1.9, preferably from about 0.2 to about 1.5, n averages

from about 10 to about 1500, preferably from about 50 to about 1000, more preferably from 100 to 800, especially from 120 to 400 and Y comprises monomer units of formula II



[0031] Such polymers are available from BASF under the trade name Sokalan^(R) CP5 (neutralized form) and Sokalan^(R) CP45 (acidic form) of which the former, however, is not a polymer as described in claim 1.

[0032] A second category belongs to the class of polycarboxylate polymers in which referring to formula I, X is CH₂, R³ is OH, p is from 0 to 0.1, preferably 0 and n averages from about 50 to about 1500, preferably from about 100 to 1000. Y, if present, can be a polycarboxylic acid such as II above, or an ethylene oxide moiety.

[0033] A third category belongs to the class of acetal polycarboxylate polymers in which, referring to formula I, X is), R³ is H, p is from 0 to 0.1, preferably 0 and n averages from 10 to 500. If present, Y again can be a polycarboxylic acid such as II above or an ethyleneoxide moiety.

[0034] A fourth category belongs to the class of polycarboxylate polymers in which referring to formula I, X is CH₂, R³ is H or C₁₋₄ alkyl, p is 0 and n averages from about 10 to 1500, preferably from about 500 to 1000.

[0035] A fifth category of polycarboxylate polymers has the formula I in which X is CH₂, R³ is H or C₁₋₄ alkyl, especially methyl, p is from 0.01 to 0.09, preferably from 0.02 to 0.06, n averages from about 10 to about 1500, preferably from about 15 to about 300 and Y is a polycarboxylic acid formed from maleic acid, citraconic acid, itaconic acid or mesaconic acid, highly preferred being maleic acid-derived comonomers of formula II above.

[0036] The bleach-stable polymer end groups in formula I suitably include alkyl groups, oxyalkyl groups and alkyl carboxylic acid groups and salts and esters thereof.

[0037] In formula I above, M is H or mixtures thereof with alkali metal, alkaline earth metal, ammonium or substituted ammonium. The proportion of M which is H is such as to ensure that the polymer meets the pH criteria described herein above.

[0038] In the above, n, the degree of polymerization of the polymer can be determined from the weight average polymer molecular weight by dividing the latter by the average monomer molecular weight. Thus, for a maleic-acrylic copolymer having a weight average molecular weight of 15,500 and comprising 30 mole % of maleic acid derived units, n is 182 (i.e. 15,500/(116 x 0.3 + 72 x 0.7)).

[0039] In case of doubt, weight-average polymer molecular weights can be determined herein by gel permeation chromatography using Water [mu] Porasil (RTM) GPC 60 A2 and [mu] Bondagel (RTM) E-125, E-500 and E-1000 in series, temperature-controlled columns at 40°C against sodium polystyrene sulphonate polymer standards, available from Polymer Laboratories Ltd., Shropshire, UK, the polymer standards being 0.15M sodium dihydrogen phosphate and 0.02M tetramethyl ammonium hydroxide at pH 7.0 in 80/20 water/acetonitrile.

[0040] Mixtures of polycarboxylate polymers are also suitable herein, especially mixtures comprising a high molecular weight component having an n value of at least 100, preferably at least 120, and a low molecular weight component having an n value of less than 100, preferably from 10 to 90, more preferably from 20 to 80. Such mixtures are optimum from the viewpoint of providing excellent bleach stability and anti-incrustation performance in the context of a zero-phosphate detergent formula.

[0041] In mixtures of this type, the weight ratio of high molecular weight component to low molecular weight component is generally at least 1:1, preferably from about 1:1 to about 20:1, more preferably from about 1.5:1 to about 10:1, especially from about 2:1 to about 8:1. Preferred polycarboxylate polymers of the low molecular weight type are polycarboxylate polymers of the fourth category (homopolyacrylate polymers) listed above.

[0042] Of all the above, highly preferred polycarboxylate polymers herein are those of the first category in which n averages from 100 to 800, preferably from 120 to 400 and mixtures thereof with polycarboxylate polymers of the fourth category in which n averages from 10 to 90, preferably from 20 to 80.

[0043] Other suitable polymers for use herein include polymers derived from amino acids such as polyglutamine acid, and polyaspartic acid, as disclosed in EP-A-0 305 282, and EP-A-0 351 629.

[0044] The particles in the compositions according to the present invention comprise from 30% to 93% by weight of the total composition of said peroxyacid bleach precursor, preferably from 70% to 88%. Furthermore, the particles in the compositions according to the present invention comprise from 7% to 70% by weight of the total composition of said binding agent, preferably from 12% to 30%.

[0045] The composition according to the invention comprises particles described hereinabove of different size. Another essential feature of the present invention is that the level of coating should be greater in the smaller particles

than in the bigger particles.

[0046] Particles of different sizes in the composition of the present invention can be separated by using sieves. The compositions according to the present invention comprise particles of from 100 micrometers to 1700 micrometers, i.e. all particles which pass through a sieve of 1700 micrometer and which do not pass through a sieve of 100 micrometer. Smaller and bigger particles are not suitable for the purpose of the present invention.

[0047] The composition according to the present invention can be separated in at least two classes, each class comprising particles within a size range. For each class, the mean coating level can be determined. Compositions according to the present invention are those where the mean coating level is greater for the particles belonging to the class of smaller particle size.

[0048] For each particle size class, the mean coating level, as used herein, is the amount of coating material expressed in weight % based on the total weight of the particles in the class, i.e. the mean coating level does not take into account the differences in particle sizes within a given class. As used herein, the mean coating level of the composition according to the present invention is the amount of coating material, expressed in weight %, based on the total weight of the composition.

[0049] Depending on the polymer used for agglomeration and coating in the compositions according to the present invention, different analytical means can be used to measure the amount of polymer in the particles, thus the coating level. Such means include colorimetric titration with ferrothiocyanate, photometric titration with chromotropes, gas chromatography, etc. A preferred and simple method is an acid-base titration calibrated with the polymer. In the preferred embodiment of the present invention where the binder material and the coating material are the same polymer, the coating level can be determined by measuring the amount of polymer in an agglomerated but uncoated sample, measuring the amount of polymer in an agglomerated and coated sample of same weight, then calculating the difference between both samples. Suitable compositions herein have a mean coating level of from 2% to 25%, preferably 5% to 20%, most preferably 5% to 15%.

[0050] Preferred composition herein can be splitted in particles belonging to three classes.

[0051] A first class comprises particles of from 1700 to 850 micrometers. Particles of said first class have a mean coating level which is of from more than 0% to 100% of the mean coating level of the composition, preferably 0% to 50%.

[0052] A second class comprises particles of from less than 850 micrometers to 500 micrometers. Particles of said second class have a mean coating level of from 0% to 150% of the mean coating level of the composition, preferably from 0% to 100%.

[0053] A third class comprises particles of from less than 500 micrometers to 250 micrometers. Particles of said third class have a mean coating level of from 50% to 300 % of the mean coating level of the composition, preferably from 75% to 275%, most preferably 100% to 250%

[0054] A process for manufacturing a preferred solid peroxyacid bleach precursor according to the present invention includes the steps of :

- co-agglomerating a peroxyacid bleach precursor with a binder material as hereinbefore defined;
- optionally drying said co-agglomerate;
- coating said dried co-agglomerate with a coating material as hereinbefore defined. Such that the level of coating in said particles is greater in particles of smaller size;
- drying said coated co-agglomerate.

[0055] According to said process the peroxyacid bleach precursor powder must be co-agglomerated into a water-soluble acidic polymer binder material as hereinbefore defined. Any agglomerating technique known to the man skilled in the art is suitable for use herein.

[0056] The co-agglomerated particulate material does not itself provide the benefits of the invention, and said co-agglomerated material needs to be coated with a water-soluble acidic polymer as hereinabove defined. The coating of the co-agglomerated material with the coating material can be carried out in several ways.

[0057] The coating material may be sprayed on as a molten material or as a solution or dispersion in a solvent/carrier liquid which is subsequently removed by evaporation. The coating material can also be applied as a powder coating e.g. by electrostatic techniques although this is less preferred as the adherence of powdered coating material is more difficult to achieve and can be more expensive.

[0058] Molten coating is a preferred technique for coating materials of Mpt<80°C but is less convenient for higher Melting Point acids (i.e. >100°C). For coating materials of Mpt>80°C, spray on as a solution or dispersion is preferred. Organic solvents such as ethyl and isopropyl alcohol can be used to form the solutions or dispersions, although this will necessitate a solvent recovery stage in order to make their use economic. However, the use of organic solvents also gives rise to safety problems such as flammability and operator safety and thus aqueous solutions or dispersions are preferred.

[0059] Aqueous solutions are particularly advantageous as the coating materials herein have a high aqueous solubility, provided the solution has a sufficiently low viscosity to enable it to be handled. Preferably a concentration of at least 25% by weight of the coating material in the solvent is used in order to reduce the drying/evaporation load after surface treatment has taken place. The treatment apparatus can be any of those normally used for this purpose, such as inclined rotary pans, rotary drums and fluidised beds, high and low speed mixers (Lödige).

[0060] In the present invention, it is essential to control the coating distribution to ensure that the smaller particles are more coated than the larger particles.

[0061] An appropriate way to control the coating level as a function of the particle size in the process to be used for the manufacturing of the particles of the present invention, is to separate the particles of the composition into several streams of particles of different sizes after the agglomeration step, and coat-treat each stream individually.

[0062] A more elegant way to control the coating level on the particles is to use a fluid bed where the particles are fluidized in an air stream. This fluidising provides a natural particle size gradient with smaller particles at the top of the bed and larger particles at the bottom. The coating material is then sprayed onto the particles, and an appropriate coating can be achieved by appropriately positioning the spray jet or jets. Specifically, increased spraying at the top of the bed will provide a higher coating level on the small particles.

[0063] Solid peroxyacid bleach precursor compositions in accordance with the invention can be used in a variety of applications. Thus the peroxyacid bleach compositions may themselves be incorporated into other solid compositions such as tablets, extrudates and agglomerates. The compositions can also be suspended in nonaqueous liquid compositions in which the organic acid surface treating material is insoluble and inert. However, the preferred application for the solid peroxybleach precursor compositions of the invention is as particulate components of granular detergent compositions, particularly the so-called concentrated detergent compositions that are added to a washing machine by means of a dosing device placed in the machine drum with the soiled fabric load. Concentrated granular detergent compositions dispensed into the wash liquor via a dosing device are more subject to dissolution problems than compositions added via the dispensing compartment of a washing machine because, in the initial stages of a wash cycle, the agitation in the immediate environment of the product is inhibited by the presence of the fabric load. Whilst this can constitute a benefit in permitting the development of high transient concentrations of builder and surfactant, the development of high transient peroxyacid concentrations can, as noted previously, lead to fabric and colour damage. The compositions of the present invention, when incorporated into concentrated detergent products delivered to the wash liquor via a dispensing device, mitigate if not eliminate this problem.

[0064] Detergent compositions incorporating the coated peroxy acid bleach precursor composition of the present invention will normally contain from 0.5% to 20% of the precursor composition, more frequently from 1% to 9% and most preferably from 3% to 8%, on a composition weight basis.

[0065] Such detergent compositions will, of course, contain a source of alkaline hydrogen peroxide necessary to form a peroxyacid bleaching species in the wash solution and preferably will also contain other components conventional in detergent compositions. Thus preferred detergent compositions will incorporate one or more of surfactants, organic and inorganic builders, soil suspending and anti-redeposition agents, suds suppressors, enzymes, fluorescent whitening agents, photo activated bleaches, perfumes and colours.

[0066] Detergent compositions incorporating the coated particulate peroxyacid precursors of the present invention will include an inorganic perhydrate bleach, normally in the form of the sodium salt, as the source of alkaline hydrogen peroxide in the wash liquor. This perhydrate is normally incorporated at a level of from 3% to 35% by weight, more preferably from 3% to 35% by weight and most preferably from 5% to 30% by weight of the composition.

[0067] The perhydrate may be any of the inorganic salts such as perborate, percarbonate, perphosphate and persilicate salts but is conventionally an alkali metal perborate or percarbonate. Whilst fabric colour damage arising from compositions in accordance with the invention is low, irrespective of whether a perborate or percarbonate salt is employed, the improvement in comparison with uncoated precursor particulates is more noticeable with percarbonate bleach as this causes greater fabric colour damage in the absence of any coating on the bleach precursor.

[0068] Sodium percarbonate, which is the preferred perhydrate, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1, 1-diphosphonic acid (HEDP) or an amino-phosphonate, that is incorporated during the manufacturing process. For the purposes of the detergent composition aspect of the present invention, the percarbonate can be incorporated into detergent compositions without additional protection, but preferred executions of such compositions utilise a coated form of the material. A suitable coating is sodium silicate of $\text{SiO}_2\text{:Na}_2\text{O}$ ratio from 1.6:1 to 3.4:1, preferably 2.8:1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Another coating is a mixed salt of an alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interlox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1:200 to 1:4, more preferably from 1:99 to 1:9, and most preferably from 1:49 to 1:19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula

$\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5. Magnesium silicate can also be included in the coating.

[0069] The particle size range of the crystalline percarbonate is from 350 micrometers to 450 micrometers with a mean of approximately 400 micrometers. When coated, 60 % to 80% by weight of the crystals have a size greater than 425 micrometers, with a mean of approximately 650 micrometers

[0070] Whilst heavy metals present in the sodium carbonate used to manufacture the percarbonate can be controlled by the inclusion of sequestrants in the reaction mixture, the percarbonate still requires protection from heavy metals present as impurities in other ingredients of the product. Accordingly, in detergent compositions utilising percarbonate as the perhydrate salt, the total level of Iron, Copper and Manganese ions in the product should not exceed 25 ppm and preferably should be less than 20 ppm in order to avoid an unacceptably adverse effect on percarbonate stability. Detergent compositions in which alkali metal percarbonate bleach has enhanced stability are disclosed in the prior art.

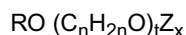
[0071] A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US-A-3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in US-A-4,259,217 issued to Murphy on March 31, 1981.

[0072] Mixtures of anionic surfactants are suitable herein, particularly blends of sulphate, sulphonate and/or carboxylate surfactants. Mixtures of sulphonate and sulphate surfactants are normally employed in a sulphonate to sulphate weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C_{12} - C_{18} fatty source, preferably from a C_{16} - C_{18} fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants in such sulphonate sulphate mixtures are alkyl sulphates having from 12 to 22, preferably 16 to 18 carbon atoms in the alkyl radical. Another useful surfactant system comprises a mixture of two alkyl sulphate materials whose respective mean chain lengths differ from each other. One such system comprises a mixture of C_{14} - C_{15} alkyl sulphate and C_{16} - C_{18} alkyl sulphate in a weight ratio of C_{14} - C_{15} : C_{16} - C_{18} of from 3:1 to 1:1. The alkyl sulphates may also be combined with alkyl ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. The cation in each instance is again an alkali metal, preferably sodium. Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula $\text{R}-\text{CON}(\text{R}')\text{CH}_2\text{COOM}$ wherein R is a C_9 - C_{17} linear or branched alkyl or alkenyl group, R' is a C_1 - C_4 alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C_{12} - C_{14}), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

[0073] One class of nonionic surfactants useful in the present invention comprises condensates of ethylene oxide with a hydrophobic moiety, providing surfactants having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

[0074] Especially preferred nonionic surfactants of this type are the C_9 - C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{14} - C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C_{12} - C_{14} primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

[0075] Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

[0076] A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_8 - C_{20} , preferably C_{10} - C_{14} N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

[0077] Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_8 - C_{16} , preferably C_{10} - C_{14} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

[0078] The detergent compositions comprise from 5% to 20% of surfactant but more usually comprise from 7% to 20%, more preferably from 10% to 15% surfactant by weight of the compositions.

[0079] Combinations of surfactant types are preferred, more especially anionic-nonionic and also anionic-nonionic-cationic blends. Particularly preferred combinations are described in GB-A-2040987 and EP-A-0087914. Although the

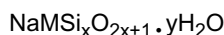
surfactants can be incorporated into the compositions as mixtures, it is preferable to control the point of addition of each surfactant in order to optimise the physical characteristics of the composition and avoid processing problems. Preferred modes and orders of surfactant addition are described hereinafter.

[0080] Another highly preferred component of detergent compositions incorporating the coated peroxy acid precursor particulates of the invention is a detergent builder system comprising one or more non-phosphate detergent builders. These can include, but are not restricted to alkali metal carbonates, bicarbonates, silicates, aluminosilicates, monomeric polycarboxylates, 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 than two carbon atoms, organic phosphonates and aminoalkylene poly (alkylene phosphonates) and mixtures of any of the foregoing. The builder system is present in an amount of from 25% to 60% by weight of the composition, more preferably from 30% to 60% by weight.

[0081] Preferred builder systems are free of boron compounds and any polymeric organic materials are preferably biodegradable.

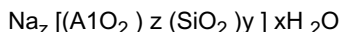
[0082] Suitable silicates are those having an $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range from 1.6 to 3.4, the so-called amorphous silicates of $\text{SiO}_2\text{:Na}_2\text{O}$ ratios from 2.0 to 2.8 being preferred. These materials can be added at various points of the manufacturing process, such as in a slurry of components that are spray dried or in the form of an aqueous solution serving as an agglomerating agent for other solid components, or, where the silicates are themselves in particulate form, as solids to the other particulate components of the composition. However, for compositions in which the percentage of spray dried components is low i.e. 30%, it is preferred to include the amorphous silicate in the spray-dried components.

[0083] Within the silicate class, highly preferred materials are crystalline layered sodium silicates of general formula



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. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α , β , γ and 5 forms of $\text{Na}_2\text{Si}_2\text{O}_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-11 and NaSKS-6. The most preferred material is 5- $\text{Na}_2\text{Si}_2\text{O}_5$, (NaSKS-6). Crystalline layered silicates are incorporated either as dry mixed solids, or as solid components of agglomerates with other components.

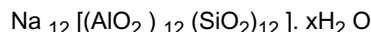
[0084] Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate zeolites have the unit cell formula



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 materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

[0085] The above aluminosilicate ion exchange materials are further characterised by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer. The aluminosilicate ion exchange materials are further characterised by their calcium ion exchange capacity, which is at least 200 mg equivalent of CaCO_3 water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterised by their calcium ion exchange rate which is at least 130 mg equivalent of CaCO_3 /litre/minute/(g/litre) [2 grains Ca^{++} /gallon/minute/gram/gallon] of aluminosilicate (anhydrous basis), and which generally lies within the range of from 130 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [2 grains/gallon/minute/(gram/gallon)] to 390 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [6 grains/gallon/minute/(gram/gallon)], based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 260 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [4 grains/gallon/minute/(gram/gallon)].

[0086] Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US-A-3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6 [(\text{AlO}_2)_6 (\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

[0087] Suitable water-soluble monomeric or oligomeric carboxylate builders include lactic acid, glycolic acid and ether derivatives thereof as disclosed in BE-A-831,368, 821,369 and 821,370. 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 described in DE-A-2,446,686, and 2,446,687 and US-A-3,935,257 and the sulfinyl carboxylates described in BE-A-840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethoxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, and aminosuccinates described in NL-A-7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in GB-A-1,387,447.

[0088] Polycarboxylates containing four carboxy groups include oxydiscuccinates disclosed in GB-A-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 GB-A-1,398,421 and 1,398,422 and in US-A-3,936,448, and the sulfonated pyrolysed citrates described in GB-A-1,439,000.

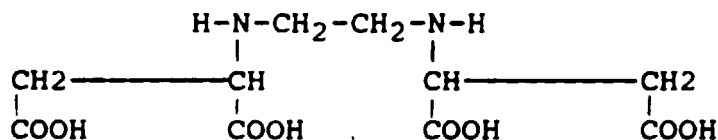
[0089] Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadiene pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB-A-1,425,343. Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

[0090] The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of detergent compositions in accordance with the present invention.

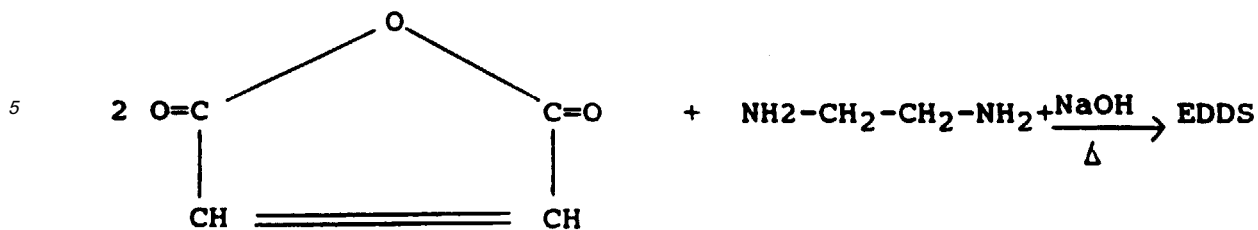
[0091] Other suitable water soluble organic salts are the homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. 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 70,000, especially about 40,000. Such builder polymeric materials may be identical to the polymeric materials as binder materials and coating materials, as described hereinabove. These materials are normally used at levels of from 0.5% to 10% by weight more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

[0092] Another preferred polycarboxylate builder is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include NaEDDS, Na_2EDDS and Na_4EDDS . Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

[0093] The structure of the acid form of EDDS is as follows :



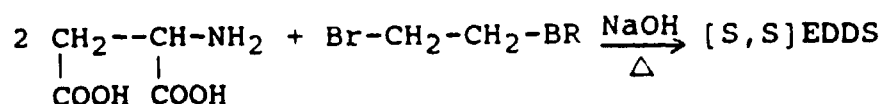
[0094] EDDS can be synthesised, for example, from readily available, inexpensive starting material such as maleic anhydride and ethylene diamine as follows :



[0095] A more complete disclosure of methods for synthesising EDDS from commercially available starting materials can be found in US -A-3,158,635, Kezerian and Ramsay, issued November 24, 1964.

[0096] The synthesis of EDDS from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R],[S,S], and [S,R], due to the two asymmetric carbon atoms. The biodegradation of EDDS is optical isomerspecific, with the [S,S] isomer degrading most rapidly and extensively, and for this reason the [S,S] isomer is most preferred for inclusion in the compositions of the invention.

[0097] The [S,S] isomer of EDDS can be synthesised from L-aspartic acid and 1,2-dibromoethane, as follows :



[0098] A more complete disclosure of the reaction of L-aspartic acid with 1,2-dibromoethane to form the [S,S] isomer of EDDS can be found in Neal and Rose, Stereospecific Ligands and Their Complexes of Ehtylenediaminediscuccinic Acid, *Inorganic Chemistry*, Vol 7 (1968), pp. 2405-2412.

[0099] Organic phosphonates and amino alkylene poly (alkylene phosphonates) include alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates, although these materials are less preferred where the minimisation of phosphorus compounds in the compositions is desired.

[0100] For the purposes of detergent compositions embodying the surface treated bleach precursor particulates of the invention, the non-phosphate builder ingredient will comprise from 25% to 60% by weight of the compositions, more preferably from 30% to 60% by weight. Within the preferred compositions, sodium aluminosilicate such as Zeolite A will comprise from 20% to 60% by weight of the total amount of builder, a monomeric or oligomeric carboxylate will comprise from 10% to 30% by weight of the total amount of builder and a crystalline layered silicate will comprise from 10% to 65% by weight of the total amount of builder. In such compositions the builder ingredient preferably also incorporates a combination of auxiliary inorganic and organic builders such as sodium carbonate and maleic anhydride/acrylic acid copolymers in amounts of up to 35% by weight of the total builder.

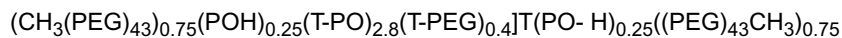
[0101] Anti-redeposition and soil-suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo-or co-polymeric polycarboxylic acids or their salts. Polymers of this type include copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

[0102] Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

[0103] Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino -4-anilino-2-triazin-6-ylaminostilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, monosodium 4',4''-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2- sulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-2-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)stilbene-2,2'-disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-

6-ylamino)stilbene- 2,2¹disulphonate and sodium 2(stilbyl-4¹¹-(naphtho-1¹,2¹:4,5)-1,2,3 - triazole-2¹¹- sulphonate.

[0104] Soil-release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US-A-4116885 and 4711730 and EP-A-0272033. A particular preferred polymer in accordance with EP-A-0272033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pCOC}_6\text{H}_4\text{CO})$.

[0105] Certain polymeric materials such as polyvinyl pyrrolidones typically of MWt 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

[0106] Another optional detergent composition ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms, exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

[0107] As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

[0108] A preferred silicone suds controlling agent is disclosed in Bartolotta et al. US-A-3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in DE-A-2,646,126 published April 28, 1977. An example of such a compound is DC0544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

[0109] The suds suppressors described above are normally employed at levels of from 0.001% to 0.5% by weight of the composition, preferably from 0.01% to 0.1% by weight.

[0110] The preferred methods of incorporation comprise either application of the suds suppressors in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation of the suds suppressors into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C₂₀-C₂₄ fatty acids, microcrystalline waxes and high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al US-A-3,933,672.

[0111] Another optional ingredient useful in the present invention is one or more enzymes.

[0112] Preferred enzymatic materials include the commercially available amylases, neutral and alkaline proteases, lipases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US-A-3,519,570 and 3,533,139.

[0113] Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0011340.

[0114] Their combination with mono C₁₂-C₁₄ quaternary ammonium salts is disclosed in EP-B-0026527 & 528. Other useful organic fabric softening agents are the dilong chain amides as disclosed in EP-B-0242919. Additional organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0299575 and 0313146.

[0115] Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight, whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. Where a portion of the composition is spray dried, these materials can be added to the aqueous slurry fed to the spray drying tower, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

[0116] The coated peroxyacid bleach precursor particulates of the present invention are particularly useful in concen-

trated granular detergent compositions that are characterised by a relatively high density in comparison with conventional laundry detergent compositions. Such high density compositions have a bulk density of at least 650 g/litre, more usually at least 700 g/litre and more preferably in excess of 800 g/litre.

[0117] Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

[0118] To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement e.g. a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide the bulk density in g/litre. Replicate measurements are made as required.

[0119] Concentrated detergent compositions also normally incorporate at least one multi-ingredient component i.e. they do not comprise compositions formed merely by dry-mixing individual ingredients. Compositions in which each individual ingredient is dry-mixed are generally dusty, slow to dissolve and also tend to cake and develop poor particle flow characteristics in storage.

[0120] Subject to the above bulk density and component content limitations, the compositions of the invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation and preferred methods involve combinations of these techniques. A preferred method of making the compositions involves a combination of spray drying, agglomeration in a high speed mixer and dry mixing.

[0121] Preferred detergent compositions in accordance with the invention comprise at least two particulate multi-ingredient components. The first component comprises at least 15%, conventionally from 25% to 50%, but more preferably no more than 35% by weight of the composition and the second component from 1% to 50%, more preferably 10% to 40% by weight of the composition.

[0122] The first component comprises a particulate incorporating an anionic surfactant in an amount of from 0.75% to 40% by weight of the powder and one or more inorganic and/or organic salts in an amount of from 99.25% to 60% by weight of the powder. The particulate can have any suitable form such as granules, flakes, prills, marumes or noodles but is preferably granular. The granules themselves may be agglomerates formed by pan or drum agglomeration or by in-line mixers but are customarily spray dried particles produced by atomising an aqueous slurry of the ingredients in a hot air stream which removes most of the water. The spray dried granules are then subjected to densification steps, e.g. by high speed cutter mixers and/or compacting mills, to increase density before being reagglomerated. For illustrative purposes, the first component is described hereinafter as a spray dried powder.

[0123] Suitable anionic surfactants for the purposes of the first component have been found to be slowly dissolving linear alkyl sulfate salts in which the alkyl group has an average of from 16 to 22 carbon atoms, and linear alkyl carboxylate salts in which the alkyl group has an average of from 16 to 24 carbon atoms. The alkyl groups for both types of surfactant are preferably derived from natural sources such as tallow fat and marine oils.

[0124] The level of anionic surfactant in the spray dried powder forming the first component is from 0.75% to 40% by weight, more usually 2.5% to 25% preferably from 3% to 20% and most preferably from 5% to 15% by weight. Water-soluble surfactants such as linear alkyl benzene sulphonates or C₁₄-C₁₅ alkyl sulphates can be included or alternatively may be applied subsequently to the spray dried powder by spray on.

[0125] The other major ingredient of the spray dried powder is one or more inorganic or organic salts that provide the crystalline structure for the granules. The inorganic and/or organic salts may be water-soluble or water-insoluble, the latter type being comprised by the, or the major part of the, water-insoluble builders where these form part of the builder ingredient. Suitable water soluble inorganic salts include the alkali metal carbonates and bicarbonates. Alkali metal silicates other than crystalline layered silicates can also be present in the spray dried granule provided that aluminosilicate does not form part of the spray dried component.

[0126] However, in concentrated detergent compositions it is preferred that water-soluble sulphate, particularly sodium sulphate, should not be present at a level of more than 2.5% by weight of the composition. Preferably no sodium sulphate is added as a separate ingredient and its incorporation as a by-product e.g. with sulph(on)ated surfactants, should be minimised.

[0127] Where an aluminosilicate zeolite forms the, or part of the, builder ingredient, it is preferred that it is not added directly by dry-mixing to the other components, but is incorporated into the multi-ingredient component(s). Where incorporation of the zeolite takes place in the spray-dried granule, any silicate present should not form part of the spray-dried granule. In these circumstances, incorporation of the silicate can be achieved in several ways, e.g. by producing a separate silicate-containing spray-dried particulate, by incorporating the silicate into an agglomerate of other ingredients, or more preferably by adding the silicate as a dry mixed solid ingredient.

[0128] The first component can also include up to 15% by weight of miscellaneous ingredients such as brighteners, anti-redeposition agents, photoactivated bleaches (such as tetrasulfonated zinc phthalocyanine) and heavy metal sequestering agents. Where the first component is a spray dried powder it will normally be dried to a moisture content of from 7% to 11% by weight, more preferably from 8% to 10% by weight of the spray dried powder. Moisture contents of powders produced by other processes such as agglomeration may be lower and can be in the range 1-10% by weight.

[0129] The particle size of the first component is conventional and preferably not more than 5% by weight should be above 1.4mm, while not more than 10% by weight should be less than 0.15 mm in maximum dimension. Preferably at least 60%, and most preferably at least 80%, by weight of the powder lies between 0.7 mm and 0.25 mm in size. For spray dried powders, the bulk density of the particles from the spray drying tower is conventionally in the range from 540 to 600 g/litre and this is then enhanced by further processing steps such as size reduction in a high speed cutter/mixer followed by compaction. Alternatively, processes other than spray drying may be used to form a high density particulate directly.

[0130] A second component of a preferred composition in accordance with the invention is another multi-ingredient particulate containing a water soluble surfactant.

[0131] This may be anionic, nonionic, cationic or semipolar in type or a mixture of any of these. Suitable surfactants are listed hereinbefore but preferred surfactants are C₁₄-C₁₅ alkyl sulphates, linear C₁₁-C₁₅ alkyl benzene sulphonates and fatty C₁₄-C₁₈ methyl ester sulphonates.

[0132] The second component may have any suitable physical form, i.e. it may take the form of flakes, prills, marumes, noodles, ribbons, or granules which may be spray-dried or non spray-dried agglomerates. Although the second component could in theory comprise the water soluble surfactant on its own, in practice at least one organic or inorganic salt is included to facilitate processing. This provides a degree of crystallinity, and hence acceptable flow characteristics, to the particulate and may be any one or more of the organic or inorganic salts present in the first component.

[0133] The particle size range of the second component should be such as to obviate segregation from the particles of the first component when blended therewith. Thus not more than 5% by weight should be above 1.4 mm while not more than 10% should be less than 0.15 mm in maximum dimension.

[0134] The bulk density of the second component will be a function of its mode of preparation. However, the preferred form of the second component is a mechanically mixed agglomerate which may be made by adding the ingredients dry or with an agglomerating agent to a pan agglomerator, Z blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050 F.R.G. By this means the second component can be given a bulk density in the range from 650 g/litre to 1190 g/litre more preferably from 750 g/litre to 850 g/litre.

[0135] Preferred compositions include a level of alkali metal carbonate in the second component corresponding to an amount of from 3% to 15% by weight of the composition, more preferably from 5% to 12% by weight. This will provide a level of carbonate in the second component of from 20% to 40% by weight.

[0136] A highly preferred ingredient of the second component is also a hydrated water insoluble aluminosilicate ion exchange material of the synthetic zeolite type, described hereinbefore, present at from 10% to 35% by weight of the second component. The amount of water insoluble aluminosilicate material incorporated in this way is from 1% to 10% by weight of the composition, more preferably from 2% to 8% by weight.

[0137] In one process for preparing the second component, the surfactant salt is formed in situ in an inline mixer. The liquid acid form of the surfactant is added to a mixture of particulate anhydrous sodium carbonate and hydrated sodium aluminosilicate in a continuous high speed blender, such as a Lodige KM mixer, and neutralised to form the surfactant salt whilst maintaining the particulate nature of the mixture. The resultant agglomerated mixture forms the second component which is then added to other components of the product. In a variant of this process, the surfactant salt is pre-neutralised and added as a viscous paste to the mixture of the other ingredients. In the variant, the mixer serves merely to agglomerate the ingredients to form the second component.

[0138] In a particularly preferred process for making detergent compositions incorporating the coated peroxyacid bleach precursor particulates of the invention, part of the spray dried product comprising the first granular component is diverted and subjected to a low level of nonionic surfactant spray on before being rebled with the remainder. The second granular component is made using the preferred process described above. The first and second components together with the coated bleach precursor particulate and the perhydrate bleach, other dry mix ingredients such as any carboxylate chelating agent, soil-release polymer, silicate of conventional or crystalline layered type, and enzyme are then fed to a conveyor belt, from which they are transferred to a horizontally rotating drum in which perfume and silicone suds suppressor are sprayed on to the product. In highly preferred compositions, a further drum mixing step is employed in which a low (approx. 2% by weight) level of finely divided crystalline material is introduced to increase density and improve granular flow characteristics.

[0139] In preferred concentrated detergent products incorporating an alkali metal percarbonate as the perhydrate salt

it has been found necessary to control several aspects of the product such as its heavy metal ion content and its equilibrium relative humidity. Sodium percarbonate-containing compositions of this type having enhanced stability are disclosed in the prior art.

[0140] Compositions in accordance with the invention can also benefit from delivery systems that provide transient localised high concentrations of product in the drum of an automatic washing machine at the start of the wash cycle, thereby also avoiding problems associated with loss of product in the pipework or sump of the machine.

[0141] Delivery to the drum can most easily be achieved by incorporation of the composition in a bag or container from which it is rapidly releasable at the start of the wash cycle in response to agitation, a rise in temperature or immersion in the wash water in the drum. Alternatively the washing machine itself may be adapted to permit direct addition of the composition to the drum e.g. by a dispensing arrangement in the access door.

[0142] Products comprising a detergent composition enclosed in a bag or container are usually designed in such a way that container integrity is maintained in the dry state to prevent egress of the contents when dry, but are adapted for release of the container contents on exposure to a washing environment, normally on immersion in an aqueous solution.

[0143] Usually the container will be flexible, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in EP-A-0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in EP-A-0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

[0144] In a variant of the bag or container form, laminated sheet products can be employed in which a central flexible layer is impregnated and/or coated with a composition and then one or more outer layers are applied to produce a fabric-like aesthetic effect. The layers may be sealed together so as to remain attached during use or may separate on contact with water to facilitate the release of the coated or impregnated material.

[0145] An alternative laminate form comprises one layer embossed or deformed to provide a series of pouch-like containers into each of which the detergent components are deposited in measured amounts, with a second layer overlying the first layer and sealed thereto in those areas between the pouch-like containers where the two layers are in contact. The components may be deposited in particulate, paste or molten form and the laminate layers should prevent egress of the contents of the pouch-like containers prior to their addition to water. The layers may separate or may remain attached together on contact with water, the only requirement being that the structure should permit rapid release of the contents of the pouch-like containers into solution. The number of pouch-like containers per unit area of substrate is a matter of choice but will normally vary between 500 and 25,000 per square metre.

[0146] Suitable materials which can be used for the flexible laminate layers in this aspect of the invention include, among others, sponges, paper and woven and non-woven fabrics.

[0147] However the preferred means of carrying out the washing process is to introduce the composition into the liquid surrounding the fabrics that are in the drum via a reusable dispensing device having walls that are permeable to liquid but impermeable to the solid composition.

[0148] Devices of this kind are disclosed in EP-A-0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing cycle. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Example

[0149] TAED powder was agglomerated and dried as described above using Sokalan^(R)CP45. The resultant dry agglomerate was then spray-coated with a further quantity (25% by weight) of Sokalan^(R)P45 in a fluid bed. The height of the spray-nozzle was adjusted so that it was above the highest particles fluidised in the air-stream. To reduce the tendency to cake and facilitate drying the temperature of the fluidising air was raised to around 85 deg.C. When the spray-on was complete the fluidisation with hot air was continued until the residual moisture was below 5% (by weight). The final dry agglomerate was then screened as before to provide a material where 95% of the particles lay between 1700 and 425 micrometers.

[0150] The agglomerate had the following composition:

TAED: 76.8%

Sokalan^(R)CP45: 18.6%, and the mean coating level determined by acid-base titration and calculated difference

was 10.4%.

Water/Misc: to 100%

5 [0151] The composition was then separated into four classes of particles and the mean coating level was determined by acid base titration and calculated difference.

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Part. Size (micrometers)	>1200	>850	>425	<425
mean coating	6.4	10.0	12.4	14.9

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[0152] A reference TAED agglomerate was prepared by agglomerating the same TAED powder with molten TAE25 as binder in the same mixing device as above. Particles were then cooled and sized to the same standards as above. Agglomerate composition was :

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TAED	87.0%
TAE25	13%

25

[0153] The detergent agglomerates were tested for colour damage potential when incorporated into the following detergent matrix (composition in parts by weight) :

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

45

* The detergent matrix already contains Sokalan^(R) CP45 as a co-builder, independently from the Sokalan^(R) CP45 present in the agglomerates.

[0154] The amount of agglomerate in the composition was such as to provide an active level of 5% by weight of TAED versus the total composition.

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[0155] The formulations containing the TAED agglomerates were subjected to a full scale washing machine test using Miele automatic washing machines (Model W754) set to the Short Wash cycle at 40°C.

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[0156] Bleach-sensitive coloured fabric swatches were used, a 43 cm² swatch being wrapped around the dispensing device in which 100g of the formulation was added. In each machine, 3.3 kg of white cotton bedsheets were used as ballast. 12 litres of water of 150 ppm hardness (expressed as CaCO₃) with a Ca:Mg ratio of 3:1 was fed to each machine. The swatches were made of 100% lambswool woven fabric with purple 48 dye (Design No. W3970) supplied by Borval Fabrics, Albert Street, Huddersfield, West Yorkshire, England. 24 replicates of each treatment were performed and the swatches were then graded visually for fabric colour damage by an expert panel using the following grading system.

[0157] Three coloured swatches demonstrating differing degrees of colour damage are used as standards to establish

a 4 point scale in which 1 represents 'virtually no damage' and 4 represents 'very damaged'. The three standards are used to define the mid points between the various descriptions of colour damage viz

- 1 virtually no damage
- 2 slight damage
- 3 damage
- 4 very damaged

[0158] Two expert panellists are used and their results are averaged.

[0159] Using this technique to compare colour damage resulting from use of the formulations above the following results were obtained:

Formulations Grade	% of swatches having grade				Overall
	1	2	3	4	
(Reference) TAE25/TAED	13	17	58	12	2.69
(Invention): Sokalan ^(R) CP45/TAED	33	33	30	4	2.05

[0160] It can be seen that the formulation incorporating the agglomerate in accordance with the invention produces appreciably less fabric colour damage than the reference agglomerate. Further testing also confirmed that there was no loss in bleaching performance for the optimised product.

Claims

1. A solid peroxyacid bleach precursor composition comprising particles of coated peroxyacid bleach precursor, wherein said composition comprises particles of different sizes, wherein said precursor comprises one or more N-, or O- acyl groups and having a Mpt>30°C, wherein said precursor is coated with a coating material, **characterized in**, that said coating material is selected from water-soluble acidic polymers, wherein said polymers have a water solubility greater than 5 g/l at 20°C, a molecular weight of from 1000 to 250,000, and wherein a 1% solution of said polymers has a pH of less than 7, and the level of coating in said particles is greater in particles of smaller size.
2. A composition according to claim 1 wherein the mean coating level is of from 2% to 25%, preferably 5% to 15%.
3. A composition according to claims 1 and 2 wherein said precursor is co-agglomerated with a binder material before it is coated with said polymer.
4. A composition according to claim 3 wherein said binder material is a said water-soluble acidic polymer.
5. A composition according to the preceding claims which comprises:
 - A first class of said particles comprising particles of from 1700 to 850 micrometers, wherein the mean coating level in said class is of from 0% to 100% of the mean coating level of the composition, preferably 0% to 50%;
 - A second class of said particles comprising particles of from less than 850 micrometers to 500 micrometers, wherein the mean coating level in said class is of from 0% to 150% of the mean coating level of the composition, preferably 0% to 100%; and
 - A third class comprising particles of from less than 500 micrometers to 100 micrometers, wherein the mean coating level in said class is of from 50% to 300% of the mean coating level of the composition, preferably 75% to 275%, most preferably 100% to 250%.
6. A solid peroxyacid bleach precursor composition according to claim 4 wherein said binder material and said coating material are identical.
7. A solid peroxyacid bleach precursor composition according to the preceding claims, wherein said water-soluble

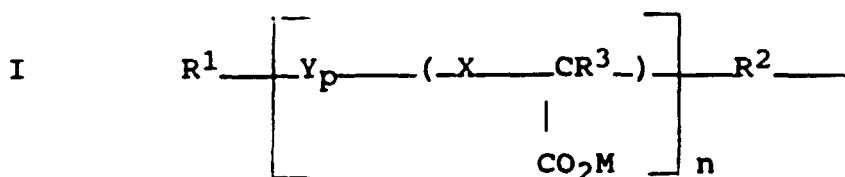
acidic polymers have a molecular weight in the range of from 1500 to 150,000.

8. A solid peroxyacid bleach precursor composition according to any of the preceding claims, wherein a 1% solution of said polymers has a pH of from less than 5.5.

9. A solid peroxyacid bleach precursor composition according to any of the preceding claims wherein said polymers have a melting point superior to 30°C.

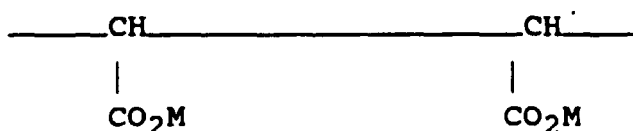
10. A solid peroxyacid bleach precursor composition according to any of the preceding claims, which comprises from 30% to 93% by weight of said composition of said peroxyacid bleach precursor, preferably 70% to 88%, and from 7% to 70% by weight of said composition of said polymer, preferably 12% to 30%.

11. A solid peroxyacid bleach precursor composition according to any of the preceding claims, wherein said polymer is a polymer according to the formula I:



wherein X is O or CH₂, Y is a comonomer or comonomer mixture; R¹ and R² are bleach- and alkali-stable polymer end groups; R³ is H, OH or C₁₋₄ alkyl; M is H, or mixtures thereof with alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, or mixtures thereof.

12. A solid peroxyacid bleach precursor composition according to claim 11 wherein, in formula I, p is 0.1 to 1.9, X is CH₂, R³ is H or C₁₋₄ alkyl, M is H, and n averages from 100 to 800, preferably from 120 to 400, Y comprises monomer units of formula II:



13. A solid peroxyacid bleach precursor composition according to any of the preceding claims wherein said peroxyacid bleach precursor is tetraacetyl ethylenediamine.

14. A bleaching composition incorporating a solid peroxyacid bleach precursor composition according to any of the preceding claims wherein said bleaching composition further comprises an inorganic perhydrate bleach

15. A bleaching composition according to claim 14 wherein the perhydrate bleach is sodium perborate or percarbonate.

16. A laundry detergent composition comprising a composition according to any of the preceding claims.

17. A process for manufacturing a composition according to claims 3-13 which comprises the steps of:

- co-agglomerating a solid peroxyacid bleach precursor as described in claims 1 and 2 with binder material;
- coating said dried co-agglomerate with a coating material as described in claim 1, such that the level of coating in said particles is greater in particles of smaller size;
- drying said coated co-agglomerate.

18. A process according to claim 17 wherein said particles are separated into several streams of particles of different

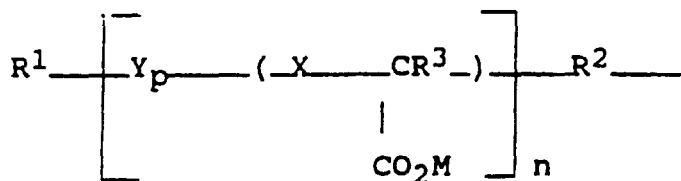
sizes after said agglomeration step, and said streams are individually coat-treated.

19. A process according to claim 17 wherein said particles are fluidized in an air stream after said agglomeration step, and said coating material is sprayed onto said fluidised particles.

Patentansprüche

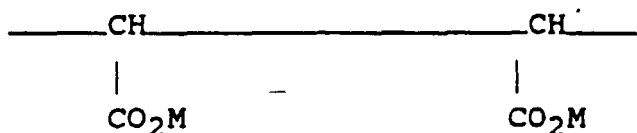
1. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung, umfassend Teilchen aus beschichtetem Peroxysäure-Bleichmittelvorläufer, wobei die Zusammensetzung Teilchen verschiedener Größen umfaßt, wobei der Vorläufer eine oder mehrere N- oder O-Acylgruppen umfaßt und einen Schmelzpunkt (Mpt) > 30°C aufweist, wobei der Vorläufer mit einem Beschichtungsmaterial beschichtet ist, dadurch gekennzeichnet, daß das Beschichtungsmaterial aus wasserlöslichen, sauren Polymeren gewählt ist, wobei die Polymere eine Wasserlöslichkeit von mehr als 5 g/l bei 20°C, ein Molekulargewicht von 1000 bis 250000 aufweisen, und wobei eine 1-prozentige Lösung des Polymeren einen pH von weniger als 7 aufweist, und wobei der Anteil der Beschichtung der Teilchen größer ist bei Teilchen geringerer Größe.
2. Zusammensetzung nach Anspruch 1, wobei der mittlere Beschichtungsanteil 2 bis 25%, vorzugsweise 5 bis 15%, beträgt.
3. Zusammensetzung nach den Ansprüchen 1 und 2, wobei der Vorläufer mit einem Bindemittelmateriel coagglomert worden ist, bevor er mit dem Polymer beschichtet worden ist.
4. Zusammensetzung nach Anspruch 3, wobei das Bindemittelmateriel das wasserlösliche, saure Polymer ist.
5. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend:
 - eine erste Klasse der Teilchen, umfassend Teilchen mit 1700 bis 850 µm, wobei der mittlere Beschichtungsanteil dieser Klasse 0 bis 100% des mittleren Beschichtungsanteils der Zusammensetzung, vorzugsweise 0 bis 50%, beträgt;
 - eine zweite Klasse der Teilchen, umfassend Teilchen von weniger als 850 µm bis 500 µm, wobei der mittlere Beschichtungsanteil in dieser Klasse 0 bis 150% des mittleren Beschichtungsanteils der Zusammensetzung, vorzugsweise 0 bis 100%, beträgt; und
 - eine dritte Klasse, umfassend Teilchen von weniger als 500 µm bis 100 µm, wobei der mittlere Beschichtungsanteil in dieser Klasse 50 bis 300% des mittleren Beschichtungsanteils der Zusammensetzung, vorzugsweise 75 bis 275%, am meisten bevorzugt 100 bis 250%, beträgt.
6. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach Anspruch 4, wobei das Bindemittelmateriel und das Beschichtungsmateriel identisch sind.
7. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach den vorangehenden Ansprüchen, wobei die wasserlöslichen, sauren Polymeren ein Molekulargewicht im Bereich von 1500 bis 150000 aufweisen.
8. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei die 1-prozentige Lösung der Polymeren einen pH von weniger als 5,5 aufweist.
9. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei die Polymeren einen Schmelzpunkt von mehr als 30°C aufweisen.
10. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 30 bis 93 Gew.-% der Zusammensetzung an dem Peroxysäure-Bleichmittelvorläufer, vorzugsweise 70 bis 88 Gew.-%, und 7 bis 70 Gew.-% der Zusammensetzung an den Polymeren, vorzugsweise 12 bis 30 Gew.-%.
11. Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei das Polymer ein Polymer der Formel (I) ist:

(I)



worin X O oder CH₂ ist, Y ein Comonomer oder eine Comonomermischung ist; R¹ und R² ein bleich- und alkalista-
bile Polymerendgruppen sind; R³ H, OH oder C₁₋₄-Alkyl ist; M H ist oder Mischungen hiervon mit Alkalimetall, Erd-
alkalimetall, Ammonium oder substituiertem Ammonium; p 0 bis 2 ist; und n mindestens 10 ist, oder Mischungen
hiervon.

- 12.** Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach Anspruch 11, wobei in der Formel I, p 0,1 bis 1,9
ist, X CH₂ ist, R³ H oder C₁₋₄-Alkyl ist, M H ist, und n im Durchschnitt 100 bis 800, vorzugsweise 120 bis 400, ist,
und Y Monomereinheiten der Formel II umfaßt:



- 13.** Feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach mindestens einem der vorangehenden Ansprü-
che, wobei der Peroxysäure-Bleichmittelvorläufer Tetraacetythyldiamin ist.

- 14.** Bleichmittelzusammensetzung, in welche eine feste Peroxysäure-Bleichmittelvorläuferzusammensetzung nach
mindestens einem der vorangehenden Ansprüche eingebracht ist, wobei die Bleichmittelzusammensetzung wei-
terhin ein anorganischen Perhydrat-Bleichmittel umfaßt.

- 15.** Bleichmittelzusammensetzung nach Anspruch 14, wobei das Perhydrat-Bleichmittel Natriumperborat oder -percar-
bonat ist.

- 16.** Wäschewaschmittelzusammensetzung, umfassend eine Zusammensetzung nach mindestens einem der vorange-
henden Ansprüche.

- 17.** Verfahren zur Herstellung einer Zusammensetzung nach den Ansprüchen 3 bis 13, umfassend die Schritte:

- Coagglomerieren eines festen Peroxysäure-Bleichmittelvorläufers, wie in den Ansprüchen 1 und 2 beschrie-
ben, mit einem Bindemittelmaterial;
- Beschichten des getrockneten Coagglomerats mit einem wie in Anspruch 1 beschriebenen Beschichtungsmat-
erial, so daß der Beschichtungsanteil bei diesen Teilchen größer ist bei Teilchen geringerer Größe;
- Trocknen des beschichteten Coagglomerats.

- 18.** Verfahren nach Anspruch 17, wobei die Teilchen nach dem Agglomerationsschritt in verschiedene Ströme von Teil-
chen mit unterschiedlichen Größen unterteilt werden und die Ströme individuell beschichtungsbehandelt werden.

- 19.** Verfahren nach Anspruch 17, wobei die Teilchen nach dem Agglomerationsschritt in einem Luftstrom fluidisiert
werden und das Beschichtungsmaterial auf die fluidisierten Teilchen gesprüht wird.

Revendications

- 1.** Composition de précurseur de blanchiment peroxyacide solide comprenant des particules de précurseur d'agent
de blanchiment peroxyacide enrobé, où ladite composition comprend des particules de tailles différentes, où ledit

précurseur comprend un ou plusieurs groupes N-ou O-acyle et ayant un point de fusion supérieur à 30°C, où ledit précurseur est enrobé dans un matériau de revêtement, caractérisé en ce que ledit matériau de revêtement est choisi parmi les polymères acides solubles dans l'eau, lesdits polymères ayant une solubilité dans l'eau supérieure à 5 g/l à 20°C, un poids moléculaire compris entre 1000 et 250 000, et où une solution à 1 % desdits polymères a un pH inférieur à 7, et le niveau d'enrobage dans lesdites particules est supérieur dans les particules de plus petite taille.

2. Composition selon la revendication 1, dans laquelle le niveau d'enrobage moyen est de 2 % à 25 %, de préférence de 5 % à 15 %.

3. Composition selon les revendications 1 et 2, dans laquelle le précurseur est coaggloméré avec un matériau liant avant d'être enrobé avec ledit polymère.

4. Composition la revendication 3, dans laquelle ledit matériau liant est un desdits polymères acides solubles dans l'eau.

5. Composition selon les revendications précédentes, qui comprend :

- une première classe desdites particules comprenant des particules de 1700 à 850 µm, où le niveau d'enrobage moyen dans ladite classe est de 0 % à 100 % du niveau d'enrobage moyen de la composition, de préférence de 0 % à 50 %;
- une seconde classe desdites particules comprenant des particules comprises entre moins de 850 µm à 500 µm, où le niveau d'enrobage moyen dans ladite classe est de 0 % à 150 % du niveau d'enrobage moyen de la composition, de préférence de 0 % à 100 % ; et
- une troisième classe comprenant des particules comprises entre moins de 500 µm à 100 µm, où le niveau d'enrobage moyen dans ladite classe est de 50 % à 300 % du niveau d'enrobage moyen dans la composition, de préférence 75 % à 275 %, mieux encore de 100 % à 250 %.

6. Composition de précurseur d'agent de blanchiment peroxyacide solide selon la revendication 4, dans laquelle ledit matériau liant et ledit matériau d'enrobage sont identiques.

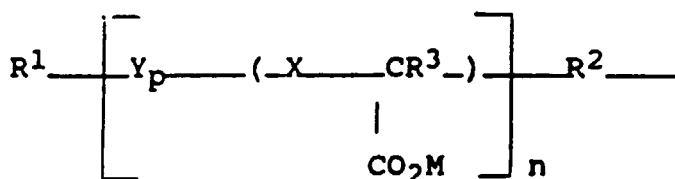
7. Composition de précurseur d'agent de blanchiment peroxyacide solide selon les revendications précédentes, dans laquelle lesdits polymères acides solubles dans l'eau ont un poids moléculaire dans la plage de 1500 à 150 000.

8. Composition de précurseur d'agent de blanchiment peroxyacide solide selon l'une quelconque des revendications précédentes, dans laquelle une solution à 1 % desdits polymères a un pH de moins de 5,5.

9. Composition de précurseur d'agent de blanchiment peroxyacide solide selon l'une quelconque des revendications précédentes, dans laquelle lesdits polymères ont un point de fusion supérieur à 30°C.

10. Composition de précurseur d'agent de blanchiment peroxyacide solide selon l'une quelconque des revendications précédentes, qui comprend de 30 % à 93 % en poids de ladite composition dudit précurseur d'agent de blanchiment peroxyacide, de préférence de 70 % à 88 %, et de 7 % à 70 % en poids de ladite composition dudit polymère, de préférence de 12 % à 30 %.

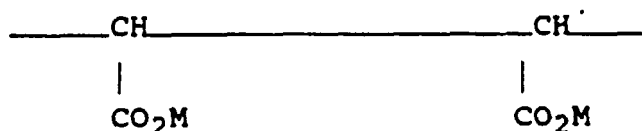
11. Composition de précurseur d'agent de blanchiment peroxyacide solide selon l'une quelconque des revendications précédentes, dans laquelle ledit polymère est un polymère selon la formule I :



dans laquelle X représente O ou CH₂, Y est un comonomère ou un mélange de comonomères ; R¹ et R² sont des

groupes d'extrémité de polymères stables vis-à-vis des agents de blanchiment et des bases ; R^3 représente H, OH ou un alkyle en C_1 à C_4 ; M représente H, ou leurs mélanges avec un métal alcalin, un métal alcalino-terreux, l'ammonium ou l'ammonium substitué, p vaut de 0 à 2, et n vaut au moins 10, ou leurs mélanges.

- 5 12. Composition de précurseur d'agent de blanchiment peroxyacide solide selon la revendication 11 dans laquelle, dans la formule I, p vaut de 0,1 à 1,9, X représente CH_2 , R^3 représente H ou un alkyle en C_1 à C_4 , M représente H, et n est compris en moyenne entre 100 et 800, de préférence entre 120 et 400, Y comprend des unités monomères de formule II :



- 20 13. Composition de précurseur d'agent de blanchiment peroxyacide solide selon l'une quelconque des revendications précédentes dans laquelle ledit précurseur d'agent de blanchiment peroxyacide est la tétraacétyléthylène diamine.

- 25 14. Composition d'agent de blanchiment incorporant une composition de précurseur d'agent de blanchiment peroxyacide solide selon l'une quelconque des revendications précédentes dans laquelle, ladite composition d'agent de blanchiment comprend en outre un agent de blanchiment perhydrate minéral.

- 15 15. Composition d'agent de blanchiment selon la revendication 14 dans laquelle l'agent de blanchiment perhydrate est le perborate ou le percarbonate de sodium.

- 30 16. Composition de détergent pour lessive comprenant une composition selon l'une quelconque des revendications précédentes.

17. Procédé de fabrication d'une composition selon les revendications 3 à 13 qui comprend les étapes de :

- 35 - coagglomération d'un précurseur d'agent de blanchiment peroxyacide solide tel que décrit dans les revendications 1 et 2 avec un matériau liant ;
 - enrobage dudit co-aggloméré séché avec un matériau d'enrobage tel que décrit dans la revendication 1, de manière que le niveau d'enrobage dans lesdites particules soit supérieur dans les particules de plus petite taille ;
 40 - séchage dudit coaggloméré enrobé.

18. Procédé selon la revendication 17 dans lequel on sépare lesdites particules en plusieurs courants de particules de tailles différentes après ladite étape d'agglutination, et on traite individuellement par enrobage lesdits courants.

- 45 19. Procédé selon la revendication 17 dans lequel on fluidise lesdites particules dans un courant d'air après ladite étape d'agglomération, et on pulvérise ledit matériau d'enrobage sur lesdites particules fluidisées.