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(54) Title: DETERGENT COMPOSITIONS (57) Abstract Detergent compositions especially suitable for laundry applications are disclosed, which contain low absorbency zeolite with a dibutyl phthalate (DBP) absorption value greater than or equal to 68g/100g, a particle size of 15 microns or below and a particle size distribution where no more than 0.09 % by weight has a particle size greater than 45 microns.		

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Detergent Compositions

Technical Field

This invention relates to detergents, in particular laundry detergents. More particularly,
5 this invention relates to solid detergents, for example in a granular or tablet form.

Background of the Invention

Detergent compositions, particularly those for use as laundry detergents are well known.
A problem associated with detergent products, particularly solid detergent products is
10 their incomplete dissolution or gelling which can lead to residues of detergent in a
dispenser drawer or during the wash process which can lead to entrapment of undissolved
product on fabrics. This is undesirable as such residues are visible on the fabrics even
after drying. This problem is exacerbated by the recent trend in the detergent industry
towards higher bulk density granular compositions which have a higher content of active
15 ingredients, for example granular detergent compositions having a bulk density of 550g/l
or even 600g/l or above.

It is well-known that water hardness ions are detrimental to the efficacy of the surfactant
cleaning systems, for example by interaction with certain soil components and the
20 detergent cleaning system. Detergent formulators address this problem by incorporating a
builder system into detergent compositions which sequesters water hardness ions, thereby
ensuring maximum cleaning performance from the surfactant system. Phosphate builder
systems are highly effective, however in view of the environmental concerns linked to
their use, alternative builders such as zeolites, have become well known and widely used.
25 Zeolites have effective building properties and have been successfully incorporated into
detergent compositions since the 1970s.

However, zeolite-builders are largely water insoluble and the nature of the zeolite, how it
is processed, interactions with other deterative components such as surfactants, carbonates

and silicates and the like, may exacerbate the problem of deposition of detergent composition residues on fabrics.

There are many disclosures of the use of zeolite builders in detergents. For example, US
5 4000094, US 4264464, JP 08/283799, WO 96/21717 all disclose such detergent
compositions, specifying preferred average particle sizes for the zeolite. WO 97/34980
relates to providing zeolite particles which give reduced fabrics residues and have an
increased liquid carrying capacity. To this effect this patent application describes
modified zeolite powder in which alkali metal silicate is deposited onto Zeolite P having
10 an average weight particle size (50% by weight of the zeolite has a particle size) from 1 -
10 μ m.

US4457854 teaches that particles of spray dried base beads made by spray-drying an
aqueous slurry of zeolite and carbonate and then mixed with a water-soluble silicate
15 powder and liquid-form nonionic detergent produce a free-flowing detergent. Fabric
residues are said to be reduced by post-addition of the hydrous alkali metal silicate rather
than by incorporation of the silicate into the crutcher mix with the zeolite and carbonate.
The patent also discloses preferred "average ultimate zeolite particle sizes" of below
15 μ m.

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In practice, although they may have the average particle sizes outlined in the references
discussed above, commercially available zeolites have a broad particle size distribution
and contain larger particles of zeolite. This may be the case in particular, for highly
absorbent zeolites because of the processing conditions for such zeolites. Highly
25 absorbent crystalline zeolite is desirable for use in detergent compositions as it permits
loading of high levels of surfactant whilst maintaining good detergent flowability. It may
be made by a method in which zeolite crystallites are formed and in the formation process
are adhered together to form a particle which comprises a cluster of crystallites which has
good absorbency. Such a method of preparation is relatively difficult to control so that

the particles of zeolite produced tend to be highly irregular in shape and with a wide particle size distribution.

The present inventors have now found that choosing a specific fraction of absorbent crystalline zeolite gives a surprisingly improved fabric residues performance when used in a detergent composition even using such irregular shaped zeolite crystallites. The inventors have surprisingly found that selection of the zeolite based on the average particle size alone does not give this benefit, but that in addition, the presence of larger particles is critical, so that a significant reduction in fabric residues results when a specific fraction of zeolite is selected.

Summary of the Invention

In accordance with the present invention there is provided a detergent composition comprising zeolite characterised in that the zeolite has a dibutylphthalate (DBP) absorption value of at least 68g/100g (as defined herein) and a particle size such that at least 99 wt % of the zeolite has a particle size of 15 μ m or below as measured by Laser Diffraction as defined below and no more than 0.09% by weight of the zeolite has a particle size of 45 μ m or above as defined by the Wet Sieve Test.

In preferred detergent compositions, the zeolite has a particle size in which no more than 0.05% by weight, and most preferably no more than 0.01% by weight of the zeolite has a particle size of 45 μ m or greater.

Also, preferably the particle size of at least 99 wt % of the zeolite is 0.05 μ m or above, most preferably, 0.1 μ m or greater. Whilst not wishing to be bound by theory, the inventors believe that the fabric residues are minimised using zeolite in which at least 99 wt % has a particle size of 0.05 μ m, preferably above 0.1 μ m or above because smaller particle size zeolite tends to be caught by fibrils on the surfaces of fabrics in the washing process and then may clump together to form larger particles which lead to fabric residues, trapped on the fabric surface.

In accordance with the invention, there is also provided use of a zeolite having a DBP absorption value of at least 68g/100g as defined herein and a particle size such that at least 99 wt % of the zeolite has a particle size of 15 μm or below as measured by the
5 Laser Diffraction as defined below and no more than 0.09wt% of the zeolite has a particle size greater than 45 μm as measured by the Wet Sieve Test, in a detergent composition for reducing fabric residues.

Detailed Description of the Invention

10 Zeolite

The particle size measurement for determining the proportion of zeolite having a particle size greater than 45 μm is carried out using a Wet Sieve Test. In accordance with the wet sieve test, from a batch of zeolite to be tested, the following test is carried out twice on each sample of zeolite to find the proportion of the zeolite having particle size greater
15 than 45 μm and the average value of the two samples is calculated. That average value provides the required particle size proportion. If the two values differ by more than 10% of the larger value, the results are discarded and the procedure repeated.

A 100g (+/-0.1g) sample of zeolite is placed in a 1000ml beaker with 500ml distilled
20 water. The liquid in the beaker is stirred until no residue remains on the bottom of the beaker. The contents of the beaker are then emptied onto a 45micron aperture sieve (200mm diameter standard brass or stainless steel sieve). The liquid is not retained. Additional distilled water is then poured into the beaker to be mixed with any residues remaining and the rinse water is poured onto the sieve. A rinsing step for the sieve is then
25 carried out: a base pan for the sieve is then filled with distilled water and the sieve placed on top of the base pan. Extra distilled water is added until the water level is approximately 5-10mm above the mesh level. The residue is washed with a gentle swirling action for 2-3 minutes. The sieve is then removed and the water in the base pan is examined. If any cloudiness remains the water is discarded and the rinsing step for the
30 sieve repeated. If the water is clear, the sieve is placed in a pre-heated oven at 105+/-2

degrees C for 1 hour. The sieve is then removed from the oven and allowed to cool for 10 minutes +/- 1 minute. The residue is then dusted off using a brass wire brush and collected in a pre-weighed petri dish. The residue weight is determined as soon as possible (within 2-3 minutes) by weighing on a balance accurate to at least 2 decimal places. The weight of the residue (g) is the percentage of zeolite having a particle size greater than 45 microns.

Since the Wet Sieve Test measures fractions of specific particle size it is not suitable for measuring the particle size distribution of the zeolite to determine whether 99 wt% of the zeolite has a particle size of 15 microns or below. Therefore, for this determination, a Laser Diffraction measurement method is used. In this test, a Sympatec Laser Diffractor comprising a HELOS/KA central unit with Paradox software system, a QUIXEL liquid dispersion system and a 2mm CUVETTE is used.

500ml of distilled water is placed into an Ultrasonics bath and a sample of zeolite is added. The liquid is left in the Ultrasonics bath operating at a frequency of 40KHz for 10 minutes during which time, the ultrasound ensures a substantially homogeneous dispersion of individual particles of zeolite is obtained. A sample of the dispersion is removed from the ultrasonics bath and added slowly into 1 litre of distilled water in a QUIXEL until the software indicates that an optimum concentration for measurement has been reached. A suitable concentration may be for example, 0.5g/l.

A 2mm CUVETTE is placed into the QUIXEL and a particle size distribution measurement of the aqueous suspension taken over a 10 second run using a 87.5µm lens. This measurement method gives the weight percentage of the sample having particle size of 15µm or below.

In order to determine the DBP absorption value of the zeolite, di-n-butyl phthalate (DBP) is automatically titrated onto a pre-weighed sample of zeolite in a mixing chamber. As DBP is titrated, the mixing and agglomeration profile is recorded to the point of saturation

using a torque rheometer. More specifically, a 25g sample of zeolite is weighed to 2 decimal places and then placed into a mixing chamber of a Brabender absorptometer with substantially even distribution. DBP is delivered into the mixing chamber from a LEWA pump, pre-calibrated to deliver DBP at a rate of 2.4ml/min(+/-0.2ml/min) with stirring from the absorptometer at a rate of 125 rpm and the torque during mixing is recorded by the Brabender chart recorder. DBP is added until the maximum torque has been reached. After a further 20-30 seconds to ensure that the saturation point has been exceeded, the Brabender chart recorder is stopped.

- 10 In order to calculate the DBP value, a horizontal line is drawn half way between the highest torque value and the base line. This horizontal line A, passes through the peak. The distance between the up-slope and the down-slope of the peak is measured along line A and a vertical line B is drawn equidistant from the up and down slopes of the peak along line A. This line B is used to determine the DBP value according to the following
- 15 formula: $\text{DBP absorption value (g/100g)} = [(D/R) \times (V) \times (100)]/M$ where $D =$ distance from start of test to saturation (mm)
- $R =$ rate of chart recorder paper (mm/min)
- $V =$ average rate of DBP delivery per minute (ml/min)
- i.e. $[(\text{g})\text{DBP delivered in 5mins before run} + (\text{g})\text{delivered in 5mins after run}]/10$
- 20 $M =$ mass of sample used (g)

Preferred DBP values are at least 70g/100g or even at least 75 or 80g/100g.

- 25 Preferred zeolites for use in the present invention have a particle size such that 99wt% of the zeolite has a particle size 0.05 μm or above, most preferably of 0.1 μm or above. In order to detect the proportion of particles of such a low particle size, these particles can be measured by Scanning Electron Microscope using stereological interpretation of data as discussed in Computer Assisted Microscopy – The Measurement and Analysis of Images by John C. Russ; Plenum Press, NY and London 1990, Chapter 8 pp. 221-265.

In order to obtain zeolites as specified, commercially available materials may be classified in any conventional way, for example using sieves to obtain the appropriate zeolite fraction. The inventors have found that it may be particularly useful to ensure that in a one tonne sample of zeolite, the particle size requirements of the claims are met.

- 5 Such a large sample of zeolite is particularly useful because it is sufficiently large that its value is not adversely affected by plant variability.

Zeolites are crystalline aluminosilicates. Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio
10 of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

- 15 The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolites A and X are preferred. Zeolite A which is particularly preferred has the formula $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$, wherein x is from 20 to 30, especially 27. Zeolite X
20 has the formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Zeolite MAP builder is also suitable for use in the present invention. Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than
25 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2. Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

Zeolite may be present in the detergent compositions of the invention or
30 components thereof in amounts from as low as 1 wt% to as high as 99 wt%.

Generally levels of zeolite in the detergent compositions of the invention are at least 2 wt % or at least 5 wt% or even at least 10 or 20 wt%. Generally in the detergent composition, zeolite as specified is present in amounts no greater than 80 wt%, or no greater than 50 wt%, or even in amounts no greater than 40wt%.

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The specified zeolite may be incorporated into the detergent composition as a dry added particle material either directly in the particle size specified or as a larger particle for example from 100 to 1500 microns, formed from the specified particle size zeolite and binder. Suitable binders include other detergent ingredients and binders conventional in the detergent field such as polymeric materials for example based on maleic acid and/or acrylic acid monomers, polyalkylene glycols such as PEG, or hydratable salts or acids of such salts, such as citric acid or alkali metal silicates or alkali metal carbonates. In such a particle the zeolite will comprise up to 99 wt% of the particle, generally from at least 90wt % of the dry-added particle.

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Such larger particle size zeolite-based granules generally contain at least 60 wt% zeolite.

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Alternatively, zeolite of the specified particle size undergoes a detergent processing step with one or more additional detergent ingredients, such as other builder components and/or surfactants to form a particulate detergent . In this case, the particulate detergent component containing the specified zeolite, generally contains up to 80 wt%, or more usually up to 70 wt% or even up to 60 wt% of the particulate detergent component. In a preferred feature of the invention, the zeolite is present as a particulate detergent composition comprising cationic surfactant. In a further preferred embodiment of the invention, zeolite is present as a particulate detergent composition comprising anionic surfactant or anionic and cationic surfactant.

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Suitable anionic surfactants are described below in the section entitled Surfactants and include alkyl benzene sulphonates. Particularly preferred anionic surfactants are those having a Kraft temperature of 45°C or below or of 40°C or below.

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In accordance with one embodiment of the invention, the zeolite is incorporated into the detergent composition via a spray-dried particle. Such particles preferably contain at least 15 wt% surfactant, or at least 20 wt% or even greater than 25 wt% surfactant. The surfactant may be anionic, cationic, nonionic, amphoteric or zwitterionic or mixtures thereof as described below. In view of the reduction in residues provided by the present invention, the spray-dried particles may also contain alkali metal silicate so that the zeolite and alkali metal silicate are both added into the crutcher mix and are spray-dried together. Therefore, in accordance with a process of the present invention, zeolite of the specified particle size and absorbency is mixed with additional detergent ingredients to form a crutcher slurry which is spray dried, the spray dried powder is then mixed with additional detergent ingredients to form a granular detergent which is optionally compressed into a tablet. Optional binders may be included at any stage of the process.

In accordance with a further embodiment of the invention, the specified zeolite is incorporated into the detergent composition via an agglomerate. The zeolite can be agglomerated with other detergent ingredients in conventional ways, retaining its high absorbency properties and also producing products with superior fabric residues performance. Agglomeration processes may be as described in any of the following patent applications: EP-A-367 339, EP-A-420 317 and EP-A-506 184.

Again, the particulate detergent components produced may be mixed with additional detergent ingredients and optionally compressed into tablets. Optional binders may be included at any stage in the process.

In accordance with a further aspect of the invention, the zeolite may be incorporated into the detergent compositions of the invention via an extrudate. Thus in a preferred process of the present invention the specified zeolite is mixed with other detergent ingredients to form a thick paste which is extruded to form extruded lengths of detergent composition. These lengths are cut into short portions and

optionally shaped to produce detergent granules. Again, the detergent particulates produced may be mixed with additional detergent ingredients and optionally compressed into tablets. The use of the zeolites as specified may be particularly beneficial in such extrusion processes. Due to the highly absorbent nature of the zeolite, high proportions of organic detergent components such as surfactants can be incorporated into the detergent paste whilst still producing a non-sticky easily extruded paste. A typical extrusion process is described in DE-A- 195 24 287.

Since the zeolites have good absorbency properties, liquid detergent ingredients may be post-dosed to the zeolite-containing detergent compositions or components thereof before addition of further detergent ingredients. In particular, anionic and/or nonionic and/or cationic surfactants in liquid form may be added to pre-formed detergent ingredients, optionally with dissolution aids such as fatty acids and their derivatives and/or esterified polyols such as glycerides and/or soap.

In the detergent compositions of the invention, a further benefit may be seen in detergent compositions which also contain percarbonate bleaching agents. Percarbonates are particularly vulnerable to loss of activity on storage due to moisture up-take and the zeolites specified have high surface area and good moisture up-take so that they can act as an improved moisture sink during storage, protecting the percarbonate from moisture and subsequent activity loss.

When present in detergent compositions, it may also be preferred that only less than 25% by weight of the detergent composition of admixed hydratable inorganic salts are present, being thus present as separate particles, or even less than 25% by weight of the detergent composition of hydratable inorganic salts in the total composition. It may be preferred that a inorganic peroxygen bleach is present, whereby it is preferred that a percarboante salt is present.

In one embodiment of the invention, it may be preferred that the detergent composition herein comprise one or more anionic surfactants and an zeolite (aluminosilicate) builder, whereby it is preferred that only small amounts of the aluminosilicate builder and the anionic surfactant are in an intimate mixture, i.e. less than 50% or even less than 30% of the total amount of the anionic surfactant and less than 50% or even less than 30% of the total amount of aluminosilicate; it may even be preferred that substantially no anionic surfactant and aluminosilicate builder are in an intimate mixture. Thus, it may be preferred that the composition comprises at least two separate particles which comprise either anionic surfactant or aluminosilicate. 'Intimate mixture' means for the purpose of the invention that the two or more ingredients the component are substantially homogeneously divided in the component or particle. Namely, it has been found that the solubility and/ or dispensing of the composition is thereby improved.

In another embodiment of the invention, it may be preferred that the composition only comprises low levels of aluminosilicate builder, for example less than 10% or even less than 5% by weight of the composition, whereby it is preferred that the composition comprises highly soluble builders, for example sodium citrate or citric acid, carbonate, and/ or crystalline layered silicate.

It may also be preferred that the composition comprises as builder system or as part of the builder system, an agglomerate comprising from 0.5% to 80% by weight a crystalline layered silicate, preferably, NaSKS-6, and from 10% to 70% by weight of a surfactant, preferably an anionic surfactant, whereby it may be preferred that less than 10% by weight of the agglomerate of free moisture, more preferably 30% to 60% by weight a crystalline layered silicate and 20% to 50% by weight of an anionic surfactant.

Other detergent ingredients

The compositions in accordance with the invention will also contain additional detergent components. The precise nature of these additional components, and levels of

incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

Surfactant

- 5 The components in accordance with the invention and the compositions herein preferably contain one or more surfactants selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

10 A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

- 15 Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic Surfactant

- 20 The components in accord with the present invention and/ or the detergent compositions herein preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for deterative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate and sulfonate
25 surfactants are preferred. The anionic surfactants is preferably present at a level of from 0.1% to 60%, more preferably from 1 to 40%, most preferably from 5% to 30% by weight.

Highly preferred are surfactants systems comprising a sulfonate and a sulfate surfactant, preferably a linear or branched alkyl benzene sulfonate and alkyl ethoxysulfates, as described herein, preferably combined with a cationic surfactants as described herein.

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

Anionic Sulfate Surfactant

- Anionic sulfate surfactants suitable for use herein include the linear and branched primary
15 and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5 - C_{17} acyl-N-(C_1 - C_4 alkyl) and -N-(C_1 - C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein). Alkyl sulfate surfactants are preferably selected from the linear and branched
20 primary C_{10} - C_{18} alkyl sulfates, more preferably the C_{11} - C_{15} branched chain alkyl sulfates and the C_{12} - C_{14} linear chain alkyl sulfates.

- Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10} - C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of
25 ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11} - C_{18} , most preferably C_{11} - C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

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

5 Anionic Sulfonate Surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures
10 thereof.

Anionic Carboxylate Surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially
15 certain secondary soaps as described herein. Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable
20 alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

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Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-

butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Certain soaps may also be included as suds suppressors.

Alkali Metal Sarcosinate Surfactant

- 5 Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

10 Alkoxyated Nonionic Surfactant

Any alkoxyated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

- Preferred alkoxyated surfactants can be selected from the classes of the nonionic
15 condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

20 Nonionic Alkoxyated Alcohol Surfactant

- The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are
25 the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic Polyhydroxy Fatty Acid Amide Surfactant

- Polyhydroxy fatty acid amides suitable for use herein are those having the structural
30 formula R^2CONR^1Z wherein : R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy

propyl, ethoxy, propoxy, or a mixture thereof, preferable C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R₂ is a C₅-C₃₁ hydrocarbyl, preferably straight-chain C₅-C₁₉ alkyl or alkenyl, more preferably straight-chain C₉-C₁₇ alkyl or alkenyl, most preferably straight-chain C₁₁-C₁₇ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

10 Nonionic Fatty Acid Amide Surfactant

Suitable fatty acid amide surfactants include those having the formula: R⁶CON(R⁷)₂ wherein R⁶ is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R⁷ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and -(C₂H₄O)_xH, where x is in the range of from 1 to 3.

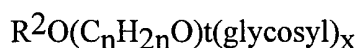
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Nonionic Alkylpolysaccharide Surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

20

Preferred alkylpolyglycosides have the formula:



25

wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric Surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

5

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is
10 from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

- 15 A suitable example of an alkyl amphocarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

- 20 Zwitterionic surfactants can also be incorporated into the detergent compositions in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

25

Suitable betaines are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C_6 - C_{18} hydrocarbyl group, each R^1 is typically C_1 - C_3 alkyl, and R^2 is a C_1 - C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the

C₁₀₋₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic Surfactants

- 5 Suitable cationic surfactants to be used herein include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

10

Another suitable group of cationic surfactants which can be used in the detergent compositions or components thereof herein are cationic ester surfactants. The cationic ester surfactant is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

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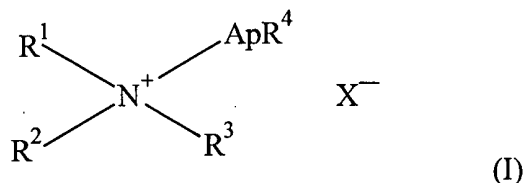
Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

- 20 In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH₂-O-CH₂- and -CH₂-NH-CH₂- linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

30

Cationic Mono-Alkoxylated Amine Surfactants

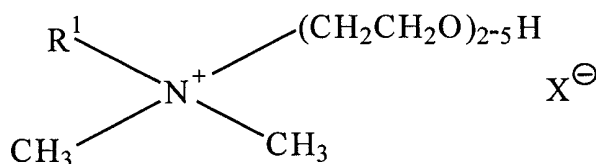
Highly preferred herein are cationic mono-alkoxylated amine surfactant preferably of the general formula I:



wherein R^1 is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 14 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both R^2 and R^3 are methyl groups; R^4 is selected from hydrogen (preferred), methyl and ethyl; X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8.

Preferably the ApR^4 group in formula I has $p=1$ and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the $-OH$ group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred ApR^4 groups are $-CH_2CH_2OH$, $-CH_2CH_2CH_2OH$, $-CH_2CH(CH_3)OH$ and $-CH(CH_3)CH_2OH$, with $-CH_2CH_2OH$ being particularly preferred. Preferred R^1 groups are linear alkyl groups. Linear R^1 groups having from 8 to 14 carbon atoms are preferred.

Another highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



wherein R^1 is C_{10} - C_{18} hydrocarbyl and mixtures thereof, especially C_{10} - C_{14} alkyl, preferably C_{10} and C_{12} alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

5

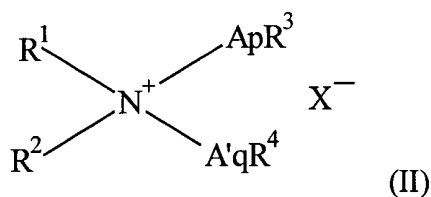
As noted, compounds of the foregoing type include those wherein the ethoxy $(\text{CH}_2\text{CH}_2\text{O})$ units (EO) are replaced by butoxy, isopropoxy $[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]$ and $[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]$ units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

10

The levels of the cationic mono-alkoxylated amine surfactants is preferably from 0.1% to 20%, more preferably from 0.2% to 7%, most preferably from 0.3% to 3.0% by weight.

Cationic Bis-Alkoxylated Amine Surfactant

15 The cationic bis-alkoxylated amine surfactant preferably has the general formula II:

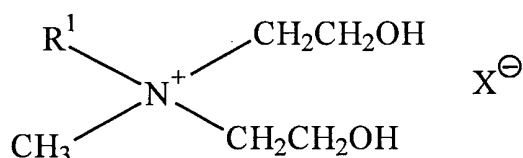


wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are

20

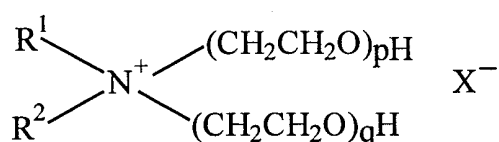
each selected from C₁-C₄ alkoxy, especially ethoxy, (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

- 5 Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



- wherein R¹ is C₁₀-C₁₈ hydrocarbyl and mixtures thereof, preferably C₁₀, C₁₂, C₁₄ alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R¹ is derived from (coconut) C₁₂-C₁₄ alkyl fraction fatty acids, R² is methyl and ApR³ and A'qR⁴ are each monoethoxy.
- 10

- Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:
- 15



wherein R¹ is C₁₀-C₁₈ hydrocarbyl, preferably C₁₀-C₁₄ alkyl, independently p is 1 to about 3 and q is 1 to about 3, R² is C₁-C₃ alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

20

Other compounds of the foregoing type include those wherein the ethoxy (CH₂CH₂O) units (EO) are replaced by butoxy (Bu) isopropoxy [CH(CH₃)CH₂O] and [CH₂CH(CH₃O)] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

Bleach Activator

The components in accord with the present invention and/ or the detergent compositions herein preferably comprises a bleach activator, preferably comprising an organic
5 peroxyacid bleach precursor. It may be preferred that the composition comprises at least two peroxy acid bleach precursors, preferably at least one hydrophobic peroxyacid bleach precursor and at least one hydrophilic peroxy acid bleach precursor, as defined herein. The production of the organic peroxyacid occurs then by an in situ reaction of the precursor with a source of hydrogen peroxide.

10

The bleach activator may alternatively, or in addition comprise a preformed peroxy acid bleach.

15

It is preferred that the bleach activator is present in a particulate component in the component or compositions herein. It may be preferred that the is present as a separate, admixed particle. Alternatively, the bleach activator or part thereof can be present in the base detergent particle.

20

Preferably, at least one of the bleach activators, preferably a peroxy acid bleach precursor, is present in a particulate component having an average particle size, by weight, of from 600 microns to 1400 microns, preferably from 700 microns to 1100 microns. More preferably, all of the activator are present in one or more particulate components having the specified weight average particle size.

25

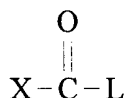
Hereby, it may be preferred that at least 80%, preferably at least 90% or even at least 95 % or even substantially 100% of the component or components comprising the bleach activator have a particle size of from 300 microns to 1700 microns, preferably from 425 microns to 1400 microns.

The hydrophobic peroxy acid bleach precursor preferably comprises a compound having a oxy-benzene sulphonate group, preferably NOBS, DOBS, LOBS and/ or NACA-OBS, as described herein.

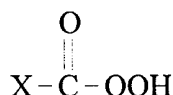
- 5 The hydrophilic peroxy acid bleach precursor preferably comprises TAED, as described herein.

Peroxyacid Bleach Precursor

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



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



- 20 For the purpose of the invention, hydrophobic peroxyacid bleach precursors produce a peroxy acid of the formula above wherein X is a group comprising at least 6 carbon atoms and a hydrophilic peroxyacid bleach precursor produces a peroxyacid bleach of the formula above wherein X is a group comprising 1 to 5 carbon atoms.
- 25 Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 30% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight. The ratio of hydrophilic to hydrophobic bleach precursors,

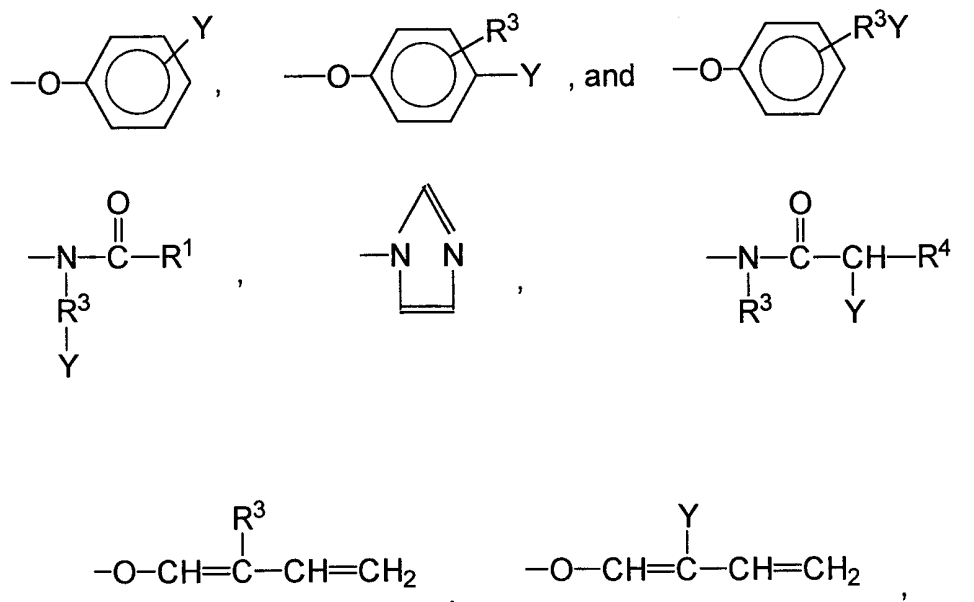
when present, is preferably from 10:1 to 1:10, more preferably from 5:1 to 1:5 or even from 3:1 to 1:3.

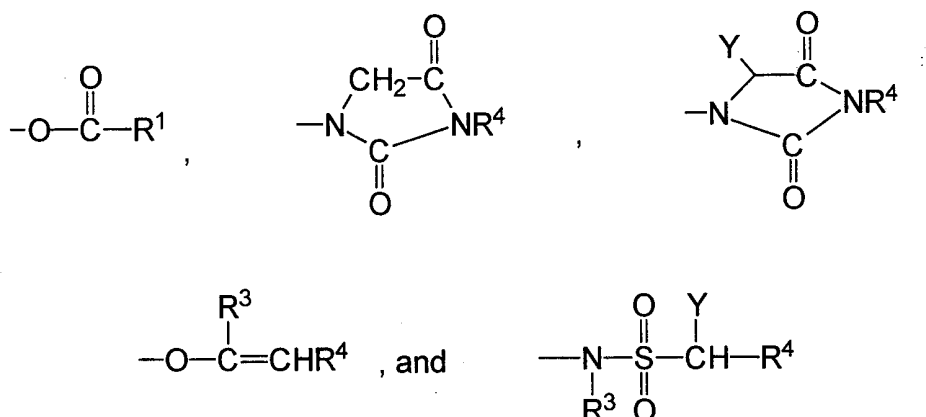
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving Groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:





and mixtures thereof, wherein R¹ is an alkyl, aryl, or alkaryl group containing from 1 to

14 carbon atoms, R³ is an alkyl chain containing from 1 to 8 carbon atoms, R⁴ is H or R³, and Y is H or a solubilizing group. Any of R¹, R³ and R⁴ may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

10 The preferred solubilizing groups are $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $-\text{N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}=\text{N}(\text{R}^3)_2$ and most preferably $-\text{SO}_3^-\text{M}^+$ and $-\text{CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and

15 potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl Percarboxylic Acid Bleach Precursors

Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis.

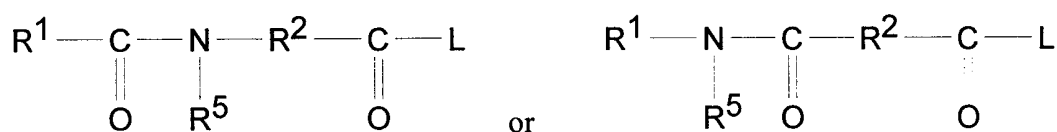
20 Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred as hydrophilic peroxy acid bleach precursor.

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

Amide Substituted Alkyl Peroxyacid Precursors

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



wherein R¹ is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from about 6 to 12 carbon atoms. R² preferably contains from about 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². R² can include alkyl, aryl, wherein said R² may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms total. Amide substituted bleach

activator compounds of this type are described in EP-A-0170386. It can be preferred that R^1 and R^5 forms together with the nitrogen and carbon atom a ring structure.

Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

10 Perbenzoic Acid Precursor

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

20

Cationic Peroxyacid Precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

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

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described
5 hereinafter.

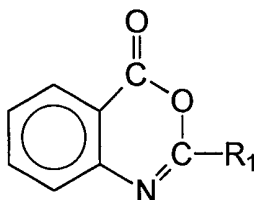
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

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

Benzoxazin Organic Peroxyacid Precursors

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



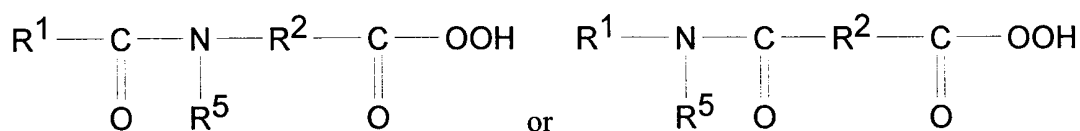
wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed Organic Peroxyacid

The components in accord with the present invention and/ or the detergent compositions herein may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:

10



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Peroxide Source

Inorganic perhydrate salts are a preferred source of peroxide. Preferably these salts are present at a level of from 0.01% to 50% by weight, more preferably of from 0.5% to 30% by weight of the composition or component.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali

metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise

5 inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

10

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate 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.

15 Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Dye

A preferred ingredients of the compositions herein are dyes and dyed particles or

20 speckles, which can be bleach-sensitive. The dye as used herein can be a dye stuff or an aqueous or nonaqueous solution of a dye stuff. It may be preferred that the dye is an aqueous solution comprising a dyestuff, at any level to obtain suitable dyeing of the detergent particles or speckles, preferably such that levels of dye solution are obtained up to 2% by weight of the dyed particle, or more preferably up to 0.5% by weight, as

25 described above. The dye may also be mixed with a non-aqueous carrier material, such as non-aqueous liquid materials including nonionic surfactants. Optionally, the dye also comprising other ingredients such as organic binder materials, which may also be a non-aqueous liquid.

The dyestuff can be any suitable dyestuff. Specific examples of suitable dyestuffs include E104 - food yellow 13 (quinoline yellow), E110 - food yellow 3 (sunset yellow FCF), E131 - food blue 5 (patent blue V), Ultra Marine blue (trade name), E133 - food blue 2 (brilliant blue FCF), E140 - natural green 3 (chlorophyll and chlorophyllins), E141 and
5 Pigment green 7 (chlorinated Cu phthalocyanine). Preferred dyestuffs may be Monastral Blue BV paste (trade name) and/ or Pigmasol Green (trade name).

The dyed detergent particles or effervescence components preferably comprise such a up to 10% or more preferably up to 2% or even up to 1% by weight of the dyed particle or
10 component.

Perfumes

Another preferred ingredient of the component of the invention or the composition herein is a perfume or perfume composition. Any perfume composition can be used herein. The
15 perfumes may also be encapsulated. Preferred perfumes contain at least one component with a low molecular weight volatile component, e.g. having a molecular weight of 150 to 450 or preferably 350. Preferably, the perfume component comprises an oxygen-containing functional group. Preferred functional groups are aldehyde, ketone, alcohol or ether functional groups or mixtures thereof.

Heavy Metal Ion Sequestrant

The components in accordance with the present invention and/or the detergent compositions herein preferably contain as an optional component a heavy metal ion sequestrant or chelant or chelating agent. By heavy metal ion sequestrant it is meant
25 herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 10%,
30 preferably from 0.1% to 5%, more preferably from 0.25% to 7.5% and most preferably

from 0.3% to 2% by weight of the compositions or component. Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates. Preferred among the above species are diethylene triamine

5 penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate, 1,1 hydroxyethane diphosphonic acid and 1,1 hydroxyethane dimethylene phosphonic acid.

10 Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino

15 diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

20

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-

25 N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Especially preferred are diethylenetriamine pentacetic acid, ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,1 hydroxyethane diphosphonic acid or the alkali

metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

In particular the chelating agents comprising a amino or amine group can be bleach-sensitive and are suitable in the compositions of the invention.

Enzyme

Another highly preferred ingredient useful in the components or compositions herein is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/ US 9703635, and in WO95/26397 and WO96/23873. Amylase enzyme may be incorporated

into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight.

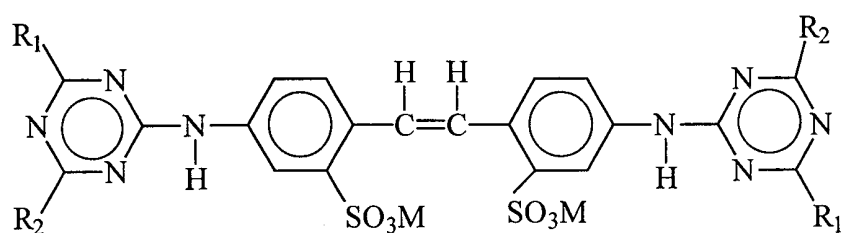
Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight. The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

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

Optical Brightener

The component or compositions herein also preferably contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners, as mentioned above.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

- 5 When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-CBS-X and Tinopal-UNPA-GX is the preferred hydrophilic
10 optical brightener useful in the detergent compositions herein.

- When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This
15 particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

- When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-
20 stilbenedisulfonic acid, sodium salt. This particular brightener species are commercially marketed under the tradename Tinopal-DMS-X and Tinopal AMS-GX by Ciba Geigy Corporation.

Photo-Bleaching Agent

- 25 Photo-bleaching agents are preferred ingredients of the compositions or components herein. Preferred photo-bleaching agent herein comprise a compounds having a porphin or porphyrin structure. Porphin and porphyrin, in the literature, are used as synonyms, but conventionally porphin stands for the simplest porphyrin without any substituents; wherein porphyrin is a sub-class of porphin. The references to porphin in this application
30 will include porphyrin. The porphin structures preferably comprise a metal element or

cation, preferably Ca, Mg, P, Ti, Cr, Zr, In, Sn or Hf, more preferably Ge, Si or Ga, or more preferably Al, most preferably Zn.

It can be preferred that the photo-bleaching compound or component is substituted with
5 substituents selected from alkyl groups such as methyl, ethyl, propyl, t-butyl group and aromatic ring systems such as pyridyl, pyridyl-N-oxide, phenyl, naphthyl and anthracyl moieties.

The photo-bleaching compound or component can have solubilizing groups as
10 substituents. Alternatively, or in addition hereto the photo-bleaching agent can comprise a polymeric component capable of solubilizing the photo-bleaching compound, for example PVP, PVNP, PVI or co-polymers thereof or mixtures thereof.

Highly preferred photo-bleaching compounds are compounds having a phthalocyanine
15 structure, which preferably have the metal elements or cations described above. Metal phthalocyanines and their derivatives have the structure indicated in Figure 1 and/or Figure 2, wherein the atom positions of the phthalocyanine structure are numbered conventionally. The phthalocyanines can be substituted for example the phthalocyanine structures which are substituted at one or more of the 1-4, 6, 8-11, 13, 15-18, 20, 22-25,
20 27 atom positions.

Water-Soluble Builder Compound

The component or compositions herein preferably contain a water-soluble builder
25 compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 60% by weight, most preferably from 15% to 40% by weight.

The detergent compositions of the invention may comprise phosphate-containing builder
30 material in addition to the specified zeolite builder. When present phosphate is generally

present at a level of from 0.5% to 60%, more preferably from 5% to 50%, more preferably from 8% to 40% by weight of the composition. The phosphate-containing builder material preferably comprises tetrasodium pyrophosphate or even more preferably anhydrous sodium tripolyphosphate.

5

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

10

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance. Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three carboxy groups is citric acid, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight.

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Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane

tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are

5 hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

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

10 contemplated as useful builder components.

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

15 Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and

20 salts of phytic acid.

Organic Polymeric Compound

Organic polymeric compounds are preferred additional herein and are preferably present as components of any particulate components where they may act such as to bind the

25 particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein, including quaternised ethoxylated (poly) amine clay-soil removal/ anti-

30 redeposition agent in accord with the invention.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.01% to 30%, preferably from 0.1% to 15%, most preferably from 0.5% to 10% by weight of the compositions or component.

5

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of
10 such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid
15 such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

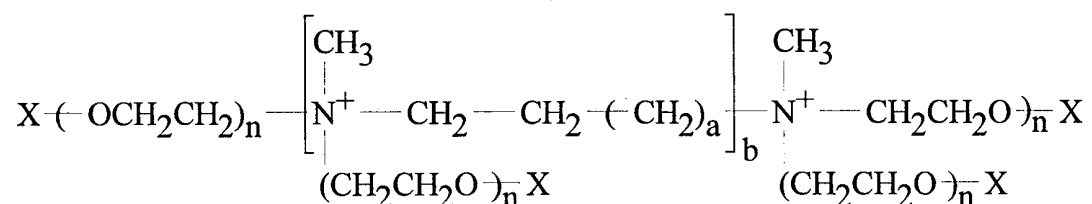
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Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

25 Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Highly preferred polymeric components herein are cotton and non-cotton soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., and U.S. Patent 5,415,807, Gosselink et al., and in particular according to US application no.60/051517.

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



- 10 wherein X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

15

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

Disintegrating Agents

20

Disintegrating agents such as effervescent particles comprising acid and alkali components with optional binders may be incorporated into the detergent compositions of the invention. Polymeric disintegrating agents such as those formed from absorbent swellable polymeric materials may also be incorporated. Suitable materials are described for example in WO98/40463 (Henkel) and WO98/40462 (Rettenmaier).

25

Suds Suppressing System

The components and detergent compositions herein, when formulated for use in machine washing compositions, may comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.02% to 10%, most preferably from 0.05% to 3% by weight of the composition or component. Suitable suds suppressing systems for use
5 herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent
10 composition, particularly in the presence of agitation of that solution. Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively
15 high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are siloxanes, particularly the polydimethylsiloxanes with trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble
20 salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

25 Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric
30 chloride with two or three moles of a primary or secondary amine containing 1 to 24

carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises: (a) antifoam compound, preferably

5 silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the
10 silicone/silica antifoam compound; wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by
15 weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight.

20

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a

monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20
25 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Other highly preferred suds suppressing systems comprise polydimethylsiloxane or mixtures of silicone, such as polydimethylsiloxane, aluminosilicate and polycarboxylic polymers, such as copolymers of laic and acrylic acid.

5 Polymeric Dye Transfer Inhibiting Agents

The component and/ or compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

10 The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

Polymeric Soil Release Agent

15 Polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present components or compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight.

20 Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

25

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more
30 positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully-anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093,

December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE
5 SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and
10 U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or
15 anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

20 Other Optional Ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include colours and filler salts, with sodium sulfate being a preferred filler salt.

25 Highly preferred compositions contain from about 2% to about 10% by weight of an organic acid, preferably citric acid. Also, preferably combined with a carbonate salt, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides and dyes, such as those described in US Patent

4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present.

Chlorine-Based Bleach

- 5 The detergent compositions can include as an additional component a chlorine-based bleach. However, since the detergent compositions of the invention are solid, most liquid chlorine-based bleaching will not be suitable for these detergent compositions and only granular or powder chlorine-based bleaches will be suitable.
- 10 Alternatively, the detergent compositions can be formulated such that they are chlorine-based bleach-compatible, thus ensuring that a chlorine based bleach can be added to the detergent composition by the user at the beginning or during the washing process.

The chlorine-based bleach is such that a hypochlorite species is formed in aqueous
15 solution. The hypochlorite ion is chemically represented by the formula OCI^- .

Those bleaching agents which yield a hypochlorite species in aqueous solution include alkali metal and alkaline earth metal hypochlorites, hypochlorite addition products, chloramines, chlorimines, chloramides, and chlorimides. Specific examples of
20 compounds of this type include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, sodium dichloroisocyanurate sodium dichloroisocyanurate dihydrate, trichlorocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, chloramine B
25 and Dichloramine B. A preferred bleaching agent for use in the compositions of the instant invention is sodium hypochlorite, potassium hypochlorite, or a mixture thereof.. A preferred chlorine-based bleach can be Triclosan (trade name).

Most of the above-described hypochlorite-yielding bleaching agents are available in solid or concentrated form and are dissolved in water during preparation of the compositions of the instant invention. Some of the above materials are available as aqueous solutions.

5 Laundry Washing Method

- Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods. Preferred washing machines may be the so-called low-fill machines.
- 15 In a preferred use aspect the composition is formulated such that it is suitable for hard-surface cleaning or hand washing. In another preferred aspect the detergent composition is a pre-treatment or soaking composition, to be used to pre-treat or soak soiled and stained fabrics.
- 20 The detergent compositions of the invention may be in the form of a liquid, gel, powder or tablet.

Examples

Abbreviations used in the effervescence component and detergent composition examples

- | | | |
|------------|---|---|
| LAS | : | Sodium linear C11-13 alkyl benzene sulfonate |
| 25 LAS (I) | : | Potassium linear or branched C11-13 alkyl benzene sulfonate |
| TAS | : | Sodium tallow alkyl sulfate |
| CxyAS | : | Sodium C1x - C1y alkyl sulfate |
| C46SAS | : | Sodium C14 - C16 secondary (2,3) alkyl sulfate |
| CxyEzS | : | Sodium C1x-C1y alkyl sulfate condensed with z moles of ethylene |
| 30 | | oxide |

	CxyEz	:	C1x-C1y predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
	QAS	:	R2.N+(CH3)2(C2H4OH) with R2 = C12 - C14
	QAS 1	:	R2.N+(CH3)2(C2H4OH) with R2 = C8 - C 11
5	APA	:	C8 - C10 amido propyl dimethyl amine
	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
	STS	:	Sodium toluene sulphonate
	CFAA	:	C12-C14 (coco) alkyl N-methyl glucamide
10	TFAA	:	C16-C18 alkyl N-methyl glucamide
	TPKFA	:	C12-C14 topped whole cut fatty acids
	STPP	:	Anhydrous sodium tripolyphosphate
	TSPP	:	Tetrasodium pyrophosphate
	Zeolite A	:	Hydrated sodium aluminosilicate of formula
15			Na ₁₂ (AlO ₂ SiO ₂) ₁₂ .27H ₂ O having an absorbency of 70g/100g and a particle size such that 99 wt% is below 15 microns and 0.04 wt % is above 45 microns.
	NaSKS-6	:	Crystalline layered silicate of formula d- Na ₂ Si ₂ O ₅
20	Citric acid I	:	Anhydrous citric acid, 80% having a particle size of from 40 microns to 70 microns, and having a volume median particle size of 55 microns
	Citric acid II	:	Anhydrous or monohydrate citric acid, 80% having a particle size of from 15 microns to 40 microns, having a volume average particle size of 25 microns
25	Malic acid	:	Anhydrous malic acid, 80% having a particle size of from 50 microns to 100 microns, having a volume median particle size of 75 microns
	Maleic acid	:	Anhydrous maleic acid, 80% having a particle size of from 5 microns to 30 microns, having a volume median particle size of 15 microns
30			

	Tartaric acid	:	Anhydrous tartaric acid, 80% having a particle size of from 25 microns to 75 microns, having a volume median particle size of 50 microns
5	Carbonate I	:	Anydrous sodium carbonate having 80% by volume of particles with a particle size from 50 microns to 150 microns with a volume median particle size of 100 microns
	Carbonate II	:	Anydrous sodium carbonate having 80% by volume of particles with a particle size from 35 microns to 75 microns, having a volume median particle size of 55 microns
10	Bicarbonate	II:	Anhydrous sodium bicarbonate having 80% by volume of particles with a particle size from 100 microns to 200 microns with a volume median particle size of 150 microns
	Bicarbonate I	:	Anydrous sodium bicarbonate having 80% by volume of particles with a particle size from 15 microns to 40 microns, having a volume median particle size of 25 microns
15	Silicate	:	Amorphous sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$)
	Sulfate	:	Anhydrous sodium sulfate
	Mg sulfate	:	Anhydrous magnesium sulfate
	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm
20	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
	MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
25	AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
	CMC	:	Sodium carboxymethyl cellulose
	Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
30	Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase

- Protease I : Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
- Alcalase : Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
- 5 Cellulase : Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
- Amylase : Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
- 10 Lipase : Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
- Lipase (1) : Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
- Endolase : Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
- 15 PB4 : Particle containing sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O}$, the particles having a weight average particle size of 950 microns, 85% particles having a particle size of from 850 microns to 950 microns
- 20 PB1 : Particle containing anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$, the particles having a weight average particle size of 800 microns, 85% particles having a particle size of from 750 microns to 950 microns
- 25 Percarbonate : Particle containing sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, the particles having a weight average particle size of 850 microns, 5% or less having a particle size of less than 600 microns and 2% or less having a particle size of more than 1180 microns
- NOBS/LOBS/DOBA : Particle comprising nonanoyloxybenzene sulfonate/lauryloxybenzene sulfonate in the form of the sodium salt or

- decanyl oxybenzoic acid, the particles having a weight average particle size of 750 microns to 900 microns
- 5 NAC-OBS : Particle comprising (6-nonamidocaproyl) oxybenzene sulfonate, the particles having a weight average particle size of from 825 microns to 875 microns
- TAED I : Particle containing tetraacetylenediamine, the particles having a weight average particle size of from 700 microns to 1000 microns
- TAED II : Tetraacetylenediamine of a particle size from 150 microns to 600 microns
- 10 DTPA : Diethylene triamine pentaacetic acid
- DTPMP : Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
- Photoactivated : Sulfonated zinc phthalocyanine encapsulated in bleach (1) dextrin soluble polymer
- 15 Photoactivated : Sulfonated aluminophthalocyanine encapsulated in bleach (2) dextrin soluble polymer
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2,2'-disulfonate
- 20 EDDS : Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
- HEDP : 1,1-hydroxyethane diphosphonic acid
- PEGx : Polyethylene glycol, with a molecular weight of x (typically 4,000)
- PEO : Polyethylene oxide, with an average molecular weight of 50,000
- 25 TEPAE : Tetraethylenepentaamine ethoxylate
- PVI : Polyvinyl imidazole, with an average molecular weight of 20,000
- PVP : Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
- PVNO : Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
- 30

- PVPVI : Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
- QEA : bis((C₂H₅O)(C₂H₄O)_n)(CH₃) -N⁺-C₆H₁₂-N⁺-(CH₃)
bis((C₂H₅O)-(C₂H₄ O))_n, wherein n = from 20 to 30
- 5 SRP 1 : Anionically end capped poly esters
- SRP 2 : Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
- PEI : Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
- 10 Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
- Opacifier : Water based monostyrene latex mixture, sold by BASF
- 15 Aktiengesellschaft under the tradename Lytron 621
- Wax : Paraffin wax
- Effervescence granule: 60 wt % citric acid; 40 wt% sodium carbonate co-compacted or malic acid/sodium carbonate/sodium bicarbonate in weight ratios 40:20:40.

In the following examples of the invention all levels are quoted as % by weight of the composition. The detergents exemplified are granular detergents, however, in order to form tablets, the granular detergents exemplified may undergo a conventional compression tableting step and may optionally be coated.

5

TABLE I

The following compositions are in accordance with the invention.

	A	B	C	D	E	F	G	H	I
<u>Spray-dried Granules</u>									
LAS	10.0	10.0	15.0	5.0	5.0	10.0	-	-	-
TAS	-	1.0	-				-	-	-
MBAS	-	-		5.0	5.0		-	-	-
C ₄₅ AS	-	-	1.0		2.0	2.0	-	-	-
C ₄₅ AE ₃ S	-	-		1.0			-	-	-
QAS			1.0	1.0			-	-	-
DTPA, HEDP and/or EDDS	0.3	0.3	0.5	0.3			-	-	-
MgSO ₄	0.5	0.5	0.1	-			-	-	-
Sodium citrate	-	-	-	3.0	5.0		-	-	-
Sodium carbonate	10.0	7.0	15.0			10.0	-	-	-
Sodium sulphate	5.0	5.0	-	-	5.0	3.0	-	-	-
Sodium silicate 1.6R	-	2.0	4.0	-	2.0		-	-	-
Zeolite A	16.0	18.0	17.0	20.0	-	-	-	-	-
SKS-6	-	-	-	3.0	5.0	-	-	-	-
MA/AA or AA	1.0	2.0	10.0	-	-	2.0	-	-	-
PEG 4000	-	2.0	-	1.0	-	1.0	-	-	-
QEA	1.0	-	-	-	1.0	-	-	-	-
Brightener	0.05	0.05	0.05	-	0.05	-	-	-	-
Silicone oil	0.01	0.01	0.01	-	-	0.01	-	-	-

effervescence granule	10	7.0	-	-	-	-	-	-	-
<u>Agglomerate</u>									
LAS			-	-	-	-	2.0	2.0	-
MBAS			-	-	-	-	-	-	1.0
C ₄₅ AS			1.5	2.5	-	-	2.0	-	-
AE ₃ or AE ₅			-	-	-	-	-	1.0	0.5
Carbonate			2.0	3.0	3.0	1.0	1.0	1.0	-
Sodium citrate			-	-	-	-	-	-	5.0
CFAA			2.0	4.0	-	-	-	-	-
Citric acid			-	-	-	4.0	-	1.0	1.0
QEA			-	-	-	2.0	2.0	1.0	-
SRP			-	-	-	1.0	1.0	0.2	-
Zeolite A			-	5.0	6.0	15.0	26.0	15.0	16.0
Sodium silicate			-	-	-	-	-	-	-
PEG	-	-	-	-	-	-	4.0	-	-
<u>Builder Agglomerates</u>									
SKS-6	6.0	12.0	-	-	6.0	3.0	-	7.0	10.0
LAS	4.0	5.0	-	-	5.0	3.0	-	10.0	12.0
<u>Dry-add particulate components</u>									
effervescence granule	-	-	-	4.0	25	8.0	12.0	2.0	4.0
QEA	-	-	-	0.2	0.5	-	-	-	-
NACAOBS	3.0	-	-	4.5	-	-	-	2.5	-
NOBS	1.0	3.0	3.0	-	-	-	-	-	5.0
TAED I	2.5	-	-	1.5	2.5	6.5	-	1.5	-
MBAS	-	-	-	8.0	-	-	8.0	-	4.0
LAS (flake)	10.0	8.0	-	-	-	-	-	8.0	-

Citric acid II	-	-	-						
<u>Spray-on</u>									
Brightener	0.2	0.2	0.3	0.1	0.2	0.1	-	0.6	0.3
Dye	-	-	-	0.3	0.05	0.1	-	-	-
AE7	-	-	-	-	-	0.5	-	0.7	-
Perfume	1.0	0.5	1.1	0.8	0.3	0.5	0.3	0.5	-
<u>Dry-add</u>									
Citrate	-	-	16.0	4.0	-	5.0	15.0	-	5.0
Percarbonate	15.0	3.0	6.0	10.0	-	-	24.0	18.0	5.0
Perborate	-	-	-	-	6.0	18.0	-	-	-
Photobleach	0.02	0.02	0.02	0.1	0.05	-	0.3	-	0.03
Enzymes (cellulase, amylase, protease, lipase)	1.3	0.3	0.5	0.5	0.8	2.0	0.5	0.16	0.2
Carbonate	0.0	10.0	-	-	-	5.0	8.0	10.0	5.0
Perfume (encapsulated)	-	0.5	0.5	-	0.3	-	0.2	-	-
Silicone antifoam	1.0	0.6	0.3	-	0.10	0.5	1.0	0.3	1.2
Soap	0.5	0.2	0.3	3.0	0.5	-	-	0.3	-
Citric acid (I or coarse)	-	-	-	6.0	5.0	-	-	-	5.0
Dyed carbonate (blue, green)	0.5	0.5	1.0	2.0	-	0.5	0.5	0.5	1.0
SKS-6	-	-	-	4.0	-	-	-	6.0	-
Fillers up to 100%									

TABLE II

The following compositions are in accordance with the invention.

	A	B	C	D	E	F	G	H	I
--	---	---	---	---	---	---	---	---	---

<u>Spray-Dried Granules</u>									
LAS or LAS (I)	10.0	10.0	16.0	5.0	5.0	10.0	-	-	-
TAS	-	1.0	-				-	-	-
MBAS	-	-	-	5.0	5.0		-	-	-
C ₄₅ AS	-	-	1.0		2.0	2.0	-	-	-
C ₄₅ AE ₃ S	-	-	-	1.0			-	-	-
QAS	-	-	1.0	1.0			-	-	-
DTPA, HEDP and/or EDDS	0.3	0.3	0.3	0.3			-	-	-
MgSO ₄	0.5	0.4	0.1	-			-	-	-
Sodium citrate	10.0	12.0	17.0	3.0	5.0		-	-	-
Sodium carbonate	15.0	8.0	15.0			10.0	-	-	-
Sodium sulphate	5.0	5.0	-	-	5.0	3.0	-	-	-
Sodium silicate 1.6R	-	-	-	-	2.0		-	-	-
Zeolite A	-	-	-	2.0	-	-	-	-	-
SKS-6	-	-	-	3.0	5.0	-	-	-	-
MA/AA or AA	1.0	2.0	10.0	-	-	2.0	-	-	-
PEG 4000	-	2.0	-	1.0	-	1.0	-	-	-
QEA	1.0	-	-	-	1.0	-	-	-	-
Brightener	0.05	0.05	0.05	-	0.05	-	-	-	-
Silicone oil	0.01	0.01	0.01	-	-	0.01	-	-	-
Effervescence granule I, III, IV VII or VIII	5	12	-	-	-	-	-	-	-
<u>Agglomerate</u>									
LAS	-	-	-	-	-	-	2.0	2.0	-
MBAS	-	-	-	-	-	-	-	-	1.0
C ₄₅ AS	-	-	-	-	-	-	2.0	-	-
AE ₃	-	-	-	-	-	-	-	1.0	0.5
Carbonate	-	-	-	-	4.0	1.0	1.0	1.0	-

QEA	-	-	-	0.2	0.5	-	-	-	-
Citrate	4.0	-	3.0	4.0	-	5.0	15.0	-	5.0
Percarbonate	15.0	3.0	6.0	10.0	-	-	12.0	18.0	5.0
Perborate	-	-	-	-	6.0	18.0	-	-	-
Photobleach	0.02	0.02	0.02	0.1	0.05	-	0.3	-	0.03
Enzymes (cellulase, amylase, protease, lipase)	1.5	0.3	0.5	0.5	0.8	2.0	0.5	0.16	0.2
Carbonate II	-	-	-	-	-	5.0	8.0	10.0	5.0
Perfume (encapsulated)	0.6	0.5	0.5	-	0.3	0.5	0.2	0.1	0.6
Suds suppressor	1.0	0.6	0.3	-	0.10	0.5	1.0	0.3	1.2
Soap	0.5	0.2	0.3	3.0	0.5	-	-	0.3	-
Citric acid II	-	-	-	-	-	-	-	5.0	5.0
Dyed carbonate (blue, green)	0.5	0.5	?	2.0	-	0.5	0.5	0.5	1.0
SKS-6	-	-	-	4.0	-	-	-	6.0	-
Fillers up to 100%									

Table III

The following are high density and bleach-containing detergent formulations according to
5 the present invention:

	A	B	C
Blown Powder			
Zeolite A	-	-	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	3.0	-	3.0

C45AS	3.0	2.0	4.0
QAS	-	-	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
effervescence granule	7.0	-	-
TAED	-	-	3.0
Agglomerates			
effervescence granule	7.0	-	7.0
QAS	1.0	-	-
LAS	-	11.0	7.0
TAS	2.0	2.0	1.0
Silicate	3.0	-	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Agglomerate			
NaSKS-6 (I) or (II)	15.0	12.0	5.0
LAS	8.0	7.0	4.0
AS	5.0	-	-
Spray On			
Perfume	0.3	0.3	0.3
C25E3	2.0	-	2.0
brightener	0.1	0.4	
photobleach	0.03	0.05	-
Dry additives			
QEA	1.0	0.5	0.5
Citric acid I	5.0	-	2.0
Bicarbonate I	-	3.0	-
Carbonate II	8.0	15.0	10.0

NAC OBS	6.0	-	5.0
Manganese catalyst	-	-	0.3
TAED I		3.0	-
NOBS	-	2.0	-
Percarbonate	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
effervesce granule	-	5.5	7.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Claims

1. A detergent composition comprising zeolite characterised in that the zeolite has a dibutyl phthalate (DBP) absorption value of at least 68g/100g as defined hererin, at
5 least 99 wt% of the zeolite has a particle size of 15 microns or below (measured as defined herein) and no more than 0.09% by weight has particle size greater than 45 microns (measured as defined herein).
2. A detergent composition according to claim 1 in which no more than 0.05% by weight of the zeolite has a particle size greater than 45 μm .
- 10 3. A detergent composition according to claim 2 in which no more than 0.01% by weight of the zeolite has a particle size greater than 45 μm .
4. A detergent composition according to any preceding claim in which the zeolite has a particle size such that 99 wt% of the zeolite has a particle size of 0.1 μm or above.
5. A detergent composition according to any preceding claim in which the zeolite is in
15 admixture with a pre-formed detergent composition or component thereof.
6. A detergent composition according to any preceding claim additionally comprising a percarbonate compound.
7. A detergent composition according to any preceding claim additionally comprising a fabric-softening clay.
- 20 8. A detergent composition according to any preceding claim in which zeolite is present as part of a pre-formed particle, the pre-formed particle additionally comprising at least 5 wt % of an anionic surfactant.
9. A detergent composition according to claim 8 in which the anionic surfactant has a Kraft point below 40°C.
- 25 10. A detergent composition according to any of the preceding claims in which the zeolite is Zeolite A or Zeolite X.
11. A detergent composition according to any of the preceding claims in which the zeolite is Zeolite A.
12. A process for manufacturing a detergent composition in which zeolite having a DBP
30 value of at least 68g/100g and a particle size distribution such that at least 99 wt% has

a particle size 15 microns or below, and less than 1 wt % of the zeolite has a particle size greater than 45 microns is mixed with additional detergent ingredient to form an agglomerate or extrudate.

- 5 13. A process for manufacturing a detergent composition in which zeolite having a DBP value at least 68g/100g and a particle size distribution such that at least 99 wt% of the zeolite has a particle size of 15 μ m or below, is classified by passing through a classification screen to removes substantially all particles of zeolite having a particle size above 45 μ m , the remaining zeolite being mixed with additional detergent ingredients in a second step.
- 10 14. Use of a zeolite having a particle size distribution such that at least 99 wt% has a particle size 15 μ m or below, and less than 1 wt % of the zeolite has a particle size greater than 45 μ m and a DBP absorption value of at least 68 in a detergent composition for reducing fabric residues.

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INTERNATIONAL SEARCH REPORT

International Application No

PL./US 99/05065

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/12 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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18/11/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/05065

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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