

"BLEACH ACTIVE DETERGENT ADDITIVE COMPOSITION"

This invention relates to granular detergent additive compositions containing a bleach active compound and an activator for the bleach active compound. More particularly, this invention relates to a method for intimately mixing two powdery mutually reactive ingredients: a bleach active compound and an activator therefor, with an inert, normally solid binder, in the form of solid particles or granules, and to the resulting particulate bleach active detergent additive composition.

The difficulties and problems encountered when attempting to incorporate in a detergent composition detergent additive ingredients, such as fluorescers, germicides, anti-tarnishing agents, enzymes, perfumes, bleach active compounds, bleach activator compounds, etc., which additives are either reactive with each other or with other components of the composition or which are liable to decompose, discolour, separate out or aggregate, have been recognised in the art.

One proposal for solving this problem has been provided in British Patent Specification 1,204,123 to Unilever Ltd. According to this proposal, the detergent additive is in the form of granules made by mechanical working of a mixture of an organic extrudable solid and the additive, with the additive being dispersed throughout the granules. The additive-containing granules may then be mixed with the remaining ingredients of the detergent composition.

- According to U.S. Patent 4,399,049 to Gray and Harris, the dispersibility or dissolution characteristics of the granular additives of the above-mentioned British Patent to Unilever are
5. improved by a detergent additive composition in the form of an extrudate comprising by weight thereof:
 - (a) from about 75% to about 95% of particulate, infusible solids having a particle size distribution such that at least about 50% thereof passes a 250
 10. micrometer screen and comprising storage-sensitive detergent additive material, and
 - (b) from about 5% to about 25% of ethoxylated nonionic surfactant melting in the range from about 20°C to about 60°C, the composition being prepared by
 15. mixing the particulate infusible solids and ethoxylated nonionic surfactant in liquid form to form a substantially homogeneous friable mass, and mechanically extruding the friable mass by means of a screw with radial discharge through an apertured
 20. screen to form extrudate in the form of elongate particles having an average lateral dimension in the range from 0.5 millimeters to 2 millimeters, and an average longitudinal dimension in the range from about 1 mm to about 6 mm.
 25. The storage-sensitive detergent additive material can be a unifunctional or multifunctional material selected from bleaching auxiliaries, photo-activators, fluoescers, dyes, perfumes, germicides, enzymes, suds controllers, fabric conditioners and
 30. the like. Preferred detergent additive materials are

organic peroxyacid bleach precursors also called bleach activators.

As described in this prior art, the above and other attempts to improve the storage-stability characteristics of detergent additive materials such as bleach activators has involved protection of the additive material from its "hostile" environment by agglomerating, coating or encapsulating the material with an organic coating material which can readily form a substantially cohesive and continuous plastic matrix in which the additive material can be embedded.

While satisfactory improvements in storage-stability characteristics have been achieved with the above-mentioned techniques, it has been found that in the case where the detergent additive is a bleach activator, the activity or action of the detergent additive is often impaired by being embedded within the organic matrix, even where the dispersibility or dissolution characteristics of the binder are good.

Accordingly, the present invention aims to provide detergent additive compositions having improved bleaching effectiveness, especially at low-wash water temperatures. More particularly, the invention aims to provide detergent additive granules in which both of the oxygen-containing bleach and bleach activator are incorporated as a result of which improved stain removal (bleach activity) is achieved without impairing the storage-characteristics of the detergent additive compositions or of the full detergent compositions to which they are

added. The invention also aims to provide the improved detergent compositions which include the detergent additive compositions as well as the method for preparing the granular detergent additive compositions.

5. The present invention is based on the quite surprising discovery that the mutually reactive bleach compound and bleach activator which will rapidly react with each other in the presence of water to form the bleach active compound can be intimately mixed with each other prior to mixing with a molten normally solid water-soluble or dispersible binder without reacting with each other and that after extrusion and cutting the resulting individual granules provide a protective coating for the active bleach forming reactants. Still further, because of the intimate association between individual particles of bleach compound and bleach activator, upon the dissolution or dispersion of the binder in the wash water, the bleach compound and bleach activator can substantially immediately come into contact with and react with each other to provide a uniform dispersion or solution of the bleach active compound throughout the wash water thereby providing more effective contact between the fabrics to be treated and the bleach active compound and consequently more effective stain removal.

The invention also provides a full detergent composition containing the granular detergent additive composition as well as a method for preparing the granular or detergent additive composition.

- According to the method aspect, the present invention provides a method for preparing a granular detergent additive which contains each of a bleach compound and an activator for the said bleach compound, the said method comprising,
- .5. mixing finely divided bleach compound and finely divided activator for the said bleach compound, and any other optional powdery additives,
10. mixing the mixture of bleach compound and activator compound with a molten, normally solid water-soluble binder,
- extruding the resulting mixture, and cooling and shaping the extruded mass to obtain the granular detergent additive product,
15. the mixing steps being carried out under anhydrous conditions, and at a temperature at which the bleach compound and activator compound are substantially non-reactive with each other, whereby the said bleach compound and activator compound in
20. the said granules will not react with each other to any significant extent until the granules are added to water at a temperature which will dissolve the said binder.
25. According to the composition aspect of the present invention, there is first provided a detergent additive comprising a mixture of particles of an oxygen-containing bleach compound and particles of an activator for said bleach compound, wherein the mixed particles are dispersed in a matrix of a molten
- 30.

water soluble binder. There is also provided a full powdery or granular detergent composition comprising at least one organic surfactant compound preferably selected from anionic, nonionic, amphoteric, or zwitterionic organic surfactants or mixtures thereof, at least one inorganic detergent builder salt, organic builder salt or mixture thereof, and the granular detergent additive containing therein each of the oxygen containing bleach compound and bleach activator compound dispersed in a water-soluble binder. Other detergent additives

and adjuncts can also be included in the detergent composition.

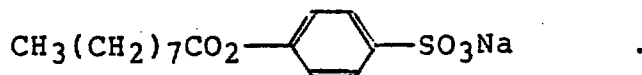
- The present invention provides bleach active granular detergent additives which when added to
5. water, e.g. an aqueous wash bath, either directly or as a component of a built laundry detergent composition, will promptly release the oxygen-containing bleach compound and activator compound to form a bleach active compound, particularly a low-temperature
 10. bleach active compound, highly effective in removing/ decolourizing oxidizable stains.

- As used herein the "oxygen-containing bleach compound" contemplates hydrogen peroxide (H_2O_2) and compounds which liberate H_2O_2 in water. Preferred
15. examples of compounds which liberate H_2O_2 in water are the percompound salts, such as the alkali metal salts of perborates, percarbonates, perpyrophosphates, persilicates and peroxides, and urea-hydrogen peroxide addition product. The alkali metal perborates are
 20. preferred, and sodium perboratemonohydrate is especially preferred.

- The bleach activators or activators for the oxygen-containing bleach compounds, i.e. percompounds, include any of the activators for percompound
25. bleaching agents, which are capable of lowering the temperature at which the percompound is effective, generally to a temperature lower than about $60^\circ C$, especially lower than about $40^\circ C$, for example 20 to $30^\circ C$. The bleach activator compounds are believed to
 30. react with hydrogen peroxide to form a bleach

species, such as peracids, which are active at lower temperatures than hydrogen peroxide. Bleach activator compounds are well known in the art and any of the bleach activator compounds mentioned in the above-mentioned U.S. Patent 4,399,049 (referred to therein as "organic peroxyacid bleach precursor") or British Patent 1,204,123, as well as those mentioned in U.S. Patent 4,290,903 and in British Patents 1,395,006 and 1,441,416 can be used in the present invention.

A preferred class of activator compounds are the esters and especially highly preferred are the acyl phenol sulphonates and acylalkyl phenol sulphonates (also known as acyloxybenzene - and alkyl acyloxybenzene sulphonates, respectively). An example of acyloxybenzene sulphonate is sodium p-acetoxybenzene sulphonate (also known as sodium acetyl phenol sulphonate). Examples of acylalkyl phenol sulphonates include sodium 2-acetoxy-5-dodecyl benzene sulphonate, sodium 2-acetoxy-5-dodecylbenzene sulphonate, sodium-2-acetoxycapryl benzene sulphonate, etc. A particularly useful bleach activator is sodium nonanoyloxybenzene sulphonate, of formula



Generally, the acyloxy substituent can have from about 2 to 20 carbon atoms and may be linear or branched. There may also be one or two substituents present on the benzene ring, such as alkyl, e.g.

C₁-C₁₅ alkyl. British Patent Specifications Nos. 963,135 and 1,147,871 disclose the preparation and use of acyloxybenzene sulphonates.

- For the purposes of the invention, the activator material will preferably have a mean particle size less than 500 microns, preferably less than 300 microns, and most preferably less than 150 microns. For example, a particle size distribution such that at least 50%, preferably at least about 80% thereof passes a 250 micrometer screen, preferably a 150 micrometer and especially preferably a 100 micrometer screen. Particle sizes down to about 1 micron or even submicron size can be used. Such particle sizes can either be achieved by adjusting the conditions under which the activator is precipitated or crystallized in the final stages of manufacturing or by milling or otherwise reducing the size of the formed crystalline material. Suitable techniques are well known in the art. The oxygen-containing bleach compound should be in the same general particle size range as described for the bleach activator. Particle sizes for the bleach compound and activator should not be so small that dusting, caking, agglomeration or insufficient particle loading levels in the granules becomes a problem.
5. material will preferably have a mean particle size less than 500 microns, preferably less than 300 microns, and most preferably less than 150 microns. For example, a particle size distribution such that at least 50%, preferably at least about 80% thereof
 10. passes a 250 micrometer screen, preferably a 150 micrometer and especially preferably a 100 micrometer screen. Particle sizes down to about 1 micron or even submicron size can be used. Such particle sizes can either be achieved by adjusting the conditions
 15. under which the activator is precipitated or crystallized in the final stages of manufacturing or by milling or otherwise reducing the size of the formed crystalline material. Suitable techniques are well known in the art. The oxygen-containing bleach
 20. compound should be in the same general particle size range as described for the bleach activator. Particle sizes for the bleach compound and activator should not be so small that dusting, caking, agglomeration or insufficient particle loading levels in the
 25. granules becomes a problem.

- The ratio of bleach compound (per salt) to activator compound will depend on the chemical natures of the respective compounds, and particularly on the number of functional reactive groups on the
30. activator which can react with hydrogen peroxide to

form the desired low temperature active oxyacid bleach active compound. Generally, the amount of activator should be sufficient to provide about 0.05 to 2 moles of activator per gram atom of active oxygen of the oxygen-containing bleach compound. On a weight basis the bleach and bleach activator are preferably present in the additive at a weight ratio of from about 4:1 to about 0.3:1.

The total amount of oxygen-containing bleach compound and bleach activator in the granular detergent additive is not especially critical except that the solids loading is desirably sufficiently high to yield adequate quantity of the bleach active compound when added to the wash water, whether directly as such, as in a separately prepared bleaching composition, or as a component of a fully built detergent composition. Furthermore, it is highly desirable to provide a sufficiently high solids loading level so that upon dissolution of the binder and release of the particles of bleach compound and activator compound the respective reactive particles will be in sufficiently close proximity to each other that substantially instantaneous reactions will occur. On the other hand, it is preferred and necessary that the solids loading levels not be so high that insufficient coverage of the particles by the binder results, e.g. some of the particles remain exposed at the surfaces of the granules. Generally, therefore, total solids content (powdery oxygen-containing bleach compound plus powdery activator compound, plus any other additives, e.g. colouring agents, builders, fillers, etc.) of the granular additive will

preferably be within the range of from about 40% to about 97% by weight, preferably from about 50% to about 95% by weight of the granules, and especially preferably from about 75 to 95% by weight of the granules. The bleach and bleach activator preferably comprise 55 to 95% by weight of the additive.

Furthermore, it will also be appreciated that within these broad ranges of solids loading levels the preferred loading levels may be more specifically determined based on such factors as the type of bleach forming reactants and especially on the nature and type of the detergent composition to which the granular detergent additive will be added. Specifically, it is important to provide a solids loading level which will result in a product density (referred to in the trade as cup weight or CW) which will match as closely as possible that of the powdery or granular detergent composition. By matching cup weights there is a reduced tendency for particle settling or separation to occur.

The normally solid water-soluble or water dispersible organic binder used as the matrix for coating and encapsulating the bleach forming reactants can be any of the water-soluble or water-dispersible extrudable solids disclosed in the above-mentioned British Patent 1,204,123 including polyglycols, polyalkylene oxides, C₁₂-C₂₀ alpha-olefin sulphonates, etc. However, the preferred organic binders are the nonionic surfactants mentioned in British Patent 1,204,123 and more particularly, the ethoxylated nonionic surfactants described in greater

- detail in the aforementioned U.S. Patent 4,399,049 which are solid at room temperature, i.e. having melting points above about 20°C, preferably above about 30°C, up to about 60°C or more, but below the
5. melting points of the oxygen-containing bleach compound and the bleach activator compound.

- With regard to the ethoxylated nonionic surfactant component, this can be broadly defined as compounds produced by the condensation of ethylene
10. oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydro-
15. soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl
20. phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 3 to
25. 30, preferably 5 to 14 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerized propylene, diisobutylene, octene and nonene. Other examples include dodecylphenol
30. condensed with 9 moles of ethylene oxide per mole of

phenol, dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and diisooctylphenol condensed with 13 moles of ethylene oxide.

5. 2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 30, preferably from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 3 to about 50 moles, preferably 5 to about 45
10. moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 3 and 30, desirably between 5 and 14 moles of ethylene oxide per mole of aliphatic alcohol or the aliphatic
15. alcohol has between 10 and 30 carbon atoms and is ethoxylated with between 30 and 50 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural
20. fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being tradenames of Shell) or Synperonics,
25. which are understood to have about 50% 2-methyl branching (Synperonic is a tradename of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the tradename Lial by Liquichimica. Specific examples of nonionic
30. surfactants falling within the scope of the invention

- include Dobanol 45-4, Dobanol 45-7, Dobanol 45-9, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Neodol 25-7, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of
5. between 5 and 12 moles or between 35 and 45 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an
10. average of between 7 and 12 moles or between 35 and 45 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series
15. having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The
20. molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the tradename of "Pluronic" supplied by
25. Wyandotte Chemicals Corporation.

- Of these, the second group of nonionic surfactants, i.e. the condensation products of primary or secondary aliphatic alcohols with ethylene oxide are preferred. It is also within the scope of the
30. present invention to use such condensation products

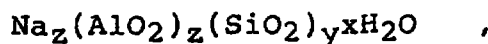
wherein a portion of the ethylene oxide is replaced by propylene oxide in amounts which do not impair the water solubility of the binder.

- The amount of the organic, normally solid, water-soluble or water-dispersible binder in the detergent additive granules should be sufficient to provide continuous coverage for the granules with the powder solids being fully embedded therein and thereby protected from exposure to the outside atmosphere.
5. Preferably, the amount of binder is also sufficient to provide a continuous coating on each individual particle, as well as providing a continuous matrix for the dispersed coated particles. Generally, an amount of the organic binder of at least 3% by weight, preferably at least 5% by weight will be sufficient. The upper limit of the amount of binder is not particularly critical but generally care should be taken to avoid using such large amounts of binder that dissolution of the granules is delayed or
10. to preclude adequate loading levels. Accordingly, the upper limit of the amount of binder will generally be about 60%, preferably no more than 50%, especially preferably no more than about 25% based on the total weight of the granules.
15. Various optional ingredients can be incorporated into the additive and detergent compositions of the present invention in order to increase efficacy, particularly in the area of detergency and stain removal. The total amount of such optional
20. ingredients lies in the range 1%-70%, preferably
- 25.
- 30.

1%-30% of the additive composition when incorporated directly therein, or in the range 40%-99.0%, preferably 90%-99.5% when incorporated in the non-additive portion of a detergent composition.

5. The detergent additive compositions of the present invention can include a particulate dispersant, either in intimate mixture with the detergent additive material, or more as a surface-coating agent on the extrudate at a level of from
10. about 1% to 3%, especially from about 1.1% to 2.5% by weight of the composition. Preferred dispersants include water-insoluble silica or silicate, water-soluble inorganic salt, or organic polyacid or salt thereof. Water-insoluble silicates include
15. aluminosilicates of the clay or zeolite classes or magnesium silicate type of material. Aluminosilicates of the clay variety include sheet-like natural clays, such as the smectite-type and kaolinite-type groups. Highly suitable smectite-type clays include alkali
20. and alkaline earth metal montmorillonites, saponites and hectorites; highly suitable kaolinite-type materials include kaolinite itself, calcined kaolin and metakaolin.

- Other suitable water-insoluble silicates include
25. aluminosilicates of the zeolite type, particularly those of the general formula



- wherein z and y are integers of at least about 6, the molar ratio of z to y is in the range from about 1.0
30. to about 0.5 and x is a number such that the moisture

content of the aluminosilicate is from about 10% to about 28% by weight thereof. Particularly preferred materials of the zeolite class are those prepared from clay themselves, especially A-type zeolites

5. prepared by alkali treatment of calcined kaolin.

Another suitable water-insoluble silicate is a magnesium silicate of formula $n \text{ MgO}:\text{SiO}_2$ where n is in the range from about 0.25 to about 4.0.

10. Suitable water-soluble inorganic salts include magnesium sulphate or chloride, sodium bicarbonate, as well as the calcium or magnesium complexing agents useful as detergency builders. These are discussed in detail below.

15. Suitable organic acids include lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patents Nos. 821,368, 821,369, and 821,370; succinic acid, malonic acid, (ethylene-dioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid, and fumaric acid;
20. citric acid, aconitic acid, citraconic acid, carboxymethyloxy succinic acid, lactoxysuccinic acid, and 2-oxa-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid, and 1,1,2,3-propane
25. tetracarboxylic acid, cyclopentane-cis, cis, cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-cis dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic
30. acid, mellitic acid, pyromellitic acid and the

phthalic acid derivatives disclosed in British Patent 1,425,343; ethylene diamine tetra(methylenephosphonic acid), diethylene triamine penta(methylenephosphonic acid) and the acid salts of the above organic acids. Of the above, the preferred organic acids are citric, glycollic and lactic acids and the two phosphonic acids.

As well as being a dispersant, the above acidic materials also have a pH regulating function, of course, and are particularly valuable for the granular extrudates containing bleach activators of the present invention.

A highly preferred ingredient of the detergent compositions of the present invention is a surfactant or mixture of surfactants, especially an anionic surfactant or a mixture thereof with nonionic, cationic, zwitterionic and ampholytic surfactant. The surfactant is preferably present in the non-additive portion of the detergent composition at a level of from about 1% to about 20%, more preferably from about 3% to about 16% of the total composition. A typical listing of the classes and species of these surfactants is given in U.S. Patent No. 3,663,961 issued to Norris on 23rd May, 1972.

The anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulphonate, sulphate, carboxy-

- late, phosphonate and phosphate. Examples of suitable anionic detergents which fall within the scope of the present invention include the soaps, such as the water-soluble salts of higher fatty acids
5. or resin acids, such as may be derived from fats, oils and waxes of animal or vegetable origin, e.g. the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulphated and
 10. sulphonated synthetic detergents, particularly those having about 8 to 26, and preferably about 12 to 22 carbon atoms to the molecule.

- As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulphonates, such as the higher
15. alkyl benzene sulphonates containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g. the sodium salts of higher alkyl benzene sulphonates or of the higher alkyl toluene, xylene and phenol sulphonates; alkyl naphthalene
 20. sulphonate, ammonium diamyl naphthalene sulphonate, and sodium dinonyl naphthalene sulphonate. In one preferred type of composition, there is used a linear alkyl benzene sulphonate having a high content of 3-(or higher) phenyl isomers and a correspondingly low
 25. content (well below 50%) of 2-(or lower) phenyl isomers; in other terminology, the benzene ring is preferably attached in large part at the 3 or higher (e.g. 4, 5, 6 or 7) position of the alkyl group and the content of isomers in which the benzene ring is
 30. attached at the 2 or 1 position is correspondingly

low. Particularly preferred materials are set forth in U.S. Patent No. 3,320,174, 16th May, 1967 of J. Rubinfeld.

- Other anionic detergents are the olefin
5. sulphonates, including long chain alkene sulphonates, long chain hydroxyalkane sulphonates or mixtures of alkenesulphonates and hydroxylalkanesulphonates. These olefin sulphonate detergents may be prepared, in known manner, by the reaction of SO_3 with long
 10. chain olefins (of 8-25, preferably 12-21, carbon atoms) of the formula RCH=CHR^1 , where R represents an alkyl group and R^1 represents an alkyl group or a hydrogen atom, to produce a mixture of sultones and alkenesulphonic acids, which mixture is then treated
 15. to convert the sultones to sulphonates. Examples of other sulphate or sulphonate detergents are paraffin sulphonates having, for example, about 10-20, preferably about 15-20, carbon atoms, such as the primary paraffin sulphonates made by reacting long
 20. chain alpha olefins and bisulphates (e.g. sodium bisulphite) or paraffin sulphonates having the sulphonate groups distributed along the paraffin chain such as the products made by reacting a long chain paraffin with sulphur dioxide and oxygen under
 25. ultraviolet light followed by neutralization with NaOH or other suitable base (as in U.S. Patents 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Patent 735,096); sulphates of higher alcohols; salts of alpha-sulphofatty esters (e.g. of about 10 to 20
 30. carbon atoms, such as methyl alpha-sulphomyristate or alpha-sulphotallowate).

Examples of sulphates of higher alcohols are sodium lauryl sulphate, sodium tallow alcohol sulphate, Turkey Red Oil or other sulphated oils, or sulphates, of mono- or di-glycerides of fatty acids

5. (e.g. stearic monoglyceride monosulphate), alkyl poly(ethenoxy) ether sulphates such as the sulphates of the condensation products of ethylene oxide and lauryl alcohol (usually having 1 to 5 ethenoxy groups per molecule); lauryl or other high alkyl glyceryl
10. ether sulphonates, aromatic poly(ethenoxy) ether sulphates such as the sulphates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule).

The suitable anionic detergents include also the

15. acyl sarcosinates (e.g. sodium lauroylsarcosinate) the acyl esters (e.g. oleic acid ester) of isethionates, and the acyl N-methyl taurides (e.g. potassium N-methyl lauroyl- or oleyol tauride).

Highly preferred water soluble anionic detergent

20. compounds are the ammonium and substituted ammonium (such as mono-, di- and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulphonates, olefin
25. sulphonates, the higher alkyl sulphates, and the higher fatty acid monoglyceride sulphates. The particular salts will be suitably selected depending upon the particular formulation and the proportions therein.

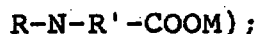
30. Nonionic surface active agents include those

- surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylates, hydroxyl, amido or amino with
5. ethylene oxide or with the polyhydration product thereof, polyethylene glycol.

- As examples of nonionic surface active agents which may be used there may be noted the condensation products of alkyl phenols with ethylene oxide. e.g.
10. the reaction product of isooctyl phenol with about 6 to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols such as tridecyl alcohol with ethylene oxide; ethylene
 15. oxide addends of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol monooleate and mannitan mono-palmitate, and the condensation products of polypropylene glycol with ethylene oxide.
 20. A particularly suitable composition, for use as a granular detergent material contains a mixture of a linear alkylbenzenesulphonate, as previously described, soap and nonionic detergent, with the soap and nonionic detergent being present in minor
 25. portions. The ratios of the amount of (A) soap, and (B) nonionic detergent, to (C) the total amount of the synthetic anionic sulphate and sulphonate detergent, in this mixture, are preferably as follows: A:C about 1:10 to 1:2, preferably about 1:4 to 1:6, on an
 30. anhydrous basis, B:C about 1:10 to 1:3, e.g. about

- 1:4 to 1:6, on an anhydrous basis. The component (C) may comprise a blend of the linear alkylbenzene-sulphonate detergent with other anionic synthetic sulphate or sulphonate detergents (e.g. olefin
5. sulphonates, paraffin sulphonates having the sulphonate groups distributed along the paraffin chain, or alkyl sulphates) with the alkylbenzene-sulphonate constituting say one-third, one-half, or two-thirds of this blend. More broadly, where the
10. detergent components (B) and (C) are present, the total level of nonionic surfactant in the instant composition of the present invention may be such as to provide a weight ratio of nonionic surfactant: anionic surfactant in the range from about 1:4 to
15. about 4:1.

- Examples of suitable amphoteric detergents are those containing both an anionic and a cationic group and a hydrophobic organic group, which is advantageously a higher aliphatic radical, e.g. of 10 to 20
20. carbon atoms. Among these are the N-long chain alkyl aminocarboxylic acids (e.g. of the formula



25. the N-long chain alkyl iminodicarboxylic acids (e.g. of the formula $RN(R'COOM)_2$) and the N-long chain alkyl betaines (e.g. of the formula



30. $R^+-N-R'-COO^-)$

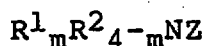


- where R is a long chain alkyl group, e.g. of about 10-20 carbons, R' is a divalent radical joining the amino and carboxyl portions of an amino acid (e.g. an alkylene radical of 1-4 carbon atoms), M is hydrogen or a salt-forming metal, R² is a hydrogen or another monovalent substituent (e.g. methyl or other lower alkyl), and R³ and R⁴ are monovalent substituents joined to the nitrogen by carbon-to-nitrogen bonds (e.g. methyl or other lower alkyl substituents).
5. Examples of specific amphoteric detergents are N-alkyl-beta-aminopropionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl glycine; the alkyl group may be, for example, that derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol (or a laurylmyristyl mixture), hydrogenated tallow alcohols, cetyl, stearyl, or blends of such alcohols. The substituted aminopropionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be
 10. used in the practice of the present invention. Examples of other amphoteric detergents are the fatty imidazolines, such as those made by reacting a long chain fatty acid (e.g. of 10 to 20 carbon atoms) with diethylene triamine and monohalocarboxylic acids
 15. having 2 to 6 carbon atoms, e.g. 1-coco-5-hydroxyethyl-5-carboxymethyl-imidazoline; betaines containing a sulphonic group instead of the carboxylic group; betaines in which the long chain substituent is joined to the carboxylic group without
 20. an intervening nitrogen atom, e.g. inner salts of 2-
 - 25.
 - 30.

trimethylamino fatty acids such as 2-trimethylamino-lauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atom is replaced by phosphorous.

5. The addition of a water-soluble cationic surfactant to the present compositions has been found to be useful for improving the greasy stain removal performance. Suitable cationic surfactants are those having a critical micelle concentration for the pure material of at least 200 ppm and preferably at least 500 ppm specified at 30°C and in distilled water. Literature values are taken where possible, especially surface tension or conductimetric values - see Critical Micelle Concentrations of Aqueous Surfactant System, P. Mukerjee and K.J. Mysels, NSRDS-NBS 37 (1971).

A highly preferred group of cationic surfactants of this type have the general formula:



20. wherein R^1 is selected from C_8 -20 alkyl, alkenyl and alkaryl groups; R^2 is selected from C_1 -4 alkyl and benzyl groups, Z is an anion in number to give electrical neutrality; and m is 1, 2 or 3; provided that when m is 2, R^1 has less than 15 carbon atoms
25. and when m is 3, R^1 has less than 9 carbon atoms.

Where m is equal to 1, it is preferred that R^2 is a methyl group. Preferred compositions of this mono-long chain type include those in which R^1 is C_{10} to C_{16} alkyl group. Particularly preferred

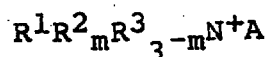
30. compositions of this class include C_{12} alkyl tri-

methyllummonium halide and C₁₄ alkyl trimethyllummonium halide.

- Where m is equal to 2, the R¹ chains should have less than 14 carbon atoms. Particularly preferred
5. cationic materials of this class include di-C₈ alkyl-dimethyllummonium halide and di-C₁₀ alkyldimethyllummonium halide materials.

- Where m is equal to 3, the R¹ chains should be less than 9 carbon atoms in length. An example is
10. trioctyl methyl ammonium chloride.

Another highly preferred group of cationic compounds have the general formula:

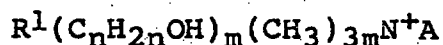


- wherein R¹ represents a C₆₋₂₄ alkyl or alkenyl group
15. or a C₆₋₁₂ alkaryl group, each R² independently represents a (C_nH_{2n}O)_xH group where n is 2, 3, or 4 and x is from 1 to 14, the sum total of C_nH_{2n}O groups in R_m² being from 1 to 14, each R³ independently represents a C₁₋₁₂ alkyl or alkenyl group, an aryl
20. group or a C₁₋₆ alkaryl group, m is 1, 2 or 3, and A is an anion.

- In this group of compounds, R¹ is selected from C₆₋₂₄ alkyl or alkenyl groups and C₆₋₁₂ alkaryl groups; R³ is selected from C₁₋₁₂ alkyl or alkenyl
25. groups and C₁₋₁₆ alkaryl groups. When m is 2, however, it is preferred that the sum total of carbon atoms in R¹ and R_{3-m}³ is no more than about 20 with R¹ representing a C₈₋₁₈ alkyl or alkenyl group. More preferably, the sum total of carbon atoms in R¹ and
30. R_{3-m}¹ is no more than about 17 with R¹ representing a

C₁₀₋₁₆ alkyl or alkenyl group. When m is 1, it is again preferred that the sum total of carbon atoms in R¹ and R³_{3-m} is no more than about 17 with R¹ representing a C₁₀₋₁₆ alkyl or alkaryl group.

5. Additionally in this group of compounds, the total number of alkoxy radicals in polyalkoxy groups (R²_m) directly attached to the cationic charge centre should be no more than 14. Preferably, the total number of such alkoxy groups is from 1 to 7 with each
10. polyalkoxy group (R²) independently containing from 1 to 7 alkoxy groups, more preferably, the total number of such alkoxy groups is from 1 to 5 with each polyalkoxy group (R²) independently containing from 1 to 3 alkoxy groups. Especially preferred are cationic
15. surfactants having the formula



wherein R¹ is as defined immediately above, n is 2 or 3 and m is 1, 2 or 3.

- Particularly preferred cationic surfactants of
20. the class having m equal to 1 are dodecyl dimethyl hydroxyethyl ammonium salts, dodecyl dimethyl hydroxypropyl ammonium salts, myristyl dimethyl hydroxyethyl ammonium salts and dodecyl dimethyl dioxyethylenyl ammonium salts. When m is equal to 2,
25. particularly preferred cationic surfactants are dodecyl dihydroxyethyl methyl ammonium salts, dodecyl dihydroxyethyl ethyl ammonium salts, myristyl dihydroxyethyl methyl ammonium salts, cetyl dihydroxyethyl methyl ammonium salts, cetyl dihydroxyethyl
30. methyl ammonium salts, stearyl dihydroxyethyl methyl

ammonium salts, oleyldihydroxyethyl methyl ammonium salts, and dodecyl hydroxy ethyl hydroxypropyl methyl ammonium salts. When m is 3, particularly preferred cationic surfactants are dodecyl trihydroxyethyl ammonium salts, myristyl trihydroxyethyl ammonium salts, cetyl trihydroxyethyl ammonium salts, stearyl trihydroxyethyl ammonium salts, oleyl trihydroxy ethyl ammonium salts, dodecyl dihydroxyethyl hydroxypropyl ammonium salts and dodecyl trihydroxypropyl ammonium salts.

In the above, the usual inorganic salt counterions can be employed, for example, chlorides, bromides and borates. Salt counterions can also be selected from organic acid anions, however, such as the anions derived from organic sulphonic acids and from sulphuric acid esters. A preferred example of an organic acid anion is a C₆₋₁₂ alkaryl sulphonate.

Of all the above cationic surfactants, especially preferred are dodecyl dimethyl hydroxyethyl ammonium salts and dodecyl dihydroxyethyl methyl ammonium salts.

Additional preferred cationic surfactants are fully disclosed in British Patent Application 79-25946.

The above water-soluble cationic surfactants can be employed in nonionic/cationic surfactant mixtures in a weight ratio of from about 10:6 to about 20:1, more preferably from about 10:2 to about 10:6, and particularly from about 10:3 to 10:5.

The detergent compositions of the present invention can _____

also contain from about 5% to about 93% of detergency builder, preferably from about 20% to about 70% thereof.

- Suitable detergent builder salts useful herein
5. can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates and bicarbonates.

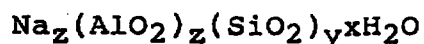
Examples of suitable organic alkaline detergency builder salts are:

- (1) water-soluble amino polyacetates, e.g. sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates, and N-(2-hydroxyethyl)nitrilotriacetates;
- (2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates;
- (3) water-soluble polyphosphonates, including,
 20. sodium, potassium, and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylenediphosphonic acid and the like;
- (4) water-soluble polycarboxylates such as the
 25. salts of lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and the
 30. fumaric acid; citric acid, aconitic acid, citraconic

- acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and
5. 1,1,2,3-propane tetracarboxylic acid; cyclopentane-cis, cis, cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid; 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexa-
 10. carboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent 1,425,343.

- Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is
15. disclosed in Canadian Patent 755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphate.

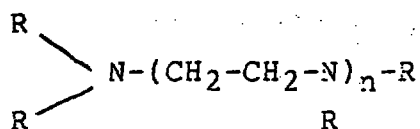
- A further class of builder salts is the
20. insoluble aluminosilicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation



25. wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5 and x is an integer from about 15 to about 264.
- Compositions incorporating builder salts of this type form the subject of British Patent Specification
30. 1,429,143 published 24th March, 1976, German Patent

Application OLS 2,433,485 published 6th February, 1975 and OLS 2,525,778 published 2nd January, 1976.

The detergent compositions of the invention can also be supplemented by from about 0.05% to about 0.6% (acid basis), preferably from about 0.06% to about 0.3% of aminopolyphosphonic acid, or salt thereof, having the general formula



wherein n is an integral number from 0 to 3, and each R is individually hydrogen or $\text{CH}_2\text{PO}_3\text{H}_2$ provided that at least half of the radicals represented by R are $\text{CH}_2\text{PO}_3\text{H}_2$. Preferred aminopolyphosphonic acids are selected from nitrilotri(methylenephosphonic acid), ethylene-diaminetetra(methylenephosphonic acid), diethylenetriamine(pentamethylenephosphonic acid), and mixtures thereof.

An alkali metal, or alkaline earth metal, silicate can also be present, preferably from about 3% to about 8%. Suitable silicate solids have a molar ratio of $\text{SiO}_2/\text{alkali metal}_2\text{O}$ in the range from about 1.0 to about 3.3, more preferably from 1.5 to 2.0.

Various other materials may be present in the granular washing products. Thus, materials, such as

- the higher fatty acid amides may be added to improve detergency and modify the foaming properties in a desirable manner. Examples thereof are the higher fatty acid alkanolamide, preferably having 2-3
5. carbons in each alkanol group and a fatty acyl radical within the range of 10-18 carbons, preferably 10-14 carbons, such as lauric or myristic monoethanolamides, diethanolamides and isopropanolamides. Tertiary higher alkyl amino oxides such as having
 10. about 10-18 carbons in one alkyl group, e.g. lauryl or myristyl dimethylamine oxides, may be added also. Fatty alcohols of 10-18 carbons, such as lauryl or coconut fatty alcohols, or cetyl alcohol are suitable additives also. A hydrotropic material such as the
 15. lower alkyl aryl sulphonates, e.g. sodium toluene or xylene sulphonates, can assist processing also. In general, these materials are added in minor amounts, usually from about 1/2 to 10%, preferably 1 to 6%, based on the total solids.
 20. The washing products may also contain optical brightening agents or fluorescent dyes (e.g. in amount in the range of about 1/20% to 1/2%); germicidal ingredients such as halogenated carbanilides, e.g. trichlorocarbanilide, halogenated
 25. salicylanilide, e.g. tribromosalicylanilide, halogenated bisphenols, e.g. hexachlorophene, halogenated trifluoromethyldiphenyl urea, zinc salt of 1-hydroxy-2-pyridinethione and the like (e.g. in amounts in the range of about 1/50% to 2%); soil-suspending agents
 30. such as sodium carboxymethyl cellulose or polyvinyl

- alcohol, preferably both, or other soluble polymeric materials such as methyl cellulose (the amount of suspending agent being, for example, in the range of about 1/20% to 2%); antioxidants such as 2,6-di-tert-butylphenol, or other phenolic antioxidant materials (e.g. in amounts in the range of about 0.001 to 0.1%), colouring agents, enzymes, and other additives.

- Preferred enzymatic materials include the commercially available amylases and neutral and alkaline proteases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in U.S. Patents 3,519,570 and 3,533,139. Examples of suitable enzymes include the materials sold under the Registered Trademarks Maxatase and Alcalase.

15. Anionic fluorescent brightening agents are well known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)-stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-2-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)-stilbene-2,2'-disulphonate and sodium 2(stilbyl-4"-(naphtho-1',2':4,5)-1,2,3-triazole-2"-sulphonate.

- Other fluorescers which can be included in the non-additive portion of the detergent composition are the 1,3-diaryl pyrazolines and 7-alkylaminocoumarins.

In general terms, the granular bleach active detergent additive compositions according to the invention are made by

(1) mixing together the powdery finely-divided oxygen containing bleach compound and the powdery finely-divided bleach activator compound and any other optional powdery additives to obtain a homogeneous powder mixture;

(2) mixing the molten normally solid watersoluble binder with the powder mixture of step (1) to coat all or substantially all of the particles of the powder mixture with the binder and obtain a homogeneous extrudable mass;

(3) extruding the mass; and

(4) cooling and shaping the extruded mass to obtain the granular detergent additive product, preferably by cutting the extrudate into granules.

In a specific preferred form of the invention there is provided a method for preparing a free-flowing non-tacky granular detergent additive comprising a perborate salt bleaching compound and an acyloxy benzene sulphonate compound as an activator for the said perborate salt bleaching compound, the said method comprising the steps of

(A) combining from about 75 to about 95 parts by weight of a mixture of powdery perborate salt bleaching compound and powdery acyloxybenzene sulphonate compound activator with from about 25 to 5 parts by weight of a normally solid, molten nonionic surfactant, as a coating and binder for the said powdery mixture;

(B) extruding the mixture from step (A) while maintaining the temperature of the extrudate below the reaction temperature at which the perborate salt and activator compound in the said extrudate are reactive with each other; and

(C) cooling the extrudate to solidify the binder and cutting the extrudate into granules.

Preferably in step (B), the temperature is maintained between the softening temperature of the binder and the solidification temperature of the binder whereby the binder assumes a wax-like consistency.

The granules of the present invention may be of various shapes. In one suitable form they are short, generally cylindrical rods, noodles or strands whose diameters are in the range of about 0.3 to 2.0 mm (preferably about 0.4 to 1.4 mm) and whose lengths are in the range of about 1.0 to 20.0 mm (preferably about 2.0 to 10.0 mm). In another suitable form the granules are of spherical form having diameters in the range of about 0.1 to 2.0 mm (preferably about 0.5 to 1.0 mm). Among other shapes mention may be made of cubes, rectangular prisms and parallelepipeds obtainable by suitable selection of the extrusion die. Generally speaking, the average particle volume of the granules is preferably within the range of

about 0.005 to 20 mm³, but may vary within the limits of 0.005 to 20 mm³. Preferably, the particles have an average longitudinal:average lateral dimension ratio of from about 1.1:1 to about 3:1, more

5. preferably from 1.3:1 to about 1.8:1. In this context, "average" refers to a simple number average.

- In one embodiment of the invention, the mixed powdered ingredients may (after grinding to eliminate large particles) be mixed with the liquid organic
10. binder to form a substantially uniform paste which can then be milled to improve its homogeneity, after which the milled product (e.g. in ribbon or flake form) can be passed through a plodder and extruded therefrom as a bundle of thin parallel threads; the
15. threads may then be surface-hardened, as by cooling, dried to remove some of their moisture, and then broken up in a granulating apparatus or otherwise cut into desired lengths. In another method, the liquid binder containing workable mass is extruded (e.g. by
20. using a single or twin screw extruder) to form thin short rods which are then rounded by rapidly rolling them while they are in plastic condition, into generally spherical shape. These procedures generally give granules that are compact and whose
25. individual granule density is about 1 gram per cubic centimeter, e.g. in the range of about 1.2 to 1.6 grams per cubic centimeter.

- In order to prevent premature reaction between the oxygen-containing bleach compound, e.g. alkali
30. metal perborate, and bleach activator, e.g. acyloxy-

- benzene sulphonate, steps (1) and (2) and preferably also steps (3) and (4) should be carried out in the substantial absence of moisture, i.e. under anhydrous conditions, including atmospheric humidity. Once the
5. active bleach forming reactants are coated with the organic binder it is not as essential to avoid contact with moisture but still the presence of moisture even during the extruding and cooling/shaping steps should be minimized or avoided all together so
10. as to prevent dissolution of the water-soluble organic binder, gelling of the binder, etc.

- For the same reason, it is important to maintain the temperatures during the mixing and extruding steps at appropriate levels to minimize the
15. possibility of reaction between the bleach forming reactants. Generally speaking for most of the useful activators it will be sufficient to maintain temperatures below about 80°C, preferably below about 70°C, especially preferably below about 65°C.

20. Naturally, during step (2) the temperature will be such as to maintain the binder in a sufficiently liquid state so as to be able to flow over and around the solid powdery particles to provide the desired coating. During step (3) the temperature can be
25. lowered, if necessary, to make the binder more plastic or wax-like in nature to increase the cohesiveness of the extrudable mass.

- It has been found that particularly good results have been achieved when the powdery mixture and
30. molten or liquid binder are mixed (step-(2)) in a

sigma blade mixer although any other type of mixing apparatus capable of providing a homogeneous extrudable mass can also be used.

- Also, good results have been achieved using a
5. single screw extruder with one or more, for example 1, 2 or 3 heating zones and one or more, for example 1, 2 or 3 cooling zones. In one preferred embodiment the homogeneous extrudable mass is extruded with a soap plodder, such as a 1¹/₂ inch-single screw
 10. Stephen Beck Soap Plodder with a specially machined 1 mm pore extrusion plate with the jacket of the extruder cooled to maintain the temperature of the extrudate at less than about 65°C. Conveniently the powder mixture and the molten or liquid binder can be
 15. fed to a preplodder or compactor or mixer associated with or directly connected to the inlet feed port of the extruder.

- The full detergent compositions to which the granular detergent additives of the present invention
20. are conveniently added are most often in the form of spray-dried hollow beads or spongy low density granules, the particle sizes of which are usually such that a major portion is at least about 0.2 mm in diameter, e.g. about 0.3 or 0.4, or even 0.5 or 1 to
 25. 2 mm.

Generally, the granular detergent additive may comprise from about 0.1 to about 49%, preferably from about 0.2 to 20% of the weight of the full detergent composition.

30. Preferred granular detergent compositions comprise:

- (a) from about 40% to about 99.9% of spray-dried powder comprising
5. (i) from about 1% to about 20% of organic surfactant selected from anionic, zwitterionic and ampholytic surfactants and mixtures thereof,
 - (ii) from about 5% to about 93.9% of detergency builder, and
 - (iii) from about 5% to about 18% moisture,
 10. (b) from about 0.1% to about 20% of the detergent additive composition, and optionally
 - (c) up to about 25% of ethoxylated nonionic surfactant in intimate mixture with the spray-dried base powder and detergent additive composition.
- The density, particle size, shape, colour and
15. composition of the granular detergent bleach-reactants containing additive should be matched to the corresponding values of the detergent spray-dried powder so as to avoid separation or aggregation of the respective particles, to enhance consumer appeal,
 20. and to maximize the compatibility between the bleach reactants and bleach active species on the one hand and the detergent and additives (e.g. builders, enzymes, etc.) on the other.
- Of course, it will be appreciated that the
25. granular detergent additives of the present invention are useful, per se, as a bleach active composition alone or for admixture with conventional detergents at the point of use. Since the bleach reactant containing granules combine chemical stability, high
 30. solubility and good granular flow characteristics,

they are eminently suitable for use alone or as a component of a full detergent composition to provide highly effective bleaching even at low wash water temperatures.

5. The invention may be put into practice in various ways and a number of specific examples will be described to illustrate the invention with reference to the accompanying examples. All parts and percentages are by weight unless otherwise noted.

10. EXAMPLES 1A to 1E

- In these examples, the nonionics, Neodol 25-7 (an aliphatic alcohol having from 12 to 15 carbon atoms condensed with 7 moles of ethylene oxide per mole of alcohol) or TA-40 (a coco fatty acid alcohol condensed with about 40 moles ethylene oxide in the amounts shown in Table 1 are melted at about 55°C and the melted nonionic is added to a powdery mixture of nonanoyloxybenzene sulphonate (NOBS) and sodium perborate (mono- or tetra-hydrate), also in the amounts shown in Table 1 while mixing in a sigma blade mixer heated to about 58°C. The resulting homogeneous mixture is fed to a 1¹/₂ inch Stephen Beck Soap plodder having a single worm screw fitted at the extrusion outlet with a 1 millimeter pore size extrusion plate. The temperature at the outlet of the extruder is maintained at about 60 to 64°C or lower by circulating water through the jacket surrounding the extrusion section. The resulting extruded 1 mm strands (spaghetti) are cut to 5 to 10 mm lengths.
30. The resulting granules are characterized by their surface condition: tacky, less tacky, friable or

strong; and by their colour: white or off-colour.
The results are also shown in Table 1.

TABLE 1

5.	<u>Ingredient</u>	<u>Example</u>				
		<u>1A</u>	<u>1B</u>	<u>1C</u>	<u>1D</u>	<u>1E</u>
				(weight%)		
	NOBS	55	50	42	58	67
	Sodium Per- borate					
10.	Monohydrate	27	25		29	24
	Tetrahydrate			42		
	Nonionic					
	Neodol 25-7	18	17			
	TA-40			16	13	9
15.	Bentonite		9			0
	Surface					
	Condition	Tacky	Less Tacky	Friable	Strong	Strong*
20.	Colour	White	Off- Colour	White	White	White

Notes on Table 1

25. *The granules were considered highly powdery.

EXAMPLE 2

- The granular detergent additive of Example 1D was added to the commercially available spray-dried
30. bead type built detergent composition sold by Colgate-Palmolive Co. under the trademark

Fresh Start to provide 6 parts of granules per 40 parts of Fresh Start beads. The Fresh Start detergent beads have a cup weight of 157 while the detergent granules of Example 1D have a cup weight of 145.

5. Three different batches of the mixture of additive and Fresh Start are stored for two weeks at temperatures of 110°F (°C), 100°F (°C) or room temperature (70°F (°C)) at a relative humidity of 0%. No decomposition (as measured by loss of oxygen) is observed.

10. When the detergent composition (Fresh Start plus granular detergent additive) is added to water at 40°C, the granules dissolve within about 60 seconds and substantially all of the perborate and AOBS

15. (NOBS) are consumed to form the corresponding low temperature active oxyacid bleach.

CLAIMS

1. A method for preparing a granular detergent additive which contains each of a bleach compound and an activator for the said bleach compound, the said method comprising

mixing finely divided bleach compound and finely divided activator for the said bleach compound, and any other optional powdery additives,

mixing the mixture of bleach compound and activator compound with a molten, normally solid water-soluble binder,

extruding the resulting mixture, and cooling and shaping the extruded mass to obtain the granular detergent additive product, the mixing steps being carried out under anhydrous conditions, and at a temperature at which the bleach compound and activator compound are substantially non-reactive with each other, whereby the said bleach compound and activator compound in the said granules will not react with each other to any significant extent until the granules are added to water at a temperature which will dissolve the said binder.

2. A method as claimed in Claim 1 in which the binder is a nonionic surface active compound.

3. A method as claimed in Claim 1 or Claim 2 in which the bleach compound is a perborate salt and the bleach activator compound is an acyloxy benzene sulphonate.



44

4. A method for preparing a free-flowing non-tacky granular detergent additive comprising a perborate salt bleaching compound and an acyloxy benzene sulphonate compound as an activator for the said perborate salt bleaching compound, the said method comprising the steps of
- (A) combining, under anhydrous conditions, from about 75 to about 95 parts by weight of a mixture of powdery perborate salt bleaching compound and powdery acyloxybenzene sulphonate compound activator with from about 25 to 5 parts by weight of a normally solid, molten nonionic surfactant, as a coating and binder for the said powdery mixture;
- (B) extruding the mixture from step (A) while maintaining the temperature of the extrudate below the reaction temperature at which the perborate salt and activator compound in the said extrudate are reactive with each other; and
- (C) cooling the extrudate to solidify the binder and cutting the extrudate into granules.
5. A method as claimed in Claim 4 in which in step (B), the temperature is maintained between the softening temperature of the binder and the solidification temperature of the binder whereby the binder assumes a wax-like consistency.



* C L N S *

6. A method, as claimed in Claim 1 substantially as specifically described herein with reference to the Examples.

5. 7. An additive whenever made by a method as claimed in any one of Claims 1 to 6.

10. 8. A powdery or granular detergent composition comprising an organic surfactant compound selected from the group consisting of anionic, nonionic, amphoteric, zwitterionic organic synthetic surfactants and mixtures thereof; at least one detergent builder salt selected from the group consisting of inorganic builder salts, organic builder salts, and mixtures thereof; and an oxygen-containing bleach and an activator compound for said bleach in the form of the granular detergent additive as claimed in Claim 7.

20. 9. A detergent additive comprising a mixture of particles of an oxygen-containing bleach and particles of an activator for the said bleach, the said mixed particles being encapsulated in a molten water-soluble binder, which is a nonionic surface active agent, which is solid at room temperature.

25. 10. An additive as claimed in Claim 9 in which the individual particles of bleach and bleach activator within each granule are substantially separated from each other by a coating layer of the said molten binder.

30.



11. An additive as claimed in Claim 9 or Claim 10 in which the water-soluble binder is a nonionic surface active agent.

5. 12. An additive as claimed in any one of Claims 9 to 11 in which the bleach is a percompound.

13. An additive as claimed in any one of Claims 9 to 11 in which the bleach is a perborate salt.

10. 14. An additive as claimed in any one of Claims 9 to 13 in which the activator is an acyloxy benzene sulphonate.

15. 15. An additive as claimed in any one of Claims 9 to 14 in which the bleach and bleach activator comprise from about 55 to about 95% by weight of the additive.

20. 16. An additive as claimed in any one of Claims 9 to 15 in which the bleach and bleach activator are present at a weight ratio of from about 4:1 to about 0.3:1.

25. 17. An additive as claimed in Claim 9 substantially as specifically described with reference to the Examples.

30.

