⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 241 962
A2

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 87200469.2

㉒ Date of filing: 12.03.87

(51) Int. Cl.4: C11D 3/39 , C11D 3/10 ,
C11D 3/12 , C11D 3/37

㉚ Priority: 25.03.86 GB 8607387

㊸ Date of publication of application:
21.10.87 Bulletin 87/43

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(71) Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(84) CH DE ES FR IT LI NL SE

(71) Applicant: UNILEVER PLC
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

(84) GB

(72) Inventor: de Bernat, James Gavin
3 Sweetfield Road
Little Sutton Cheshire L66 1HY(GB)
Inventor: Robb, Ian Donald
22 The Kings Gap
Hoylake Wirral Merseyside L47 1HF(GB)
Inventor: Wilde, Raymond John
9 Stanley Avenue Higher Bebington
Wirral Merseyside L63 5QE(GB)

(74) Representative: Tan, Bian An, Ir. et al
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) Granular non-phosphorus detergent bleach compositions.

(57) Granular detergent bleach compositions substantially free of phosphorus-containing material comprising as builder 1) a carbonate/calcite mixture, 2) an aluminosilicate cation exchange material, 3) a nitrilotriacetic acid compound or a mixture of 2) and 3); a peroxygen bleaching agent and a granular non-phosphorus bleach activator composition comprising:

(a) 50-90% by weight of a bleach activator;
(b) 5-45% by weight of an inert non-alkaline, non-phosphate water-soluble salt; and
(c) 1-15% by weight of a water-soluble, low-to non-carboxylate containing film-forming polymeric material of average molecular weight of from 500-1,000,000.

The granular non-phosphorus bleach activator composition has the advantage that it does not cause poisoning of calcite.

GRANULAR NON-PHOSPHORUS DETERGENT BLEACH COMPOSITIONS

This invention relates to granular non-phosphorus bleach activator containing detergent bleach compositions. Particularly it pertains to granular compositions containing activators for peroxygen bleaching agents in the form of organic peroxyacid bleach precursors usable in phosphorus-free granular detergent bleach compositions.

Granular detergent compositions which contain organic bleach activators in addition to the usual detergent substances having a cleaning action, builders and peroxygen bleaching agents are known in the art. The peroxygen bleaching agents commonly used are those which release hydrogen peroxide in aqueous solution, such as alkali metal perborates, persilicates, percarbonates, perphosphates and urea peroxide. These peroxygen bleaching agents will hereinafter also be referred to as "persalts". The most commonly used persalt in detergent compositions is alkali metal perborate, particularly sodium perborate, tetrahydrate or monohydrate.

The organic bleach activators referred to herein are generally organic N-acyl or O-acyl compounds, or carbonic or pyrocarbonic esters, which react with hydrogen peroxide (e.g. from the persalts) in solution forming a peroxy acid or percarbonic acid, a bleaching species which, unlike the persalts, is effective in bleaching at lower temperatures, e.g. from ambient to 60°C.

Such bleach activators are amply described in literature, for example in a series of articles by Allan H. Gilbert in Detergent Age, June 1967, pages 18-20, July 1967, pages 30-33, and August 1967, pages 26, 27 and 67, and further in British Patent Specifications 836,988; 855,735; 907,356; 907,358; 970,950; 1,003,310 and 1,246,339; US Patent Specifications 3,332,882, 3,277,750, 4,128,494 and 4,412,934.

A representative, but by no means comprehensive, list of activators which can be used in the present invention is given below:

(a) N-diacylated and N,N'-tetraacylated amines, such as N,N,N',N'-tetraacetyl methylene diamine or -ethylene diamine, N,N'-diacetyl aniline and N,N'-diacetyl-p-toluidine or 1,3-diacylated hydantoins as, for example, the compounds 1,3-diacetyl-5,5-dimethylhydantoin and 1,3-dipropionyl hydantoin;

(b) N-alkyl-N-suphonyl carbonamides, for example the compounds N-methyl-N-mesyl acetamide, N-methyl-N-mesyl benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide;

(c) N-acylated cyclic hydrazides, acylated triazoles or urazoles, for example monoacetyl maleic acid hydrazide;

(d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-acetyl-N,N-succinyl hydroxylamine, O-p-methyoxybenzoyl, N,N-succinyl hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl hydroxylamine and O,N,N-triacetyl hydroxylamine;

(e) N,N'-diacyl sulphurylamides, for example N,N'-dimethyl-N,N'-diacetyl sulphuryl amide and N,N'-diethyl-N,N'-dipropionyl sulphurylamide;

(f) Triacyl cyanurates, for example triacetyl cyanurate and tribenzoyl cyanurate;

(g) Carboxylic acid anhydrides, such as benzoic anhydride, m-chlorobenzoic anhydride, phthalic anhydride and 4-chlorophtalic anhydride;

(h) Sugar esters, for example glucose pentaacetate;

(i) 1,3-diacyl-4,5-diacyloxy-imidazolines, for example 1,3-diformyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-dipropionyloxy imidazoline;

(j) Tetraacetyl glycoluril and tetraproprionyl glycoluril;

(k) Diacylated 2,5-diketopiperazines, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and 1,4-dipropionyl-3,6-dimethyl-2,5-diketopiperazine;

(l) Acylation products of propylene diurea and 2,2-dimethyl propylene diurea, especially the tetraacetyl or tetrapropionyl propylene diurea and their dimethyl derivatives;

(m) Carbonic acid esters, for example the sodium salts of p-(ethoxycarbonyloxy) benzonic acid and p-(propoxycarbonyloxy) benzene sulphonic acid;

(n) Alpha-acyloxy-(N,N')polyacyl malonamides, such as alpha-acetoxy-(N,N')-diacetyl malonamide.

Since these bleach activator compounds are generally hydrolysable materials, they need to be protected from the surrounding media when incorporated in detergent compositions. On the other hand, any proper method of protecting the bleach activator from the environment must allow a relatively quick release or dissolution of the activator in the wash liquor. Release of the activator must be achieved at a period well before the end of the wash cycle so as to give time for the activator to react with the persalt forming the peroxyacid. Preferably this should occur as early as possible in the wash cycle for maximum bleaching to occur.

The most common way of protecting bleach activators is by presenting them in the form of granules or agglomerates.

Various compositions and forms of bleach activator granules have been proposed in the art, most of them using a phosphate, particularly sodium triphosphate, as an essential component of the granulating agent because of its typical property of imparting good structure combined with quick dispersion to the granule. A representative example of such bleach activator granule compositions having good storage stability and satisfactory release is that which comprises a mixture of sodium triphosphate and potassium triphosphate as the granulating agent, currently used in the majority of commercial detergent powder formulations.

For many years, phosphates, such as sodium triphosphate, have indeed been used as detergency builders.

With the increasing trend of legislation in a number of countries to ban phosphorus from detergent compositions, because of the general belief that phosphates and phosphorus-containing compounds can lead to environmental problems, it has become desirable and necessary to provide detergent compositions which are free, or essentially free, of phosphorus.

Consequently, in formulating such phosphorus-free detergent bleach compositions comprising a bleach activator, it has also become necessary to look for a reasonable alternative to bleach activator granule compositions which are free of phosphorus but which should have the physical properties and performance characteristics comparable to phosphorus-containing bleach activator granules when used in detergent compositions under non-phosphorus conditions.

A number of alternative non-phosphorus builders have been proposed, especially a mixture of an alkali metal carbonate, such as sodium carbonate, with a water-insoluble calcium carbonate seed material, such as calcite, as disclosed for example in GB Patent Specifications 1,437,950 (Unilever), 1,481,516 (Unilever) and 1,481,685 (Unilever), and it is for use in compositions containing such builders that the present non-phosphorus bleach activator granule composition is particularly designed.

Non-phosphorus-containing bleach activator granule compositions are known in the art and various methods of preparing such granules and their use in detergent compositions have been proposed.

In the majority of cases an organic compound or a mixture of organic compounds were proposed as the binding or coating agent, such as for example nonionic compounds, fatty acids, fatty alcohols, waxes and polymeric materials with or without the optional use of inorganic salts.

German DE-OS 2,657,042 discloses a detergent composition comprising tetraacetyl ethylene diamine (TAED) in the form of granules, which consist of said TAED activator and a nonionic surfactant having a melting point of at least 35°C as the binding agent.

European EP-B-0051987 (Procter & Gamble) discloses bleach activator granule compositions comprising a bleach activator and a nonionic surfactant having a melting point of not more than 40°C as binding agent.

A major disadvantage of nonionics is that they tend to bleed and cause stickiness, giving rise to caking problems, especially under hot summer temperature conditions. Migration of nonionics in the formulation would also tend to aid decomposition of bleach-sensitive ingredients owing to interaction with the oxidising bleach system. Higher melting nonionics will have poor dispersing ability, resulting in a poor release of the bleach activator, with the deleterious consequence of the granules sedimenting and being lost in the dead spaces of the washing machines, known as mechanical loss. The same applies to fatty acids, fatty alcohols and waxes.

European Patent Specification EP-0070474 and EP-0037026 (Henkel) disclose methods of using water-soluble cellulose ether, starch or starch ether as granulation binder for preparing bleach activator granules having a bleach activator content of from 90-99% by weight. The methods as described here are only viable if coarse particle size bleach activators are used.

European Patent Application EP-0075818 (BASF) discloses water-free activator granules comprising a) 70-99.5% bleach activator and b) 0.5-30% of a swelling agent, prepared by compacting the compounds a) and b) without the addition of water, optionally followed by breaking into smaller particles.

As swelling agents are mentioned high molecular weight carbohydrates, such as starch, powdered cellulose, wood pulp; cross-linked polyvinyl pyrrolidone (PVP) and also starch ether and carboxymethyl cellulose.

All these proposals have been made without the object of using such bleach activator granules in non-phosphorus detergent formulations, especially in detergent compositions containing an alkali metal carbonate and calcium carbonate seed material as the builder system.

Accordingly, it is an object of the present invention to provide an effective and stable granular non-phosphorus-containing bleach activator composition which can be used in non-phosphorus granular detergent bleach compositions containing as builders a mixture of an alkali metal carbonate with a water-insoluble particulate carbonate material, which is capable of acting as a seed crystal for the precipitate resulting from the reaction between the calcium hardness ions of the water and the water-soluble carbonate, e.g. a mixture of sodium carbonate and calcite without poisoning the water-insoluble carbonate material, especially calcite, whereby its seed activity is reduced.

It is another object of the invention to provide a stable and effective granular non-phosphorus-containing bleach activator composition usable in non-phosphorus granular detergent bleach compositions comprising a non-phosphate builder selected from the group of aluminosilicate cation exchange materials, nitrilotriacetic acid compounds and mixtures thereof.

These and other objects, which will be apparent from the further description of the invention, can be achieved if a finely divided particulate bleach activator is granulated to a size of from about 0.2-2.0 mm, using an inert non-alkaline, non-phosphate inorganic or organic salt and a water-soluble, low-to non-carboxylate containing film-forming polymeric material having average molecular weight of from 500-1,000,000, as granulating agent.

It is known that calcite is sensitive to poisoning, which will result in a marked detrimental effect on calcite precipitation. In this respect the type of polymeric material used in the invention is crucial.

Thus the granular bleach activator composition of the invention is essentially free of phosphorus materials and comprises:

(i) a finely divided particulate bleach activator;

(ii) an inert non-alkaline, non-phosphate, water-soluble inorganic or organic salt; and

(iii) a water-soluble, low-to non-carboxylate containing film-forming polymeric material of average molecular weight of from 500-1,000,000.

Preferred bleach activators are the N-diacylated and N,N′-tetraacylated amines mentioned under a) above, particularly N,N,N′,N′-tetraacetyl ethylene diamine, the esters of carbonic or pyrocarbonic acids mentioned under m) and the reactive phenol esters as described in US Patent Specification 4,412,934 and GB Patent Specifications 836,988 and 864,798.

The inert non-alkaline, non-phosphate inorganic or organic salts which can be used in the invention are, for example, sodium sulphate, sodium nitrate, sodium chloride, sodium citrate, calcium sulphate and calcium chloride. A preferred salt is sodium sulphate.

The low-to non-carboxylate film-forming polymeric material usable in the invention will be any polymer, both homo-and co-polymers, which have a carboxyl group to polymer weight ratio of less than 1:5. They may be composed of monomers such as vinyl acetate, vinyl pyrrolidone, methyl vinylether, styrene and styrene sulphonate, alkyl acrylates, etc. Examples of suitable polymeric materials include polyvinylpyrrolidone, polyvinyl alcohol, co-polymers of polyvinyl alcohol/polyvinyl acetate, carbohydrates and carbohydrate ethers such as carboxymethyl cellulose, and dextrin-modified vinylacetate polymers. Polymers having average molecular weight of less than 500,000, particularly less than 100,000, are preferred.

Other polymeric materials outside those as defined in the present invention are not suitable as they tend to cause serious poisoning of calcite.

Effectively, the granular bleach activator composition will comprise:

(a) from 50-90%, preferably from 55-85% by weight, of the bleach activator;

(b) from 5-45%, preferably from 10-35% by weight, of the inorganic or organic salt; and

(c) from 1-15%, preferably from 5-10% by weight, of of the low-to non-carboxylate polymeric material.

Water may be present in an amount of up to about 5%, preferably up to 4%.

As explained hereinbefore, the granular bleach activator composition has particular applicability to non-phosphorus detergent compositions containing as builders a mixture of an alkali metal carbonate, such as sodium carbonate, with a water-insoluble carbonate seed material, such as calcium carbonate, e.g. calcite.

Accordingly, in one aspect the invention provides a detergent bleach composition which is substantially free of phosphorus-containing material, comprising:

(i) a detergent active material;

(ii) a water-soluble carbonate material which is a detergency builder;

(iii) a water-insoluble particulate carbonate material which is a seed crystal for calcium carbonate;

(iv) a peroxygen bleaching agent; and

(v) a non-phosphorus granular bleach activator composition as hereinbefore defined;

The detergent-active material can be anionic, nonionic, cationic or zwitterionic or a mixture of such agents.

Nonionic surfactants suitable for use in the present invention include water-soluble sompounds produced by the condensation of ethylene oxide with a hydrophobic compound such as an alcohol, alkyl phenol, polypropoxy glycol or polypropoxy ethylene diamine. Also suitable are alkyl amine oxides, alkyl polyglucosides and alkyl methylsulphoxides. Preferred nonionic surfactants are polyethoxy alcohols formed as the condensation products of 1 to 30 moles of ethylene oxide with 1 mole of ethylene oxide with 1 mole of branched-or straight-chain, primary or secondary aliphatic alcohols having from about 8 to about 22 carbon atoms; more especially, 6 to 15 moles of ethylene oxide are condensed with 1 mole of straight-or branched-chain, primary or secondary aliphatic alcohol having from about 10 to about 16 carbon atoms. Certain polyethoxy alcohols are commercially available under the trade-names "Neodol", "Synperonic" and "Tergitol".

Anionic surfactants suitable for use in formulating the detergent bleach compositions of the invention include water-soluble alkali metal alkylbenzenesulphonates, alkyl sulphates, alkylpolyethoxyether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulphocarboxylates and their esters, alkylglycerylether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkylphenolpolyethoxy ethersulphates, 2-acyloxyalkane-1-sulphonates and beta-alkyloxyalkane sulphonates. Soaps can also be used as anionic surfactants. Preferred anionic surfactants are alkylbenzenesulphonates with about 9 to about 15 carbon atoms in a linear or branched alkyl chain, more especially about 11 to about 13 carbon atoms; alkylsulphates with about 8 to about 22 carbon atoms in the alkyl chain, more especially from about 12 to about 18 carbon atoms; alkylpolyethoxy ethersulphates with about 10 to about 18 carbon atoms in the alkyl chain and an average of about 1 to about 12 -CH_2CH_2O-groups per molecule; linear paraffin sulphonates with about 8 to about 24 carbon atoms, more especially from about 14 to about 18 carbon atoms and alpha-olefin sulphonates with about 10 to about 24 carbon atoms, more especially about 14 to about 16 carbon atoms; and soaps having from 8 to 24, especially 12 to 18 carbon atoms.

Cationic surface-active agents suitable for use in the invention include the quaternary ammonium compounds, e.g. cetyltrimethylammonium bromide or chloride and distearyldimethylammonium bromide or chloride, and the fatty alkyl amines.

Zwitterionic surfactants that can be used in the present invention include water-soluble derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium cationic compounds in which the aliphatic moieties can be straight or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, especially alkyldimethylammonium propanesulphonates and carboxylates (betaines) and alkyldimethylammoniohydroxy propanesulphonates and carboxylates wherein the alkyl group in both types contains from about 8 to 18 carbon atoms.

Typical listings of the classes and species of surfactants useful in this invention appear in "Surface Active Agents", Vol. I, by Schwartz & Perry (Interscience 1949) and "Surface Active Agents", Vol. II, by Schwartz, Perry & Berch (Interscience 1958).

The preferred detergent active compounds are fully described in GB 1,437,950 referred to above.

The effective amount of the detergent active compound or compounds used in the composition is generally in the range from 5 to 40% by weight, preferably not more than 30% by weight of the composition.

A second essential ingredient of the composition is a water-soluble carbonate material as a builder. This is preferably sodium or potassium carbonate or a mixture thereof, for reasons of cost and efficiency. The carbonate salt is preferably fully neutralised but it may be partially neutralised, for example a sesquicarbonate may be used in partial replacement of the normal carbonate salt; the partial salts tend to be less alkaline and therefore less efficient. The amount of water-soluble carbonate material in the detergent composition can be varied widely, but the amount should be at least 5% by weight, such as from 10% to 40%, preferably 10% to 30% by weight, though an amount of up to 75% could possibly be used, if desired, in special products. The amount of the water-soluble carbonate material is determined on an anhydrous basis, though the salts may be hydrated either before or when incorporated in the detergent composition. It should be mentioned that within the preferred range the higher levels tend to be required under conditions of use at low product concentrations, as is commonly the practice in North America, and the converse applies under conditions of use at higher product concentrations, as tends to occur in Europe. It should be noted that it may also be desirable to limit the carbonate content to a lower level within the range mentioned, so as to decrease the risk of internal damage following any accidental ingestion, for example by children.

In addition to the water-soluble carbonate material it is possible to include minor amounts of other non-phosphorus detergency builders, provided that the total amount of the detergency builders does not exceed 85% by weight, so as to leave room in the detergent composition for other desirable ingredients.

Where a soap is used as a detergent active material, it may be present in such a quantity that it will also contribute as an additional builder.

The composition further necessarily contains a water-insoluble particulate carbonate material. This material must be capable of acting as a seed crystal for the precipitate which results from the reaction between the calcium hardness ions of the water and the water-soluble carbonate. Thus this water-insoluble particulate material is a seed crystal for calcium carbonate, such as calcium carbonate itself.

The water-insoluble particulate carbonate material should be finely divided and should have a surface area of at least 10 m^2/g, and preferably at least 15 m^2/g.

The particularly preferred material has a surface area from 30-100 m^2/g. Insoluble carbonate material with surface areas in excess of 100 m^2/g may be used if such materials are economically available.

Surface area is measured by nitrogen absorption using the standard Bruauer, Emmet & Teller (BET) method. A suitable machine for carrying out this method is a Carlo Erba Sorpty 1750 instrument operated according to the manufacturer's instructions.

It is most preferred that the high surface area material be prepared in the absence of poisons, so as to retain its seed activity.

The insoluble carbonate material will usually have an average particle size of less than 10 microns, as measured by sieve analysis.

When the insoluble carbonate material is calcium carbonate, any crystalline form thereof may be used or a mixture thereof, but calcite is preferred as aragonite and vaterite are less readily available commercially, and calcite is a little less soluble than aragonite or vaterite at most usual wash temperatures. When any aragonite or vaterite is used, it is generally in admixture with calcite. In the following general description, the term 'calcite' is used to mean either calcite itself or any other suitable water-insoluble calcium carbonate seed material.

The selected level of calcite in the overall composition depends on the specific surface area as described above. The amount of calcite used in the compositions should be from 5% to 60%, more preferably from 5% to 30%.

In another aspect the detergent bleach composition of the invention comprises:

(i) a detergent-active material;

(ii) a non-phosphate builder selected from the group consisting of aluminosilicate cation exchange materials, nitrilotriacetic acid compounds, and mixtures thereof;

(iii) a peroxygen bleaching agent; and

(iv) a non-phosphorus granular bleach activator composition as hereinbefore defined.

The non-phosphate builder is selected from the group of:

i) Aluminosilicate cation exchange materials, both crystalline and amorphous, having the general formula:

$$(Cat_{2/n}\,O)_x.Al_2O_3.(SiO_2)_y.Z\ H_2O$$

wherein Cat is a cation having valency n that is exchangeable with calcium (e.g. Na^+ or K^+); x is a number from 0.7-1.5; y is a number from 1.3-4; and z is such that the bound water content is from 10% to 28% by weight.

Preferred aluminosilicates are the crystalline materials of the zeolite type of the following general formula:

$$Na_x(AlO_2)_x{:}(SiO_2)_y.z.H_2O$$

wherein x and y are integers of at least 6, the ratio of x to y being in the range of 1:1 to 1:2; and z is such that the bound water content is from 10% to 28% by weight.

Particularly preferred materials of the zeolite class are the A-type zeolites.

ii) Nitrilotriacetetic acid compounds, particularly sodium nitrilotriacetate (NTA), and

(iii) mixtures thereof.

These builders can be present in an amount of from 5 to 80% by weight, preferably from 10 to 60% by weight of the composition. A preferred builder is a mixture comprising zeolite and sodium nitrilotriacetate.

In addition thereto, other non-phosphorus detergency builders known in the art and described in a number of patent publications, such as the sodium carboxy methyl-oxy disuccinates, citric acid, mellitic acid, benzene polycarboxylic acids, and the polyacetalcarboxylates as disclosed in US Patent Specification 4,144,226 may be incorporated.

The amount of peroxygen bleaching agent used in the compositions of the invention will generally be from 5% to 30% by weight, preferably from 7% to 25% by weight.

The amount of non-phosphorus bleach activator granules incorporated in the compositions will depend on the bleach activator content of the granule composition and may be from 0.5% to 15% by weight, more preferably from 1.5% to 10% by weight, calculated as pure bleach activator.

With regard to the bleach activator as used in preparing the granular bleach activator compositions, it is preferred that its particle size should be less than 200 micrometre, more preferably up to 150 micrometre.

Suitable bleach activators are those having a major proportion of particle size of between 50 micrometre and 150 micrometre. Particle size distribution as described in US Patent Specification 4,283,302 are especially suitable.

The detergent compositions in which the granular non-phosphorus bleach activator compositions are incor-porated can optionally contain any of the conventional ingredients in the amounts in which such ingredients are normally employed in fabric washing detergent com-positions.

One such optional ingredient is an alkali metal silicate, particularly sodium, neutral, alkaline, meta-or orthosilicate. A low level of silicate, for example from about 2-10% by weight, is usually advantageous in decreasing the corrosion of metal parts in fabric washing machines and it may give processing benefits. If higher levels of silicate are used up to a practical maximum of 30%, for example from 10% to 20% by weight, there can be a more noticeable improvement in detergency, which may permit some decrease in the water-soluble carbonate material content. This effect appears to be particularly beneficial when the wash liquor is used in water with appreciable levels of magnesium hardness. The amount of silicate can also be used to some extent to control the equilibrium pH of the wash liquor, which is generally within the range of 9-11, preferably 10-11, for an aqueous solution of the composition at the recommended concentration. It should be noted that a higher pH (i.e. over pH 10.5) tends to be more efficient as regards detergency, but it may be less desirable for domestic safety. Sodium silicate is commonly supplied in concentrated aqueous solution or in concentrated powder form, but the amounts are calculated on an anhydrous basis.

Examples of other optional ingredients include the lather boosters, such as alkanolamides, particularly the monoethanolamides derived from palmkernel fatty acids and coconut fatty acids, lather depressants, fabric softening agents, inorganic salts, such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes, such as proteases and amylases, germicides and colourants. Particularly when the composition does not contain an anionic detergent active material, it can be beneficial to include an anti-ashing material to reduce the deposition of calcium carbonate on to fabrics.

The detergent compositions may be produced by any of the techniques commonly employed in the manufacture of fabric washing detergent compositions, including particularly slurry-making and spray-drying processes for the manufacture of detergent powders.

The invention will now be further illustrated by reference to the following non-limiting Examples.

Example I

The following granular non-phosphorus bleach activator composition was prepared:

Composition I	% by weight
TAED (bleach activator)	83.8
Sodium sulphate	9.4
Vinylacetate polymer	3.1
Water	3.7

A solid feed consisting of a mixture of 90% TAED (average particle size of 50-150 micrometre) and 10% sodium sulphate was sprayed in a Schugi® Flexomix 160 apparatus with the proper amount of an aqueous solution consisting of 15% polymer and 85% water. The product was aerated to dry and obtain a product of the above composition with the following properties:

	Comp. I	Control Comp. A
Bulk density g/l	418	500-640
Dynamic flow rate ml/s	120	80
Compressibility %	8.2	20
Granulometry:		
Mean particle size micrometre	619	600-800
% > 1700 micrometre	nil	1
% < 250 micrometre	5.2	5
% < 125 micrometre	1.2	2

Storage properties in NTA/zeolite base powder containing sodium perborate monohydrate stored in wax laminated cartons at 37°C/70°RH.

Detergent Powder Composition	% by weight
Sodium C_{12} alkylbenzene sulphonate	9.0
Primary C_{13}-C_{15} alcohol/ 7 ethylene oxide	4.0
Zeolite	30.4
Sodium nitrilotriacetate (NTA)	4.0
Alkaline sodium silicate	5.7
Sodium succinate	4.4
Sodium carbonate	5.0
Sodium carboxymethyl cellulose	0.5
Sodium sulphate	15.4
Water	8.0
Anti-foam granule	5.0
Sodium perborate monohydrate	5.5
TAED granules	3.5

	Comp. I	Control Comp. A
TAED decomposition %:		
after 4 weeks	32.3	13-27
after 8 weeks	35.5	20-38
Perborate decomposition %:		
after 4 weeks	46.1	58-63
after 8 weeks	70.3	55-89
TAED delivery:		
Peracid yield, peak value m-mole/l	1.29	1.20
Peracid yield, peak time minutes	21.0	12.5

Control granule Comp. A	% by weight
TAED (bleach activator)	58-62
Sodium triphosphate	18-22
Potassium triphosphate	13-15
Water	5-7

Example II

The following granular non-phosphorus bleach activator (TAED) composition was prepared:

Composition of Granule II	% by weight
TAED	67.8
Sodium sulphate	22.6
Vinyl Dextrin polymer	5.6
Water	4.0

A solid feed consisting of a mixture of 75% TAED (averaqge particle size of 50-150 micrometre) and 25% sodium sulphate was sprayed in a Schugi® Flexomix 160 apparatus with the proper amount of an aqueous solution of polymer. The product was dried in a fluid bed to yield a product of the above composition with the following properties:

	Composition II
Bulk density (g/l)	460
Dynamic flow rate (ml/s)	89
Compressibility (%)	9
Granulometry:	
Mean particle size (micrometre)	748
% > 1700 micrometre	nil
% < 250 micrometre	1.0
% < 125 micrometre	0.1

TAED Delivery

	Composition II
Peracid yield, peak value m mol/l	1.18
Peracid yield, peak time minutes	15

Storage Results

Storage properties of these granules in a calcite/ carbonate base powder containing sodium perborate monohydrate stored in non-laminated cartons at 37°C/70 % RH:

	Composition II
TAED decomposition %	
after 2 weeks	40.4
after 4 weeks	59.6
Perborate decomposition %	
after 2 weeks	10.2
after 4 weeks	19.4

Poisoning of Calcite

A test procedure was adopted whereby to a solution containing 20°H Ca (as $CaCl_2$) was added 1.5 g/l sodium carbonate and 0.5 g/l calcite (Socal U3) in the presence of 10 ppm STP to simulate poisons occurring in a practical wash liquor. The effect of TAED granules at 0.15 g/l (100% basis) was noted. The experiment was carried out at 25°C using Na_2SO_4 to bring the ionic strength of the medium to 0.1.

	°H Ca at 15 minutes
(i) No TAED granule	0.31
(ii) Granule II	0.35
(iii) Control granule A	1.96

It can be seen that the granule made according to the invention has no effect on water softening, whereas a granule containing a poison causes a drastic reduction in the water softening achieved.

Washing Machine Performance

Calcite/carbonate + Granule II vs. Commercially available Phosphate Powder and Control Granule A

[The commercially available phosphate powder used was German Omo base powder.]

Calcite/carbonate powder composition	% by weight
Sodium C_{12}-alkyl benzene sulphonate	7.7
Nonionic ethoxylate	3.4
Sodium stearate	3.4
Sodium carbonate	30.0
Calcite	20.2
Sodium silicate	6.0
Enzyme	0.5
Sodium perborate monohydrate	5.5
TAED (100% basis)	2.3
Sodium sulphate/SCMC/water to 100%	

The two compositions were used to wash 2.5 kg of a soiled fabric load in washing machines having a capacity of 18 litres, the load including a number of bleach-sensitive test cloths. The reflectance of these cloths was measured both before and after the wash and the difference (ΔR_{460*}) calculated. The wash conditions were a pre-wash followed by a 35 minute wash cycle heating up from 15°C to 60°C. The water hardness was 40°FH (Ca:Mg molar ratio 4:1). 80 g each composition was used in the pre-wash, 100 g for the main wash. The pH of the wash liquor was measured both before and after the wash. The results were as follows, being averaged over 6 washes:

	Calcite/Carbonate + Granule II	Phosphate + Control A
Initial pH	10.6	10.1
Final pH	10.4	9.4
ΔR_{460*}	17.8	13.0

Example III

Similar good results were obtained with the following granular non-phosphorus bleach activator (TAED) composition:

Composition (% by weight)	II
TAED	83.4
Sodium sulphate	8.6
Vinyl acetate homopolymer	8.0
Water	–

The granular bleach activator granules were used in carbonate/calcite base powder compositions. No poisoning of calcite was observed.

Claims

1. Detergent bleach composition substantially free of phosphorus-containing material comprising:
(i) a detergent-active material;
(ii) a water-soluble carbonate material which is a detergency builder;
(iii) a water-insoluble particulate carbonate material which is a seed crystal for calcium carbonate;
(iv) a peroxygen bleaching agent; and
(v) a non-phosphorus granular bleach activator composition comprising:
(a) from 50-90% by weight of a bleach activator;
(b) from 5-45% by weight of an inert non-alkaline,non-phosphate, water-soluble inorganic or organic salt; and
(c) from 1-15% by weight of a water-soluble, low-to non-carboxylate containing film-forming polymeric material of average molecular weight from 500-1,000,000.

2. Detergent bleach composition substantially free of phosphorus-containing material comprising:
(i) a detergent-active material;
(ii) a non-phosphate builder selected from the group consisting of aluminosilicate cation exchange material, nitrilotriacetic acid compounds, and mixtures thereof;
(iii) a peroxygen bleaching agent; and
(iv) a non-phosphorus granular bleach activator composition comprising:
(a) from 50-90% by weight of a bleach activator;
(b) from 5-45% by weight of an inert, non-alkaline,non-phosphate, water-soluble inorganic or organic salt; and
(c) from 1-15% by weight of a water-soluble, low-to non-carboxylate containing film-forming polymeric material of average molecular weight of from 500-1,000,000.

3. Detergent bleach composition according to claim 1 or 2, characterized in that said water-soluble salt is sodium sulphate.

4. Detergent bleach composition according to claim 1, 2 or 3, characterized in that said polymeric material is a homo-or copolymer having a carboxyl group to polymer weight ratio of less than 1:5.

5. Detergent bleach composition according to claim 1, 3 or 4, characterized in that said water-insoluble carbonate material is calcite.

6. Detergent bleach composition according to claim 1, 3, 4, or 5, characterized in that it comprises 5-40% by weight of detergent-active material, 5-75% by weight of water-soluble carbonate material, 5-60% by weight of calcite, 5-30% by weight of peroxygen bleaching agent, and from 0-5-15% by weight of bleach activator.

7. Detergent bleach composition according to claim 2, characterized in that said non-phosphate builder is a mixture of zeolite and sodium nitrilotriacetate.

8. Detergent bleach composition according to claim 2, 3, 4 or 7, characterized in that it comprises:
from 5-40% by weight of detergent-active material;
from 5-80% by weight of non-phosphate builder;
from 5-30% by weight of peroxygen bleaching agent; and
from 0.5-15% by weight of bleach activator.