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(54) Granular non-phosphorus-containing bleach activator compositions and use thereof in granular detergent bleach compositions.

(57) Improved granular non-phosphorus-containing bleach activator composition and detergent bleach composition comprising said granular composition are disclosed. The granular bleach activator composition comprises (i) a finely divided bleach activator; (ii) an inert, non-alkaline, non-phosphate, water-soluble inorganic or organic salt; (iii) a water-soluble, film-forming polymeric material of average molecular weight of from about 500-1,000,000; and (iv) a smectite or alumino silicate clay material. The granular bleach activator composition can be stably and effectively used in substantially phosphorus-free granular detergent compositions.

Granular non-phosphorus-containing bleach activator compositions and use thereof in granular detergent bleach compositions

This invention relates to granular non-phosphorus-containing bleach activator compositions, their manufacture and use in granular detergent compositions. Particularly it pertains to granular compositions containing activators for peroxygen bleaching agents in the form of organic peroxyacid bleach precursors usable in low phosphorus or 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 alkalimetal 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 alkalimetal 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, phtalic 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 substantially 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.

Examples of such non-phosphorus-containing detergency builders are the alkalimetal carbonates, such as sodium carbonate; the alkalimetal silicates, such as sodium silicate; the alumino silicates, such as the various zeolite types of alumino silicates; the nitrilotriacetic acid compounds, such as sodium nitrilotriacetate (NTA); the carboxymethyloxy succinates; sodium citrate; the various polymeric carboxylate builders, such as the oxydisuccinates, hydrofuran tetracarboxylates, O-, S-or N-linked sulphosuccinates, oxydiacetic acid, oxidised polysaccharides, polyacrylic acids, alkyl and alkenyl succinates; soaps and sulpho fatty acid soaps; and mixtures thereof.

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 Specifications EP-0070474 and EP0037026 (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.

It is an object of the present invention to provide an improved granular non-phosphorus-containing bleach activator composition which can be stably and effectively used in substantially phosphorus-free granular detergent compositions.

This 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 with a mixture comprising an inert non-alkaline, non-phosphate inorganic or organic salt, a water-soluble, film-forming polymeric material of average molecular weight of from about 5001,000,000, and a smectite or alumino silicate clay material, to form granules of a size of from about 0.2 to 2.0 mm.

Accordingly, the invention provides a granular bleach activator composition which is substantially free of phosphorus materials, the composition comprising:

(i) a finely divided bleach activator;

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

(iii) a water-soluble, film-forming polymeric material of average molecular weight of from about 500-1,000,000; and

(iv) a smectite or alumino silicate clay material.

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. One single activator or mixtures of two or more activators may be used as desired.

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

Film-forming polymeric materials which can be used in the invention are, for example, carbohydrates and derivatives, such as carbohydrate ethers; polymers or copolymers from vinyl monomers, such as vinylacetate (and its hydrolysate vinyl alcohol), vinyl pyrrolidone, methyl acrylate, acrylic acid, methacrylic acid, maleic acid (anhydride), styrene, styrene sulphonate or mixtures thereof. Specific examples of suitable polymeric materials are polyvinyl acetate, polyvinyl pyrrolidone, copolymers of polyvinyl alcohol/polyvinyl acetate; carboxy methyl cellulose; dextrine modified vinylacetate polymers; and homo-or copolymeric polycarboxylic acids or salts thereof, such as the polyacrylic acids or polyacrylates, copolymers of maleic acid (anhydride) and acrylic or methacrylic acid, and copolymers of maleic acid (anhydride) and vinylmethyl ether.

The smectite clay materials usable in the present invention are preferably selected from the group consisting of alkali and alkaline earth metal montmorillonites, saponites and hectorites, and particularly those having an ion-exchange capacity of at least about 50 meq/100 g. However, illite, attapulgite and kaolinite clays can also be used in the instant invention. $

The clay minerals used in the instant compositions can be described as expandable, three-layer clays, in which a sheet of aluminium/oxygen atoms or magnesium/oxygen atoms lies between two layers of silicon/oxygen atoms, i.e. alumino-slicates and magnesium silicates. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used therein are examples of the clay minerals classified geologically as smectites.

There are two distinct classes of smectite clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in the outer layers. The dioctahedral minerals are primarily trivalent metal ion-based clays and are comprised of the prototype pyrophyllite and the members montmorillonite $(OH)_4Si_{8-y}Al_y(Al_{4-x}Mg_x)O_{20}$,
nontronite $(OH)_4Si_{8-y}Al_{4-x}Fe_x)O_{20}$ and
volchonkoite $(OH)_4Si_{8-y}Al_y(Al_{4-x}Cr_x)O_{20}$,
where x has a value of from 0 to about 2.0.

The trioctahedral minerals are primarily divalent metal ion based and comprise the prototype talc and the members hectorite $(OH)_4Si_{8-y}Al_y(Mg_{6-x}Li_x)O_{20}$,
saponite $(OH)_4(Si_{8-y}Al_y)(Mg_{6-x}Al_x)O_{20}$,
sauconite $(OH)_4$-$Si_{8-y}Al_y(Zn_{6-x}Al_x)O_{20}$,
vermiculite $(OH)_4Si_{8-y}Al_y(Mg_{6-x}Fe_x)O_{20}$,
wherein y has a value of 0 to about 2.0 and x has a value of 0 to about 6.0.

It is to be recognized that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected.

Specific non-limiting examples of smectite clay minerals are:

- Sodium Montmorillonite
  - Brock
  - Volclay BC
  - Gelwhite GP
  - Thixo-Jel 1
  - Ben-A-Gel
- Sodium Hectorite
  - Veegum F
  - Laponite SP
- Sodium Saponite
  - Barasym NAS 100
- Calcium Montmorillonite
  - Soft Clark
  - Gel White L
- Lithium Hectorite
  - Barasym LIH 200

Most of the smectite clays useful in the compositions herein are commercially available under various trade-names, for example, Thixo-Jel 1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay 325, from American Colloid Co., Skokie, Illinois; and Veegum F, from R.T.Vanderbilt. It is to be recognized that such smectite minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Within the classes of montmorillonite, hectorite, and saponite clay minerals, certain clays are preferred. For example, Gelwhite GP, Volclay BC and certain smectite clays marketed under the name "bentonite".

Bentonite, in fact, is a rock type originating from volcanic ash and contains montmorillonite (one of the smectite clays) as its principal clay component. The Table shows that materials commercially available under the name bentonite can have a wide range of cation exchange capacities. Each of these bentonites can in principle be used in the present invention without problems arising.

Bentonite	Supplier	Exchange capacity meq/100 g
Brock	Georgia Kaolin Co, USA	63
Soft Clark	Georgia Kaolin Co, USA	84
Bentonite L	Georgia Kaolin Co, USA	68
Clarolite T-60	Georgia Kaolin Co, USA	61
Granulare Naturale Bianco	Seven C. Milan Italy	23
Thixo-Jel 4	Georgia Kaolin Co, USA	55
Granular Naturale Normale	Seven C. Milan Italy	19
Clarsol FB 5	Ceca Paris France	12
PDL 1740	Georgia Kaolin Co, USA	26
Versuchs Product FFI	Sud-Chemie Munich Germany	26

* Low colloid content (≤ 50%)

The alumino silicate clay materials usable in the present invention are normally commercially available and can be naturally occurring or synthetically derived. Preferred synthetic crystalline alumino silicate ion-exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof.

The level of such clay materials for use as binder component in the granular bleach activator composition may be as low as about 0.5% and can be increased up to about 15% by weight.

Not only will the presence of small amounts of clay enhance the dispersibility, but it is also economically attractive as a partial replacement of the polymeric material without affecting the overall physical properties of the bleach activator granules.

Effectively, the granular bleach activator compositions will comprise:

(a) from 55-90% by weight of the finely divided bleach activator;
(b) from 3-20% by weight of the inorganic or organic salt;
(c) from 1-10% by weight of the film-forming polymeric material; and
(d) from 0.5-15% by weight of the smectite or alumino silicate clay material.

Water may be present in an amount of up to about 4.5%, preferably up to 3%.

As explained hereinbefore, the invention has particular applicability to non-phosphorus detergent compositions, although it should be appreciated that its use in other detergent compositions is not excluded.

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

i) a detergent active material;
(ii) a non-phosphorus-containing detergency builder;

(iii) a peroxygen bleaching agent; and

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

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 non-phosphorus-containing detergency builder which may be present in an amount of from 5-80% by weight of the composition. Preferred non-phosphorus-containing detergency builders are:

i) the alumino silicate 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) Polycarboxylate polymers as described in EP A-0137669; and mixtures of (i) + (ii); (i) + (iii); or (i) + (ii) + iii).

In addition thereto, 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 80% by weight, so as to leave room in the detergent composition for other desirable ingredients.

Groups of other non-phosphorus detergency builders are known in the art and described in a number of patent publications, such as the sodium carboxy methyloxy disuccinates; citric acid; mellitic acid; benzene polycarboxylic acids; and the polyacetalcarboxylates as disclosed in US Patent Specification 4,144,226.

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 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 should 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 150 micrometre. Bleach activators having a major proportion of particle size of between 50 micrometre to 150 micrometre as described in GB Patent Specification 2,053,998 are particularly suitable.

The detergent compositions in which the granular nonphosphorus bleach activator compositions are incorporated can optionally contain any of the conventional ingredients in the amounts in which such ingredients are normally employed in fabric washing detergent compositions.

One such optional ingredient is an alkalimetal silicate, particularly sodium, neutral, alkaline, metaor orthosilicate. A low level of silicate, for example 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 compsitions 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)	84.9
Sodium sulphate	10.4
Polymer*	1.1
Kaolin clay	2.2
Water	1.4

*Gantrez® AN 119, a copolymer of maleic anhydride and vinyl methyl ether. (Gantrez is a registered Trade Mark).

A solid feed consisting of a mixture of 90% TAED and 10% sodium sulphate was sprayed with the proper amount of an aqueous mixture consisting of 5% Gantrez AN 119, 10% kaolin and 85% water in a Schugi Flexomix 160 Apparatus. The product was aerated to dry and obtain a product of the above composition with the following properties:

	Comp. I	Control Comp. A	B
Bulk density g/l	404	500-640	458
Dynamic flow rate ml/s	120	80	114
Compressibility %	12.9	20	12.4
Granulometry:			
Mean particle size micrometre	721	600-800	848
% 1700 micrometre	nil	1	nil
% 250 micrometre	8.8	5	9.4
% 125 micrometre	2.9	2	3.8

Storage properties in NTA/zeolite detergent 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	30.0
Na-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

		Control	
	Comp. I	Comp. A	B
TAED decomposition %:			
after 4 weeks	15.6	13-27	13.5
after 8 weeks	18.5	20-38	51.3
Perborate decomposition %:			
after 4 weeks	16.3	58-63	8.5
after 8 weeks	34.7	55-89	36.2
TAED delivery:			
Peracid yield, peak value m-mole/1	0.96	1.20	0.94
Peracid yield, peak time minutes	11.5	12.5	20.0

Control granule Comp.	A	B
	% by weight	
TAED (bleach activator)	58-62	85.0
Sodium triphosphate	18-22	-
Potassium triphosphate	13-15	-
Water	5-7	1.5
Sodium sulphate	-	7.6
Polymer*	-	5.9

* Copolymer of maleic anhydride and acrylic acid (Sokalan CP 5 ex BASF).

Examples II and III

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

Compositions (% by weight)	II	III
TAED	80.5	87.3
Sodium sulphate	4.8	8.4
Polymer 1)	3.7	1.0
Clay 2)	8.5	1.9
Water	2.5	1.4

1) Polymer in II is Sokalan ® CP 5 ex BASF, a maleic acid/acrylic acid copolymer; Polymer in III is Gantrez ® AN 119.

2) Clay in II and III is calcium bentonite.

Claims

1. Granular non-phosphorus-containing bleach activator composition comprising :
   (i) a finely divided bleach activator;
   (II) an inert, non-alkaline, non-phosphate, water-soluble inorganic or organic salt;
   (iii) a water-soluble, film-forming polymeric material of average molecular weight of from about 500-1,000,000; and
   (iv) a smectite or alumino silicate clay material.
2. Granular bleach activator composition according to Claim 1, characterized in that it comprises :

(i) from 55-90% by weight of the finely divided bleach activator;
(ii) from 3-20% by weight of the inorganic or organic salt;
(iii) from 1-10% by weight of said polymeric material; and
(iv) from 0.5-15% by weight of said clay material.

3. Granular bleach activator composition according to Claim 1 or 2, characterized in that said salt is sodium sulphate.

4. Granular bleach activator composition according to Claim 1, 2 or 3, characterized in that said clay material is bentonite.

5. A detergent bleach composition which is substantially free of phosphorus-containing material, comprising :
(a) a detergent active material;
(b) a non-phosphorus-containing detergency builder;
(c) a peroxygen bleaching agent; and
(d) a granular non-phosphorus-containing bleach activator composition according to any of the above Claims 1-4.

6. A detergent bleach composition according to Claim 5, characterized in that it comprises :
(a) from 5-40% by weight of said detergent-active material;
(b) from 5-80% by weight of said detergency builder;
(c) from 5-30% by weight of said peroxygen bleaching agent; and
(d) from 0.5-15% by weight of bleach activator contained in said granular composition.

7. A detergent bleach composition according to Claim 5 or 6, characterized in that said non-phosphorus detergency builder is selected from the group consisting of 1) alumino silicate cation-exchange materials, 2) nitrilotriacetic acid compounds, 3) polycarboxylate polymers, and 4) mixtures thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 20 0466

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 098 108 (UNILEVER PLC) * page 8, line 12 - page 10, line 6; page 21, table 6A, claims 1-12 * ---	1-3,5-7	C 11 D 3/39 C 11 D 3/12 C 11 D 3/00
A	FR-A-2 500 475 (COLGATE-PALMOLIVE CO.) * claims 1-3 * ---	1,4	
D,A	EP-A-0 051 987 (PROCTER & GAMBLE CO.) * page 39, examples, claims 1-6 * ---	1,3	
D,A	EP-A-0 075 818 (BASF AG) * claims 1-4 * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	22-06-1987	SCHULTZE D

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