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(54) Granulated bleach activator particles.

(57) Stable bleach activator composition in the form of spray-dried granules comprising from 50-98% by weight of a water-soluble peroxyacid bleach precursor, from 2-50% by weight of a film-forming polymeric material, and from 0-48% by weight of an inert organic or inorganic salt. The spray-dried bleach activator granules show the combined characteristics of excellent storage stability, improved mechanical strength and attrition resistance, as well as good dispersibility and dissolution rate.

Bleach and laundry compositions containing the bleach activator granules are also disclosed.

EP 0 415 472 A2

GRANULATED BLEACH ACTIVATOR PARTICLES

Technical field

This invention relates to bleach activator granules, method of making such granules and use thereof in bleaching and/or detergent compositions. More particularly it relates to improved bleach activator particles prepared by spray-drying for use in or with a detergent and/or bleach composition.

Background and prior art

It is well known that peroxide compounds, such as perborates, percarbonates, perphosphates and persilicates, are highly useful for chemical bleaching of stains found on both coloured and white fabrics, and are thus also useful as bleaching agents for incorporation in laundry detergent compositions. Said peroxide compounds are most effective at high wash temperatures, i.e. at or near the boil wash temperature, but are substantially ineffective at lower temperatures of e.g. below 60 ° C. Many substances are known in the art which are referred to as bleach activators rendering peroxide compound bleaches effective at bleach solution temperatures of below 60 ° C, by forming an organic peroxyacid in situ . A bleach activator can thus generally be described as an organic peroxyacid bleach precursor which in the bleaching solution reacts with the inorganic or organic peroxide compound, thereby releasing the corresponding peroxyacid.

Many such bleach activators are known in the art, most of which contain perhydrolysable N-acyl or O-acyl residues. Examples of these include both the water-insoluble compounds such as succinic, benzoic and phthalic anhydrides, N,N,N′,N′-tetraacetyl-ethylene diamine (TAED) and tetraacetyl-glycoluril (TAGU), as well as the water-soluble compounds such as acetyl salicylic acid, glucose penta-acetate (GPA), and the various esters of phenols and substituted phenols, e.g. sodium acetoxy benzene sulphonate (SABS), sodium benzoyloxy benzene sulphonate (SBOBS) and sodium nonanoyloxy benzene sulphonate (SNOBS).

Hydrolytic instability requires that these bleach activators be protected from the surrounding media, e.g. when incorporated in detergent compositions, particularly from moisture and alkaline ingredients. On the other hand, any proper method of protecting the bleach activator from chemical attack must still allow a relatively quick release or dissolution of the activator in the wash liquor so as to enable the beneficial reaction with the peroxide compound to occur without undue delay. The most common way of protecting bleach activators is by methods wherein the powdered bleach activator material is presented in the form of agglomerated, granulated and/or coated particles. Spray-drying is another route which has been proposed to convert bleach activators into a useful particulate product form.

It is known to prepare granules of water-insoluble bleach activators, e.g. TAED, TAGU, by spray-drying an aqueous slurry comprising said water-insoluble bleach activator (see US Patent 4,457,858). It is also known to incorporate water-insoluble bleach activators in a detergent slurry for spray-drying (see GB-A-1 540 832), whereby the resulting granular detergent composition comprises the bleach activator homogeneously distributed therein.

It is further known in the art to prepare granules comprising water-soluble bleach activators by spray-drying. GB-A-963 135 and US Patent 4,681,695 describe granules of water-soluble bleach activators prepared by spray-drying an aqueous slurry comprising said water-soluble bleach activator and an inorganic (hydratable) salt, e.g. disodium dihydrogen pyrophosphate. Contrary to the granules prepared from water-insoluble bleach activators, the spray-dried granules of water-soluble bleach activators as disclosed in the process of the art contain relatively high proportions of diluent and/or stabilising salts and a relatively low level of the reactive peroxyacid bleach precursor material. This level is normally up to about 50% by weight and, for stability reasons, preferably lower. Nevertheless, the chemical and physical stabilities of such granules of the art are in many cases still far from ideal. Normally, these spray-dried granules suffer from poor attrition resistance, resulting in breakdown to fines upon handling, whereby chemical stability is affected.

Description of the invention

It has now been found that water-soluble bleach activators can be successfully formed into spray-dried granules with high bleach activator contents of satisfactory stability if the water-soluble bleach activator is

spray-dried from a crutcher slurry mix comprising said bleach activator and a film-forming polymeric material. Preferably an acidic film-forming polymeric material is used.

The present invention therefore provides a stable bleach activator composition in the form of spray-dried granules of a water-soluble bleach activator, comprising in homogeneous distribution:

(i) from 50% to about 98% by weight of a water-soluble peroxyacid bleach precursor material;
(ii) from 2% to about 50% by weight of a film-forming polymeric material; and
(iii) from 0% to about 48% by weight of an inert organic or inorganic salt.

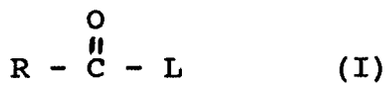
Preferred spray-dried granule compositions will comprise:

(i) from 60% to about 90% by weight of said water-soluble peroxyacid bleach precursor;
(ii) from 5% to about 30% by weight of said film-forming polymeric material; and
(iii) from 5% to about 35% by weight of said inert organic or inorganic salt.

In another aspect the invention provides a process for preparing bleach activator granules by spray-drying an aqueous slurry comprising a water-soluble bleach activator, wherein said aqueous slurry comprises from about 30-50% by weight of water, from about 25-69% by weight of a water-soluble peroxyacid bleach precursor, from about 1-10.5% by weight of a film-forming polymeric material, and from 0 to about 44% by weight of an inert organic or inorganic salt.

The water-soluble bleach activators used in the present invention are those materials which are soluble in water to an extent of at least 1% by weight, preferably at least about 5% by weight, at a temperature of 25 ° C and pH 7.

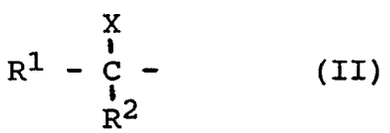
Preferred water-soluble bleach activators are peroxyacid bleach precursors having the general formula I:



(I)

wherein R is an optionally substituted alkyl group containing 1-12 carbon atoms or an optionally substituted phenyl group containing 6-10 carbon atoms, and L is a leaving group containing an anionic moiety, the conjugate acid of the leaving group having a pK_a in the range of from 6 to 13.

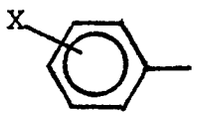
The alkyl group R can be either linear or branched and, in preferred embodiments, it is unsubstituted and contains either 1 or 7-9 carbon atoms. In another group of suitable bleach activators, the alkyl group R is substituted and has the general formula II:



(II)

wherein R^1 is a straight or branched chain alkyl containing from 4 to 10, preferably 6 to 10, more preferably 6 to 8 carbon atoms, R^2 is H, CH_3, C_2H_5 or C_3H_7 and X is halogen (Cl or Br), $-OCH_3$ or OC_2H_5.

Particularly preferred bleach activators are those in which R has the general formula III:



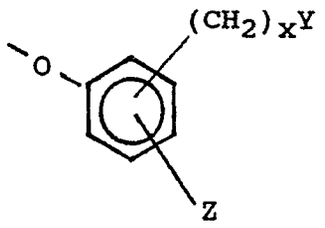
(III)

wherein X is H, a halogen (Cl, Br or F) or a straight or branched chain alkyl group containing from 1-4 carbon atoms, expecially wherein X is H.

L can be essentially any suitable leaving group containing a moiety which is anionic at pH 7. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydroxide anion. Generally, for a group to be a suitable leaving group it must exert an electron-attracting effect. Leaving groups that exhibit such behaviour are those in which their conjugate acid has a pK_a in the range of from 6 to 13, preferably from 7 to 11 and most preferably from 8 to 11. Also, in order for the activator to have the desired level of solubility in wash water it is essential that the leaving group contain an anionic moiety. Non-limiting examples of suitable anionic moieties are $-SO_3M$, -COOM and $-OSO_3M$ wherein M is a proton or a compatible cation.

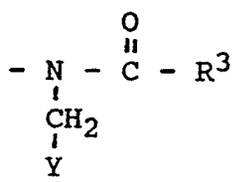
Preferred bleach activators are those of the general formula I wherein L is selected from

(a)



and

(b)



wherein Z is H, R^3 or halogen, R^3 is an alkyl group having from 1 to 4 carbon atoms, x is 0 or an integer of from 1 to 4 and Y is selected from SO_3M, OSO_3M and CO_2M and wherein M is H, alkali metal, alkaline earth metal, ammonium or substituted ammonium.

The preferred leaving group L has the formula (a) in which Z is H, x is O and Y is sulphonate or carboxylate. A highly preferred bleach activator is sodium p-benzoyloxy benzene sulphonate (SBOBS).

The film-forming polymeric material should preferably be non-oxidizable. Such suitable film-forming materials are, for example, the non-oxidizable polymers, which can be in the acid form or in the form of their alkali metal salts. Acidic polymers are preferred.

Acidic polymers usable in this invention can be any non-cellulosic homo- or copolymeric mono- and polycarboxylic acids having an average molecular weight of from 500 to about 1,000,000, preferably from 2,000 to 250,000, more preferably from 10,000 to 50,000.

Suitable polymers include those derived from acrylic acid, methacrylic acid, maleic acid, citraconic acid, aconitic acid, fumaric acid, mesaconic acid, phenyl maleic acid, benzyl maleic acid, itaconic acid, methylene malonic acid, alpha-C_1-C_4 alkyl acrylic acid, alpha-hydroxy acrylic acid and acetalcarboxylic acid monomers, or from the anhydrides of the above monomers where these exist. The polymers can be homopolymers of the above mono- or polycarboxylic monomers; or copolymers of two or more of the above mono- or polycarboxyl monomers; or copolymers of one or more of the above carboxyl monomers with an unsaturated polymerizable monomer other than the specified mono- and polycarboxyl monomers; or modified homo- or copolymers of the above classes having, for example, a non-oxidizable phosphinic acid or sulphinic acid group.

Preferred acidic, polymeric materials are the polyacrylic acids, phosphinate-modified polyacrylic acids, such as described in GB patents 1,485,235 and 1,595,688 and EP-A-0182411; copolymers of maleic acid (anhydride) and acrylic or methacrylic acid; and acidic copolymers containing hydrophobic groups, such as copolymer based on polymethacrylic acid and polyacrylic acid esters in which the ratio of free carboxyl groups to ester groups is at least 1:1. Commercially available polyacrylic acid polymers are, for example, the products sold under the trade name "Versicol", supplied by Allied Colloids, e.g. Versicol E7 and Versicol E9.

As explained hereinbefore, the aqueous slurry prior to spray-drying to form the bleach activator granules may or may not contain an inert inorganic or organic salt. A preferred inert salt is an inert inorganic salt. Suitable inorganic salts include disodium dihydrogen pyrophosphate, sodium dihydrogen orthophosphate, sodium sulphate, sodium bisulphate, magnesium sulphate and mixtures thereof. A particularly preferred inert salt usable in this invention is sodium sulphate.

There are no particular requirements for the spray-drying process other than conventional. The slurry is normally heated to a temperature of from about 60 °C to about 90 °C, preferably from about 80 °C to 90 °C, and spray-dried in a counter-current of air having an inlet temperature of from about 250 °C to about 350 °C, preferably from about 275 °C to about 325 °C, and an outlet temperature of from about 90 °C to 125 °C, preferably from 95 °C to about 110 °C.

The pH of the slurry is not critical, which means that the aqueous slurry composition as defined comprising the preferably acidic film-forming polymeric material can be spray-dried at its natural pH.

The high active content spray-dried bleach activator granules of the invention show the combined characteristics of excellent stability when stored in a detergent or bleach composition, improved mechanical strength and attrition resistance upon handling, as well as good dispersibility and dissolution rate on

addition to the wash and/or bleach solution.

In addition, they generally have a bulk density which can be varied within the range of 300 to about 850 grams/litre, and a weight average particle size of from about 150 μm to 2000 μm, preferably from about 500 μm to 1500 μm, thereby matching the values of particulate detergent or cleaning compositions so as to be usable for direct incorporation therein without undue segregation. The adjustments of these values are not part of the invention, but are measures within the routine skill of the artisan.

The present invention also encompasses bleaching compositions, laundry detergent and laundry additive compositions comprising the bleach activator granules detailed herein. Bleaching compositions according to the invention suitably contain from 5% to 99.5%, preferably from 20% to 90% by weight of peroxide compound bleaching agent and from 0.5% to 95%, preferably from 10% to 80% by weight of bleach activator composition. Laundry compositions according to the invention generally contain from 2% to 40%, preferably from 5% to 25% by weight of detersive surfactant selected from anionic, nonionic, cationic, ampholytic and zwitterionic surfactants and mixtures thereof and from 0.1% to 20%, preferably from 0.5% to 10% by weight of the water-soluble organic peroxyacid bleach precursor. In such laundry compositions the bleach activator granules generally comprise from 0.5% to 40%, preferably from 1% to 10% by weight of the laundry composition, and the base composition comprises from 25% to 99.5%, preferably from 35% to 75% by weight of the laundry composition. In addition, the laundry compositions generally comprise one or more inorganic or organic detergency builders in a total level of from 15% to 90%, preferably from 20% to 60% by weight of the laundry composition, and peroxide compound bleaching agent at a level of from 5% to 35%, preferably from 8% to 20% by weight of the laundry composition.

A wide range of surfactants can be used in the laundry compositions of the invention. US-A-4,111,855 and US-A-3,995,669 contain detailed listing of typical detersive surfactants.

Suitable synthetic anionic surfactants are water-soluble salts of C_8-C_{22} alkyl benzene sulphonates, C_8-C_{22} alkyl sulphates, C_{10}-C_{18} alkyl polyethoxy ether sulphates, C_8-C_{24} paraffin sulphanates, alpha-C_{12}-C_{24} olefin sulphonates, alpha-sulphonated C_6-C_{20} fatty acids and their esters, C_{10}-C_{18} alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, especially those prepared from coconut oil, C_8-C_{12} alkyl phenol polyethoxy ether sulphates, 2-acyloxy C_9-C_{23} alkane-1-sulphonates, and beta-alkyloxy C_8-C_{20} alkane sulphonates.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from 8 to 22, especially from 10 to 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)

Examples of this group of synthetic detergents are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_{8-18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from 9 to 15, especially 11 to 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in US-A-2,220,099 and US-A-2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS, and C_{12}-C_{15} methyl branched alkyl sulphates.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred.

Suitable fatty acid soaps herein can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylolammonium salts of higher fatty acids containing from 8 to 24, preferably from 10 to 22 and especially from 16 to 22 carbon atoms in the alkyl chain. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:5, preferably from 5:1 to 1:1, more preferably from 5:1 to 1.5:1. Especially preferred is a mixture of an alkyl benzene sulphonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium; and either an alkyl sulphate having from 10 to 20, preferably 12 to 18 carbon atoms in the alkyl radical or an ethoxy sulphate having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, having an alkali metal cation, preferably sodium.

The nonionic surfactants useful in the present invention are condensates of ethylene oxide with a

hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5.

Examples of suitable nonionic surfactants include the condensation products of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to 40 moles, preferably 2 to 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 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 fats or prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols (RTM), Dobanols (RTM) and Neodols (RTM) which have about 25% 2-methyl branching (Lutensol (RTM) being a Trade Name of BASF, Dobanol (RTM) and Neodol (RTM) being Trade Names of Shell), or Synperonics (RTM), which are understood to have about 50% 2-methyl branching (Synperonic (RTM) is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol (RTM) 45-4, Dobanol (RTM) 45-7, Dobanol (RTM) 45-9, Dobanol (RTM) 91-2.5, Dobanol (RTM) 91-3, Dobanol (RTM) 91-4, Dobanol (RTM) 91-6, Dobanol (RTM) 91-8, Dobanol (RTM) 23-6.5, Synperonic (RTM) 6, Synperonic (RTM) 14, the condensation products of coconut alcohol alcohol with an average of between 5 and 12 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 average of between 7 and 12 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 having from 9 to 15 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

Other suitable nonionic surfactants include the condensation products of C_6-C_{12} alkyl phenols with from 3 to 30, preferably 5 to 14 moles of ethylene oxide, and the compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol, such synthetic nonionic detergents being available on the market under the Trade Name of "Pluronic (RTM)" supplied by Wyandotte Chemicals Corporation.

Especially preferred nonionic surfactants for use herein are the C_9-C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{12}-C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants and surfactants of a semi-polar nature, for example amine oxides. Suitable quaternary ammonium surfactants are selected from mono C_8-C_{16}, preferably C_{10}-C_{14} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl and the corresponding di-C_6-C_{10} N-alkyl or alkenyl ammonium surfactants. Suitable amine oxides are selected from mono C_8-C_{20}, preferably C_{10}-C_{14} N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are again substituted by methyl, hydroxyethyl or hydroxypropyl.

Suitable detergent builder salts useful herein 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, pyrophosphates, tripolyphosphates and bicarbonates.

Organic builder/chelating agents that can be incorporated include citric acid, nitrilotriacetic and ethylenediamine tetraacetic acids and their salts, organic phosphonates derivatives such as those disclosed in US-A-3,213,030, US-A-3,433,021, US-A-3,292,121 and US-A-2,599,807, and carboxylic acid builder salts such as those disclosed in US-A-3,308,067. Preferred chelating agents include nitrilotriacetic acid (TNA), nitrilo(trimethylene phosphonic acid) (NTMP), ethylenediamine tetra(methylene phosphonic acid) (EDTMP) and diethylenetriamine penta(methylene phosphonic acid) (DETPMP). Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in CA-A-755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

A further class of builder salts is the 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 $Na_z(AlO_2)_z(SiO_2)y.xH_2O$ 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 0.5 and x is an integer from 15 to 264. Compositions incorporating builder salts of this type form the subject of GB-A-1,429,143, DE-A-2,433,485 and DE-A-2,525,778.

An alkali metal, or alkaline earth metal, silicate can also be present in granular compositions of the invention. The alkali metal silicate is preferably from 3% to 15%. Suitable silicate solids have a molar ratio

of SiO_2/alkali metal$_2$O in the range from 1.0 to 3.3, more preferably from 1.5 to 2.0.

The compositions herein will normally contain peroxide compounds as bleaching components. In general, the bleach is selected from inorganic peroxy salts, hydrogen peroxide, hydrogen peroxide adducts, and organic peroxyacids and salts thereof. Suitable inorganic peroxygen bleaches include sodium perborate mono- and tetrahydrate, sodium percarbonate, sodium persilicate, urea-hydrogen peroxide addition products and the clathrate $4Na_2SO_4:2H_2O_2:1NaCl$. Suitable organic bleaches include peroxylauric acid, peroxyoctanoic acid, peroxynonanoic acid, peroxydecanoic acid, diperoxydodecanedioic acid, diperoxyazelaic acid, mono-and diperoxyphthalic acid and mono- and diperoxyisophthalic acid.

The compositions of the invention can be supplemented by all manner of detergent and laundering components, inclusive of suds suppressors, enzymes, fluorescers, soil-suspending agents, anti-caking agents, pigments, perfumes, fabric-conditioning agents etc.

Suds suppressors are represented by materials of the silicone, wax, vegetable and hydrocarbon oil and phosphate ester varieties. Suitable silicone suds-controlling agents include polydimethylsiloxanes having a molecular weight in the range from 200 to 200,000 and a kinematic viscosity in the range from 20 to 2,000,000 mm^2/s, preferably from 3000 to 30,000 mm^2/s, and mixtures of siloxanes and hydrophobic silanated (preferably trimethylsilanated) silica having a particle size in the range from about 10 nm to 20 nm and a specific surface area above 50 m^2/g. Suitable waxes include microcrystalline waxes having a melting point in the range from 65 °C to 100 °C, a molecular weight in the range from 4000-1000, and a penetration value of at least 6, measured at 77 °C by ASTM-D1321, and also paraffin waxes, synthetic waxes and natural waxes. Suitable phosphate esters include mono- and/or di-C_{16}-C_{22} alkyl or alkenyl phosphate esters, and the corresponding mono- and/or di-alkyl or alkenyl ether phosphates containing up to 6 ethoxy groups per molecule.

Enzymes suitable for use herein include those discussed in US-A-3,519,570 and US-A-3,533,139. Suitable fluorescers include Blankophor (RTM) MBBH (Bayer AG) and Tinopal (RTM) CBS and EMS (Ciba-Geigy). Suitable fabric-conditioning agents include smectite-type clays as disclosed in GB-A-1,400,898 and di-C_{12}-C_{24} alkyl or alkenyl amines and ammonium salts.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclose in GB-A-1,596,765. Preferred polymers include copolymers or salts thereof of maleic anhydride with ethylene, methylvinyl ether, acrylic acid or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These polymers are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Laundry additive products comprising bleaching or laundry detergent compositions in water-releasable combination with a non-particulate carrier as described in EP-A-96566 and EP-A-99197, are also suitable herein.

Laundry products comprising a laundry detergent composition and a bleaching composition comprising the bleach activator granules and peroxide bleach in separate packs or in two-compartment sachets are also suitable herein.

Example I

A spray-dried granular bleach activator of the following composition:

	% by weight
Sodium-p-benzoyloxybenzene sulphonate (SBOBS)	65
Polyacrylic acid (Versicol ® E9) *	5
Sodium sulphate	30
Trace water	up to 100%

* M.W. ~ 75,000

was prepared in the following manner:

100 Kg of an aqueous slurry composition was prepared consisting of about 40% by weight of water, 39% by weight of SBOBS, 3% by weight of polyacrylic acid and 18% sodium sulphate. This slurry was heated to a temperature of about 85 °C and pumped to a 1.8 m diameter spray-drying tower through a nozzle of size 2 mm at a pressure of about 35 bar. Counter-current air of about 275-300 °C was let in at a velocity of 0.4 meter/sec, which left the tower at a temperature of about 100 °C.

The spray-dried bleach activator particles collected at the bottom of the spray-drying tower were non-dusty granules of regular, somewhat rounded shape of a size varying from about 300 to 1000 μm, which upon cooling and storage showed no substantial sign of attrition and degradation, i.e. the product had good particle strength.

Upon addition to a wash solution with some stirring, a rapid dissolution rate was observed.

Example II

The following granular laundry detergent compositions were prepared by a combined spray-drying and dry-mixing process.

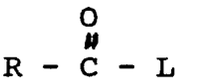
Composition (% by weight)	A	B	C
Spray-dried base powder			
Sodium alkylbenzene sulphonate	6.0	6.5	9.0
Fatty alcohol-7 ethoxylate	3.0	3.0	1.5
Sodium soap	5.0	5.0	-
Sodium triphosphate	33.0	-	-
Sodium aluminosilicate (Zeolite A)	-	40.0	24.0
Sodium carbonate	-	-	2.0
Maleic acid/acrylic acid copolymer (Sokalan ® CP5 ex BASF)	-	-	4.0
Alkaline silicate	6.0	8.0	-
Sodium sulphate	21.0	16.0	30.0
Sodium carboxymethyl cellulose	0.5	0.5	0.5
EDTA	0.2	0.2	0.2
Fluorescer	0.3	0.3	0.2
Water and minor ingredients	6.0	9.5	8.6
Dry-mixing ingredients			
Anti-foaming agent	-	-	2.5
Sodium perborate monohydrate	15.0	8.0	13.0
Spray-dried bleach activator granules of Example I (65% active)	4.0	3.0	4.0
Proteolytic enzyme (Savinase ® ex Novo)	-	-	0.5

The above products show excellent bleach activator stability upon storage and handling.

Claims

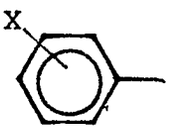
1. A bleach activator composition in the form of spray-dried granules comprising a water-soluble organic peroxyacid bleach precursor, characterized in that it comprises in homogeneous distribution :
   (i) from 50% to about 98% by weight of a water-soluble peroxyacid bleach precursor;
   (ii) from 2% to about 50% by weight of a film-forming polymeric material; and
   (iii) from 0% to about 48% by weight of an inert organic or inorganic salt.
2. A composition according to Claim 1, characterized in that it comprises ;
   (i) from 60% to 90% by weight of said water-soluble peroxyacid bleach precursor;
   (ii) from 5% to 30% by weight of said film-forming polymeric material; and
   (iii) from 5% to 35% by weight of said inert organic or inorganic salt.

3. A composition according to Claim 1 or 2, characterized in that the water-soluble organic peroxyacid bleach precursor has the general formula:



wherein R is an optionally substituted alkyl group containing 1-12 carbon atoms or an optionally substituted phenyl group containing 6-10 carbon atoms, and L is a leaving group containing an anionic moiety, the conjugate acid of the leaving group having a pK_a in the range of from 6 to 13.

4. A composition according to Claim 3, characterized in that R has the formula :



wherein X is H, a halogen (Cl, Br or F) or a straight or branched chain alkyl group containing from 1-4 carbon atoms.

5. A composition according to Claim 4, characterized in that the water-soluble peroxyacid bleach precursor is sodium p-benzoyloxy benzene sulphonate.

6. A composition according to any of Claims 1-5, characterized in that the film-forming polymeric material is a non-oxidizable acidic polymer.

7. A composition according to Claim 6, characterized in that said polymer is a non-cellulosic homo- or copolymer of mono- or poly-carboxylic acids, having an average molecular weight of from 500 to about 1,000,000.

8. A composition according to Claim 6 or 7, characterized in that said polymeric material is selected from the group consisting of polyacrylic acids, phosphinate-modified polyacrylic acids, copolymers of maleic acid (anhydride) and acrylic or methacrylic acid, and acidic copolymers based on polymethacrylic acid and polyacrylic acid esters.

9. A composition according to any of Claims 1-8, characterized in that the inert salt is sodium sulphate.

10. A process for preparing a granular bleach activator composition according to Claims 1-8, by spray-drying an aqueous slurry comprising a water-soluble bleach activator, characterized in that said aqueous slurry comprises from about 30-50% by weight of water, from about 25-69% by weight of water-soluble peroxyacid bleach precursor, from about 1-10.5% by weight of a film-forming polymeric material, and from 0 to about 44% by weight of an inert organic or inorganic salt.

11. A bleaching composition comprising from 5% to 99.5% by weight of peroxide compound bleaching agent and from 0.5% to 95% by weight of a bleach activator composition according to any of Claims 1-10.

12. A laundry composition comprising 2-40% by weight of a detersive surfactant selected from anionic, nonionic, cationic, ampholytic and zwitterionic surfactants and mixtures thereof, from 15-90% by weight of a detergency builder, from 5-35% by weight of a peroxide compound bleaching agent and from 0.5-40% by weight of a bleach activator composition according to any of Claims 1-10.

13. A laundry composition according to Claim 12, characterized in that it comprises from 5-25% by weight of said surfactant, from 20-60% by weight of said detergency builder, from 8-20% by weight of said peroxide compound bleach and from 1-10% by weight of said bleach activator composition.