United States Patent Office
3,833,506
Patented Sept. 3, 1974

3,833,506

BLEACHING ASSISTANTS AND THE PREPARATION THEREOF

Walter Fries, Erkrath-Unterbach, Klaus Hachmann, Hilden, Rhineland, Dieter Jung, Monheim-Baumberg, Rhineland, Peter Neuhausen, Krefeld-Fischeln, and Dieter Walter, Hilden, Rhineland, Germany, assignors to Henkel & Cie GmbH, Dusseldorf-Holthausen, Germany

No Drawing. Filed July 31, 1972, Ser. No. 276,727
Claims priority, application Germany, Aug. 2, 1971, P 21 38 584.2; Feb. 21, 1972, P 22 07 974.9
Int. Cl. C11d 7/18, 7/38
U.S. Cl. 252—99 17 Claims

ABSTRACT OF THE DISCLOSURE

A bleaching assistant suitable for use in pulverulent washing and bleaching compositions comprising particulate matter consisting essentially of (A) 10% to 70% by weight of an activator for active oxygen and (B) from 30% to 90% by weight of a mixture of (1) fatty acids and (2) polyethylene glycol.

The process of forming this bleaching assistant comprises spraying a homogeneous liquid mixture of the activator, fatty acid and polyethylene glycol into a solidification zone to form particles thereof of which at least 70% have an average diameter of 0.1 to 1 mm.

PRIOR ART

Washing compositions which contain so-called bleaching activators in addition to the usual detergent substances having a cleaning action, builder salts and bleaching percompounds are known. These activators comprise carboxylic acid derivatives which react with the percompounds with the formation of peracids and therefore increase the bleaching action of the mixtures or make it possible to effect bleaching at relatively low washing temperatures. The storage of such washing compositions, however, poses considerable problems, since under the influence of relatively high humidity, the percompounds and bleaching activators can react together even at room temperature, thereby leading to a loss of active oxygen. When substances sensitive to oxygen are present, for example optical brighteners, these may be decomposed by oxidation. At the same time an unpleasant smell frequently occurs, which is due to volatile oxidation products. But in washing compositions in which the percompounds are provided with protective coatings or are stored separately from the other washing composition components, in order to exclude a reaction with the other constituents, no difficulty occurs. Since the bleaching activators represent very reactive acylation agents, they can react with sensitive washing composition components, for example perfumes or optical brighteners, and impair the properties of these.

It has already been proposed to purify the optical brighteners in a specified way in order to prevent the formation of unpleasant smelling products. This does not solve the problem of a reduction of the active oxygen content, however. Further, it has been suggested that the powder particles of the bleaching activator should be provided with a coating, in order to suppress a reaction between the activator and percompounds. Suggested coating materials are inorganic, crystalline salts, for example sodium sulfate, high molecular substances such as polyethylene glycol, polyvinyl alcohol and cellulose ethers or fatty substances such as fatty acids, fatty alcohols or fatty acid alkylolamides. In such a case the coating material in solution should be sprayed or granulated on the activator. It has been found, however, that this pretreatment does not lead to an appreciable improvement in the stability during storage, especially when the coating material consists of water-soluble compounds. The use of a water-insoluble coating material in the known process only leads to an insignificant improvement of the storage stability; the covered particle, however, does not dissolve or only dissolves very slowly in cold water or in moderately heated washing liquors, and so a uniform distribution of the particles in the washing liquor or a bleaching at low temperatures is difficult.

OBJECTS OF THE INVENTION

An object of the invention is to develop a bleaching assistant which is protected against decomposition during storage and has sufficient solubility to be employed in cold water bleaching baths.

It is another object of the present invention to provide a bleaching assistant suitable for use in pulverulent washing and bleaching compositions, which comprises particles of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm., and which particles consist essentially of an intimate mixture containing (A) 10% to 70% by weight of at least one compound acting as an activator for active oxygen selected from the group consisting of N-acyl compounds having 2 to 9 carbon atoms in the acyl, O-acyl compounds having 2 to 9 carbon atoms in the acyl, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Peracid Formation Test, and (B) 30% to 90% by weight of a mixture consisting essentially of (1) fatty acids consisting of from 80% to 100% by weight of saturated fatty acids having 12 to 24 carbon atoms and saturated hydroxy fatty acids having from 12 to 24 carbon atoms and from 0% to 20% by weight of a mixture of saturated fatty acids having from 8 to 10 carbon atoms and unsaturated fatty acids having 12 to 24 carbon atoms and (2) a polyethylene glycol with an average molecular weight of 1000 to 20,000, the weight ratio of fatty acids to polyethylene glycol ranging from 5:1 to 1:4.

It is a further object of the present invention to provide a process for the preparation of a bleaching assistant suitable for use in pulverulent washing and bleaching compositions, which comprises particles of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm., and which particles consist essentially of an intimate mixture containing (A) 10% to 70% by weight of at least one compound acting as an activator for active oxygen selected from the group consisting of N-acyl compounds having 2 to 9 carbon atoms in the acyl, O-acyl compounds having 2 to 9 carbon atoms in the acyl, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Peracid Formation Test, and (B) 30% to 90% by weight of a mixture consisting essentially of (1) fatty acids consisting of from 80% to 100% by weight of saturated fatty acids having 12 to 24 carbon atoms and saturated hydroxy fatty acids having from 12 to 24 carbon atoms and from 0% to 20% by weight of a mixture of saturated fatty acids having from 8 to 10 carbon atoms and unsaturated fatty acids having 12 to 24 carbon atoms and (2) a polyethylene glycol with an average molecular weight of 1000 to 20,000, the weight ratio of fatty acids to polyethylene glycol ranging from 5:1 to 1:4; comprising the steps of spraying a homogeneous mixture of said activator, said fatty acid and said polyethylene glycol at a temperature above the melting point of at least one of said ingredients into a zone space at a temperature of at least 10° C. below the solidification point of the mixture, under atomizing conditions whereby particles are formed of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm.; and collecting said particles.

Other and further objects of the invention will become apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The present invention is directed to a bleaching assistant suitable for use in pulverulent washing and bleaching compositions, which comprises particles of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm., and which particles consist essentially of an intimate mixture containing (A) 10% to 70% by weight of at least one compound acting as an activator for active oxygen selected from the group consisting of N-acyl compounds having 2 to 9 carbon atoms in the acyl, O-acyl compounds having 2 to 9 carbon atoms in the acyl, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Peracid Formation Test, and (B) 30% to 90% by weight of a mixture consisting essentially of (1) fatty acids consisting of from 80% to 100% by weight of saturated fatty acids having 12 to 24 carbon atoms and saturated hydroxy fatty acids having from 12 to 24 carbon atoms and from 0% to 20% by weight of a mixture of saturated fatty acids having from 8 to 10 carbon atoms and unsaturated fatty acids having 12 to 24 carbon atoms and (2) a polyethylene glycol with an average molecular weight of 1000 to 20,000, the weight ratio of fatty acids to polyethylene glycol ranging from 5:1 to 1:4.

The present invention also provides a solid, pulverulent to granular composition useful in the preparation of aqueous cold-bleaching baths, especially cold-bleaching washing liquors for textiles consisting essentially of (I) from 5% to 95% by weight based upon the total weight of the aforesaid bleaching assistant and (II) from 5% to 95% by weight based upon the total weight of at least one compound selected from the group consisting of (a) alkali metal builder salts, (b) precompounds giving H_2O_2 in aqueous solutions and stabilizers for percompounds, (c) tensides selected from the group consisting of anionic surface-active compounds, nonionic surface-active compounds and amphoteric surface-active compounds, (d) optical brighteners, and (e) water-soluble organic builder salts.

The present invention also provides a process for the preparation of the said bleaching assistant comprising the steps of spraying a homogeneous mixture of said activator, said fatty acid and said polyethylene glycol at a temperature above the melting point of at least one of said ingredients into a zone space at a temperature of at least 10° C. below the solidification point of the mixture, under atomizing conditions whereby particles are formed of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm.; and collecting said particles.

The bleaching assistants are preferably present in admixture with further pulverulent bleaching agent components, especially granular to pulverulent percompounds, which in aqueous solution liberate hydrogen peroxide. In these mixtures the proportion by weight of the bleaching assistant to the percompound should be from 1:5 to 5:1 and should be chosen so that 0.05 to 2 mol of activator are present per gram atom of active oxygen.

Certain N-acyl and O-acyl compounds, forming with the H_2O_2 organic peracids, as well as carbonic acid or pyrocarbonic acid esters, which have an activation value for the percompounds in the Peracid Formation Test (=titer) of at least 3, preferably of at least 4.5, serve as activators for the percompounds which release H_2O_2 in water. The Peracid Formation Test activation value is determined in the following manner.

Solutions that contain 0.615 gm./liter of

$$NaBO_2 \cdot H_2O_2 \cdot 3H_2O$$

(4 mmol/liter) and 2.5 gm./liter of $Na_4P_2O_7 \cdot 10H_2O$ are mixed, after heating to 60° C., with 4 mmol/liter of activator and kept for 5 minutes at this temperature with stirring. Then 100 ml. of this liquid is added to a mixture of 250 gm. of ice and 15 ml. of glacial acetic acid and titrated, immediately after the addition of 0.35 gm. of potassium iodide, with 0.1N sodium thiosulfate solution with starch as indicator. The amount of thiosulfate solution used in ml. is the activation value (=titer). At a 100% activation of the peroxide used, it would amount to 8.0 ml.

Of the types of activators described below, particularly those compounds are suitable which have a melting point of at least 70° C., preferably at least 100° C., and especially at least 150° C. Furthermore, the equivalent weight of these compounds (under equivalent weight is here understood the quotient from the molecular weight and the number of acyl residues, or carbonic acid or pyrocarbonic acid residues in the molecule) should be at most 170, preferably at most 130 and especially at most 110.

The activators, usable according to the invention, include:

(a) The N-diacylated and N,N'-tetraacylated amines, described in the German Pats. 1,162,967 and 1,291,317, such as N,N,N',N'-tetraacetyl-methylenediamine, N,N,N',N'-tetraacetyl-ethylenediamine, N,N-diacetylaniline and N,N-diacetyl-p-toluidine or 1,3-diacylated hydantoins, such as the compounds 1,3-diacetyl-5,5-dimethylhydantoin and 1,3-dipropionyl-hydantoin;

(b) The N-alkyl-N-sulfonyl-carbonamides, described in the British Pat. 1,003,310; for example, the compounds N-methyl-N-mesyl-acetamide, N-methyl-N-mesylbenzamide, N-methyl-N-mesyl-p-nitrobenzamide and N-methyl-N-mesyl-p-methoxybenzamide;

(c) The N-acylated cyclic hydrazides, acylated triazoles or urazoles, described in the Swiss Pat. 407,387, such as the monoacetylmaleic acid hydrazide;

(d) The O,N,N-tri-substituted hydroxyl amines, described in the German Published Patent Application P 17 19 574.3–43, such as O-benzoyl-N,N-succinylhydroxyamine. O-acetyl-N,N - succinylhydroxyamine, O-p-methoxybenzoyl-N,N - succinyl-hydroxylamine, O-p-nitrobenzoyl-N,N-succinylhydroxylamine and O,N,N-triacetylhydroxylamine;

(e) The N,N'-diacyl-sulfurylamides, described in the German Published Application DOS 1,801,713, such as N,N'-dimethyl-N,N'-diacetyl-sulfurylamide and N,N'-diethyl-N,N'-dipropionyl-sulfurylamide;

(f) The triacylcyanurates, such as triacetylcyanurate and tribenzoylcyanurate described in German Published Patent Application DAS 1,294,919;

(g) The carboxylic acid anhydrides, described in the Swiss Pat. 347,930, or the German Pat. 893,049, or the German Published Application DOS 1,444,001, such as benzoic acid anhydride, m-chlorobenzoic acid anhydride, phthalic acid anhydride, 4-chlorophthalic acid anhydride;

(h) The sugar esters, described in the Swiss Pat. 348,682, such as glucosepentaacetate;

(i) The 1,3-diacyl-4,5-diacyloxy-imidazolidines, described in the German Published Application DOS 1,801,141, such as the compounds 1,3-diformyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5 - diacetoxy-imidazolidine. 1,3-diacetyl-4,5-dipropionyloxyimidazolidine;

(j) The acylated glycoluril compounds, described in the German Published Application DOS 1,594,865, such as tetraacetylglycoluril and tetrapropionylglycoluril;

(k) The diacylated 2,5-diketopiperazines, described in the German Published Patent Application P 20 38 106.0, such as 1,4-diacetyl-2,5-diketo-piperazine,1,4-dipropionyl-2,5-diketopiperazine, 1,4 - dipropionyl-3,6-dimethyl-2,5-diketo-piperazine;

(l) The acylation products, described in the German Published Patent Application P 21 12 557.5, of propylenediurea of 2,2-dimethylpropylenediurea (2,4,6,8-tetraazabicyclo-(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), particularly tetraacetyl-propylenediurea, tetrapropionyl-propylenediurea or their dimethyl derivatives;

(m) The carbonic acid esters, described in the German Published Application DOS 1,444,024, for example, the sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxycarbonyloxy)-benzenesulfonic acid.

Of particularly practical interest are the activator types named under (j).

In the activation of the percompounds by the named N-acyl and O-acyl compounds, carboxylic acids, such as acetic acid, propionic acid, benzoic acid, are liberated, and it is recommended to add corresponding amounts of alkalis to neutralize these carboxylic acids. In effective activators, an activation is visible already in using amounts of 0.05 mols of activator per gm.-atom of active oxygen. Preferably 0.1 to 1 mol of activator are used. The amount may, however, be raised up to 2 mols of activator per gm.-atom of active oxygen if desired.

Suitable fatty acids which are present in the activator-containing powder particles, are saturated fatty acids and saturated hydroxy-fatty acids with 12 to 24 carbon atoms, as well as mixtures thereof, such as lauric, myristic, palmitic, stearic, arachidic, behenic and lignoceric acids and the hydroxystearic and dihydroxystearic acids. If mixtures of naturally occurring or hydrogenated fatty acids are used, these may also contain saturated fatty acids with 8 to 10 carbon atoms and unsaturated fatty acids, for example oleic acid, but the fraction of the low-molecular weight and unsaturated acids should be less than 20% by weight and especially less than 10% by weight of the total fatty acids present. The composition of the fatty acid mixtures is preferably such that the softening point or melting point lies above 50° C.

The polyethyleneglycols present in admixture with the bleaching activator and the fatty acids should melt at a temperature above 35° C. Polyethyleneglycols with a molecular weight of 1000 to 20,000, preferably from 2000 to 10,000, are suitable. The proportion by weight of fatty acid to polyethyleneglycol should amount to 5:1 to 1:4, preferably 3:1 to 1:2.5.

The activator-containing particles should be present approximately in drop form to globular form and have at least 70% by weight, preferably more than 90% by weight with an average diameter of 0.1 to 1 mm. Its composition should be largely homogeneous and the surface should be smooth. Particles of powder which fulfil these conditions, are obtainable by homogenizing the bleaching activator, the fatty acid and the polyglycol at a temperature which lies above the melting point of at least one of the ingredients, and preferably above the melting point of the fatty acid and the polyglycol so as to form a suspension of the bleaching activator. This suspension is then sprayed through a nozzle under high pressure under atomizing conditions into a space zone, the temperature of which lies below the solidification point of the mixture. The aperture of the spray nozzle should have a diameter of 0.3 to 2.5 mm., and preferably from 0.6 to 1.8 mm. The pressure at which the molten material is fed to the nozzle should be 10 to 30 kg./cm.^{2}, and preferably 15 to 25 kg./cm.^{2}. Instead of a nozzle, a rotating spray disc may also be used which may be provided with round or slot-like apertures so as to apply an angular velocity to this molten material. The peripheral speed of such a disc, which usually has a diameter of 150 to 300 mm. and rotates at 800 to 10,000 revolutions per minute, should be 5 to 150 m./sec., preferably 10 to 100 m./sec. The space, in which the sprayed particles solidify, preferably comprises a cylindrical chamber which is fitted with supply lines for cooling air and a discharge device for the powder at the conical base of the chamber. The cooling air, which has a temperature of at least 10° C. below the solidifying temperature of the mixture and may be for example −10° to +40° C., may be fed in cocurrent or countercurrent.

When technically pure starting materials are used, the sprayed particles may have a natural color. This may be masked or altered by addition of dyestuffs or color pigments before the spraying or by dusting the grains obtained with pigments, for example titanium dioxide.

The bleaching assistants may be present alone in admixture with percompounds or mixed with pulverulent to granular washing compositions with or without bleaching agents. These washing compositions consist of at least one compound selected from anionic, amphoteric and nonionic detergent substances, at least one compound selected from polymeric phosphates, sequestering agents and washing alkalis, and at least one optical brightener.

In addition to these above named washing composition compounds, it is possible to utilize antimicrobial agents, soil suspension agents, enzymes, foam stabilizers, non-surface-active foam inhibitors, textile softeners, corrosion inhibitors, and water as components in the washing compositions.

Besides alkali metal peroxides, the most suitable percompounds which liberate hydrogen peroxide in aqueous solution are perhydrates, for example alkali metal perborates, such as sodium perborate containing water of crystallization or anhydrous sodium perborate, and also alkali metal percarbonates, perpyrophosphates and persilicates as well as urea perhydrate. Sodium perborate tetrahydrate is preferably used.

The average grain size of the percompounds and the optionally additionally used powder components should be from 0.1 to 2 mm. The grain size of the percompounds as well as optionally further powder components is not critical in itself, but should be so chosen that at least 50% and preferably more than 80% of the grains have a diameter of at least 0.05 and not more than 2.5 mm., so as to prevent dust on the one hand, and on the other hand to keep the powder mixture easily transportable and pourable. Relatively large deviations in the grain size of the single powder components should be avoided in order to avoid the unwanted settling of fine and specifically heavy grains at the bottom of the packing container during transportation.

Uniting of the different powder components into a homogeneous powder mixture or the addition of further powder constituents is effected in known way with the usual mixing devices, while the shape and size of the individual constituents should be preserved as far as possible.

Detergent compositions are usually comprised by a mixture containing from 5% to 95% by weight based on the total detergent composition weight of the above described bleaching assistant and from 5% to 95% by weight based upon the total detergent composition weight of suitable detergent substances. Suitable detergent ingredient substances may be further contained in the washing composition containing the bleaching assistant powder component.

The further constituents of the detergent compositions according to the invention are described below in more detail according to the class of substance.

The anionic, amphoteric or non-ionic tensides contain in the molecule at least one hydrophobic residue mostly containing 8 to 26, preferably 10 to 22 and especially 10 to 18, carbon atoms and at least one anionic, non-ionic or amphoteric water-solubilizing group. The preferably saturated hydrophobic residue is mostly aliphatic, but possibly also alicyclic in nature. It may be combined directly with the water-solubilizing group or through intermediate members. Suitable intermediate members are, for example, benzene rings, carboxylic acid ester or carboxylic acid amide groups, residues of polyhydric alcohols linked in ether or ester-like form, such as, for example, those of ethylene glycol, propylene glycol, glycerine or corresponding polyether residues.

The hydrophobic residue is preferably an aliphatic hydrocarbon residue with 10 to 18, preferably 12 to 18, carbon atoms but deviations from the preferred range of carbon atoms are possible, depending on the nature of the surface-active compound in question. The anionic tenside may be present in the form of their alkali metal salts, such as sodium and potassium, ammonium salts and salts of organic bases such as mono-, di- and triethanolamines.

Soaps from natural or synthetic fatty acids, possibly also from resin or naphthenic acids, are utilizable as anionic detergent substances, especially when these acids have iodine values of not more than 30, and preferably of less than 10, for example the sodium soaps of coconut, palm kernel or tallow fatty acids.

Of the synthetic anionic surface-active compounds, the sulfonates and sulfates possess special practical importance.

The sulfonates include, for example, the alkylaryl sulfonates, especially alkylbenzene sulfonates, which are obtained from preferably straight-chain aliphatic hydrocarbons having 9 to 15, especially 10 to 14 carbon atoms, by chlorinating and alkylating benzene or from corresponding terminal or non-terminal olefins by alkylation of benzene and sulfonation of the alkylbenzenes obtained. Further, aliphatic sulfonates are of interest, such as are obtainable, for example, from preferably saturated hydrocarbons containing 8 to 18 and preferably 12 to 18 carbon atoms in the molecule by sulfochlorination with sulfur dioxide and chlorine or sulfoxidation with sulfur dioxide and oxygen, and conversion of the products thereby obtained into the sulfonates. As aliphatic sulfonates, mixtures containing alkene sulfonates, hydroxyalkane sulfonates and disulfonates are useful, which are obtained from terminal or non-terminal C_{8-18} and preferably C_{12-18} olefins by sulfonation with sulfur trioxide and acid or alkaline hydrolysis or the sulfonation products. In the aliphatic sulfonates thus prepared, the sulfonate group is frequently found attached to a secondary carbon atom; however, sulfonates with a terminal sulfonate group obtained by reaction of terminal olefins with bisulfite can also be used.

Furthermore, salts, preferably dialkali metal salts of α-sulfo-fatty acids, and salts of esters of these acids with mono- or poly-hydric alcohols containing 1 to 4, and preferably 1 to 2 carbon atoms belong to the sulfonates to be used according to the invention.

Further useful sulfonates are salts of fatty acid esters of hydroxyethanesulfonic acid or dihydroxypropane sulfonic acid, the salts of the fatty alcohol esters of lower aliphatic or aromatic sulfomono- or di-carboxylic acids containing 1 to 8 carbon atoms, alkylglycerylether sulfonates and the salts of the amide-like condensation products of fatty acids or sulfonic acids with aminoethanesulfonic acid.

As tensides of the sulfate type are fatty alcohol sulfates, especially those prepared from coconut fat alcohols, tallow fat alcohols or oleyl alcohol. Useful sulfonation products of the sulfate type are also obtainable from terminal or non-terminal C_{8-18} olefins. Sulfated fatty acid alkylolamides or fatty acid monoglycerides, and sulfated alkoxylation products of alkylphenols (C_{8-15} alkyl), fatty alcohols, fatty acid amides or fatty acid alkylolamides, which may contain in the molecule 0.5 to 20, preferably 1 to 8 and especially 2 to 4 ethylene and/or propylene glycol residues, also belong to this group of surface-active compounds.

Suitable anionic surface-active compounds of the carboxylate type are the fatty acid esters or fatty alcohol ethers of hydroxycarboxylic acids, and the amide-like condensation products of fatty acids or sulfonic acids with aminocarboxylic acids, for example, with glycocoll, sarcosin or protein hydrolysates.

The non-ionic surface-active compounds, here called "non-ionics," for the sake of simplicity, include products which owe their solubility in water to the presence of polyether chains, amineoxide, sulfoxide or phosphineoxide groups, alkylolamide groups and very generally, to an accumulation of hydroxyl groups.

The products obtainable by addition of ethylene oxide and/or glycide to fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty acid and sulfonic acid amides are of special practical interest. These non-ionics may contain per molecule 4 to 100, preferably 6 to 40 and especially 8 to 20 ether residues, particularly ethylene glycol ether residues. Moreover, propylene or butylene glycol ether residues or polyether chains may be present in or at the ends of these polyether residues.

Further, products known by the trade name of "Pluronics" of "Tetronics" belong to the non-ionics. They are obtained from water-insoluble polypropylene glycols or from water-insoluble propoxylated lower aliphatic alcohols containing 1 to 8, preferably 3 to 6 carbon atoms and/or from water-insoluble propoxylated alkylenediamines. These water-insoluble (i.e. hydrophobic) propylene oxide derivatives are converted into the said non-ionics by ethoxylation until they become soluble in water. Finally, the reaction products of the above-mentioned aliphatic alcohols with propylene oxide known as "Ucon-Fluid" some of which are still water-soluble, are useful as non-ionics.

The non-ionics also include fatty acid or sulfonic acid alkylolamides which are derived, for example, from mono- or di-ethanolamine, dihydroxypropylamine or other polyhydroxyalkylamines, for example the glycamines. They can be replaced by amides from higher primary or secondary alkylamines and polyhydroxycarboxylic acids.

The surface-active amineoxides include, for example, the products derived from higher tertiary amines having a hydrophobic alkyl residue and two shorter alkyl and/or alkylol residues containing up to 4 carbon atoms each.

Suitable as non-ionic dispersing agents are possibly non-surface-active water-soluble compounds or compounds emulsifiable or dispersible in water, such as, for example, fatty acid part glycerides and also compounds which do not contain hydrophobic residues within the meaning of the above-described surface-active compounds, as for example, solid or liquid polyethylene glycols, ethylene oxide adducts of glycerine and other polyalcohols.

The preferred non-ionic surface-active detergent substances are polyglycolether derivatives of alcohols, fatty acids and alkylphenols which contain 3 to 30 glycolether groups and 8 to 20 carbon atoms in the hydrocarbon residue. Polyglycolether derivatives, in which the number of ethyleneglycolether groups is from 5 to 15 and the hydrocarbon residues of which are derived from straight-chain primary alcohols with 12 to 18 carbon atoms or from alkylphenols with a straight alkyl chain containing 6 to 14 carbon atoms, are specially suitable. Washing agents which are marked by a particularly low foaming power may be obtained by the addition of 3 to 15 mol of propylene oxide to the last-mentioned polyethyleneglycolether or by conversion into the acetals.

Other suitable non-ionic washing substances are the water-soluble polyethylene oxide adducts of polypropylene glycol, ethylenediaminopolypropyleneglycol and alkylpolypropyleneglycol, with 1 to 10 carbon atoms in the alkyl chain, containing 20 to 250 ethyleneglycolether groups and 10 to 100 propyleneglycolether groups. The said compounds usually contain 1 to 5 ethylene-glycol units per propyleneglycol unit. Non-ionic compounds of the amine oxide and sulfoxide type, which if desired may also be ethoxylated, are also useful.

Amphoteric surface-active compounds contain the molecule both acid and basic hydrophilic groups. Carboxyl, sulfonic acid, sulfuric acid half ester, phosphonic acid and phosphoric acid partial ester groups are the acid groups. Basic groups include primary, secondary, tertiary and quaternary ammonium groups, Amphoteric compounds with quaternary ammonium groups belong to the betaine type.

Carboxy, sulfate and sulfonate betaines have particular practical interest on account of their good compatibility with other surface-active compounds. Suitable sulfobetaines are obtained, for example, by reacting tertiary amines containing at least one hydrophobic alkyl residue with sultones, for example, propane- or butane-sultone. Corresponding carboxybetaines are obtained by reacting the said tertiary amines with chloroacetic acid, or its salts or with chloroacetic acid esters and splitting the ester linkage. Preferred are 3-(N,N-dimethyl-N-alkylammonium)-propane-1-sulfonate and 3-(N,N-dimethyl-N-alkylammonium)-2-hydroxypropane-1-sulfonate.

In addition, polymeric phosphates, especially pentasodium triphosphate, may also be present in the powder component containing washing compositions. The triphosphates may also be present in admixture with higher condensed phosphates such as tetraphosphates, or their hydrolysis products such as acid or neutral pyrophosphates.

The condensed phosphates may also be wholly or partly replaced by sequestering agents, for example aminopolycarboxylic acids. These include alkali metal salts of nitrilotriacetic acid and ethylenediaminotetraacetic acid. Further, the salts of diethylenetriaminopentaacetic acid and the higher homologues of the said aminopolycarboxylic acids are suitable. These homologues may be prepared, for example by polymerization of an ester, amide or nitrile of N-acetic acid aziridine followed by subsequent saponification to form carboxylic acid salts or by reaction of polyamines having a molecular weight of 500 to 10,000 with salts of chloracetic acids or bromacetic acids in an alkaline medium. Other suitable aminopolycarboxylic acids are poly-(N-succinic acid)-ethyleneimines and poly-(N-tricarballylic acid)-ethyleneimines of average molecular weight 500 to 500,000, which are obtainable in an analogous way to the N-acetic acid derivatives.

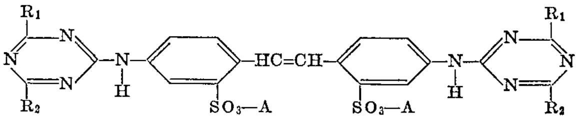
In addition, nitrogen-free compounds can be used as sequestering agents, for example the water-soluble potassium and especially sodium salts of polyvalent hydroxycarboxylic acids or ethercarboxylic acids, such as citric acid, gluconic acid, glucuronic acid and hydroxydiacetic acid, and also of higher molecular weight polycarboxylic acids, for example polymerizates of ethylenically unsaturated mono-, di and tri-carboxylic acids such as acrylic acid, maleic acid, fumaric acid, itaconic acid, citric acid, aconitic acid, mesaconic acid and methylenemalonic acid. Also utilizable are copolymerizates of these carboxylic acids with one another or with other copolymerizable substances, for example olefinic hydrocarbons such as ethylene, propylene, isobutylene and styrene, with olefinic monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid and 3-butene-carboxylic acid, or with other olefinic alcohols, ethers, esters, amides and nitriles such as vinyl alcohol, allyl alcohol, vinylmethylether, acrolein, vinyl acetate, acrylamide and acrylonitrile. Copolymerizates from olefinic mono-, di- and tricarboxylic acids and polyolefinic compounds of various structure are also suitable. The polymerizates and copolymerizates have an average degree of polymerization of 3 to 6000 and should contain 1 to 9, preferably 2 to 9 (referred to 3 monomer units) carboxyl groups capable of forming salts.

Builder salts which may be used are the so-called washing alkalis such as alkali metal silicates, especially sodium silicates, in which the proportion of Na_2O to SiO_2 is from 1:3.5 to 1:1, and also carbonates, bicarbonates and borates of alkali metals such as sodium or potassium. The amount of alkaline-reacting substances including the washing alkalis and phosphates should be such that the pH value of a utilizable liquor is from 9 to 11 and during the washing process does not fall below 8 owing to consumption of alkali by the hydrolysis of the bleaching activator.

Increased activity, for example an improved washing power or a reduced foaming power, may be obtained in many cases by suitable combination of different surface-active washing substances or builder salts with one another. Such improvements are possible, for example by a combination of anionic with non-ionic and/or amphoteric compounds with one another or by mixtures of washing substances of the same type, which in regard to their structure differ in the number of carbon atoms, the number and position of double bonds or chain branchings in the hydrocarbon residue. Also mixtures of inorganic and organic builder salts having a synergistic action may be used or may be combined with the aforementioned mixtures.

In some cases the washing compositions may contain known foam-inhibiting substances such as saturated fatty acids or their alkali metal soaps having 20 to 24 carbon atoms, higher molecular weight fatty acid esters or triglycerides, trialkylmelamines or dialkyl- or tetraalkylureas.

Particularly important representatives of optical brighteners are the diaminostilbene sulfonic acid derivatives of the general formula



I

in which A represents hydrogen, sodium, potassium, ammonium or an ammonium group derived from an organic base, for example, mono-, di- and tri-ethanolamine or morpholine, and in which R_1 and R_2 may represent halogen atoms, lower alkoxy groups, the amino group or radicals of aliphatic, aromatic or heterocyclic primary or secondary amines as well as radicals of aminosulfonic acids where the aliphatic radicals, present in the above groups, contain preferably 1 to 4, and particularly 2 to 4 carbon atoms, while the heterocyclic ring systems are primarily rings with 5 or 6 members. As aromatic amine radicals preferably aniline, anthranilic acid or aniline-sulfonic acid are of interest. Brighteners derived from the diaminostilbene sulfonic acids are mostly used as brighteners for cotton. The following products, derived from formula I, are commercially available, where R_1 and R_2 may be the same or different and represent

$—NH_2$, $—NH—CH_3$, $—NH—C_2H_5$, $—NH—CH_2—CH_2OH$,

$—NH—CH_2—CH_2—OH—CH_3$, $—NH—CH_2—CH_2—CH_2—O—CH_3$,

$CH_3—\overset{|}{N}—CH_2—CH_2OH$, $—N{=}(CH_2—CH_2OH)_2$, morpholine, dimethy morpholino, $—NH—C_6H_5$, $—NH—C_6H_4—SO_3H$, $—OCH_3$

Some of the brighteners are, in regard to their fiber affinity, to be considered as transitional types to the polyamide brighteners, such as when the brightener has R_2 equal to $—NH—C_6H_5$. To the cotton brighteners of the diaminostilbene sulfonic acid type also belongs the compound 4,4-bis-(4-phenyl-vicinal-triazolyl-2) stilbene disulfonic acid-2,2'.

Compounds in which R_1 is an anilino and R_2 is a methylamino, diethanolamino, methoxyethylamino or morpholino group are specially suitable. Mixtures of the aforementioned brighteners are also suitable, for example combinations of a compound in which R_1 represents an anilino group and R_2 a morpholino group with a second compound in which R_1 represents an anilino group and R_2 a methylamino, methoxyethylamino or methoxypropylamino group. The optical brighteners are preferably present as their sodium salts.

Other suitable optical brighteners are those of the carbostyril, N-dialkylaminocoumarin, thiophen-bis-benzoxazole and ethylene-bis-benzoxazole type. Mixtures of such brighteners with the above mentioned brighteners of the triazinylstilbenedisulfonic acid type are also suitable.

These optical brighteners are present in the products of the invention, particularly in the washing agents, according to the invention, generally in amounts of from 0.05% to 1.5%, preferably from 0.07% to 1% by weight.

Other constituents which may be present in the powder constituents mentioned above are neutral salts, especially sodium sulfate, bacteriostatic substances such as halogenated phenolethers and thioethers, halogenated carbanilides and salycylanides and halogenated diphenylmethanes, and also stabilizers for percompounds such as magnesium silicate. Known greying inhibitors, especially sodium cellulose glycollate (carboxymethylcellulose) may be added to increase the dirt-carrying power.

The powder component of the washing compositions are preferably in the form of homogeneous particles. Such particles for example, are obtainable by spray drying or granulation from aqueous concentrates or preformed powders and granulation of the other constituents thereof in known manner. The powder component, however, may also consist of granular mixtures, in which the powder particles have a variable composition. Thus, for example, a certain fraction of the powder particles may contain the detergent substances and a part of the builder salts and may have been obtained by hot spray drying, while a further part of the particles, for example prepared by granulation, contains the residue of the builder salts and those active substances which decompose, volatilize, or lose activity under the conditions of the hot spray drying, as for example, perfumes, biocides and certain foam inhibitors.

In complex mixtures the proportion by weight of the powder components to the sum of bleaching assistants and percompound according to the invention may be from 1:2 to 10:1, preferably from 1:1 to 5:1.

The bleaching assistant according to the invention as well as their mixtures with percompounds and/or washing compositions are marked by a very high stability on storage, i.e. the decrease of the bleaching activity takes place considerably more slowly than with known mixtures. The formation of undesired odors by decomposition of components sensitive to oxidation is thereby avoided. In use the mixtures show good solubility properties, i.e. when used in fully automatic washing machines during the rinsing process, they dissolve in a short time without leaving a residue.

The preparation of the powder particles is readily accomplished, as compared with the known process in which the bleaching activators are granulated or coated with coating substances, since it is not necessary in the present invention to use solvents for the powder or to recover the solvents, which are always combined into the resulting prior art losses. Another advantage of the present invention over the known processes is that the melt of fatty acid, polyglycol and bleaching activator specifically utilized for the spraying has little or no tendency to separate into the components of the mixture. After the mixing, therefore, it can be stored and transported or conveyed in pipe lines over a relatively long time, i.e. more than an hour, without any problems occurring through the settling or deposition of the constituents. If fatty acids are used exclusively as the carrier for the bleaching activator instead of the mixture consisting of fatty acid and polyglycol, a substantial separation of the melt into its substituents occurs within a few minutes resulting in the deposition of the bleaching activator. Molten mixtures of polyglycol and bleaching activator also separate within a short time. Such mixtures have the disadvantage, moreover, that the sprayed particles stick together and therefore the sprayed material is not sufficiently flowable.

In contrast to the known bleaching activators coated with fatty acids, the powder particles of the present invention are sufficiently soluble as well as quickly soluble in cold or moderately warm washing liquors; and this solubility is of special importance for their use in washing machines with programmed working cycles. The bleaching activators enclosed in the particles are protected against decomposition, especially by oxidizing agents or moisture, and do not undergo any loss of effectiveness even after prolonged periods of storage.

The present invention will be illustrated with reference to the following examples which are not to be deemed limitative in any manner thereof.

EXAMPLE 1

46 parts by weight of a fatty acid mixture consisting of 94% by weight of stearic acid and 6% by weight of palmitic acid and 17 parts by weight of a polyethyleneglycol of molecular weight 10,000 (melting point 63° C.) were melted at 80° C. and were homogenized after the addition of 37 parts by weight of tetraacetylglycoluril. The melt, which had a viscosity of 340 cp. at 80° C. and which at this temperature showed no tendency to separate into its components over a period of 30 minutes, was sprayed through a nozzle with an aperture diameter of 1 mm. at a pressure of 20 atm. into a spraying chamber. The temperature of the cooling air passing in counter current was 19° C. on entry and that of the issuing air 21° C. The easily pourable nonadhering sprayed powder had mostly a spherical structure and on a screen analysis gave the following grain size distribution:

Screen size (mm.)	Percent wt.
<2.0	2.6
1.6	4.0
0.8	22.5
0.4	52.5
0.2	17.3
<0.2	0.6

The average grain size was 0.6 mm.

EXAMPLE 2

A molten mixture of 38.5% by weight of tetraacetylglycoluril, 23.0% by weight of stearic acid and 38.5% by weight of polyethylene glycol (molecular weight 10,000) was fed at a temperature of 84° C. to a spray disc provided with rectangular outlet slots and rotating at 7000 revolutions per minute, and was atomized. The disc had a diameter of 200 mm. and the peripheral speed was 73 m./sec. The cooling air passing in the same direction had a temperature of 12° C. at the entrance of the cylindrical spray chamber and at the outlet a temperature of 25° C. An easily pourable powder consisting of globular particles with the following grain size distribution was obtained: 1.6 mm.=0.1%; 0.8 mm.=0.8%; 0.4 mm.=16.8%; 0.2 mm.=69.5%; 0.1 mm.=11.1%; under 0.1 mm.=1.0%.

EXAMPLE 3

27 parts by weight of the sprayed product (a) prepared according to Example 1 were mixed with 10 parts by weight of sodium perborate tetrahydrate (b) with a weight per liter of 1000 g. and an average grain size of 0.3 mm. and with 63 parts by weight of a washing composition mixture (c) obtained by hot spray drying, the weight per liter of which was 420 g. and the average grain size was 0.65 mm. The finished powdered mixture had the following composition (quantities in weight percent):

(a)

	Percent
Tetraacetylglycoluril	10.0
Fatty acid	12.4
Polyglycol	4.6

(b)

	Percent
Sodium perborate tetrahydrate	10.0

(c)

	Percent
n-Dodecylbenzenesulfonate (Na salt)	7.0
Oleyl alcohol with 10 ethyleneglycolether groups	2.0
Pentasodium triphosphate	33.0
Soda	6.0
Sodium silicate ($Na_2O:SiO_2=1:2$)	3.5
Magnesium silicate	2.5
Sodium ethylenediaminotetraacetate	0.2
Optical brightener	0.3
Sodium carboxymethylcellulose	1.0
Water	7.5

The mixture was filled into folding boxes, 650 g. per box and stored at 20° C. and 70% relative humidity. During the observation period of 10 weeks no decline in the available active oxygen took place.

COMPARATIVE EXAMPLES 3(A) to 3 (E)

For comparative purposes the packages were stored in a conditioning cabinet at 30° C. and 80% relative humidity. In a first comparative experiment 3(A) a washing composition of the same composition was used, in which, however, the tetraacetylglycoluril was not melted with the powder particles consisting of fatty acid and polyglycol, but was added to the mixture (c) before the spraying of the liquid concentrate (slurry).

In a second comparative experiment 3(B) a tetraacetylglycoluril covered with stearic acid was was used, for the preparation of which 75 g. of tetraacetylglycoluril was sprayed on a granulating dish with a solution of 25 g. of stearic acid in 75 ml. of carbon tetrachloride and was granulated until the solvent was removed. The particle size distribution of this granulate was 1.6 mm.=1%; 0.8 mm.=14% 0.4 mm.=8%; 0.2 mm.=29%; 0.1 mm.= 42%; under 0.1 mm.=6%.

In a further comparative experiment 3(C) 40 parts by weight of tetraacetylglycoluril were dispersed in 60 g. of molten polyethyleneglycol of molecular weight 10,000 and sprayed according to the method indicated in Example 1. The screen analysis of the powder consisting of globular particles was: 0.8 mm.=1%; 0.4 mm.=4%; 0.2 mm.=76%; 0.1 mm.=18%; under 0.1 mm.=1%.

In a comparative experiments 3(D) and 3(E) 50 parts by weight of tetraacetylglycoluril were dispersed in a melt of 50 parts by weight of a coconut fatty alcohol (chain lengths C_{12}–C_{16}) reacted with 30 mol of ethylene oxide, and sprayed. Two different screen fractions with the following size distribution were examined:

Screen size (mm.)	Experiment 3(D), percent	Experiment 3(E), percent
1.6	25	----------
0.8	27	----------
0.4	35	2
0.2	11	42
0.1	1	47
<0.1	1	9

The fraction of active perborate was determined by titration at weekly intervals and the half life time $t=\frac{1}{2}$ was determined therefrom at which half of the perborate had decomposed.

The stability factor F gives the quotients from the half life time found and the half life time for a washing composition according to experiment 3(A), in which, as described, the bleaching activator was incorporated by addition of the powder component (c) to the washing composition slurry. A factor over 1 denotes a better, and a factor of less than 1 a worse, perborate stabilization. The results are shown in the following Table.

Example	Protective substance for activator	Percent perborate after weeks— 1	2	3	4	5	$t\frac{1}{2}$	Factor F
3	(See example)	98	96	91	84	68	6.1	2.9
3(A)		82	54	23	1	------	2.1	1.0
3(B)	Stearic acid	86	59	22	3	------	2.5	1.2
3(C)	Polyglycol	88	56	17	------	------	2.2	1.1
3(D)	Ethoxylated fatty alcohol	77	27	5	------	------	1 6	0.8
3(E)	Same as 3(D)	63	7	------	------	------	1.3	0.7

The comparative experiments show the superiority of the compositions according to the invention, as exemplified by Example 3.

EXAMPLE 4

30.3% by weight of the sprayed product obtained according to Example 2 were mixed with 10% by weight of sodium perborate tetrahydrate and 57.7% by weight of the pulverulent washing composition mentioned in Example 3 (component C) and, as there described, tested for stability. At 20° C. and 70% relative humidity no decline in active oxygen occurred over a period of 10 weeks, while at 30° C. and 80% relative humidity the following values were found:

	Percent perborate after weeks— 1	2	3	4	5	6	$t\frac{1}{2}$	F
Example 4	98.0	93.5	90.0	84.0	63.0	40.0	5.7	2.6
Comparison	88.5	55.0	18.5	------	------	------	2.1	------

A mixture, which had been prepared as in Example 3 comparative experiment 3(A), served for comparison.

EXAMPLE 5

A molten mixture consisting of 40.0% by weight of tetraacetylglycoluril, 30.0% by weight of polyethylene glycol (molecular weight 4000) and 30.0% by weight of a mixture of 8 parts by weight of palmitic acid, 72 parts by weight of searic acid, 8 parts by weight of arachidic acid and 12 parts by weight of behenic acid, was sprayed by means of a nozzle, as described in Example 1. The temperature of the melt was 85° C. and that of the cooling air at the inlet was 20° C. and at the outlet 23° C. The particle size distribution of the sprayed material was: 1.6 mm.=5.5%; 0.8 mm.=20.5%; 0.4 mm.=54.3%; 0.2 mm.=18.1%; under 0.2 mm.=1.6%.

28% by weight of the sprayed product was mixed with 10% by weight of sodium perborate tetrahydrate and 62% by weight of a spray dried washing composition according to Example 3 (component c). The measurement of the stability during storage compared with a mixture prepared according to Example 3, comparative experiment

3(A), gave at 30° C. and 80% relative humidity the following values:

	Percent perborate after weeks—							
	1	2	3	4	5	6	t½	F
Example 5	96	91	88	82	63	25	5.3	3.5
Comparison	74	20					1.5	

In a further series of experiments mixtures of

(I)

	Percent by weight
Tetraacetylglycoluril	40
Stearic acid	30
Polyethyleneglycol (mol. wt. 10,000)	30

(II)

	Percent by weight
Tetraacetylglycoluril	40
Stearic acid	60

(III)

	Percent by weight
Tetraacetylglycoluril	40
Polyethyleneglycol (mol. wt. 10,000)	60

were heated at 85° C. for a relatively long time. While Mixture I was still homogeneous after 1 hour, in Mixture II the tetraacetylglycoluril had noticeably settled after 4 minutes and after 30 minutes was almost completely deposited on the bottom. In the case of Mixture III a settling of the bleaching activator was perceptible after 8 minutes.

Although the present invention has been disclosed in connection with a few preferred embodiments thereof, variations and modifications may be resorted to by those skilled in the art without departing from the principles of the new invention. All of these variations and modifications are considered to be within the true spirit and scope of the present invention as disclosed in the foregoing description and defined by the appended claims.

We claim:

1. A process for the preparation of bleaching assistants suitable for use in pulverulent washing and bleaching compositions, having particles consisting essentially of an intimate mixture containing (A) 10% to 70% by weight of at least one compound acting as an activator for active oxygen selected from the group consisting of N-acyl compounds having 2 to 9 carbon atoms in the acyl, O-acyl compounds having 2 to 9 carbon atoms in the acyl, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Peracid Formation Test, and (B) 30% to 90% by weight of a mixture consisting essentially of (1) fatty acids consisting of from 80% to 100% by weight of saturated fatty acids having 12 to 24 carbon atoms and saturated hydroxy fatty acids having 12 to 24 carbon atoms and from 0% to 20% by weight of a mixture of saturated fatty acids having from 8 to 10 carbon atoms and unsaturated fatty acids having 12 to 24 carbon atoms and (2) a polyethylene glycol with an average molecular weight of 1000 to 20,000, the weight ratio of fatty acids to polyethylene glycol ranging from 5:1 to 1:4, which comprises the steps of spraying a homogeneous mixture of said activator, said fatty acid and said polyethylene glycol at a temperature above the melting point of at least one of said ingredients into a zone space at a temperature of at least 10° C. below the solidification point of the mixture, under atomizing conditions whereby particles are formed of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm.; and collecting said particles.

2. A bleaching assistant suitable for use in pulverulent washing and bleaching compositions, produced by the process of claim **1**.

3. The bleaching assistant of claim **2**, in which the activator is tetraacetylglycoluril.

4. The bleaching assistant of claim **2**, in which the weight ratio of fatty acid to polyethylene glycol is from 3:1 to 1:2.5.

5. The bleaching assistant of claim **2**, in which at least 90% by weight of the powder particles have a diameter of 0.1 to 1.6 mm.

6. A solid, pulverulent to granular composition useful in the preparation of aqueous cold-bleaching baths, especially cold-bleaching washing liquors for textiles consisting essentially of (I) from 5% to 95% by weight based upon the total weight of the bleaching assistant of claim **2** and (II) from 5% to 95% by weight based upon the total weight of at least one compound selected from the group consisting of (a) alkali metal builder salts, (b) percompounds giving H_2O_2 in aqueous solutions and stabilizers for percompounds, (c) tensides selected from the group consisting of anionic surface-active compounds, nonionic surface-active compounds and amphoteric surface-active compounds, (d) optical brighteners, and (e) water-soluble organic builder salts.

7. The composition of claim **6**, in which at least one compound of (II) is a granular pulverulent percompound, which liberates hydrogen peroxide in aqueous solution.

8. The composition of claim **7**, in which the weight ratio of the bleaching assistant to the percompound is from 1:5 to 5:1 and is chosen so that 0.05 to 2 mol of activator is present per gram atom of active oxygen.

9. The composition of claim **8**, in which 0.1 to 1 mol of activator is present per gram atom of active oxygen.

10. The composition of claim **9** in which the percompound is selected from the group consisting of anhydrous sodium perborate and sodium perborate containing water of crystallization.

11. The process of claim **1**, in which said atomizing conditions are affected by spraying said mixture through an aperture having a diameter of 0.3 to 2.5 mm. under a pressure of 10 to 30 kg./cm.^{2}.

12. The process of claim **11**, in which the spraying pressure is from 15 to 25 kg./cm.^{2}.

13. The process of claim **11**, in which the aperture has a diameter of 0.6 to 1.8 mm.

14. The process of claim **2**, in which said zone space has a temperature of from −10° C. to +40° C.

15. The process of claim **2**, in which said atomizing conditions are affected by introducing a fine stream of said mixture into said zone space by applying an angular velocity to said stream through a peripheral speed of 5 to 150 m./sec.

16. The process of claim **15** in which the peripheral speed is from 10 to 100 m./sec.

17. A process for the preparation of bleaching assistants suitable for use in pulverulent washing and bleaching compositions, having particles consisting essentially of an intimate mixture containing (A) 10% to 70% by weight of at least one compound acting as an activator for active oxygen selected from the group consisting of N-acyl compounds having 2 to 9 carbon atoms in the acyl, O-acyl compounds having 2 to 9 carbon atoms in the acyl, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Peracid Formation Test, and (B) 30% to 90% by weight of a mixture consisting essentially of (1) fatty acids consisting of from 80% to 100% by weight of saturated fatty acids having 12 to 24 carbon atoms and saturated hydroxy fatty acids having 12 to 24 carbon atoms and from 0% to 20% by weight of a mixture of saturated fatty acids having from 8 to 10 carbon atoms and unsaturated fatty acids having 12 to 24 carbon atoms and (2) a polyethylene glycol with an average molecular weight of 1000 to 20,000, the weight ratio of fatty acids to polyethylene glycol ranging from 5:1 to 1:4, which

comprises the steps of spraying a homogeneous mixture of said activator, said fatty acid and said polyethylene glycol at a temperature above the melting point of at least one of said ingredients into a zone space at a temperature of from −10° C. to +40° C. and at least 10° C. below the solidification point of the mixture, under atomizing conditions selected from the group consisting of (I) introducing a fine stream of said mixture into said zone space by applying an angular velocity to said stream through a peripheral speed of 5 to 150 m./sec. and (II) spraying said mixture through an aperture having a diameter of 0.3 to 2.5 mm. under a pressure of 10 to 30 kg./cm.^{2}, whereby particles are formed of which at least 70% have an average diameter of 0.1 to 1 mm. and not more than 30% have a diameter of not less than 0.01 and not more than 2.5 mm.; and collecting said particles.

References Cited

UNITED STATES PATENTS

3,715,184	2/1973	Kuhling et al. ______	252—95 X
3,525,695	8/1970	Mouret et al. ________	252—95
3,441,507	4/1969	Schiefer et al. ______	252—99 X

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—95, 186

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,833,506 Dated September 3, 1974

Inventor(s) Walter Fries, Klaus Hachmann, Dieter Jung, Peter Neuhausen and Dieter Walter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column	Line	
4	39 & 40	"succinylhydroxyamine" should read --succinylhydroxylamine--
4	40	"succinylhydroxyamine" should read --succinylhyroxylamine--
4	73	"of" should read --or--
8	9	"of" should read --or--
10	48	"-OH-" should read --O--
10	50	"morpholine" should read --morpholino--
10	71	"thiophen-" should read --thiophene--
11	9	"salycylanides" should read --salycylanilides--
11	35	"assistant" should read --assistants
11	59	"problems" should read --problem--
13	59	delete the word "a"
16	44 & 46	should depend from claim 1, not claim 2

Signed and sealed this 17th day of June 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U S GOVERNMENT PRINTING OFFICE : 869-930

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,833,506 Dated September 3, 1974

Inventor(s) Walter Fries, Klaus Hachmann, Dieter Jung, Peter Neuhausen and Dieter Walter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column	Line	
4	39 & 40	"succinylhydroxyamine" should read --succinylhydroxylamine--
4	40	"succinylhydroxyamine" should read --succinylhyroxylamine--
4	73	"of" should read --or--
8	9	"of" should read --or--
10	48	"-OH-" should read --O--
10	50	"morpholine" should read --morpholino--
10	71	"thiophen-" should read --thiophene--
11	9	"salycylanides" should read --salycylanilides--
11	35	"assistant" should read --assistants
11	59	"problems" should read --problem--
13	59	delete the word "a"
16	44 & 46	should depend from claim 1, not claim 2

Signed and sealed this 17th day of June 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE: 869-930