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(54) MIXED METAL COLLOIDS AS BLEACH BOOSTING AGENTS

(57) The aim of the invention is to improve bleaching agents so that they may use atmospheric oxygen as a source of bleaching active species. This is substantially achieved by employing a combination of an aqueous mixed colloid of Au and Pt metal with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions.

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Description

[0001] This invention relates to compositions and methods for catalytically bleaching substrates, such as fabrics and hard surfaces, with atmospheric oxygen using certain transition metal colloids in combination with conventional bleach activators. The present invention especially relates to the removal of colored stains from fabrics or hard surfaces by mixed gold/platinum colloids in combination with said conventional bleach activators.

[0002] Peroxygen bleaches are well known for their ability to remove stains from substrates. Traditionally, the substrate is subjected to hydrogen peroxide, or to substances which can generate hydrogen peroxide in aqueous systems, such as inorganic or organic peroxides. Generally, these systems need to be activated. One method of activation is to employ wash temperatures of 60 °C or higher. However, these temperatures are not preferred due to high energy consumption. A preferred approach to generating hydroperoxy bleach-active species is the use of inorganic peroxides in combination with organic precursor compounds. These systems are employed for many commercial laundry detergents, especially in solid detergents such as powders. For example, various bleach systems are based on tetraacetyl ethylenediamine (TAED) as the organic precursor, which is employed in combination with sodium perborate or sodium percarbonate, whereas other bleach products are based on sodium nonanoyloxybenzenesulphonate (SNOBS) or analogous compounds as the organic precursor, also combined with sodium perborate or sodium percarbonate.

[0003] Such precursor systems are generally effective but still exhibit some disadvantages. For example, the combination of bleach and bleach precursor has considerable formulation space requirements so that a significant proportion of a detergent is devoted to the bleach components, leaving less room for other active ingredients. Moreover, precursor systems sometimes do not bleach very efficiently when low dosage, short wash times, cold temperatures and low wash liquor to substrate ratios are entailed.

[0004] Alternatively to the use of peroxoacid-precursors, or additionally to it, hydrogen peroxide and peroxy systems can be activated by bleach catalysts, such as for example by complexes of iron and the ligand N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, disclosed in the international patent application WO 95/34628 A1. This still does not do away with the amounts of peroxgen componds necessary in the detergent.

[0005] The international patent application WO 00/12677 A1 discloses the use of atmospheric oxygen, that is air, as the source for a bleaching species generated from a transition metal complex such as the iron complex mentioned before. While the latter method does not rely on the presence of rather large amounts of hydrogen peroxide or its precoursors in the detergent, is still suffers from the disadvantage that the activating agents require specifically adapted ligands which are synthesized in a couple of steps in rather costly procedures.

[0006] Accordingly, it would be desirable to be able to provide a bleaching system based on atmospheric oxygen or air that does not require the presence of rather sophisticated organic components.

[0007] We have surprisingly found that it is possible to use atmospheric oxygen or air for bleaching substrates without the disadvantages referred to above, when aqueous mixed colloids of gold and platinum are employed in combination with conventional bleach activators.

[0008] Accordingly, in a first aspect, the present invention provides a bleaching composition comprising, in an aqueous medium, atmospheric oxygen and a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based bleach system.

[0009] In a second aspect, the present invention provides a method of bleaching a substrate comprising applying to the substrate, in an aqueous medium in the presence of atmospheric oxygen or air, a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions.

[0010] Furthermore, in a third aspect, the present invention provides the use of a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions as a bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or of a peroxy-based bleach system.

[0011] Aqueous Pt colloids may be prepared by methods known in the art, for example by reducing Pt salts in aqueous solution with reducing agents, such as alkali borohydrides, alcohols, ascorbic acid or alcali citrates. Such aqueous colloids may be stabilized by known polymeric stabilising agents, such as polyvinylpyrrolidone, polyvinylalcohol, sodium polyacrylate, polyallylamine hydrochloride, polyallylamine, their thiol and phosphine capped derivatives and their mixtures. Such stabilising agents preferably are present in the aqueous metal colloids in weight ratios of stabilising agent to metal of from 1:10 to 3:1, in particular of from 3:10 to 8:10.

[0012] In preferred embodyments of all aspects of the invention, the Au/Pt-colloids may be immobilized on solid support materials, such as for example TiO_2, SiO_2, MgO, NiO, CeO_2, ZrO_2, and their mixtures, by methods known to the person skilled in the art. If present, the weight ratio of the amount of such support material, relative to the combined amounts of Au and Pt, preferably is in the range of from 200:1 to 50:1, in particular 100:1.

[0013] As part of the combinations employed according to the invention, compounds that under perhydrolysis conditions afford optionally substituted perbenzoic acid and/or peroxycarboxylic acids containing 1 to 10 carbon atoms, in particular

2 to 4 carbon atoms, are preferred. Customary bleach activators, which carry O- and/or N-acyl groups are suitable, for example polyacylated alkylenediamines, in particular tetraacetylethylenediamine (TAED), acylated glycolurils, in particular tetraacetyl glycoluril, acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated phenylsulfonates and - carboxylates, in particular nonanoyloxy- or isononanoyloxybenzenesulfonate or -benzoate, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran as well as acetylated sorbitol and mannitol, and acylated sugar derivatives, in particular pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. A compound that forms peroxycarboxylic acid under perhydrolysis conditions is preferably employed in concentrations of from 0.1 mg/l to 100 mg/l, in particular from 1 mg/l to 20 mg/l, in the aqueous medium for the use to bleach substrates. Detergents according to the invention preferably comprise compounds that form peroxycarboxylic acids under perhydrolysis conditions in amounts of up to 8 wt %, particularly in the range of from 2 wt % to 6 wt %, each relative to the total detergent. Preferably the weight ratio of the combined amount of Au and Pt metal to the compound that under perhydrolysis conditions form peroxyacids is in the range of from 1:100 to 1:10, in particular from 1:35 to 1:50.

[0014] Advantageously, the present invention permits all or the majority of the bleaching species in the medium (on an equivalent weight basis) to be derived from atmospheric oxygen. Thus, the medium can be made wholly or substantially devoid of peroxygen bleach or of a peroxy-based bleach system. Moreover, the bleaching system according to the invention is operable under unfavourable wash conditions which include low temperatures, short contact times, and low dosage requirements. When the bleaching composition according to the invention is used, the aqueous medium comprising it advantageously is insensitive or stable to catalase, which acts on peroxy species. Furthermore, as the method according to the invention is effective in an aqueous medium, the invention is therefore particularly applicable to bleaching of hard surfaces occuring in the household and to launder fabrics. Therefore, whilst the composition and method according to the present invention may be used for bleaching any suitable substrate, the preferred substrate is a household hard surface or a fabric. Preferably the bleaching is to achieve the removal of colored stains from fabrics or hard surfaces.

[0015] As the invention does rely on the presence of gaseous oxygen, air may be employed, or a mixture of gases that comprise a higher concentration of oxygen than normal air. The latter will reduce the reaction time required to obtain a desired bleaching result, as will an increase in pressure of the gas employed. The method and use according to the invention are preferably performed at gas pressures, especially at air pressures, in the range of from 1 bar to 10 bar, in particular from 5 bar to 10 bar.

[0016] The bleaching method may be carried out by simply leaving the substrate in contact with the medium for a sufficient period of time. Preferably, however, the aqueous medium on or containing the substrate is agitated. This may be achieved by known household appliances, such as washing machines or automatic dishwashing machines, or by manually agitating the substrate or the aqueous medium, such as in manual washing or manual dishwashing, or in wiping soiled hard surfaces, such as tiles, floor tiles, dishes, windows, or mirrors. Preferably, the aqueous medium used to bleach substrates has a pH in the range of from pH 5 to pH 10, more preferably from pH 7 to pH 10.

[0017] The inventive method or use is preferably carried out at temperatures in the range of from 10 °C to 60 °C, in particular 40 °C to 60 °C. The water hardness of the water used for preparing the aqueous washing or cleaning liquor is preferably in the range of from 0° dH to 16° dH, in particular from 0° dH to 3° dH.

[0018] The bleaching compositions according to the present invention may be used for laundry cleaning (including carpets or cushion materials that normally are cleaned in place), hard surfaces cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing, etc.). As is generally known in the art, bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, and for dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations, and/or contact lens disinfection. In the context of the present invention bleaching should be understood as relating generally to the decolourisation of stains or of other materials attached to or associated with a substrate. However, it is envisaged that the present invention can be applied where a requirement is the removal and/or neutralisation by an oxidative bleaching reaction of malodours or other undesirable components attached to or otherwise associated with a substrate.

[0019] The bleaching composition of the present invention has particular application in detergent formulations, especially for laundry cleaning. Accordingly, in another preferred embodiment, the present invention provides a bleaching detergent composition, particularly a liquid bleaching detergent composition, and especially a bleaching laundry detergent composition, being substantially devoid of peroxygen bleach or of a peroxy-based bleach system, comprising an aqueous mixed colloid of gold and platinum and additionally a surface-active material, optionally together with any other ingredient conventionally employed in detergents, that does not unfavourably interact with the metal colloid.

[0020] Detergents according to the invention preferably comprise the mixed metal colloid defined above in amounts of from 0.005 %to 0.5 wt %, particularly from 0.03 wt % to 0.2 wt %, each expressed as the combined amount of Au and Pt metal relative to the total detergent. In typical compositions the combined amount of colloidal gold metal and colloidal platinum metal is such that the in-use content in the aqueous medium is from 1 mg/l to 1 g/l, with preferred in-use levels for domestic laundry and dishwashing operations falling in the range of from 10 mg/l to 200 mg/l of the combined metals. In aquoeus liquid compositions the aqueous mixed colloid preferably is contained as such, whereas in solid compositions the mixed colloid preferably is present in immobilized form, as described above.

[0021] The detergent according to the present invention may for example contain a surface-active material in an amount of from 10 wt % to 50 wt %. The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic and cationic surfactants and mixtures thereof.

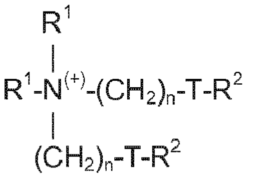
[0022] Detergents, which can be present in particular as powdery solids, in the form of post-compacted particles, as homogeneous solutions or suspensions, can comprise in principle all known and customary ingredients for such detergents. In particular, they can comprise builders, surface active surfactants, water-miscible organic solvents, enzymes, sequestrants, electrolytes, pH adjusters, polymers with special effects, such as soil release polymers, color transfer inhibitors, graying inhibitors, crease-reducing polymeric active substances and shape-retaining polymeric active substances, and further auxiliaries, such as optical brighteners, foam regulators, dyes and fragrances.

[0023] The inventive compositions can comprise one or more surfactants, wherein particularly anionic surfactants, non-ionic surfactants and their mixtures come into consideration, but also cationic and/or amphoteric surfactants can be comprised. Suitable non-ionic surfactants are particularly alkyl glycosides and ethoxylation and/or propoxylation products of alkyl glycosides or of linear or of branched alcohols, each with 12 to 18 carbon atoms in the alkyl moiety and 3 to 20, preferably 4 to 10 alkyl ether groups. Moreover, corresponding ethoxylation and/or propoxylation products of N-alkylamines, vicinal diols, fatty acid esters and fatty acid amides, which in regard to the alkyl moiety correspond to the cited long chain alcohol derivatives, as well as alkyl phenols with 5 to 12 carbon atoms in the alkyl group can be used.

[0024] Suitable anionic surfactants are particularly soaps and such that comprise sulfate or sulfonate groups, preferably with alkali metal ions as the cations. Useable soaps are preferably the alkali metal salts of the saturated or unsaturated fatty acids containing 12 to 18 carbon atoms. These types of fatty acids can also be used in a not completely neutralized form. The useable surfactants of the sulfate type include the salts of sulfuric acid half esters of fatty alcohols with 12 to 18 carbon atoms and the sulfation products of the mentioned non-ionic surfactants with a low degree of ethoxylation. The useable surfactants of the sulfonate type include linear alkylbenzene sulfonates with 9 to 14 carbon atoms in the alkyl moiety, alkyl sulfonates with 12 to 18 carbon atoms, as well as olefin sulfonates with 12 to 18 carbon atoms, which result from the reaction of the corresponding monoolefins with sulfur trioxide, as well as alpha-sulfofatty acid esters that result from the sulfonation of fatty acid methyl or ethyl esters.

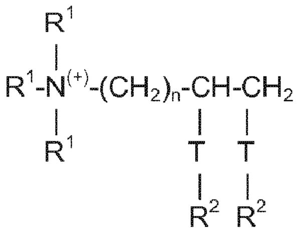
[0025] These types of surfactants are preferably comprised in washing agents in amounts of 5 wt % to 50 wt %, particularly 8 wt % to 30 wt %, whereas disinfectants as well as cleaning agents for hard surfaces comprise preferably 0.1 wt % to 20 wt %, particularly 0.2 to 5 wt % surfactants.

[0026] The detergents, in particular when they concern those intended for the treatment of fabrics, can comprise in particular one or more of the cationic, fabric softeners of the general Formulas X, XI or XII as the cationic active substances with fabric softening action:



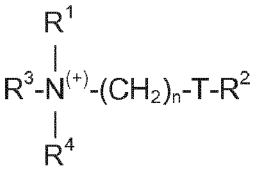
$$R^1\text{-}\underset{(CH_2)_n\text{-}T\text{-}R^2}{\overset{R^1}{N^{(+)}}}\text{-}(CH_2)_n\text{-}T\text{-}R^2$$

(X)



$$R^1\text{-}\underset{R^1}{\overset{R^1}{N^{(+)}}}\text{-}(CH_2)_n\text{-}\underset{\underset{R^2}{T}}{CH}\text{-}\underset{\underset{R^2}{T}}{CH_2}$$

(XI)



$$R^3\text{-}\underset{R^4}{\overset{R^1}{N^{(+)}}}\text{-}(CH_2)_n\text{-}T\text{-}R^2$$

(XII)

in which each group R^1, independently of one another, is selected from C_{1-6} alkyl, -alkenyl or - hydroxyalkyl groups; each group R^2, independently of one another, is selected from C_{8-28} alkyl or -alkenyl groups; $R^3 = R^1$ or $(CH_2)_n\text{-}T\text{-}R^2$;

R^4 = R^1 or R^2 or $(CH_2)_n$-T-R^2; T = -CH_2-, -O-CO- or-CO-O- and n is an integer from 0 to 5. The cationic surfactants possess the usual number and type of anions required to compensate the charge, wherein these can be selected, besides for example halides, also from the anionic surfactants. In preferred embodiments, hydroxyalkyl-trialkylammonium compounds, particularly C_{12-18} alkyl(hydroxyethyl)dimethylammonium compounds, and preferably their halides, in particular chlorides, are used as the cationic surfactants. The detergent preferably comprises 0.5 wt % to 25 wt %, particularly 1 wt % to 15 wt % of cationic surfactant.

[0027] A detergent preferably comprises at least one water-soluble and/or water-insoluble organic and/or inorganic builder. The water-soluble organic builders include polycarboxylic acids, particularly citric acid and sugar acids, monomeric and polymeric amino polycarboxylic acids, particularly methylglycine diacetic acid, nitrilotriacetic acid and ethylenediaminetetraacetic acid as well as polyaspartic acid, polyphosphonic acids, particularly amino tris(methylenephosphonic acid), ethylenediaminetetrakis(methylenephosphonic acid) and 1-hydroxyethane-1,1-diphosphonic acid, polymeric hydroxy compounds such as dextrin as well as polymeric (poly)carboxylic acids, particularly those polycarboxylates obtained from the oxidation of polysaccharides or dextrins, and/or polymeric acrylic acids, methacrylic acids, maleic acids and mixed polymers thereof, which can also comprise small amounts of copolymerized polymerizable substances exempt from carboxylic acid functionality. The relative molecular weight of the homopolymers of unsaturated carboxylic acids lies generally between 5000 and 200 000, that of the copolymers between 2000 and 200 000, preferably 50 000 to 120 000, each relative to free acid. A particularly preferred acrylic acid-maleic acid copolymer has a relative molecular weight of 50 000 to 100 000. Suitable, yet less preferred compounds of this class, are copolymers of acrylic acid or methacrylic acid with vinyl ethers, such as vinyl methyl ether, vinyl esters, ethylene, propylene and styrene, in which the content of the acid is at least 50 wt %. Terpolymers, which comprise two unsaturated acids and/or their salts as monomers as well as vinyl alcohol and/or an esterified vinyl alcohol or a carbohydrate as the third monomer, can also be used as the water-soluble organic builders. The first acidic monomer or its salt is derived from a monoethylenically unsaturated C_3-C_8 carboxylic acid and preferably from a C_3-C_4 monocarboxylic acid, particularly from (meth)acrylic acid. The second acidic monomer or its salt can be a derivative of a C_4-C_8 dicarboxylic acid, maleic acid being particularly preferred, and/or a derivative of an allyl sulfonic acid, which is substituted in the 2-position with an alkyl or aryl residue. These types of polymer generally have a relative molecular weight between 1000 and 200 000. Other preferred copolymers are those, which preferably contain acrolein and acrylic acid/acrylic acid salts or vinyl acetate as monomers. The organic builders, especially for the manufacture of liquid detergents, can be employed in the form of aqueous solutions, preferably in the form of 30 to 40 weight per cent aqueous solutions. In general, all the cited acids are added in the form of their water-soluble salts, particularly their alkali metal salts.

[0028] These types of organic builders can be comprised as desired in amounts of up to 40 wt %, particularly up to 25 wt % and preferably from 1 wt % to 8 wt %. Amounts close to the cited upper limit are preferably incorporated in pasty or liquid, particularly aqueous detergents.

[0029] The water-soluble inorganic builders particularly concern polymeric alkali metal phosphates that can be present in the form of their alkaline, neutral or acidic sodium or potassium salts. Examples of these are tetrasodium diphosphate, disodium dihydrogen diphosphate, pentasodium triphosphate, so-called sodium hexametaphosphate as well as the corresponding potassium salts or mixtures of sodium and potassium salts. In particular, crystalline or amorphous alkali metal alumosilicates in amounts of up to 50 wt %, preferably not more than 40 wt % and in liquid dertergents not more than 1 wt % to 5 wt % are added as the water-insoluble, water-dispersible inorganic builders. Among these, the detergent-quality crystalline sodium alumosilicates, particularly zeolites A, P and optionally X, are preferred. Amounts close to the cited upper limit are preferably incorporated in solid, particulate detergents. Suitable alumosilicates particularly exhibit no particles with a particle size above 30 μm and preferably consist to at least 80 wt % of particles smaller than 10 μm. Their calcium binding capacity, which can be determined according to the indications of German patent DE 24 12 837, generally lies in the range of 100 to 200 mg CaO per gram.

[0030] Suitable substitutes or partial substitutes for the cited alumosilicate are crystalline alkali metal silicates that can be present alone or in a mixture with amorphous silicates. The alkali metal silicates that can be used as builders preferably have a molar ratio of alkali metal oxide to SiO_2 below 0.95, particularly 1:1.1 to 1:12 and can be amorphous or crystalline. Preferred alkali metal silicates are the sodium silicates, particularly the amorphous sodium silicates, with a molar ratio Na_2O:SiO_2 of 1:2 to 1:2.8. Crystalline silicates that can be present alone or in a mixture with amorphous silicates are preferably crystalline, layered silicates corresponding to the general Formula $Na_2Si_xO_{2x+1}$ y H_2O, wherein x, the so-called module, is a number from 1.9 to 4 and y is a number from 0 to 20, preferred values for x being 2, 3 or 4. Preferred crystalline layered silicates are those in which x assumes the values 2 or 3 in the cited general formula. In particular, both β- as well as δ-sodium disilicates ($Na_2Si_2O_5$ y H_2O) are preferred. Practically anhydrous crystalline alkali metal silicates of the abovementioned general Formula, in which x is a number from 1.9 to 2.1 can be employed and can also be manufactured from amorphous alkali metal silicates. In a further preferred embodiment, a crystalline sodium layered silicate with a module of 2 to 3 is employed, as can be manufactured from sand and soda. In a further preferred embodiment, crystalline sodium silicates with a module in the range 1.9 to 3.5 are employed. In a preferred development, a granular compound of alkali metal silicate and alkali metal carbonate is added, as is commercially available, for example under the name Nabion® 15. In the case that alkali metal alumosilicate, in particular zeolite, is also present as the additional builder, then the weight ratio alumosilicate to silicate, each relative to anhydrous active substances, is preferably 1:10 to 10:1. In detergents that comprise both amorphous and crystalline alkali metal silicates, the weight ratio of amorphous alkali metal silicate to crystalline alkali metal silicate is preferably 1:2 to 2:1 and particularly 1:1 to 2:1.

[0031] Builders are preferably comprised in amounts of up to 60 wt %, particularly from 5 wt % to 40 wt %.

[0032] In a preferred development, the detergent possesses a water-soluble builder block. The use of the term "builder block" is intended to emphasize that the detergents do not comprise other builders than water-soluble builders, i.e. all of the builders comprised in the detergent are summarized in the stated "block", wherein at the most, allowance is made for the amounts of materials that can be comprised in the customary ingredients of commercial materials as impurities or minor amounts of added stabilizers. The term "water-soluble" is intended to mean that the builder block, in the amount comprised in the detergent, under normal conditions, dissolves without residue. The detergents preferably comprise at least 15 wt % and up to 55 wt %, particularly 25 wt % to 50 wt %, of the water-soluble builder block. This is preferably composed of the components

> 5 wt % to 35 wt % of citric acid, alkali metal citrate and/or alkali metal carbonate that can also be replaced at least in part by alkali metal hydrogen carbonate,
> up to 10 wt % alkali metal silicate with a module in the range of 1.8 to 2.5,
> up to 2 wt % phosphonic acid and/or alkali metal phosphonate,
> up to 50 wt % alkali metal phosphate, and
> up to 10 wt % polymeric polycarboxylate,

wherein the indicated quantities are based on the total detergent. This is also true for all of the following indicated quantities, when not otherwise stated.

[0033] In a preferred embodiment, the water-soluble builder block comprises at least 2 of the components b), c), d) and e) in amounts of greater than 0 wt %.

[0034] With regard to the component a), in a preferred embodiment, there are comprised 15 wt % to 25 wt % alkali metal carbonate that can be replaced at least in part by alkali metal hydrogen carbonate, and up to 5 wt %, particularly 0.5 wt % to 2.5 wt % citric acid and/or alkali metal citrate. In an alternative embodiment, the component a) comprises 5 wt % to 25 wt %, particularly 5 wt % to 15 wt % citric acid and/or alkali metal citrate and up to 5 wt %, particularly 1 wt % to 5 wt % alkali metal carbonate that can be replaced at least in part by alkali metal hydrogen carbonate. If both alkali metal carbonate and also alkali metal hydrogen carbonate are present, then the component a) preferably includes alkali metal carbonate and alkali metal hydrogen carbonate in the weight ratio of 10:1 to 1:1.

[0035] With regard to the component b), in a preferred embodiment there are comprised 1 wt % to 5 wt % alkali metal silicate with a modulus in the range 1.8 to 2.5.

[0036] With regard to the component c), in a preferred embodiment there are comprised 0.05 wt % to 1 wt % phosphonic acid and/or alkali metal phosphonate. Phosphonic acids are also understood to include optionally substituted alkyl phosphonic acids that may also possess a plurality of phosphonic acid groups (so-called polyphosphonic acids). They are preferably selected from the hydroxy and/or aminoalkyl phosphonic acids and/or their alkali metal salts, such as, for example, dimethylaminomethane diphosphonic acid, 3-aminopropane-1-hydroxy-1,1-diphosphonic acid, 1-amino-1-phenyl-methane diphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, amino-tris(methylene phosphonic acid), N,N,N',N'-ethylenediamine-tetrakis(methylene phosphonic acid) and acylated derivatives of the phosphorous acids, which can also be employed in any mixtures.

[0037] With regard to the component d), in a preferred embodiment there are comprised 15 wt % to 35 wt % alkali metal phosphate, in particular trisodium polyphosphate. "Alkali metal phosphate" is here the collective term for the alkali metal (more particularly sodium and potassium) salts of the various phosphoric acids, in which metaphosphoric acids $(HPO_3)_n$ and orthophosphoric acid (H_3PO_4) can be differentiated among representatives of higher molecular weight. The phosphates combine a plurality of inherent advantages: They act as alkalinity sources, prevent lime deposits on machine parts and lime incrustations in fabrics and, in addition, contribute towards the cleaning power. Sodium dihydrogen phosphate NaH_2PO_4 exists as the dihydrate (density 1.91 gcm^{-3}, melting point 60 °C) and as the monohydrate (density 2.04 gcm^{-3}). Both salts are white, readily water-soluble powders that on heating, lose the water of crystallization and at 200 °C are converted into the weakly acidic diphosphate (disodium hydrogen diphosphate, $Na_2H_2P_2O_7$) and, at higher temperatures into sodium trimetaphosphate ($Na_3P_3O_9$) and Maddrell's salt. NaH_2PO_4 shows an acidic reaction. It is formed by adjusting phosphoric acid with sodium hydroxide to a pH value of 4.5 and spraying the resulting "mash". Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium diphosphate, KDP), KH_2PO_4, is a white salt with a density of 2.33 gcm^{-3}, has a melting point of 253 °C (decomposition with formation of potassium polyphosphate $(KPO_3)_x$) and is readily soluble in water. Disodium hydrogen phosphate (secondary sodium phosphate), Na_2HPO_4, is a colorless, very readily water-soluble crystalline salt. It exists in anhydrous form and with 2 mol (density 2.066 gcm^{-3}, water loss at 95 °C), 7 mol (density 1.68 gcm^{-3}, melting point 48 °C with loss of 5 H_2O) and 12 mol of water (density 1.52 gcm^{-3}, melting point 35 ° with loss of 5 H_2O), becomes anhydrous at 100 °C and, on fairly intensive heating, is converted into the diphosphate $Na_4P_2O_7$. Disodium hydrogen phosphate is prepared by neutralization of phosphoric acid with soda solution using phenolphthalein as the indicator. Dipotassium hydrogen phosphate (secondary or dibasic potassium phosphate), K_2HPO_4, is an amorphous white salt, which is readily soluble in water. Trisodium phosphate, tertiary sodium phosphate, Na_3PO_4, are colorless crystals with a density of 1.62 gcm^{-3} and a melting point of 73-76 °C (decomposition) as the dodecahydrate, as the decahydrate (corresponding to 19-20% P_2O_5) a melting point of 100 °C, and in anhydrous form (corresponding to 39-40% P_2O_5) a density of 2.536 gcm^{-3}. Trisodium phosphate is readily soluble in water with an alkaline reaction and is manufactured by evaporating a solution of exactly 1 mole disodium phosphate and 1 mole NaOH. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K_3PO_4, is a white deliquescent granular powder with a density of 2.56 gcm^{-3}, has a melting point of 1340 °C and is readily soluble in water through an alkaline reaction. It is produced by e.g. heating Thomas slag with carbon and potassium sulfate. Despite their higher price, the more readily soluble and therefore highly effective potassium phosphates are often preferred to corresponding sodium compounds in the detergent industry. Tetrasodium diphosphate (sodium pyrophosphate), $Na_4P_2O_7$, exists in anhydrous form (density 2.534 gcm^{-3}, melting point 988 °C, a figure of 880 °C has also been mentioned) and as the decahydrate (density 1.815-1.836 gcm^{-3}, melting point 94 °C with loss of water). Both substances are colorless crystals that dissolve in water with an alkaline reaction. $Na_4P_2O_7$ is formed when disodium phosphate is heated to more than 200 °C or by reacting phosphoric acid with soda in a stoichiometric ratio and dehydrated by spray drying the solution. The decahydrate complexes heavy metal salts and hardness salts and, hence, reduces the hardness of water. Potassium diphosphate (potassium pyrophosphate), $K_4P_2O_7$, exists in the form of the trihydrate and is a colorless hygroscopic powder with a density of 2.33 gcm^{-3}, which is soluble in water, the pH of a 1% solution at 25 °C being 10.4. Relatively high molecular weight sodium and potassium phosphates are formed by condensation of NaH_2PO_4 or KH_2PO_4. They may be divided into cyclic types, namely the sodium and potassium metaphosphates, and chain types, the sodium and potassium polyphosphates. In particular, the latter are known by various different names: fused or calcined phosphates, Graham's salt, Kurrol's salt and Maddrell's salt. All higher sodium and potassium phosphates are known collectively as condensed phosphates. The industrially important pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate), is anhydrous or crystallizes with 6 H_2O to a non-hygroscopic white water-soluble salt, which has the general formula $NaO\text{-}[P(O)(ONa)\text{-}O]_n\text{-}Na$ where n=3. Around 17 g of the salt free from water of crystallization dissolve in 100 g of water at room temperature, around 20 g at 60 °C and around 32 g at 100 °C. After heating the solution for 2 hours at 100 °C, around 8% orthophosphate and 15% diphosphate are formed by hydrolysis. In the preparation of pentasodium triphosphate, phosphoric acid is reacted with soda solution or sodium hydroxide in a stoichiometric ratio and the solution is dehydrated by spray-drying. Similarly to Graham's salt and sodium diphosphate, pentasodium triphosphate solubilizes many insoluble metal compounds (including lime soaps, etc.). $K_5P_3O_{10}$ (potassium tripolyphosphate), is marketed for example in the form of a 50 wt % conc. solution (>23% P_2O_5, 25% K_2O). The potassium polyphosphates are widely used in the washing and cleaning industry. Sodium potassium tripolyphosphates also exist and are also usable in the scope of the present invention. They are formed for example when sodium trimetaphosphate is hydrolyzed with KOH:

$$(NaPO_3)_3 + 2\ KOH \rightarrow Na_3K_2P_3O_{10} + H_2O$$

[0038] They may be used in exactly the same way as sodium tripolyphosphate, potassium tripolyphosphate or mixtures thereof. Mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphosphate may be used.

[0039] With regard to the component e), in a preferred embodiment of the detergent, there are comprised 1.5 wt % to 5 wt % of polymeric polycarboxylate, particularly selected from the polymerization or copolymerization products of acrylic acid, methacrylic acid and/or maleic acid. Among these are the homopolymers of acrylic acid and more specifically those with an average molecular weight in the range of 5000 Da to 15 000 Da (PA standard) are particularly preferred.

[0040] Enzymes that can be used in the detergents are those from the class of proteases, lipases, cutinases, amylases, pullulanases, mannanases, cellulases, hemicellulases, xylanases, oxidases and peroxidases as well as their mixtures, for example proteases like BLAP®, Optimase®, Opticlean®, Maxacal®, Maxapem®, Alcalase®, Esperase®, Savinase®, Durazym® and/or Purafect® OxP, amylases like Termamyl®, Amylase-LT®, Maxamyl®, Duramyl® and/or Purafect® OxAm, lipases like Lipolase®, Lipomax®, Lumafast® and/or Lipozym®, cellulases like Celluzyme® and/or Carezyme®. Enzymatic active materials obtained from bacterial sources or fungi such as Bacillus subtilis, Bacillus licheniformis, Streptomyceus griseus, Humicola lanuginosa, Humicola insolens, Pseudomonas Pseudoalcaligenes or Pseudomonas cepacia are particularly suitable. The enzymes can be adsorbed on carriers and/or embedded in encapsulants in order to protect them against premature inactivation. They are comprised in detergents or disinfectants preferably in amounts of up to 10 wt %, particularly 0.2 wt % to 2 wt %, wherein enzymes that are stabilized against oxidative decomposition are particularly preferably employed.

[0041] In a preferred embodiment, the detergent comprises 5 wt % to 50 wt %, particularly 8 to 30 wt % anionic and/or non-ionic surfactant, up to 60 wt %, particularly 5 wt % to 40 wt % builder and 0.2 wt % to 2 wt % enzyme, selected from the proteases, lipases, cutinases, amylases, pullulanases, mannanases, cellulases, oxidases and peroxidases as well as their mixtures. Organic solvents that can be employed in the detergents, particularly when the detergents are in liquid or paste form, include alcohols with 1 to 4 carbon atoms, particularly methanol, ethanol, isopropanol and tert-butanol, diols with 2 to 4 carbon atoms, particularly ethylene glycol and propylene glycol, as well as their mixtures and the ethers derived from the cited classes of compounds. These types of water-miscible solvents are preferably present in the detergents in amounts of not more than 30 wt %, particularly 6 wt % to 20 wt %.

[0042] To adjust a pH to a desired level that does not itself result from mixing the usual components, the detergents can comprise acids that are compatible with the system and the environment, particularly citric acid, acetic acid, tartaric acid, malic acid, lactic acid, glycolic acid, succinic acid, glutaric acid and/or adipic acid, but also mineral acids, particularly sulfuric acid, or bases, particularly ammonium hydroxide or alkali metal hydroxides. These types of pH adjustors are preferably comprised in the detergents in amounts of not more than 20 wt %, particularly 1.2 wt % to 17 wt %.

[0043] "Soil release" polymers, often called soil release substances, which provide the treated surface, for example fibers, with soil repellency are known as "soil repellents" and are non-ionic or cationic cellulose derivatives, for example. The particularly active polyester soil release polymers include copolyesters of dicarboxylic acids, for example adipic acid, phthalic acid or terephthalic acid, diols, for example ethylene glycol or propylene glycol, and polydiols, for example polyethylene glycol or polypropylene glycol. The preferred soil release polyesters employed include such compounds that are formally obtained by the esterification of two monomeric moieties, wherein the first monomer is a dicarboxylic acid HOOC-Ph-COOH and the second monomer is a diol $HO-(CHR^{11}-)_a)_bOH$ that can also be present as the polymeric diol $H-(O-(CHR^{11}-)_a)_bOH$. Here, Ph means an o-, m- or p-phenylene group that can carry 1 to 4 substituents, selected from alkyl residues with 1 to 22 carbon atoms, sulfonic acid groups, carboxyl groups and their mixtures, R^{11} is hydrogen, an alkyl residue with 1 to 22 carbon atoms and their mixtures, a is a number from 2 to 6 and b is a number from 1 to 300. Preferably, both monomer diol units $-O-(CHR^{11}-)_aO-$ and also polymeric diol units $-(O-(CHR^{11}-)_a)_bO-$ are present in the resulting polyesters. The molar ratio of monomeric diol units to polymeric diol units is preferably in the range 100:1 to 1:100, particularly 10:1 to 1:10. The degree of polymerization b in the polymeric diol units is preferably in the range 4 to 200, particularly 12 to 140. The molecular weight or the average molecular weight or the maximum of the molecular weight distribution of preferred soil-releasing polyesters is in the range 250 to 100 000, particularly 500 to 50 000. The acid, based on the Ph group, is preferably selected from terephthalic acid, isophthalic acid, phthalic acid, trimellitic acid, mellitic acid, the isomers of sulfo phthalic acid, sulfo isophthalic acid and sulfo terephthalic acid and their mixtures. As long as their acid groups are not part of the ester linkages in the polymer, then they are preferably present in salt form, particularly as the alkali metal or ammonium salt. Among these, sodium and potassium salts are particularly preferred. If desired, instead of the monomer HOOC-Ph-COOH, small amounts, particularly not more than 10 mol % of other acids that possess at least two carboxyl groups, based on the fraction of Ph with the abovementioned meaning, can be comprised in the soil release polyester. Exemplary alkylene and alkenylene dicarboxylic acids include malonic acid, succinic acid, fumaric acid, maleic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid. The preferred diols $HO-(CHR^{11}-)_aOH$ include those in which R^{11} is hydrogen and a is a number from 2 to 6, and those, in which a has the value 2 and R^{11} is selected from hydrogen and alkyl residues with 1 to 10, particularly 1 to 3 carbon atoms. The last named diols are particularly preferably those of the formula $HO-CH_2-CHR^{11}-OH$, in which R^{11} has the abovementioned meaning. Exemplary diol components are ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,8-octane diol, 1,2-decane diol, 1,2-dodecane diol and neopentyl glycol. Polyethylene glycol with an average molecular weight of 1000 to 6000 is particularly preferred among the polymeric diols. If desired, these polyesters can be end blocked, wherein the blocking groups can be alkyl groups with 1 to 22 carbon atoms and esters of monocarboxylic acids. The end groups bonded through ester linkages can be based on alkyl, alkenyl and aryl monocarboxylic acids containing 5 to 32 carbon atoms, particularly 5 to 18 carbon atoms. They include valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, undecenoic acid, lauric acid, lauroleic acid, tridecanoic acid, myristic acid, myristoleic acid, pentadecanoic acid, palmitic acid, stearic acid, petroselic acid, petroselaidic acid, oleic acid, linoleic acid, linolaidic acid, linolenic acid, elaiostearic acid, arachic acid, gadoleic acid, arachidonic acid, behenic acid, erucic acid, brassidic acid, clupanodonic acid, lignoceric acid, cerotic acid, melissic acid, benzoic acid that can carry 1 to 5 substituents with a total of up to 25 carbon atoms, particularly 1 to 12 carbon atoms, for example *tert*-butylbenzoic acid. The end groups can also be based on hydroxymonocarboxylic acids containing 5 to 22 carbon atoms, examples of which include hydroxyvaleric acid, hydroxycaproic acid, ricinoleic acid, its hydrogenation product hydroxystearic acid, and *o*-, *m*- and p-hydroxybenzoic acid. The hydroxymonocarboxylic acids can themselves be linked with one another through their hydroxyl group and their carboxyl group and thus be present several fold in an end group. Preferably, the number of hydroxymonocarboxylic acid units per end group, i.e. their degree of oligomerization, is in the range 1 to 50, particularly 1 to 10. In a preferred development of the invention, polymers of ethylene terephthalate and polyethylene oxide terephthalate are used, in which the polyethylene glycol units have a molecular weight 750 to 5000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 50:50 to 90:10, alone or in combination with cellulose derivatives.

[0044] Color transfer inhibitors that can be used in detergents for washing textiles particularly include polyvinyl pyrrolidones, polyvinyl imidazoles, polymeric N-oxides such as polyvinyl pyridine-N-oxide and copolymers of vinyl pyrrolidone with vinyl imidazole and optionally further monomers. As fabric surfaces, particularly of rayon, spun rayon, cotton and their mixtures, can crease of their own accord because the individual fibers are sensitive to flection, bending, pressing and squeezing at right angles to the fiber direction, laundry detergents can comprise anti-crease agents. They include for example synthetic products based on fatty acids, fatty acid esters, fatty acid amides, fatty acid alkylol esters, fatty acid alkylol amides or fatty alcohols that have mainly been treated with ethylene oxide, or products based on lecithin or modified phosphoric acid esters.

[0045] Graying inhibitors have the task of ensuring that the dirt removed from hard surfaces and particularly from textile fibers is held suspended in the wash liquor. Water-soluble colloids of mostly organic nature are suitable for this, for example glue, gelatins, salts of ether carboxylic acids or ether sulfonic acids of starches or celluloses, or salts of acidic sulfuric acid esters of celluloses or starches. Water-soluble, acid group-containing polyamides are also suitable for this purpose. Moreover, aldehyde starches, for example, can be used instead of the abovementioned starch derivatives. Preference, however, is given to the use of cellulose ethers such as carboxymethyl cellulose (Na salt), methyl cellulose, hydroxyalkyl cellulose, and mixed ethers, such as methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, methyl carboxymethyl cellulose and mixtures thereof, which can be employed, for example in amounts of 0.1 to 5 wt %, based on the detergent.

[0046] The detergents may comprise optical brighteners, in particular derivatives of diaminostilbene disulfonic acid or alkali metal salts thereof. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-)stilbene-2,2'-disulfonic acid or compounds of similar structure which contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Optical brighteners of the substituted diphenylstyryl type may also be present, for example the alkali metal salts of 4,4'-bis(2-sulfostyryl)diphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)diphenyl. Mixtures of the abovementioned optical brighteners may also be used.

[0047] Particularly when used in automatic washing or cleaning processes, it can be advantageous to add conventional foam inhibitors to the detergents. Suitable foam inhibitors include for example, soaps of natural or synthetic origin, which have a high content of C_{18}-C_{24} fatty acids. Suitable non-surface-active types of foam inhibitors are, for example, organopolysiloxanes and mixtures thereof with microfine, optionally silanized silica and also paraffins, waxes, microcrystalline waxes and mixtures thereof with silanized silica or bis-fatty acid alkylenediamides. Mixtures of various foam inhibitors, for example mixtures of silicones, paraffins or waxes, are also used with advantage. Preferably, the foam inhibitors, especially silicone-containing and/or paraffin-containing foam inhibitors, are loaded onto a granular, water-soluble or dispersible carrier material. Especially in this case, mixtures of paraffins and bis stearylethylene diamide are preferred.

[0048] The manufacture of solid detergents is not difficult and in principle can be made by known methods, for example by spray drying or granulation. For manufacturing detergents with an increased bulk density, particularly in the range of 650 g/l to 950 g/l, a preferred process is one with an extrusion step. Detergents in the form of aqueous solutions or other solutions comprising standard solvents are particularly advantageously manufactured by simply mixing the ingredients, which can be added as such or as a solution into an automatic mixer. In another preferred embodiment of detergents, in particular for the automatic washing of tableware, they are in the form of tablets.

Examples

Example 1: Catalyst Preparation

[0049] 0.407 ml of an aqueous solution of $AuCl_4$, comprising 0.005 g of Au calculated as the metal, and 0.507 ml of an aqueous solution of H_2PtCl_6, comprising 0.005 g of Pt calculated as the metal, were added to 400 ml of de-ionized water. 0.65 ml of a 1 wt.% aqueous solution of polyvinylpyrrolidone (PVP, average molecular weight 360,000 g/mol) was added. After 2 min to 3 min of stirring, 5.43 ml of a freshly prepared 0.1 M sodium borohydride solution was added, and the resulting colloid was stirred (1000 rpm) for 30 minutes to ensure complete reduction to metallic form. 0.99 g of TiO_2 and some drops of sulphonic acid were added, and strirring was continued for an additional hour. The catalyst so obtained was filtered, washed with 1.2 l of de-ionized water, and dried at 110 °C for 16 hours.

Example 2: Wash Tests

[0050]

a) Comparative Test 1: A Cotton substrate (2.5 cm x 2.5 cm) that had been stained with standardized tea soil was put in a 75 ml autoclave reactor. 50 ml of pH 10 buffer solution were added, the reactor was pressurized with oxygen (10 bar) and kept with stirring its content (1000 rpm) at 60 °C for 30 minutes. Then the reactor was allowed to cool for 40 minutes, the cotton substrate was removed, washed with 100 ml of water, dried, and its color was measured.

b) Comparative Test 2: The experiment described in a) was repeated, but this time 2 ml of 0.179 g/l of TAED and 48 ml of the pH 10 buffer solution replaced the 50 ml buffer solution.

c) Comparative Test 3: The experiment described in a) was repeated, but this time 8.3 mg of the catalyst prepared in Example 1 were added to the buffer solution.

d) Test (invention): The experiment described in b) was repeated, but this time but this time 8.3 mg of the catalyst prepared in Example 1 were added to the buffer solution.

e) Results

Table 1: Bleaching Power [remission value in %]

Comparative Test 1	68.3
Comparative Test 2	67.9
Comparative Test 3	67.8
Test (invention)	70.4

[0051] The combination of the colloid and the bleach activator used according to the invention were superior to the added effect of each of them.

Claims

1. Bleaching composition, comprising, in an aqueous medium, atmospheric oxygen and a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based bleach system.

2. Method of bleaching a substrate comprising applying to the substrate, in an aqueous medium in the presence of atmospheric oxygen or air, a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions, the aqueous colloid catalysing bleaching of the substrate by atmospheric oxygen.

3. Use of a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions, the colloid catalysing bleaching of a substrate by the atmospheric oxygen as a catalytic bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or of a peroxy-based bleach system.

4. Method according to claim 2 or use according to claim 3, **characterized in that** the combined content of gold and platinum metal in the aqueous medium is from 1 mg/l to 1 g/l, in particular from 10 mg/l to 200 mg/l.

5. Method according to claim 2 or 4, or use according to claim 3 or 4, **characterized in that** it is carried out at temperatures in the range of from 10 °C to 60 °C, in particular from 40 °C to 60 °C.

6. Method according to claim 2, 4 or 5, or use according to any of claims 3 to 5, **characterized in that** it is performed at gas pressures, especially at air pressures, in the range of from 1 bar to 10 bar, in particular from 5 bar to 10 bar.

7. Method according to claim 2, 4, 5 or 6, or use according to any of claims 3 to 6, **characterized in that** the aqueous medium used to bleach the substrates has a pH in the range from pH 5 to pH 10, in particular from pH 7 to pH 10.

8. Bleaching detergent composition, being substantially devoid of peroxygen bleach or of a peroxy-based bleach system, comprising a combination of an aqueous mixed colloid of gold and platinum with a compound that forms a peroxycarboxylic acid under perhydrolysis conditions, the colloid catalysing bleaching of a substrate by the atmos-

pheric oxygen and additionally a surface-active material.

9. Detergent according to claim 8, comprising the mixed colloid in amounts of from 0.005 % to 0.5 wt %, particularly from 0.03 wt % to 0.2 wt %.

10. Detergent according to claim 8 or 9, **characterized in that** it comprises, in amounts of up to 8 wt %, particularly in the range of from 2 wt % to 6 wt %, compounds that form peroxycarboxylic acids under perhydrolysis conditions.

11. Composition, use or method according to any preceeding claim, **characterized in that** the mixed colloid is immobilized on a solid support material, in particular TiO_2, SiO_2, MgO, NiO, CeO_2, ZrO_2, and their mixtures.

12. Composition, use or method according to claim 11, **characterized in that** the weight ratio of the amount of solid support material, relative to the combined amounts of Au and Pt, is in the range of from 200:1 to 50:1, in particular 100:1

13. Composition, use or method according to any preceeding claim, **characterized in that** the aqueous mixed colloid is stabilized by polymeric stabilising agents, such as polyvinylpyrrolidone, polyvinylpyrrolidone, polyvinylalcohol, sodium polyacrylate, polyallylamine hydrochloride, polyallylamine, their thiol and phosphine capped derivatives, and their mixtures.

14. Composition, use or method according to claim 13, **characterized in that** the stabilising agent is present in the aqueous metal colloid in weight ratios of stabilising agent to metal of from 1:10 to 3:1, in particular of from 3:10 to 8:10.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 19 3112

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 00/36065 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 22 June 2000 (2000-06-22) * page 5, line 9; claims 1,10 * -----	1-14	INV. C11D3/04 C11D3/395
A	WO 02/072747 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 19 September 2002 (2002-09-19) * claim 1 * -----	1-14	
A	WO 2013/167602 A1 (HENKEL AG & CO KGAA [DE]) 14 November 2013 (2013-11-14) * claim 1 * -----	1-14	
A	DE 10 2009 001692 A1 (HENKEL AG & CO KGAA [DE]) 23 September 2010 (2010-09-23) * claims 1,2 * -----	1-14	
A	WO 2010/105961 A1 (HENKEL AG & CO KGAA [DE]; NORDSKOG ANETTE [NO]; GHOSH ROBIN [DE]; SPUH) 23 September 2010 (2010-09-23) * claims 1,2 * -----	1-14	TECHNICAL FIELDS SEARCHED (IPC)
A	WO 2006/093792 A1 (SOLUTIONS BIOMED LLC [US]; TICHY DARYL J [US]; LARSON BRIAN G [US]) 8 September 2006 (2006-09-08) * claims 1,13,14 * -----	1-14	C11D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	8 February 2019	Richards, Michael

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
……………………………………………………………
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 18 19 3112

08-02-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0036065 A1	22-06-2000	AU 3148300 A	03-07-2000
		US 6140298 A	31-10-2000
		WO 0036065 A1	22-06-2000
WO 02072747 A1	19-09-2002	AR 035442 A1	26-05-2004
		AT 363528 T	15-06-2007
		AU 2002304851 B2	09-06-2005
		BR 0206044 A	11-11-2003
		CA 2431006 A1	19-09-2002
		CN 1496399 A	12-05-2004
		DE 60220381 T2	27-09-2007
		EP 1368451 A1	10-12-2003
		ES 2287279 T3	16-12-2007
		MY 126188 A	29-09-2006
		US 2003054967 A1	20-03-2003
		WO 02072747 A1	19-09-2002
		ZA 200303004 B	16-04-2004
		ZA 200306413 B	18-08-2004
WO 2013167602 A1	14-11-2013	DE 102012207949 A1	14-11-2013
		EP 2847314 A1	18-03-2015
		WO 2013167602 A1	14-11-2013
DE 102009001692 A1	23-09-2010	DE 102009001692 A1	23-09-2010
		WO 2010105962 A1	23-09-2010
WO 2010105961 A1	23-09-2010	DE 102009001691 A1	23-09-2010
		WO 2010105961 A1	23-09-2010
WO 2006093792 A1	08-09-2006	AU 2006218874 A1	08-09-2006
		BR PI0608399 A2	29-12-2009
		CA 2599010 A1	08-09-2006
		CN 101163784 A	16-04-2008
		DK 1856236 T3	04-12-2017
		EP 1856236 A1	21-11-2007
		IL 185506 A	31-10-2012
		JP 4971198 B2	11-07-2012
		JP 2008531583 A	14-08-2008
		KR 20070110394 A	16-11-2007
		US 2006198798 A1	07-09-2006
		US 2006263239 A1	23-11-2006
		US 2008233005 A1	25-09-2008
		WO 2006093792 A1	08-09-2006
		ZA 200707893 B	31-12-2008

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 9534628 A1 **[0004]**
- WO 0012677 A1 **[0005]**
- DE 2412837 **[0029]**