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(71) Applicant *(for AU CA GB only):* UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant *(for all designated States except AU CA GB US):* UNILEVER N.V. [NL/NL]; P.O. Box 137, NL-3000 DK Rotterdam (NL).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)* : VAN DE PAS, Johannes, Cornelis [NL/NL]; Philips Willemstraat 6, NL-3136 CV Vlaardingen (NL).

(74) Agent: JOPPE, Hermina, L., P.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).

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(57) Abstract

An aqueous liquid detergent composition comprising (a) 2-60 % by weight of detergent active materials; (b) a peroxygen bleach in an amount corresponding to 0.1 to 15 % by weight of the composition of active oxygen, at least part of said bleach being present as solid particles suspended in the system; and (c) 0.05 % to 25 % by weight of ingredients for providing softness to fabrics.

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LIQUID DETERGENTS

The present invention is concerned with aqueous liquid detergent compositions. In particular the present invention relates to liquid detergent compositions for the washing of fabrics which contain a peroxygen bleach compound.

It has been proposed in EP 293 040 and EP 294 904 to use solid water-soluble peroxygen bleach compounds in aqueous liquid detergent compositions. A disadvantage of the compositions as disclosed in these patent applications is that they are often not fully capable of providing a softening effect to fabrics.

There has been a desire to provide single liquid detergent compositions which would be capable of both washing and softening the fabrics to overcome the inconvenience of using separate products for in-the-rinse softening.

US 4,430,236 (Chandler Franks) discloses low pH single phase aqueous liquid laundry products containing a hydrogen peroxide bleach and nonionic surfactants. Cationic surfactants may be included for providing softening properties.

The present invention provides liquid detergent compositions providing a very desirable combination of good washing performance and softness of the fabrics after washing. Compositions in accordance to the invention can be formulated in a broad pH range, especially at alkaline pH values, and may contain a broad range of fabric softening ingredients in combination with bleach materials other than hydrogen peroxide.

Accordingly the present invention relates to an aqueous liquid detergent composition comprising
(a) 2-60 % by weight of detergent active materials;
(b) a peroxygen bleach in an amount corresponding to 0.1 to 15 % by weight of the composition of active oxygen, at least part of said bleach being present as solid particles suspended in the system; and
(c) 0.05 to 25 % by weight of ingredients for providing softness to fabrics.

Preferred fabric softening ingredients for incorporation in liquid detergent compositions of the invention are selected from the groups of fabric softening clays, fabric softening cellulose ether materials, particles comprising a quaternary ammonium fabric softener, an amine softener material, an amphoteric fabric softener material or mixtures thereof.

Compositions according to the present invention comprise a peroxygen bleach which is not or only partly present in the system in solubilised form, the remaining part being present as solid peroxygen particles which are suspended in the system. Preferably at least 80 % by weight, more preferably more than 90 %, more preferably from 98 to 100 % of the bleach is present in undissolved form.

Preferably the weight average diameter of the undissolved bleach particles is from 0.5 to 100 micrometer, especially 5 to 60 micrometer. A method for obtaining these small particles is described in EP 294 904.

One way of ensuring that the bleach is present in undissolved form is to increase the amount of electrolyte in the composition, therewith reducing the solubility of the bleach component in the system. Suitable electrolytes for this purpose are for instance the at least partially water soluble carbonate, sulphate and halogenide salts and metaborate. Other preferred electrolytes are salting out electrolytes.

For the purpose of the present invention the expression salting out electrolyte has the same meaning as in EP 79 646, namely those electrolytes which have a lyotropic number of less than 9.5.

For ensuring an adequate reduction in solubility of the bleach component, the dissolved part of the electrolyte constitutes preferably more than 2 % by weight of the composition, more preferred more than 5% by weight, especially preferred between 10 and 50 % by weight.

Examples of suitable peroxygen compounds include the perborates, persulfates, peroxy disulfates, perphosphates and the crystalline peroxyhydrates formed by reacting hydrogen peroxide with urea or alkali metal carbonate. Also encapsulated bleaches may be used.

The bleach component is preferably added in an amount corresponding to 0.1 to 15% by weight of the composition of active oxygen, more preferred from 0.5 to 5% active oxygen, typically from 1.0 to 3.0 % active oxygen.

Especially preferred is the use of bleaches such as diperoxydodecandioic acid (DPDA) or other peracid crystals and perborate (preferably perborate-tetrahydrate) or percarbonate bleaches. Preferably these bleaches are used in an amount of from 5 to 40 % by weight of the composition, more preferably from 10 to 30%.

The bleach ingredients may for example be added to the composition as a dry particulate material or as a predispersion of bleach particles. If perborate-tetrahydrate bleaches are used, a suitable commercial available bleach dispersion is Proxsol (ex ICI), alternatively perborate-tetrahydrate crystals may be formed in-situ for example as described in EP 294 904.

The present invention seeks to provide liquid detergent compositions which contain a bleach ingredient and which are capable of providing softness to fabrics to overcome the inconvenience of using separate products for in-the-rinse softening

British patent application GB 1,400,898 (Procter and Gamble) describes the use of smectic-type clays in granular detergent compositions for obtaining softening in the wash. Hitherto, however, it has been difficult to incorporate clay softeners in liquid aqueous detergent compositions.

EP 225 142 (UNILEVER) proposes to use a fabric softening clay material having a limited swellability.

EP 291 261 (UNILEVER) describes the use of fabric softening clay material in combination with non-peptising/non-building electrolytes such as sodium formates, chloride or sulphate.

EP 213 730 (UNILEVER) proposes to provide the desired softening in the wash, by combining a detergent active material, a fabric softening agent and specific low gel-point cellulose ether derivatives. These specific cellulose ethers are capable of enhancing fabric softening in the wash step.

EP 265 187 discloses the use of imidazoline particles having an average particle diameter of from about 20 to 200 microns for softening-in-the wash.

EP 294 893 discloses the use of imidazoline-anionic surfactant ion-pair/wax composites as fiber- and fabric conditioning agent. EP 294 894 discloses the similar use of amine-anionic ion pair/wax composites having a particle size of 1 to 1000 nanometer in liquid compositions.

Preferred fabric softening ingredients for incorporation in compositions of the invention are selected from the groups of

(i) fabric softening clays;

(ii) fabric softening cellulose ether materials;

(iii)particles comprising a quaternary ammonium fabric softener, an amine softener material, an amphoteric fabric softener material or mixtures thereof;

(iv) mixtures thereof.

Particularly preferred is the use of fabric softening clays. Surprisingly it has been found that clay materials which are known for their impurities such as metal traces, do not affect in an unacceptable degree the stability of the bleach materials as presently claimed. This is surprising as it would be expected that the impurities of the clay material would be dissolved in the aqueous phase of the liquid detergent composition and function as a catalyst for the decomposition of the bleach.

Another surprising benefit of using fabric softening clay materials in combination with solid bleach materials is that this sometimes increases the solid suspending properties of liquid detergent compositions.

Suitable fabric softening clays include low, medium or high swelling clays. Examples of suitable clay materials are Hectorites/ Na Bentonites, for example BENTONE EW and CLARSOL W100; Ca Bentonites, for example CLARSOL KC1, MDO 77/84, LAUNDROSIL DG, LAPORTE CP 103 and MARMORA, or their sodium carbonate activated forms; commercially sodium carbonate activated Ca Bentonite, for example CLARSOL KC2, MDO 81/84, LAUNDROSIL DG AC and DOKUM KARAKAYA; acid activated Ca Bentonites, for example BENTONITE DC and white bentonites, for example STREETLEY NO's 1 and 2. Other suitable clay materials are disclosed in the above mentioned British patent 1,400,898.

Other suitable fabric softening clays are VOLCLAY SPV (origin USA), SURREY NO. 1 (origin USA), EARTH (origin UK), ENVIRONETICS (origin Argentina), CULVIN (origin South Africa), SAN FRAN (origin Argentina), BERKBOND 1 (origin UK), STREETLEY WYOMING (originh USA), MDO 77/84 and ECC (ASB) (both origin Morocco), UBM (origin Brasil), CSM (high CEC Prassa) (origin Greece), GELLWHITE (origin TEXAS USA) and WILLEMSE (origin South Africa). Also hydrophobically modified clay materials may be used.

Preferred clay materials for use in compositions of the invention are montmorrilonite clays, more preferably bentonite clays, especially preferred white bentonite clays.

The amount of fabric softening clays in compositions of the invention is preferably from 0.1-25 %, more preferred from 0.5-15 %, most preferred from 1-10 % by weight of the composition, suitable amounts are for example about 2 % or about 3 % by weight.

Preferred fabric softening cellulose ether materials are nonionic substituted cellulose ethers having an HLB of between 3.1 and 4.3, a gel point of less than 58 ^{o}C, said cellulose ether material being substituted with C_{1-3} alkyl and/or hydroxyalkyl groups.

Preferably the substituent groups are selected from the C_2-C_3 alkyl and C_2-C_3 mono- or polyhydric hydroxy alkyl groups, or combinations thereof. Especially the use of alkyl hydroxyalkyl cellulose ethers is preferred. Most preferred is the use of ethyl hydroxyethyl substituted cellulose ethers. The choice and percentage of substituent groups has a direct influence on the HLB value of the cellulose ether. A suitable method for determining the HLB value of cellulose ethers is the method as described for emulsifiers by J T Davies, 2nd Int Congress of Surface Activity 1957, I pp 426-439. This method has been adopted to derive a relative HLB ranking for cellulose ethers by summation of Davies's HLB assignments for substituent groups at the three available hydroxyl sites on the anhydroglucose ring of the polymer. The HLB assignments for the substituents groups include the following:

Residual Hydroxyl	1.9
Methyl	0.825
Ethyl	0.350
Hydroxy ethyl	1.63
Hydroxy propyl	1.15
Hydroxy butyl	0.67.

The cellulose ethers useful herein are polymers. The gel point of polymers can be measured in a number of ways. In the present context the gel point is measured on a polymer solution prepared at 10 g/l concentration in deionised water by heating 50 ml solution placed in a beaker, with stirring, at a heating rate of approximately 5°C/minute. The temperature at which the solution clouds is the gel point of the cellulose ether being tested and is measured using a Sybron/Brinkmann colorimeter at 80% transmission/450 nm.

Provided that the HLB and gel point of the polymer fall within the required ranges, the degree of substitution (DS) of the anhydroglucose ring may be any value up to the theoretical maximum value of 3, but is preferably from about 1.7-2.9, there being a maximum of 3 hydroxyl groups on each anhydroglucose unit in cellulose. The expression 'molar substitution' (MS) is sometimes also used in connection with these polymers and refers the number of hydroxyalkyl substituents per anhydroglucose ring and may be more than 3 when the substituents themselves carry further substituents.

The most highly preferred polymers have an average number of anhydrogluclose units in the cellulose polymer, or weight average degree of polymerisation, from about 50 to about 1,200. For liquids, it may be desirable to include polymers of relatively low degree of polymerisation to obtain a satisfactory product viscosity.

A number of cellulose ethers suitable for use in the present invention are commercially avaiable, as follows:

Trade Name	Gel point °C	HLB (Davies)	DS/MS alkyl/hydroxalkyl
BERMOCOLL CST035 (ex Berol Nobel)	35	3.40	)1.4 ethyl)0.5 hydroxyethyl
DVT 88 004 (ex Berol Nobel)	37	3.11	)1.5 ethyl)1.0 hydroxyethyl
TYLOSE MHB 1000 (ex Hoechst)	54	3.52	)2.0 methyl)0.1 hydroxyethyl

The amount of cellulose ether be employed in compositions according to the invention is preferably from 0.05 to 5%, more preferably from 0.5 to 3% by weight of the composition.

Preferred cellulose ethers for use in compositions of the present invention have an HLB of between 3.3 and 3.8 and a gel point of between 30 and 55°C. Especially preferred is the use of Bermocoll CST035.

Preferred particles comprising a quaternary ammonium fabric softener and/or an amine softener material and/or an amphoteric fabric softener material are discrete composites of one or more conventional softening ingredients. Also lamellar droplets of fabric softening materials are considered as particles in accordance with the present invention; preferably however solid particles are used.

Suitable quaternary ammonium softeners, amines and amphoteric fabric softening ingredients are for example disclosed in EP 322 270. Most preferably the particles comprise an ion-pair softener complex such as for example an imidazoline-anionic surfactant ion-pair softener complex as disclosed in for example 294 893, or an amine-anionic ion pair softener complex as for example disclosed in EP 294 894.

Preferably the particles have a weight average particle size of 5 nanometer to 1000 micrometer, more preferred from 10 nanometer to 10 micrometer, most preferred from 50 nanometer to 5 micrometer.

Preferably the amount of fabric softening particles is from 1 to 25 % by weight of the composition, more preferred from 2 to 15 %, most preferred from 3 to 10 %.

Compositions of the invention are aqueous liquid detergent compositions. Aqueous detergent compositions comprise at least 10 % by weight of water, more preferably from 15 to 80 % of water, most preferably from 20 to 50 %. Embraced within the scope of the present invention are so-called isotropic liquid detergent compositions, wherein all ingredients are present in solubilised form and anisotropic liquid detergent compositions. Preferably compositions of the invention are structured liquid detergent compositions, such structured liquids can be "internally structured" whereby the structure is formed by primary ingredients and/or they can be structured by secondary additives such as certain cross-linked polyacrylates or clays, which can be added as "external structurants" to compositions of the invention.

Such structuring is very well known in the art and may be deliberately brought about to endow properties such as consumer preferred flow properties and/or turbid appearance. Many structured liquids are also capable of suspending particulate solids such as detergency builders and abrasive particles.

Some of the different kinds of active-structuring which are possible are described in the reference H.A. Barnes, "Detergents", Ch.2. in K. Walters (Ed), "Rheometry: Industrial Applications", J. Wiley & Sons, Letchworth 1980. In general, the degree of ordering of such systems increases with increasing surfactant and/or electrolyte concentrations. At very low concentrations, the surfactant can exist as a molecular solution, or as a solution of spherical micelles, both of these being isotropic. With the addition of further surfactant and/or electrolyte, structured (antisotropic) systems can form. They are referred to respectively, by various terms such as rod-micelles, planar lamellar structures, lamellar droplets and liquid crystalline phases. Often, different workers have used different terminology to refer to the structures which are really the same. For instance, in European patent specification EP-A-151 884, lamellar droplets are called "spherulites". The presence and identity of a surfactant structuring system in a liquid may be determined by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, x-ray or neutron diffraction, and sometimes, electron microscopy.

Electrolyte may be only dissolved in the aqueous continuous phase or may also be present as suspended solid particles. Particles of solid materials which are insoluble in the aqueous phase may be suspended alternatively or in addition to any solid electrolyte particles.

Three common product forms in this type are liquids for heavy duty fabrics washing and liquid abrasive and general purpose cleaners. In the first class, the suspended solid can comprise suspended solids which are substantially the same as the dissolved electrolyte, being an excess of same beyond the solubility limit. This solid is usually present as a detergency builder, i.e. to counteract the effects of calcium ion water hardness in the wash. In the second class, the suspended solid usually comprises a particulate abrasive, insoluble in the system. In that case the electrolyte, present to contribute to the structuring of the active material in the dispersed phase, is generally different from the abrasive compounds. In certain cases, the abrasive can however comprise partially soluble salts which dissolve when the product is diluted. In the third class, the structure is usually used for thickening the product to give consumer-preferred flow properties, and sometimes to suspend pigment particles.

Compositions of the first kind are described in for example our patent specification EP-A-38,101 whilst examples of those in the second category are described in our specification EP-104,452. Those in the third category are for example, described in US 4,244,840.

The dispersed structuring phase in these liquids is generally believed to consist of an onion-like configuration comprising concentric bilayers of detergent active molecules, between which is trapped water (aqueous phase). These configurations of active material are sometimes referred to as lamellar droplets.

It is believed that the close-packing of these droplets enables the solid materials to be kept in suspension. The lamellar droplets are themselves a sub-set of lamellar structures which are capable of being formed in detergent active/aqueous electrolyte systems. For the purpose of the present invention, detergent compositions of the lamellar droplet type are preferred.

Compositions of the invention also comprise one or more detergent active materials. In the widest definition the detergent active materials in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 and "Surface Active Agents" Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in Tensid-Taschenburch", H. Stache, 2nd Edn., Carl Hanser Verlag, Munchen & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Also possible is the use of salting-out resistant active materials, such as for example described in EP 328 177, especially the use of alkyl polyglycoside surfactants, such as for example disclosed in EP 70 074.

Preferably the level of nonionic surfactants is more than 1 % by weight of the composition, preferably from 2.0 to 20.0 %.

Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulponate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Generally the level of the above mentioned non-soap anionic surfactant meterials is from 1-40 % by weight of the composition.

Preferably the weight ratio of synthetic anionic surfactants to nonionic surfactants is from 10 : 1 to 1 : 10.

It is also possible, and sometimes preferred, to include an alkali metal soap of a mono- or di-carboxylic acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil, alk(en)yl succinates e.g. dodecyl succinates or mixtures thereof. The sodium or potassium soaps of these acids can be used.

Preferably the level of soap in compositions of the invention is from 0-40 % by weight of the composition, more preferred from 1-30 %, most preferred 5-25 %.

In many (but not all) cases, the total detergent active material may be present at from 2% to 60% by weight of the total composition, for example from 5% to 40% and typically from 10% to 30% by weight. However, one preferred class of compositions comprises at least 20%, most preferably at least 25% and especially at least 30% of detergent active material based on the weight of the total composition.

Compositions according to the invention are preferably physically stable in that they yield no more than 2% by volume phase separation when stored at 25°C for 21 days from the time of preparation. Especially preferred are compositions which do not yield any phase separation upon storage for 21 days at 25 °C.

Compositions according to the invention, preferably have solid-suspending properties in that they yield less than 5 % by volume of sediment after storage for 21 at 25°C, more preferably less than 2 % by volume sediment is formed, most preferably substantially no visible sediment is formed.

When a solid peroxygen bleach component is present in an aqueous system, generally part of the bleach material will be solubilized in the form of peracid and/or hydrogen peroxide in the aqueous phase. One of the problems sometimes observed in these systmes is the occurence of oxygen evolution, due to the decomposition of this peracid or hydrogen peroxide into acid and/or water and oxygen. The oxygen bubbles thus formed may either emerge from the liquid or be trapped in the liquid, thereby causing a volume increase.

Liquid detergent compositions according to the invention are preferably volume stable in that they show less than 25% preferably less than 10%, more preferably less than 5% volume increase during storage at a temperature between 20 and 37°C for a period of three months after preparation.

Although the type of container for storage is believed not to be critical, generally liquid detergent compositions according to the invention will be stored in closed bottles, say of 1.5 litre, which optionally may include venting means, for releasing generated oxygen.

For obtaining good volume stability, preferably the compositions according to the present invention also comprise a stabilising agent for the bleach component. Suitable stabilisers are well-known in art and include EDTA, Magnesium silicates and phosphonates such as for instance the Dequest range ex Monsanto and Naphthol ex Merck. Preferably the amount of stabilising agent is from 0.05 to 5 % by weight of the composition, more preferred from 0.05 to 1% of the composition.

Compositions of the present invention may comprise one or more bleach activator agents. These materials when combined with a peroxy bleach in the wash, will activate hydrogen peroxide at a low temperature of from 15 to 55°C therewith allowing the effective use of peroxide bleaches at low washing temperatures.

The bleach activators used in the present invention, often also referred to as peroxyacid bleach precursors are conventionally organic compounds having one or more reactive acyl groups, which at relatively low temperature react with hydrogenperoxide causing the formation of organic peroxyacids, the latter providing for a more effective bleaching action at lower temperatures than hydrogen peroxide itself.

The best known organic bleach activator of practical importance is N,N,N,N'-tetraacyl ethylene diamine, normally referred to as TAED. Another well-known bleach activator is sodium-4-benzoyl oxybenzene sulphonate normally referred to as BOBS, as disclosed in GB 836,988.

Examples of other organic bleach activators are other n-acyl substituted amides, for example tetraacetyl methylene diamine; carboxylic acid anhydrides for example succinic, benzoic and phthalic anhydrides; carboxylic acid esters, for example sodium acetoxy benzene sulphonate; acetates such as glycerol-triacetate, glucose pentaactetate and xylose-tetraacetate and acetyl salicylic acid.

Preferably TAED is used as the bleach activator. The preferred level of bleach activator in the liquid detergent is from 0.1 to 10 % by weight preferably from 0.5 to 5 % by weight of the composition.

Preferably the bleach activator is present in the system in at least partly undissolved form. Preferably at least 10% by weight, more preferably at least 30%, especially preferred more than 50% by weight of the activator is present in undissolved form.

One way of ensuring that the activator is present in undissolved form is the use of encapsulated activator materials. Another method is to increase the amount of electrolyte in the composition, therewith reducing the solubility of the activator in the system. Suitable electrolytes for this purpose are for instance the at least partially water soluble carbonate, sulphate and halogenide salts and metaborate. Other preferred electrolytes are salting out electrolytes as defined hereabove.

For ensuring an adequate reduction in solubility, the dissolved part of the electrolyte constitutes preferably more than 2 % by weight of the composition, more preferred more than 5% by weight, especially preferred between 10 and 50 % by weight.

Compositions of the invention preferably have a pH between 4 and 12, more preferred 7 and 11, most preferred more than 8 and less than 10, for example from 8.5 to 9.5.

As to the viscosity of the product directly after preparation, it has been found that a lower value for the viscosity generally increases the volume stability of the bleach containing product. Also lower viscosities are generally preferred by the consumer. However, for providing solid-suspending properties, low viscosities should preferably be avoided. Therefore in selecting the most appropriate viscosity of the product, a balance should be sought between better stability and consumer-acceptance at lower viscosities and increased solid suspending properties at higher viscosities.

Generally it is preferred that for good volume stability and good consumer-acceptance, the viscosity is preferably less than 5,000 mPas at 21 s^{-1}, more preferred less than 1,500, most preferred between 20 and 1,000, especially preferred from 30 to 500. For good solid suspending properties, it is preferred that the viscosity is more than 1,000 mPas at 10^{-4} s^{-1}, more preferred more than 10,000, especially preferred more than 100,000.

The techniques for obtaining the initial viscosity as desired are well-known in the art, and include for example the appropriate choice of active ingredients, the adaptation of the level of dissolved electrolyte and the inclusion of viscosity modifying agents. A preferred way for regulating the viscosity of the product is the inclusion of polymers in the composition.

Viscosity and/or stability regulating polymers which are preferred for incorporation in compositions according to the invention include deflocculating polymers e.g those having a hydrophilic backbone and at least one hydrophobic side chain. Such polymers are for example described in our copending British patent applications 8813978.7 (corresponding to EP 346 995).

Other polymers which could advantageously be used for viscosity regulation are described in EP 301,882 (Unilever PLC) and EP 301,883 (Unilever PLC). Preferably the amount of viscosity regulating polymer, especially deflocculating polymers, is from 0.1 to 5% by weight of the total composition, more preferred from 0.2 to 2%.

Especially when the compositions are of lamellar structure it is preferred for the aqueous continuous phase to contain dissolved electrolyte. As used herein, the term electrolyte means any ionic water soluble material. However, in lamellar dispersions, not all the electrolyte is necessarily dissolved but may be suspended as particles of solid because the total electrolyte concentration of the liquid is higher than the solubility limit of the electrolyte. Mixtures of electrolytes also may be used, with one or more of the electrolytes being in the dissolved aqueous phase and one or more being substantially only in the suspended solid phase. Two or more electrolytes may also be distributed approximately proportionally, between these two phases. In part, this may depend on processing, e.g.

the order of addition of components. On the other hand, the term "salts" includes all organic and inorganic materials which may be included, other than surfactants and water, whether or not they are ionic, and this term encompasses the sub-set of the electrolytes (water soluble materials).

The only restriction on the total amount of detergent active material and electrolyte (if any) is that in the lamellar compositions embraced in the present invention, together they must result in formation of an aqueous lamellar dispersion. Thus, within the ambit of the present invention, a very wide variation in surfactant types and levels is possible. The selection of surfactant types and their proportions, in order to obtain a physically stable liquid with the required structure will be fully within the capability of those skilled in the art. However, it can be mentioned that an important sub-class of useful compositions is those where the detergent active material comprises blends of different surfactant types. Typical blends useful for fabric washing compositions include those where the primary surfactant(s) comprise nonionic and/or a non-alkoxylated anionic and/or an alkoxylated anionic surfactant.

In the case of blends of surfactants, the precise proportions of each component which will result in such physical stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids.

The compositions optionally also contain electrolyte in an amount sufficient to bring about structuring of the detergent active material. Preferably though, the compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included, provided it is of a kind and in an amount compatible with the other components and the composition is still in accordance with the definition of the invention claimed herein. Some or all of the electrolyte (whether salting-in or salting-out), or any substantially water insoluble salt which may be present, may have detergency builder properties.

In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. The builder material is any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric.

Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used. Sometimes, however, it is preferred to minimise the amount of phosphorous-containing builders.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilitriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, CMOS, tartrate mono succinate, tartrate di succinate and citric acid.

Preferably the level of non-soap builder material is from 5-50 % by weight of the composition, more preferred from 5 to 35 %.

Although it is possible to incorporate minor amounts, of hydrotropes other than water-miscible solvents, we prefer that the compositions of the present invention contain low levels or are substantially free from hydrotropes. By hydrotrope is meant any water soluble agent which tends to enhance the solubility of surfactants in aqueous solution.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase (Trade Mark) ex Novo), germicides and colourants.

Compositions of the invention may be prepared by any conventional method for the preparation of liquid detergent compositions. A preferred method involves the dispersing of the electrolyte (non-builder) -if any- together with the minor ingredients except for the temperature sensitive ingredients -if any- in water of elevated temperature, followed by the addition of the builder material -if any-, the detergent active materials (optionally as a pre-mix) under stirring and thereafter cooling the mixture and adding any temperature sensitive minor ingredients such as enzymes or perfumes and the bleach. The deflocculating polymer - if any- may for example be added after the elctrolyte ingredient or as the final ingredient.

When perborate monohydrate is used as the bleaching agent, it may be preferred to cool the final product to a temperature just above the freezing point, in order to accelerate the recrystallisation of the perborate in tetrahydrate form.

In use the liquid detergent compositions of the invention will generally be diluted with wash water to form a wash liquor, which may be used for detergency purposes, for example for the washing process in a washing machine. The concentration of liquid detergent composition in the wash liquor is preferably from 0.1 to 10 % by weight, more preferred from 0.1 to 3 %.

The invention will now be illustrated by way of the following Examples. In all Examples, unless stated to the contrary, all percentages are by weight.

Examples 1-3

The following compositions may be prepared by adding the electrolyte together with the minor ingredients except for the perfume and the enzymes to water of elevated temperature, followed by the addition of the deflocculating polymer and then the detergent active materials as a premix under stirring and thereafter cooling the mixture and adding the enzymes the perfumes, the bleach and the fabric softener ingredient.

Ingredient (% wt)	I	II	III
Na-Dobs	<--------	21	--------->
Synperonic A7	<--------	9	--------->
Sodium metaborate	<--------	2.6	--------->
Nacitrate/citric acid1)	<--------	9.8	--------->
Dequest 2060S (as 100%)	<--------	0.4	--------->
Na-perborate tetra2)	<--------	17	--------->
Bentone 14 3)	3.0	-	-
Clarsol KCl4)	-	3.0	-
Bermocoll CST 35	-	-	0.5
Enzyme (Alcalase)	<--------	0.8	--------->
$CaCl_2.2H_2O$	<--------	0.2	--------->
Tinopal CBSX	<--------	0.1	--------->
Silicon DB 100	<--------	0.3	--------->
Perfume	<--------	0.3	--------->
polymer5)	<--------	1	--------->
water	<------	balance	--------->
pH	<----------	9	----------->

-1- This mixture is used to adjust the pH.

-2- as 100% perborate added as a dispersion (Proxsol ex ICI) of approximately 65 % perborate in water with an average perborate particle size of 40 micron.

-3- Hydrophobic clay ex NL industries

-4- Bentonite clay ex CECA

-5- deflocculating polymer of formula I of EP 346 995 (ex National Starch) wherein x=50, y=0, R^5=H, R^1=-CO-O, R^2 and R^3 are absent, R^4 = $-C_{12}H_{2}5$, Mw= 7,500.

Examples 4-9

The following compositions were made as in examples 1-3.

INGREDIENT (%wt)	4	5	6	7	8	9
NaLAS	20.4	19.6	20.0	19.9	18.6	18.0
Synperonic A7	8.8	8.4	8.6	8.6	8.0	7.8
Na-citrate.2aq	14.6	14.0	14.4	14.3	13.4	12.9
Na-metaborate.4aq	3.7	3.5	3.6	3.6	3.3	3.2
Dequest 2060S	0.3	0.3	0.3	0.3	0.3	0.3
Silicon DB100	-	-	-	-	0.2	0.2
Naperborate mono	7.3	7.0	5.0	7.2	-	-
Naperborate tetra	-	-	-	-	13.4	16.2
polymer	1.0	1.0	1.0	1.0	1.0	1.0
Clarsol KC1	-	4.2	4.3	2.9	2.7	2.6
water	<-----------		balance		------------>	
pH	9.3	9.1	9.2	9.2	9.1	9.1
Visc (mPa.s $21s^{-1}$)	620	1380	640	2630	210	270
Volume stability	0%	6%	0%	0%	0%	0%
Physical stability						
phase separation	s	s	s	s	s	s
solid sedimentation	us	s	s	s	us	us
Bleach stability	94	90	93	95	96	

In the above table NaLas refers to sodium linear C_{12} alkyl benzene sulphonate, the perborate tetra was added as a predispersion (Proxsol ex ICI), the polymer was deflocculating polymer A-44 as described in EP 346 995, the pH was adjusted to the value indicated -if necessary- with citric acid, the volume stability indicates the maximum volume increase during 3 months storage at ambient temperature, s indicated stability, us instability, the bleach stability indicates the wt % of perborate left after 1 month storage at ambient temperature, for example 8 the value is extrapolated.

These examples show that surprisingly fabric softening clays may be incorporated into bleach containing aqueous liquid detergent compositions, without unduly affecting bleach stability, while the resulting products are still pourable and do not show a significant degree of phase separation. Furthermore examples 5-7 compared to example 4 (comparative) show that surprisingly the combined use of fabric softening clays and bleach materials may provide increased solid suspending properties.

Examples 10-14

The following compositions were prepared as in example 1-3, the ingredients used and the method of assessment of the product was as in examples 4-9.

Ingredient (%wt)	10	11	12	13	14
NaLas	20.4	20.1	20.7	18.9	18.3
Synperonic A7	8.8	8.6	8.9	8.2	7.8
Na-citrate 2aq	14.6	14.4	14.8	13.6	13.0
Nametaborate 4aq	3.7	3.6	3.7	3.4	3.2
Dequest 2060S	0.3	0.3	0.3	0.3	0.3
Silicon DB100	-	-	-	0.2	0.2
Naperborate mono	7.3	7.2	5.2	-	-
Naperborate tetra	-	-	-	13.6	16.3
polymer	1.0	1.0	1.0	1.0	1.0
Bentone 34	-	1.7	1.1	1.0	1.0
Water	<-------- balance ---------->				
pH	9.3	9.4	9.3	9.1	9.8
Viscosity (mPa.s $21s^{-1}$)	620	7310	390	240	310
Volume stability	0%	>12%	1%	0%	nm
Physical stability					
phase separation	s	s	s	s	nm
solid sedimentation	us	s	us	s	nm
Bleach stability	94	92	98	99	85

These examples show that surprisingly fabric softening clays may be incorporated into bleach containing aqueous liquid detergent compositions, without unduly affecting bleach stability. Furthermore example 11 compared to example 10 (comparative) shows that surprisingly the combined use of fabric softening clays and bleach materials may provide increased solid suspending properties. Example 13 gives an extrapolated value for bleach stability.

Example 15-17

The following compositions were prepared as in example 1-3, the ingredients used and the method of assessment of the product was as in examples 4-9.

Ingredient (% wt)	15	16	17
NaLas	20.4	20.3	20.8
Synperonic A7	8.8	8.7	8.9
Na-citrate 2aq	14.6	14.5	14.8
Na Metaborate 4aq	3.7	3.6	3.7
Naperborate mono	7.3	7.3	5.2
polymer	1.0	1.0	1.0
Laponite RD	-	0.7	0.7
Water	<-------	balance	--------->
pH	9.3	9.4	9.3
Viscosity	620	5430	290
Volume stability	0%	0%	0%
Physical stability			
phase separation	s	s	s
solid sedimentation	us	s	us
Bleach stability	94	94	98

These examples show that surprisingly fabric softening clays may be incorporated into bleach containing aqueous liquid detergent compositions, without unduly affecting bleach stability. Furthermore example 16 compared to example 15 (comparative) shows that surprisingly the combined use of fabric softening clays and bleach materials may provide increased solid suspending properties.

Claims

1. An aqueous liquid detergent composition comprising

   (a) 2-60 % by weight of detergent active materials;

   (b) a peroxygen bleach in an amount corresponding to 0.1 to 15 % by weight of the composition of active oxygen, at least part of said bleach being present as solid particles suspended in the system; and

   (c) 0.05 to 25 % by weight of ingredients for providing softness to fabrics.

2. An aqueous liquid detergent composition according to claim 1, wherein the ingredients for providing softness are selected from the groups of :

   (i) fabric softening clays;

   (ii) fabric softening cellulose ether materials;

   (iii) particles comprising a quaternary ammonium fabric softener, an amine softener material, an amphoteric fabric softener material or mixtures thereof;

   (iv) mixtures thereof.

3. An aqueous liquid detergent composition according to claim 1 comprising from 1 to 60 % by weight of electrolytes.

4. An aqueous liquid detergent composition according to claim 1, wherein the bleach material is selected from the group consisting of perborates and percarbonates.

5. An aqueous liquid detergent composition according to claim 1, comprising from 0.1 to 5 % by weight of viscosity regulating polymers.

6. An aqueous liquid detergent composition according to claim 1, wherein the ingredient for providing softness is a fabric softening clay material.

7. An aquoeus liquid detergent composition according to claim 1, comprising

(a) 2-60 % by weight of detergent active materials;

(b) a peroxygen bleach in an amount corresponding to 0.1 to 15 % by weight of the composition of active oxygen, at least part of said bleach being present as solid particles suspended in the system;

(c) 0.05 to 25 % by weight of ingredients for providing softness to fabrics;

(d) 1 to 60 % by weight of electrolyte materials;

(e) 5 to 50 % by weight of non-soap builder materials;

(f) 0.1 to 5 % of viscosity regulating polymers; said product having a viscosity at 21 s^{-1} of less than 2,000 mPa.s, said product having a volume increase of less than 25% when stored for three months after preparation and said product having a pH of 4 to 12.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/00212

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 11 D 3/39, 17/00, 3/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 11 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	EP, A, 0160342 (UNILEVER N.V.) 6 November 1985 see the whole document --	1-3
Y	US, A, 3996152 (J.B. EDWARDS) 7 December 1976 see the whole document; particularly column 8, line 5 --	1,2
Y	EP, A, 0122141 (UNILEVER PLC) 17 October 1984 see claims; page 8, line 24 --	1,2
Y	EP, A, 0301882 (UNILEVER N.V.) 1 February 1989 see claims; page 4, line 30; page 5, lines 25-26 --	1,2
	./.	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 12th April 1991	Date of Mailing of this International Search Report 11. 06. 91
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer M. PEIS M. Peis

International Applicatic .o PCT/EP 91/00212

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A,P	EP, A, 0368575 (IMPERIAL CHEMICAL INDUSTRIES) 16 May 1990 see the whole document	1,2,4
A	EP, A, 0120659 (IMPERIAL CHEMICAL INDUSTRIES) 3 October 1984 see claims	1,2,4,6
A	US, A, 4891147 (R.L. GRAY et al.) 2 January 1990 see claims 1-6,11-13	1
A	US, A, 4166794 (S. GREY) 4 September 1979 see claims	1,2,4

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

EP 9100212
SA 43972

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/06/91
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9100212

SA 43972

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82