⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 037 184**
B1

⑫ **EUROPEAN PATENT SPECIFICATION**

㊺ Date of publication of patent specification: **23.01.85**

(51) Int. Cl.^{4}: **C 11 D 3/39,** C 11 D 17/00

㉑ Application number: **81300964.4**

㉒ Date of filing: **09.03.81**

(54) **Liquid detergent compositions, their manufacture and their use in washing processes.**

㉚ Priority: **01.04.80 GB 8010885**
01.04.80 GB 8010887

㊸ Date of publication of application:
07.10.81 Bulletin 81/40

㊺ Publication of the grant of the patent:
23.01.85 Bulletin 85/04

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(56) References cited:
FR-A-2 175 922
FR-A-2 321 302
US-A-4 051 058

The file contains technical information submitted after the application was filed and not included in this specification

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EP 0 037 184 B1

Courier Press, Leamington Spa, England.

Description

The present invention relates to liquid detergent compositions and more particularly to built liquid detergents compositions containing an active oxygen-containing compound.

For many years, many solid heavy duty washing compositions have contained one or more active oxygen-containing compounds (sometimes called per-compounds or peroxygen compounds) in order to oxidise and de-colourise various stains commonly encountered in household laundry, and to thereby complement the other components of the washing composition. However, it has been recognised that even in such solid compositions where the active oxygen-containing compounds and the alkaline components of the washing composition are both in solid form, there is a tendency for the activity of the active oxygen-containing compound to diminish during storage of the washing composition, on account of interaction of the percompound with the alkaline components and water vapour in the air surrounding the composition. The rate of loss of activity of the solid active oxygen-containing compound can be significantly reduced to acceptable levels by contacting the compound with various peroxygen compound stabilisers, of which a particularly appropriate sort comprises alkali or alkaline earth metal silicates, as described for example in GB—A—1553505 to Interox Chemicals Ltd., and alternatively or additionally coating the solid particles of the compound with a suitable organic or inorganic barrier to prevent the compound coming into contact with the other components of the washing composition. Examples of compositions stabilised by coating are described in US—A—3847830 assigned to Laporte Industries Limited and US—A—3992317 and US—A—4105827, both assigned to Interox S.A.

Examination of the prior art demonstrates a marked reluctance on the part of producers of detergent compositions to employ built aqueous alkaline liquid detergent compositions containing a peroxygen compound. For example, US—A—3850831 assigned to Mo Och Domsjo Aktiebolag deliberately employs non-aqueous compositions instead of aqueous compositions because they were unable to prevent rapid decomposition of the peroxygen compound during storage of the aqueous composition. In US—A—3852210, assigned to Flow Pharmaceuticals Inc., the liquid detergent composition described was builder-free, and its pH was adjusted by addition of acid to pH 4 in the example in which the stability of that composition was tested. More recently, in US—A—4,166,794, assigned to Colgate-Palmolive liquid bleach-softener compositions containing hydrogen peroxide were described, but such compositions contained cationic compounds instead of anionic surfactants, did not include a builder and their pH was adjusted to pH 4 to 5.

It is not surprising that the prior art sought ways to side-step the problems of providing a storage-stable heavy duty alkaline liquid detergent composition containing an active oxygen-containing compound such as hydrogen peroxide, because the problems are much greater than for solid compositions. By virtue of the fact that all the components are in the liquid phase, they are inevitably always in intimate contact with each other and cannot be separated from the others simply by a coating technique. This would not matter if the other components in combination were compatible with hydrogen peroxide, but in practice this is not the case. Two of the main contributors to hydrogen peroxide instability are anionic surfactants and builders such as polyphosphate which are both time-honoured, readily available and cost effective components of washing compositions, but which generate mildly alkaline conditions in an aqueous concentrate, often from pH 8.5 to 9.5 when present in the ranges of concentrations suitable for a detergent concentrate. The instability of hydrogen peroxide under such conditions can be seen from the following results. A solution of 10 percent tetra-potassium pyrophosphate and 5 percent hydrogen peroxide in demineralized water lost 62 percent of the available oxygen (activity of the active oxygen-containing compound) within a fortnight and a similar composition containing the corresponding sodium salt lost 44 percent within a week.

The significance of this becomes more plain when it is recalled that pyrophosphate in low concentrations, and especially under acidic conditions, is employed as a stabilizer for hydrogen peroxide. It will, thus, be recognised that the problem of providing a storage stable aqueous alkaline detergent composition and especially a built detergent composition presents difficulties that are peculiar to such compositions.

It has also been suggested that detergent compositions can include organic complexing agents as builders. When small amounts of organic complexing agents, such as about 1 percent by weight were tested at 32°C for long-term storage compatibility with hydrogen peroxide under mildly alkaline conditions, the result was, in general, an unacceptable loss of peroxidic activity. For example, an aqueous hydrogen peroxide solution containing 1 percent of ethylenediamine tetraacetic acid, tetra sodium salt lost a remarkable 96 percent within two weeks and that containing 1 percent of nitrilotriacetic acid, trisodium salt lost an incredible 79 percent in one week. A solution of hydrogen peroxide containing 1.3 percent of ethylene diamine tetra(methylene phosphonic acid), potassium salt lost 50 percent within a week. Clearly, the aforementioned results demonstrate that in such compositions the hydrogen peroxide is not storage stable under such alkaline conditions. Moreover, when alkali metal silicates which acts as stabilisers for solid percompounds are introduced even at 1% into stabilised alkaline detergent compositions described hereinafter a more rapid loss of available oxygen occurs. Therefore, the need for a storage-stabilised aqueous alkaline detergent composition is still to be satisfied.

There is a further complicating factor to be borne in mind when considering the feasibility of producing a useful liquid detergent composition that is stabilised against loss of peroxide activity. When such liquid compositions are used for laundering, their primary use, they are merely diluted so that there is no change in the physical state of the composition such as occurs when a solid composition is dissolved. Hence, those compounds which are included in the concentrated detergent composition to prevent interaction of the peroxide with other components during storage inevitably are still present in the wash solution in the same weight ratio to the peroxide and with continuing capability to prevent interaction. It would therefore be expected that if a high ratio of stabiliser to peroxide is employed in order to obtain a mix of improved storage stability, the rate and extent of utilisation of the peroxide would be impaired, which would manifest itself in impaired washing performance.

It is an object of the present invention to provide a liquid detergent composition in a concentrated form which can be diluted to form a washing and laundering solution.

It is a further object of some embodiments of the present invention to provide aqueous alkaline detergent compositions containing a builder and hydrogen peroxide stabilised sufficiently to avoid the use of special vented containers.

It is a still further object of certain embodiments of the present invention to provide aqueous alkaline detergent compositions containing a builder and hydrogen peroxide stabilised against excessive decomposition during storage, which provide a washing performance substantially the same as for the corresponding unstabilised composition.

According to the present invention there is provided a stabilised aqueous built liquid detergent composition comprising a surfactant, builder, water, hydrotrope and if desired one or more detergent adjuvants characterised in that contains

- (i) at least 3% surfactant selected from anionic sulphate or sulphonate surfactants and non-ionic ethoxylate surfactants;
- (ii) at least 5% of a builder selected from alkali metal polyphosphates and carboxylic complexing builders;
- (iii) at least 2% hydrogen peroxide;
- (iv) sufficient alkali metal aryl sulphonate hydrotrope to maintain the composition in a single phase, either by itself or in conjunction with other components; and
- (v) a stabilising amount of a combination comprising
  - (a) from 0.075 to 1% of an aminomethylene phosphonate or hydroxyalkyl diphosphonate, together with
  - (b) from 0.08 to 1% of a polyhydroxy aliphatic carboxylate in a weight ratio to (a) of from 3:1 to 1:3 and/or up to 15% of a low molecular weight mono-hydroxy aliphatic alcohol in a weight ratio to (a) of at least 2.5:1.

Percentages for any component herein are by weight, based on the composition, unless specifically stated to the contrary.

The anionic surfactant, especially suitably, is an alkyl aryl sulphonate and in order to assist its biodegradability is preferably a linear alkyl aryl sulphonate. The alkyl group preferably contains from 9 to 18 carbon atoms, particularly the decyl, dodecyl or tetradecyl groups. Although other aryl groups can be used, the aryl group is normally benzene. Examples of suitable commercially available alkali metal alkyl aryl sulphonates are available under the trade names Warcodet K54 from Warwick Chemicals, England, Nansa SS60 from Albright and Wilson, England and especially Hetsulf 60S from Heterene Chemicals Co., New Jersey. Other anionic surfactants that demonstrate compatibility with hydrogen peroxide include alkyl sulphosuccinamate, the alkyl group preferably containing from 12 to 18 carbon atoms, a commercially available example of such a compound is available under the tradename Alcopol FA from Allied Colloids, England. Suitable anionic sulphate surfactants include primary alcohol sulphates and primary alcohol ether sulphates, the alkyl group in the alcohol moiety of such compounds normally containing from 9 to 18 and frequently from 12 to 15 carbon atoms. Commerically available examples of such compounds include Perlankrol D.S.A., E.S.D and E.A.D. being respectively a sodium primary alcohol sulphate, sodium primary alcohol ether sulphate, and ammonium primary alcohol ether sulphate, all available from Diamond Shamrock. Other useable sulphonate surfactants include n-alkane and olefin sulphonates, the aliphatic moiety normally containing at least 12 and often from 13 to 18 carbon atoms. Examples of such compounds are available under the trade name Hostapur S.A.S. and O.S. from Hoechst (UK). Mixtures of any two or more of the foregoing anionic surfactants can be employed. Generally the concentrate contains at least 3% of the anionic sulphate and/or sulphonate surfactant and usually not more than 15%.

In many embodiments of the present invention, the non-ionic surfactant component of the composition is selected from primary alcohol ethoxylates and linear secondary alcohol ethoxylates. The alcohol component in each of these compounds preferably has a carbon chain length of R in the general formula $RO(C_2H_4O)_nH$ of at least 9 and frequently not more than 18 carbon atoms, extending away from the ethoxylate moiety. In many commercially available compounds, the linear carbon chain of R is in the range of from 11 to 16 carbon atoms and in many cases the surfactant is derived from a mixture of alcohols.

In the ethoxylate moiety of such compounds, the degree of ethoxylation n is generally in the range of from 5 to 20 and in many very desirable ethoxylates, n is from 7 to 12. However, it is desirable also to take into account the relative proportions of the two moieties in the non-ionic surfactant involved, and this is often expressed in terms of the weight proportion of the ethoxylate moiety in the molecule. The proportion is desirably at least 50%, normally not more than 85% and preferably at least 60% up to 80%. A most desirable range of surfactants contains from 60 to 80%, preferably 65 to 75% by weight of the ethoxylate moiety and the alcohol moiety is a linear C_{12}, C_{13}, C_{14}, C_{15} or C_{16} or a mixture of linear alcohols having an average carbon chain length within the range of 12 to 16. It will be recognised that in many preferred alcohol ethoxylates, the ratio of the number of carbon atoms in R to the degree of ethoxylation n in the ethoxylate moiety is generally in the range of from 3:2 to 2:1. Examples of suitable commercially available alcohol ethoxylates are available under the tradenames Synperonic A.7, A.9, and A.11, all from I.C.I., England, in which R is a mixture of C_{13} and C_{15} and the degree of ethoxylation are respectively 7, 9 and 11, Tergitol 15-S-9 and 15-S-12, from Union Carbide, U.S.A., being C_{11-15} linear secondary alcohol ethoxylates, having degrees of ethoxylation of respectively 9 and 12, Lubrol 12 A.9 and 17 A.10 from I.C.I., England, the average chain lengths of R being respectively 12 and 17 and the degrees of ethoxylation 9.5 and 10, Ethylan CD9112 and D259, both from Diamond Shamrock, and Brij 35, 78 and 98, being respectively the lauryl, stearyl and oleyl ethers of polyoxyethylenes from I.C.I., and Renex 20 being a polyoxyethylene mixed fatty acid ester available from Honeywell Atlas. A further polyethylene oxide condensate that can be employed is available under the trade name Mykon 100 from Warwick Chemicals. Mixtures of two or more ethoxylated surfactants can be used. The amount of nonionic surfactant used is normally at least 3% and frequently not more than 15%.

A third essential component of the built liquid detergent composition of the present invention is a builder selected from polyphosphate and carboxylic acid complexing builders. Amongst the polyphosphates, it is especially suitable to employ pyrophosphates, and more particularly the tetrapotassium or tetrasodium salts or mixtures thereof. In many embodiments, the tetra-potassium pyrophosphate salt is selected, by virtue of its solubility being superior to that of the corresponding sodium salt in concentrated liquid detergent compositions. Although it is possible to employ a di-alkali metal di-hydrogen pyrophosphate as a proportion of the polyphosphate builder, its incorporation e.g. 30—60% of the polyphosphate builder mix tends to produce a lower pH in the washing solution obtained simply by dissolution of the liquid detergent composition, providing a wash and stain removal detectably inferior to that obtained when the tetra alkali metal salt is employed instead, in otherwise identical compositions. The polyphosphate can be introduced into the detergent composition either as a solid which is dissolved, or in the form of an aqueous solution, but the percentages given herein are of a dry weight basis.

The organic complexing builders contemplated herein tend to fall into three classes, hydroxycarboxylic acid, aminocarboxylic acid and oxacarboxylic acid. Amongst hydroxycarboxylic acid builders, a particularly suitable one is citric acid, usually introduced as the tri-alkali metal salt, and on cost grounds, as the trisodium salt. Mixtures of the hydroxycarboxylic acid builders and polyphosphates, for example citric acid and tetrapyrophosphate both in salt form, can also be used, often in a weight ratio of 2:1 to 1:2. Where a rather higher pH of the mix is desired, an alkaline adjuster, sodium metaborate is very suitable. It is desirable to use not more than about 20% of pyrophosphates and where tripolyphosphate is used not more than about 10 to 15%.

Within the class of aminocarboxylic acid builders, nitrilo triacetic acid, normally alkali metal salt thereof, (NTA) is most prominent. Generally use of the salt tends to produce a somewhat higher pH than of a corresponding weight of hydroxycarboxylic acid complexing builder and probably as a result thereof the resultant built detergent composition tends to show slightly inferior hydrogen peroxide stability. At higher concentrations within the aforementioned range for builders, it is preferable to downwardly adjust the pH of the mix by introducing it in part acid form. In practice, often not more than 10% NTA is employed. It can be employed to complement hydroxycarboxylic acid builders, the resulting mixture therewith generating an intermediate pH, for example a mixture of 12 to 6% sodium citrate and 3 to 9% NTA. Similar mixtures of NTA with polyphosphates such as tetrapyrophosphates can also be utilised.

Within the class of oxacarboxylic acids, carboxymethyloxysuccinate deserves mentioned. For practical reasons it is preferable to employ from 5 to 8% of this builder. Where higher than 8% builder is desired, the balance above 8% is more advantageously provided by one of the other aforementioned builders.

The sulphonate hydrotropes are suitably the alkali metal salts of benzene or methyl-substituted benzene sulphonates, most commonly xylene sulphonate and toluene sulphonate. Preferably the sodium or potassium salt is employed. A proportion of the hydrotrope can be provided by incorporation of one or more ethoxylated phosphate esters. Such esters chemically can be regarded as phosphate ester derivatives of the aforementioned non-ionic ethoxylate surfactants described hereinbefore. In many embodiments, the product used is a mixture of the two. The degree of ethoxylation in the ethoxylated moiety is generally the range from 2 to 12 and often in the range of 2 to 6, and the carbon chain length of the hydrophobic alkyl group R is normally from 9 to 18. Whilst it is possible to employ the closely related ethoxylated alkyl phenol phosphate esters, in which the alkyl group is often from C_8 to C_{12}, their use for such purposes is being increasingly viewed with hostility by water authorities because suitable methods have not yet been found to degrade them biologically. The phosphate esters often are available in the acid form and they can be employed as such in the liquid detergent compositions of the present invention, but their use in that way does tend to lower the pH of the composition and of the subsequent washing solution and if desired, the phosphate ester can be partially or completely neutralised with alkali metal hydroxide, especially sodium or potassium hydroxide or ammonium hydroxide.

In general, the total proportion of sulphonate hydrotrope plus ethoxylated phosphate ester is normally selected within the range of from 3% to 12%, of which the sulphonate hydrotrope is frequently from 3 to 9% and the ethoxylated phosphate ester the balance. A small proportion of ethoxylated phosphate ester, for example from 1 to 3% can be advantageous in improving the washing ability of the composition for certain commonly encountered stains like cocoa, for example where the ratio of the anionic to non-ionic surfactant is relatively high, such as at approximately 1:1 or higher.

The stabiliser system for hydrogen peroxide in the composition comprises an amino methylene phosphonate or hydroxyalkyl diphosphonate and either or both of a low molecular weight aliphatic alcohol, and a polyhydroxy aliphatic carboxylate. The low molecular weight aliphatic alcohol is most preferably ethanol, particularly in the view of its combination of properties in that, not only does it effectively and surprisingly improve the storage stability of hydrogen peroxide in the composition, in combination with the other components despite the fact that its presence tends to increase the alkalinity of the solution, as measured by a standard pH electrode, but it also cooperates with the aforementioned hydrotropes in retaining a one phase system and consequently provides higher flexibility in formulating compositions. The low molecular weight aliphatic alcohol is employed, preferably in an amount of at least 5% of the composition and is not more than 15%. In many embodiments it is employed within the range of from 7 to 12%. The higher weight aliphatic alcohols such as propanol and butanol are considerably less desirable by virtue, it is believed, of their poorer water solubility so that the compounds can be employed to only a much smaller proportion of the composition than can ethanol. By way of example, many of the compositions described herein containing comparatively high amounts of surfactant and builder can remain in a single-storage stable phase when they contain 10% of ethanol, but when the same amount of butanol or propanol is employed instead, phase separation occurs.

The polyhydroxyaliphatic carboxylate generally contains at least 5 carbon atoms and normally up to 10 carbon atoms. Although the carbon chain in the molecule can be branched, in many effective examples the compound is linear, terminating at one end in a carboxylate group, and preferably having a chain length of 5, 6 or 7 carbon atoms. Desirably all, or at least the majority of the remaining carbon atoms are substituted by an hydroxyl group. The compound can be in acid form, but preferably is neutralised with an alkali metal, preferably sodium or potassium. Preferred compounds of this class include the acid or neutralised forms of gluconic acid and glycero-ido heptonate. The polyhydroxy compound is employed in an amount of at least 0.08% of the composition and not more than 1%.

The phosphonate component of the stabilised system can be introduced in the acid form, but it will be recognised that, if the acid form is employed initially, to a certain extent the resultant solution will have a lower pH and impairment of overall washing performance can thereby ensue. The phosphonate component is therefore introduced preferably in an at least partial alkali metal salt form. By the term "amino methylene phosphonates" is meant any compound containing an amino group substituted by a methylene phosphonic acid group or a salt thereof. Many suitable phosphonates can be represented by the general formula, in acid form:—

$$[H_2O_3PCH_2]-[N(CH_2PO_3H_2)(CH_2)_p]_q-[N(MePO_3H_2)_2]$$

in which p is normally from 2 to 6 and q is normally from 0 to 2. Highly desirable examples are ethylene diamino tetra (methylene phosphonic acid) hexa potassium salt, and diethylene triamino penta (methylene phosphonic acid) or hexa potassium salt. Further suitable examples include hexamethylene diamino tetra (methylene phosphonic acid), penta sodium salt and amino tri(methylene phosphonic acid) penta sodium salt. Where desired, one or more of the methylene groups linking the amino groups can be substituted at the carbon atom by a lower alkyl group or at one carbon only by an hydroxyl group or the substituents of two such suitably spaced, preferably adjacent carbon atoms can combine to form cycloaliphatic ring preferably containing 5 or 6 carbon atoms.

The aliphatic diphosphonates can conveniently be represented in acid form by the formula $YZC(PO_3H_2)_2$ in which Y represents an hydroxyl or amino group, the amino group itself optionally being substituted by a lower alkyl, a lower alkylamino or a lower hydroxyalkyl group, lower indicating from 1 to 4 carbon atoms, and Z represents a lower alkyl, preferably methyl group. Examples of such diphosphonates include 1-amino ethane-1,1-diphosphonic acid and 1-hydroxyethane-1,1-diphosphonic acid, and preferably the alkali metal salts thereof. Mixtures of any two or more of the aforementioned amino-methylene phosphates and/or diphosphonates can be employed, as desired. Such a compound or compounds are employed in an amount of at least 0.075% by weight of the composition and not more than 1% and often the amount is selected from the range of 0.1% to 0.4%. Use of larger amounts than 1% do not in general repay the additional cost of their incorporation, and for each phosphonate an amount is reached beyond which increasing the amount leads to impaired stabilisation.

When it is desired to include both the polyhydroxycarboxylate and the phosphonate in the composition, an extremely convenient and desirable way of so doing is to first obtain or produce a premix of these two components in the desired weight ratio e.g. 4:3 of the former to the latter and then use the premix.

In the detergent compositions of the present invention, the weight ratio of the polyhydroxy compound to the phosphonate is within the range of 3 to 1 to 1 to 3 and often within the range of 2 to 1 to 1 to 1, and their combined % is preferably from 0.2 to 1.0%. In other highly desirable embodiments of the present invention, the lower molecular weight aliphatic alcohol is selected within a weight ratio to the phosphonate of from 50:1 to 2.5:1, and preferably from 50 to 1 to 20 to 1, when the stabiliser system consists of the phosphonate and the alcohol, preferably employing a comparatively high amount of the phosphonate, namely at least 0.15% generally up to 0.4%. Most desirably the weight ratio is varied inversely to variation in the phosphonate concentrate. The product of the weight ratio of alcohol to phosphonate and the concentration of the phosphonate expressed as a percentage in the two component stabiliser system is preferably at least 8 and often from 9 to 12. It is specially desirable to employ all three stabiliser components together in the detergent composition especially in a combined amount of at least 0.2% for the polyhydroxy compound and the phosphonate, and at least 5% of the aliphatic alcohol. In many embodiments, it is convenient and advantageous to select the components within the ranges of 0.1 to 0.4% for each of the polyhydroxy and phosphonate components and from 5 to 12 and particularly from 8 to 12% for the aliphatic alcohol, especially ethanol.

The hydrogen peroxide can conveniently be incorporated in the form of the appropriate amount of concentrated hydrogen peroxide, e.g. 35 to 85% W/W hydrogen peroxide commercially available, which often contains from 10 ppm pyrophosphate. It is often incorporated in the solution in the range of from 3 to 10%, frequently from 5 to 8% and for industrial uses often from 10 to 20% (expressed as 100%). Lower concentration of hydrogen peroxide could be employed, but in general these would not enable a desirable amount of active oxygen to be provided in the washing solution unless the concentration of the other components in the detergent composition were correspondingly reduced also. It will be recognised that the concentration of hydrogen peroxide in the range 5 to 8% in the detergent composition when diluted to form a washing solution by a factor selected within the range of 100:1 to 1000:1 and often preferably from 200:1 to 500:1 can readily provide active oxygen concentrations commensurate with those provided by normal concentrations of many heavy duty solid detergent compositions or by the addition of an active oxygen bleach at recommended levels to commercially obtainable active oxygen-free liquid detergents.

In practice, the total proportion of components other than water and hydrogen peroxide normally is selected to be not greater than 52%. Use of a higher proportion, particularly where the composition contains relatively high proportions of builder and anionic surfactants tends to become more sensitive to phase separation. Although a total proportion, e.g. below 20% of such components could be employed in compositions, whether built or not, it is more desirable to provide such components to a total proportion of at least 20% and more preferably at least 30% of the liquid composition, not only from the point of view of reducing the volume of unnecessary water to be transported but also because the user often associates dilute products with inferior products. In many embodiments, the totaled proportions of components other than water and hydrogen peroxide in the built compositions is at least 35% and frequently not more than 45%.

The preferred concentration of polyphosphate or citrate in the detergent compositions is from 9 to 16%. The proportion of anionic sulphate or sulphonate surfactant plus ethoxylated non-ionic surfactant in the concentrate is preferably within the range of from 6 to 15%, the weight ratio of anionic to non-ionic surfactants normally being selected within the range of 5:2 to 2:5, in order to produce a balanced surfactant mix for the treatment of the general mix of household stains. Where the composition is intended for a more specific stain, one that is known to be sensitive to a particular type of surfactant, then anionic to non-ionic surfactant weight ratios outside the aforementioned range can be readily contemplated. Hence, e.g. where the product is intended primarily for greasy stains, a lower anionic to non-ionic ratio can be more desirable, for example in the range of 1 to 2.5 to 1 to 5. Additionally, in determining the actual amounts of various components to be incorporated in the mixture, it is desirable to maintain the builder e.g. polyphosphate or citrate to anionic surfactant ratio within the range of 1:1 to 5:1 and particularly from 2:1 to 4:1 so as to take advantage of the synergistic interaction between those two components. The anionic surfactants are present preferably in an amount from 3 to 8%, and often at least 4%, and the builder is preferably polyphosphate or citrate, frequently at from 9 to 16%, and the non-ionic surfactant content is normally at least 3% and again often at least 4%, with the result that the anionic sulphonate or sulphate surfactant and nonionic ethoxylated surfactant are present in such compositions in total amount advantageously of at least 8%.

Additionally, it is desirable for the customary reasons to incorporate in the detergent composition a small proportion of detergent adjuvants, the total amount of adjuvants, generally up to 8% and in many cases, being from 1 to 5%. Examples of adjuvants include soil anti-redeposition agents, for example polyvinylpyrrolidone, and sodium carboxymethylcellulose, often in an amount of from 0.1 to 0.3% and an optical brightener or a range of brighteners to allow for the various sorts of fibres from which household laundry articles are made, to a total amount often in the range of 0.5 to 2% of the composition. It is generally desirable to select as brightener those of the stilbene type which have demonstratable storage compatibility with hydrogen peroxide in solution. In general, the composition will also contain a very small proportion of alkali metal sulphate formed during the neutralisation of the anionic surfactant during its preparation. The compositions can also include a small amount of mono- or di or tri ethanolamine, or alkali metal borates as pH adjusters, but alkali metal silicates and carbonates are excluded, or of amphoteric surfactants such as imidazoline based fatty acid carboxysulphates, e.g. from 0.5 to 2%. The adjuvants can also include a small amount of foam regulators, for example ethylene oxide/propylene oxide copolymers such as are available from Ugine Kuhlmann, France under the Tradename Pluronic, grades L42 and F.108, and soaps i.e. alkali metal salts of aliphatic carboxylic acids, having a chain length of at least 8 carbon atoms and normally from 10 to 20 carbon atoms, examples of which include stearate, and soaps derived from natural sources, particularly tallow and coconut oils, again often up to 2% by weight. Other adjuvants can comprise compatible tarnish inhibitors, cationic softeners, dyes, perfumes and thickeners, such as xanthan gum for citrate-built formulations. The amounts of the adjuvants can be varied by the skilled worker within or outside the exemplified ranges.

Some especially preferred built compositions according to the present invention comprise from 8 to 12% in total of anionic sulphate or sulphonate surfactant and nonionic ethoxylated surfactants of which preferably from 3 to 8% is anionic sulphate or sulphonate surfactant and preferably from 2 to 8% is non-ionic ethoxylated surfactant, from 9 to 15% alkali metal preferably, potassium tetrapyrophosphate; from 3 to 6% alkali metal aryl sulphonate hydrotrope; from 5 to 12%, preferably 8 to 12% ethanol; from 5 to 10%, preferably 5 to 8% hydrogen peroxide; from 0.2 to 1% in total of a polyhydroxy linear C_6 or C_7 aliphatic carboxylate, preferably an alkali metal gluconate and an alkali metal methylene phosphonate complexing agent, preferably ethylene diaminetetra methylene phosphonate or hexamethylene diamine tetra methylene phosphonate or diethylene triamine penta methylene phosphonate, preferably in a weight ratio of from 2:1 to 1:1; up to 3% of detergent adjuvants such as described herein, including a soil antiredeposition agent and an optical brightener; and the balance, water, preferably from 55 to 65%. Other compositions include corresponding compositions containing at least 5% builder and in which all or part of the 9—16% polyphosphates or citrate builder is replaced by 4 to 7% carboxymethyloxy succinate or 3 to 9% NTA.

In a modification of the invention, no builder is employed, and instead the compositions contain additional surfactant, mainly nonionic surfactant. Consequently, unbuilt detergent compositions according to the present invention contain at least 5% nonionic surfactant and in total at least 10% surfactants. The presence of the extra surfactants means that the balance of anionic to nonionic generally favours the nonionic to a much greater extent than in built compositions according to the present invention. Thus, in unbuilt compositions, the anionic surfactant is normally selected in the range of 3 to 15%, but the nonionic is normally selected in the range of 5 to 35%. The weight ratio of anionic surfactant to nonionic surfactant is preferably selected in the range of 1:1 to 1:6, and in practice is often likely to be in the range of 1:3 to 1:6. The anionic surfactant often represents from 3 to 10% of the unbuilt composition and the nonionic surfactant at least 15% and frequently from 20 to 35%. In a specially preferred unbuilt compositions, the surfactants concentration is not more than 40% and particularly is from 25 to 40%, of which the anionic comprises from 3 to 8% and the nonionic from 22 to 35%. The unbuilt compositions can, in practice, be slightly more concentrated than the bulit compositions. Thus, the total proportion of components other than water and hydrogen peroxide is generally up to 65% and frequently from 40 to 60%.

In the other respects, for examle selection of and concentrations of hydrotrope, stabiliser, hydrogen peroxide and adjuvants, the aforementioned description for the built compositions applies likewise to the unbuilt compositions according to the present invention.

It is especially desirable that the compositions, either built or unbuilt, be free from alkali metal carbonates or silicates.

The compositions described herein can be made conveniently by mixing the components in the desired proportions in a mixing tank, and to avoid and minimise loss of hydrogen peroxide by decomposition it is preferable to add it as the last step, or at least after the two stabiliser components have been introduced. The surfactants are preferably mixed at a moderately elevated temperature, often from 35 to 60°C, and then combined with the other components which brings the mixture to near ambient for the introduction of the hydrogen peroxide. Preferably the polyphosphate is introduced in aqueous solution, either supplied as such by the manufacturer or prepared on site by dissolution. The minor components, detergent adjuvants and sulphonate hydrotrope can be mixed in with the surfactant mix. The various solutions and water can be introduced consecutively or concurrently into the mixing tank except as mentioned hereinbefore that the hydrogen peroxide solution is preferably introduced last or starting last. Although the process has been described in a batch manner it will be readily apparent to a skilled engineer how to carry out the process on a continuous basis. The composition, when thoroughly mixed, can then be poured into containers or dispensers. By virtue of the superior storage stability of at least some of the embodiments, of the invention, such as those losing less than 1% Avox a week the containers or dispensers for such embodiments need not be of the specially vented and thus expensive types, but instead containers having a slightly loose fitting closure means, such as cap or stopper can be used.

According to a further aspect of the present invention, washing processes, or laundering, according to the present invention can be carried out by diluting the liquid concentrate of the present invention with water to a desired extent, and contacting the aqueous washing solution with the articles to be washed at any temperature from ambient to the boiling point of the solution. In many processes, the process is carried out at hand hot temperature or hotter, often a temperature of at least 45°C and, depending on local washing customs, frequently at a temperature of at least 60°C.

It is a feature of the present invention that there is provided a one shot liquid detergent composition containing not only hydrogen peroxide, but also a high concentration of anionic and non-ionic surfactants of the order needed to form a washing solution without the addition of any further components. However, if it is desired, the detergent composition described hereinbefore can be employed in conjunction with one or more bleach activators, i.e. compounds which react in aqueous solution with hydrogen peroxide to generate peroxy acids, preferably added separately to the washing solution to prevent premature interaction. Such compounds are normally N-acyl or O-acyl compounds. Typical examples of the classes of each activator which each represents, includes N,N,N',N'-tetraacetyl-ethylene-diamine of N-acylated alkyleneamines, benzoic or phthalic anhydride, tetra acetyl glycoluril, N-alkyl-N-sulphonyl-carbonamide, N-acylhydantoins, carbonic acid esters, triacetyl cyanurate, O,N,N'-tri substituted hydroxylamines and diacyl peroxides such as benzoyl glutaryl peroxide and diphthaloyl peroxide. In comparison with the use of such activators in conjunction with solid detergent compositions, inter-reaction between the active oxygen containing compound and the activator can occur more quickly by virtue of the fact that the hydrogen peroxide is already in solution whereas for solid peroxygen compounds, and especially the commonly used sodium perborate tetrahydrate at hand-hot temperatures or cooler, its rate of dissolution can be a restraining factor. If an activator is employed in conjunction with the detergent composition, then the preferred washing temperatures tend to be somewhat lower, preferably falling in the range from ambient to 60°C. Naturally, a convenient mole ratio of activator to hydrogen peroxide is from 2 to 1 to 1 to 2, and especially 1 to 1 in the washing solution.

Generally, the concentrates of the present invention are diluted to produce washing solutions containing from 0.1 to 1.5 gpl surfactant. In many cases, the concentration of surfactants is within the range of 0.2 to 0.6 gpl and such concentrations can be obtained from many of the preferred detergent compositions of the present invention such as those containing at least 8% surfactants at a dilution of greater than 100 to 1, and often at a dilution of from 200 to 1 to 300 to 1.

The washing period can range from as low as a minute or a few minutes e.g. 5 minutes at washing temperature at or near the boiling point of the washing solution, e.g. from 90 to 100°C up to a period of several hours at cooler wash temperatures, such as overnight steeping at ambient temperature. The washing period can be varied at the discretion of the user. Typical washing times at a temperature of 40 to 70°C are of the order from 5 to 40 minutes.

In addition to laundry use, the compositions can be used neat or after dilution to cleanse hard surfaces, such as those of enamel, paint, metal, plastic, wood, glass or ceramics.

Having described the invention in general terms, specific embodiments will be described hereinafter more fully by way of example only. It will be recognised that by employing his general knowledge and the information contained hereinbefore, the expert in the field of liquid detergents will be able to vary the proportions of components in the composition.

Examples 1—34 and 43—64

Liquid detergent compositions according to the present invention were prepared by the following general route, employing the weight proportions summarised in Tables 1, 2 and 3 below.

First, a mixture of the anionic and nonionic surfactants in the correct proportions was heated to approximately 40 to 45°C with constant stirring until a clear solution occurred. The sulphonate hydrotrope and ethoxylated phosphate ester when employed were then introduced in the desired proportions with stirring followed by the builder, often together with a proportion of the total deionised water content of the mixture which cooled the mixture. Next the ethanol the residual amount of water the polyhydroxy carboxylate and the phosphonate components were added as well as the detergent adjuvants, where employed. Finally, the hydrogen peroxide solution was introduced. The mixture was vigorously stirred.

The components used in the compositions were as follows, for many of which the tradename, including grade designation letters and numbers are also given, as well as their supplier if reference to the tradename has not been made hereinbefore:—

anionic surfactants

A_1	sodium dodecyl benzene sulphonate "Hetsulf 60S"
A_2	sodium linear alkyl benzene sulphonate "Nansa SS60"
A_3	sodium primary alcohol sulphate "Perlankrol DSA"

amphoteric surfactant

A_4	imidazoline based-coconut carboxysulphate hydrophile "Miranol 3MCT" (Miranol Inc.)

nonionic surfactants

N_1	C_{15} sec alcohol ethoxylate ($n=9$) "Tergitol 15S9"
N_2	middle cut primary C_{12}—C_{15} alcohol ethoxylate ($n=9$) "Ethylan D259"
N_3	synthetic primary alcohol ethoxylate ($n=7$) "Synperonic A7"
N_4	lower cut primary alcohol ethoxylate ($n=9$) "Ethylan CD19"

Hydrotropes

HX_1	sodium xylene sulphonate "SX96" (Pilot Chemical Co., Los Angeles)
HX_2	sodium xylene sulphonate "Eltesol SX30" (Albright & Wilson, England)

Phosphate esters

HE_1	ethoxylated phosphate ester "Triton QS30"
HE_2	ethoxylated phosphate ester ($n=2$) "Briphos L2D" (Albright & Wilson),

polyhydroxycarboxylate

SG	sodium gluconate

phosphonate stabiliser

SP_1	hexapotassium ethylene diamine tetra (methylene phosphonate)
SP_2	aminotris(methylene phosphonic acid)
SP_3	diethylenetriamine penta(methylene phosphonic acid)
SP_4	hexamethylenediaminetetra(methylenephosphonate) hexapotassium salt
SE	Ethanol-industrial grade methylated spirits
HP	Hydrogen peroxide—35% W/W aqueous solution containing 50 ppm pyrophosphate

Builder

B_1	Potassium tetrapyrophosphate (solid)
B_2	Potassium tetra pyrophosphate (aqueous solution) "Kalipol 4KP" (Albright & Wilson)
B_3	Potassium polyphosphate (chain length 4) "Kalipol 18" (Albright & Wilson)
B_4	Sodium Citrate
B_5	Nitrilotriacetic acid, sodium salt
B_6	Trisodium carboxymethyloxysuccinate.
Water	Deionised except where the marked * in which Widnes, Cheshire municipal water was used untreated.

Similar compositions to one or more of the exemplified compositions were obtained by substituting alternative nonionic surfactants such as poly oxyethylene alkyl ethers or poly oxyethylene alkyl ethers for the specified ethoxylates, and/or substituting ammonium primary alcohol ether sulphate for the specified sulphate surfactant, and/or by substituting ethoxylated phosphate mono ester of higher degree of ethoxylation for the specified di-ester, and or by substituting other polyphosphate builders for those specified.

The storage stability trial for Tables 1 and 2 was effected by transferring a small sample of the given composition into a clean plastic bottle housed in a constant temperature enclosure at 32°C. The available oxygen concentration (Avox) in the composition was determined by the standard acidified potassium permanganate titration method on a small portion extracted from the sample and the result obtained after storage for a given period compared with the original content. The result given in Tables 1 and 2, is the percentage of Avox lost from the hydrogen peroxide after 3 weeks storage, except in Examples 43 to 52 in which it is after 4 weeks storage. The storage stability trials for Table 3 were carried out in the same manner as that for Tables 1 and 2 except that the temperature of the enclosure was 50°C in order to accelerate proceedings. The result is given after 24 hours, approximately. The gluconate and phosphonate were introduced separately, except in Examples 1 to 30 and 43 to 58 where they were provided in the form of a premix of SG and SP_1 available under the gradename Polyron 1020.

TABLE 1

Weight % of component in composition

Ex.	Surfactant				Hydrotrope			Builder		
	Nonionic		Anionic							
No.	N_1	N_4	A_1	A_2	HX_1	HX_2	HE_1	B_1	B_2	B_4
1	6		4		5			15		
2	6		4		5			15		
3	5		5		5			15		
4	5		5		5			15		
5	4		6		5			15		
6	4		6		5			15		
7	3		7		5			15		
8	3		7		5			15		
9	3		7		5		10	15		
10	3		7		5		10	15		
11	7				5		3	15		
12	7				5		3	15		
13	5			5		5			15	
14	5			5		5			15	
15	5			5		5			15	
16	5			5		5			15	
17	5			5		5			15	
43	4		6		6			15		
44	4			6		6		15		
45		4		6		6				10
46		4		6		6				10
47		4		6		6				15
48		4		6		6				15
49	4			6		6		15		
50	4			6		6		15		

TABLE 1 (Continued)

	Weight % of component							
	Stabiliser							
Ex. No.	SE	SG	SP_1	SP_2	HP	Water	pH	Avox loss
1		0.20	0.15		7	Balance	9.3	4
2	10	"	"		7		9.5	2
3		"	"		7		9.3	7
4	10	"	"		7		9.4	4
5		"	"		7		9.2	2
6	10	"	"		7		9.2	2
7		"	"		7		9.2	4
8	10	"	"		7		9.3	3
9		"	"		7		8.2	4
10	10	"	"		7		8.3	2
11		"	"		7		7.8	2
12	10	"	"		7		8.0	1
13	10	0.05	0.04		7		9.4	12
14	10	0.10	0.08		7		9.2	10
15	10	0.20	0.15		7		9.0	3
16	10	0.30	0.23		7		9.0	3
17	10	0.40	0.30		7		9.0	5
43	10	0.20	0.15		7		9.4	2
44	10	0.20	0.15		7		9.1	3
45		0.20	0.15		7		7.4	3
46	10	0.20	0.15		7		7.4	2
47		0.20	0.15		7		7.6	3
48	10	0.20	0.15		7		7.7	2
49		0.20	0.15		7	*	9.4	4
50	10	0.20	0.15		7	*	9.2	3

TABLE 2

Weight % of component in composition

	Surfactants									
Ex.	Nonionic		Anionic		Amph.	Hydrotrope		Builder		
No.	N_2	N_3	A_2	A_3	A_4	HX_2	HE_2	B_1	B_2	B_3
18	3		7			5			15	
19	3		7			5	1		15	
20	3		7			5	2		15	
21	3		7			5	3		15	
22	3		7			5			15	
23	7		3			5			15	
24	4		6			5			15	
25	6		4			5			15	
26	5		5			5			15	
27	3					5	7		15	
28	4					5	6		15	
29	7		7			5			10	
30	6		4			5			10	
31		10		3.3		2			6.5	
32		10	3.3			2			6.5	
33		10		3.3		3				6.5
34		10	3.3			3				13.5
51	5		4			5		15		
52	6		6			5		15		

TABLE 2 (Continued)

Ex. No.	Weight % of component Stabiliser Se	SG	SP_1	SP_2	HP	Water	pH	Avox loss
18		0.20	0.15		7	b	8.9	18
19		"	"		7	a	8.2	14
20		"	"		7	l	8.1	8
21		"	"		7	a	8.7	10
22	10	"	"		7	n	9.1	4
23	10	"	"		7	c	9.2	3
24	10	"	"		7	e	9.2	2
25	10	"	"		7		9.2	4
26	10	"	"		7		9.1	2
27		"	"		7		7.8	4
28		"	"		7		8.0	6
29		"	"		7		8.1	4
30		"	"		7		8.5	4
31	6.5			to pH	3.3		7	2
32	6.5			to pH	3.3		7	1
33	6.5			to pH	3.3		7	6
34	6.5			to pH	3.3		7	3
51		0.2	0.15		7		9.4	2
52	10	0.2	0.15		7		9.5	3

TABLE 3

Weight % of component in composition

Ex. No.	Surfactant Nonionic N_4	Anionic A_2	Hydrotrope HX_2	Builder B_1	B_4	B_5	B_6	HP
53	4	6	6	15				7
54	4	6	6		15			7
55	4	6	6			15		7
56	4	6	6				5	7
57	4	6	6	15				7
58	4	6	6	15				7
59	4	6	6	15				7
60	4	6	6	15				7
61	4	6	6	15				7
62	4	6	6	15				7
63	4	6	6	15				7
64	4	6	6	15				7

TABLE 3 (Continued)

Weight of components in composition

Ex. No.	Stabiliser S_E	S_G	SP_1	SP_3	SP_4	Water	pH	Avox loss %
53	10	0.2	0.15			B	9.3	7
54	10	0.2	0.15			a	9	7
55	10	0.2	0.15			l	8	13
56	10	0.2	0.15			a	8.3	10
57	10	0.2	0.15			n		4
58	10	0.2	0.15			c		3
59		0.2	0.15			e		6
60	10	0.2	0.15					5
61		0.2		0.15				5
62	10	0.2		0.15				4
63		0.2			0.15			6
64	10	0.2			0.15			5

Under the storage conditions, it was observed that almost all the compositions exemplified remained throughout storage in a single phase despite the presence of both hydrogen peroxide and polyphosphate builder in high concentrations, and that phase stable compositions similar to those (18) which separated after several months, were obtainable by a modest reduction in the polyphosphate concentration or addition of ethanol in amounts sufficient to enhance the stability of the hydrogen peroxide in the composition or slightly more hydrotrope.

From Tables 1, 2 and 3 it can be seen that incorporation of ethanol within the limits specified herein in conjunction with phosphonate or phosphonate/gluconate improves the storage stability of the alkaline composition, and that as the level of gluconate/phosphonate stabiliser mix is increased, the storage stability of the composition increases up to certain level and thereafter declines.

The washing capability of various of the above mentioned compositions have been tested and the results are summarised in Tables 4, 5 and 6.

The washing trials were carried out in the following manner:

Prestained swatches of cotton were washed in a laboratory scale washing machine, sold under the name Tergotometer (US Testing Corporation) which simulates the action of a vertical agitator type of domestic washing machine. The machine trials were carried out under standard conditions of two stained swatches, each of 5 g, being washed at a temperature maintained at 60°C with one litre of an aqueous washing solution containing 4 grams of the selected detergent composition. For the compositions according to the present invention this resulted generally in an initial surfactant concentration in the range of about 0.3 to 0.5 gpl, and an initial builder concentration in the range of from 0.2 gpl to 0.8 gpl. The first washed swatches were removed from the wash water after 10 minutes washing, rinsed with cold water and dried, and the second removed after 20 or 30 minutes washing and similarly rinsed and dried. The extent of stain removal from each swatch was determined by measuring the reflectance of the swatches before and after washing, using a Zeiss Elrepho Reflectance Photometer having a Xenon lamp light source equipped with a y-tristimulus filter. Each swatch was measured four times with a backing of three thicknesses of material. The reflectance readings were averaged and the % stain removal (abbreviated to %SR) was obtained using the following formula:

$$\% \text{ Stain removal} = 100 \times (R_f - R_i)/(R_u - R_i)$$

where R_u represents reflectance of the unstained cloth, R_i reflectance of the cloth after staining, and R_f reflectance of the stained cloth after bleaching. Swatches of cotton stained with red wine were obtained from E.M.P.A., St. Gallen, Switzerland. Swatches of other stained fabrics were obtained by padding the appropriate fabric through an appropriate stain solution, partially drying the fabric with an infra red drier, and repeating the padding and drying cycle twice more.

In the washing trials summarised in Table 4 and 5, the washing solution water had a hardness of 150 ppm as calcium carbonate in a Ca:Mg ratio of 2:1 and in those summarised in Table 6, a hardness of 250 ppm as calcium carbonate in a Ca:Mg ratio of 3:1.

In Tables 5, and 6 the detergent composition of the present invention additionally contained 0.5% by weight of a bleach stable stilbene optical brightener obtainable from Ciba Geigy under the tradename Uvitex BHT. Washing trials using compositions C41, and C42 are present by way of comparison only. The composition C41 was a commercially available built liquid detergent composition from Lever Bros. under the tradename Wisk, and C42 was an approximately 50/50 W/W mixture of Wisk with an active-oxygen containg bleach additive from Clorox under the tradename Colorox 2. Analysis of the products C41 and C42 showed that at the levels of detergent composition employed, the washing solution contained total surfactants in the range of 0.3 to 0.4 gpl and an initial builder plus pH adjuster concentration of about 0.4 gpl. These concentrations are very comparable with the concentrations of surfactants and builders present under standard conditions of use of the invention compositions (4 gpl) and in broad terms double those when the invention compositions are used at only 2 gpl.

TABLE 4

Example/ comparison composition used	Washing conditions	Stain	% Stain removal after 10 min	20 min
48	Standard	Red wine	61	67
48	,,	Cocoa	28	30
48	,,	Tea	52	58
48	,,	EMPA 101	42	47
C42	4 g/l	Red wine	56	63
C42	,,	Cocoa	14	19
C42	,,	Tea	51	60
C42	,,	EMPA101	27	32
48	2 g/l	Red wine	56	63
48	,,	Cocoa	25	27
48	,,	Tea	47	54
48	,,	EMPA 101	33	39
C41	2 g/l	Red wine	52	60
C41	,,	Cocoa	16	20
C41	,,	Tea	40	43
C41	,,	EMPA 101	34	41

TABLE 5

Example/ comparison composition used	Washing conditions	Stain	% Stain removal after 10 min	20 min
4	Standard	Red wine	63.4	65.4
4	„	Cocoa	28.7	33.3
4	„	Tea	53.5	55.8
4	„	EMPA Standard	51.7	57.4
2	„	Red wine	59.6	64.5
2	„	Cocoa	38.5	43.8
2	„	Tea	42.9	56.5
2	„	EMPA Standard	52.4	59.6
6	„	Red wine	59.7	66.2
6	„	Cocoa	33.0	37.3
6	„	Tea	49.7	59.8
6	„	EMPA Standard	52.5	59.1
12	„	Red wine	57.6	61.8
12	„	Cocoa	25.6	36.6
12	„	Tea	49.1	55.5
12	„	EMPA Standard	50.0	54.8
2	2 g/l	Red wine	50.8	54.6
2	„	Cocoa	6.6	8.6
2	„	Tea	28.5	33.8
4	„	Red wine	53.1	56.5
4	„	Cocoa	6.0	9.5
4	„	Tea	26.5	29.9
6	„	Red wine	50.1	52.6
6	„	Cocoa	6.5	9.1
6	„	Tea	26.3	29.4
C41	„	Red wine	38.5	40.6
C41	„	Cocoa	2.2	3.6
C41	„	Tea	4.4	10.9
C42	4 g/l mix	Red wine	44.9	53.4
C42	„	Cocoa	−1.5	7.8
C42	„	Tea	6.2	31.6

TABLE 6

Example/ comparison composition used	Washing conditions	Stain	% Stain removal after 10 min	20 min
18	Standard	Red wine	71.8	79.7
18	„	Cocoa	23.7	39.1
18	„	Tea	46.9	62.0
19	„	Red wine	72.7	79.8
19	„	Cocoa	16.4	33.0
19	„	Tea	46.6	61.2
21	„	Red wine	71.9	80.4
21	„	Cocoa	29.0	37.8
21	„	Tea	47.3	63.2
26	„	Red wine	74.9	81.9
26	„	Cocoa	22.2	37.4
26	„	Tea	50.4	66.4
29	„	Cocoa	14.0	24.0
30	„	Cocoa	15.0	14.0
C41	2 g/l	Red wine	60.4	66.2
C41	„	Cocoa	17.6	29.1
C41	„	Tea	23.9	27.6
C41	4 g/l	Red wine	65.2	67.0
C41	„	Cocoa	18.2	33.9
C41	„	Tea	18.2	33.9
C42	4 g/l mix	Red wine	66.3	76.6
C42	„	Cocoa	12.2	26.9
C42	„	Tea	25.2	62.3

From Tables 4, 5 and 6 it can be readily seen that the invention compositions were very effective and, in several, better stain removers on the range of stains tested than were comparison compositions C41, C42 and C43. It will be recognised therefore, that the compositions of the instant invention combine the advantages of good storage stability with good washing performance. Moreover, when washing trials were repeated employing washing compositions that omitted the phosphonate and gluconate stabilisers, but were otherwise identical, the washing results were also identical, being within 1% stain removal, i.e. within the limits of reproducibility of the washing tests, indicating that the presence of the phosphonate and gluconate stabiliser had not impaired the washing performance even though they had considerably improved the storage stability of the composition.

Examples 65 to 69

Compositions were prepared by the method for Examples 1 to 64 except that the step relating to incorporating builder was omitted. The Avox of the compositions was required after 4 weeks storage at

32°C and the washing trials were carried out in exactly the same manner as those whose results are summarised in Tables 4 to 6, in hard water having a hardness of 150 ppm as calcium carbonate in a Ca:Mg ratio of 2:1.

The compositions and results are summarised in Table 7 below.

TABLE 7

Example No.		65	66	67	68	69
Composition weight %						
Surfactant	N_1	30	30	35	25	20
	A_2	5	5	5	10	
Hydrotrope	HX_2	5	5	5	5	5
Ethanol	SE	10	10	10	10	10
Hydrogen peroxide		7	7	7	7	7
Gluconate	SG	0.20	0.20	0.20	0.20	0.20
Phosphonate	SP_1	0.15	0.15	0.15	0.15	0.15
Water		balance				
Stability Avox lost		3.9	1.8	1.8	3.4	2.2
% Soil Removal						
Red wine	10 mins	63	63	66	66	68
Red wine	30 mins	68	67	72	71	73
Cocoa	10 mins	10	9	8	9	8
Cocoa	30 mins	13	11	10	11	11

The effectiveness of the soil removal can be judged by comparison with commercially available detergent compositions in the USA, viz the aforementioned "Wisk" and a product available from Colgate-Palmolive under the trade "Dynamo", each at 2 gpl, on further examples of the stains under the same conditions of wash temperature, water hardness and wash duration, either alone or in 50:50 weight mix with the aforementioned bleach additive "Clorox 2".

The comparative results are summarised below in Table 8.

TABLE 8

	Red wine 10 mins	30	Cocoa 10 mins	30
Wisk	37	40	1	6
Wisk+Clorox	44	61	3	6
Dynamo	50	54	5	10
Dynamo+Clorox	45	62	8	9

From the above it can be seen that the invention compositions obtained significantly better results in the respected red wine stain than did the commerical compositions and in respect of the cocoa stain obtained much better result than did the sample of Wisk, alone or with added bleach and comparable with or better than the results obtained using Dynamo, alone or with added bleach.

Claims

1. A stabilised aqueous built liquid detergent composition comprising a surfactant, builder, water, hydrotrope and if desired one or more detergent adjuvants characterised in that it contains

- (i) at least 3% surfactant selected from anionic sulphate or sulphonate surfactants and non-ionic ethoxylate surfactants;
- (ii) at least 5% of a builder selected from alkali metal polyphosphates and carboxylic complexing builders;
- (iii) at least 2% hydrogen peroxide;
- (iv) sufficient alkali metal aryl sulphonate hydrotrope to maintain the composition in a single phase, either by itself or in conjunction with other components; and
- (v) a stabilising amount of a combination comprising
  - (a) from 0.075 to 1% of an aminomethylene phosphonate or hydroxyalkyl diphosphonate, together with
  - (b) from 0.08 to 1% of a polyhydroxy aliphatic carboxylate in a weight ratio to (a) of 3:1 to 1:3 and/or up to 15% of a low molecular weight mono-hydroxy aliphatic alcohol in a weight ratio to (a) of at least 2.5:1, %'s being by weight of the composition.

2. A composition according to claim 1 characterised in that the proportion of anionic sulphate or sulphonate surfactant is selected within the range of 3 to 15% weight.

3. A composition according to claim 1 or 2 characterised in that the proportion of nonionic alcohol ethoxylate is selected within the range of 3 to 15% by weight.

4. A composition according to any preceding claim characterised in that the weight proportion of ethoxylate in the nonionic alcohol ethoxylate is from 60 to 80% of the molecule.

5. A composition according to any preceding claim characterised in that the total proportion of anionic sulphate or sulphonate and nonionic alcohol ethoxylate surfactants is from 6 to 15%.

6. A composition according to any preceding claim characterised in that the weight ratio of anionic sulphate or sulphonate surfactant to nonionic alcohol ethoxylate surfactant is from 5:2 to 2:5.

7. A composition according to any preceding claim characterised in that the builder is a polyphosphate or an hydroxy carboxylic acid complexing builder.

8. A composition according to claim 7 characterised in that the proportion of builder is selected within the range 9 to 16% by weight.

9. A composition according to claim 7 or 8 characterised in that the polyphosphate is potassium tetra pyrophosphate.

10. A composition according to claim 7 or 8 characterised in that the builder is an alkali metal citrate.

11. A composition according to any of claims 1 to 6 characterised in that the builder comprises up to 10% nitrilotriacetic acid, alkali metal salt or up to 8% carboxymethylsuccinate, alkali metal salt.

12. A composition according to any preceding claim characterised in that the total proportion of all components except for water and hydrogen peroxide is from 30 to 45% by weight.

13. A stabilised aqueous liquid detergent composition comprising a surfactant, hydrotrope, water and if desired one or more detergent adjuvants characterised in that it contains

- (i) at least 10% surfactant selected from anionic surfactants and non-ionic ethoxylate surfactants, of which at least 5% is nonionic surfactant,
- (ii) at least 2% hydrogen peroxide,
- (iii) sufficient alkali metal aryl sulphonate hydrotrope to maintain the composition in a single phase, either by itself or in conjunction with other components, and
- (iv) a stabilising amount of a combination comprising
  - (a) from 0.075 to 1% of an aminomethylene phosphonate or hydroxyalkyl diphosphonate, together with
  - (b) from 0.08 to 1% a polyhydroxy aliphatic carboxylate in a weight ratio to (a) of 3:1 to 1:3 and/or up to 15% of a low molecular weight mono-hydroxyaliphatic alcohol in a weight ratio to (a) of at least 2.5:1, %'s being by weight of the composition.

14. A composition according to claim 13 characterised in that the proportion of anionic sulphate or sulphonate surfactant is selected within the range of 3 to 15% weight.

15. A composition according to claim 13 or 14 characterised in that the proportion of nononic alcohol ethoxylate is selected within the range of 5 to 35% by weight.

16. A composition according to any of claims 13 to 15 characterised in that the weight proportion of ethoxylate in the nonionic alcohol ethoxylate is from 60 to 80% of the molecule.

17. A composition according to any of claims 13 to 16 characterised in that the total proportion of anionic sulphate or sulphonate and nonionic alcohol ethoxylate surfactants is from 25 to 40%.

18. A composition according to any of claims 13 to 17 characterised in that the weight ratio of anionic sulphate or sulphonate surfactant to nonionic alcohol ethoxylate surfactant is from 1:3 to 1:6.

19. A composition according to any of claims 13 to 18 characterised in that the total proportion of all components except for water and hydrogen peroxide is from 40 to 65% by weight.

20. A composition according to any preceding claim characterised in that the proportion of hydrogen peroxide is selected within the range 3 to 20% by weight.

21. A composition according to any preceding claim characterised in that the proportion of sulphonate hydrotrope is selected within the range 3 to 9% by weight.

22. A composition according to any preceding claim characterised in that it contains from 1 to 3% by weight of an ethoxylated phosphate ester.

23. A composition according to any preceding claim characterised in that the proportion of low molecular weight aliphatic alcohol is selected within the range 5 to 15% by weight.

24. A composition according to any preceding claim characterised in that the low molecular weight aliphatic alcohol is ethanol.

25. A composition according to claim 24 characterised in that the ethanol is introduced into the form of methylated spirits.

26. A composition according to any preceding claim characterised in that the proportion of polyhydroxy carboxylate as from 0.1 to 0.4% by weight.

27. A composition according to any preceding claim characterised in that the polyhydroxy carboxylate is an alkali metal gluconate.

28. A composition according to any preceding claim characterised in that the phosphonate is an ethylene diamine tetra (methylene phosphonic acid) or hexamethylene diamine tetra (methylene phosphonic acid) or diethylene triamine penta (methylene phosphonic acid) or an alkali metal salt thereof.

29. A composition according to any preceding claim characterised in that it contains from 5 to 12% by weight ethanol, a polyhydroxy carboxylate and a phosphonate.

30. A composition according to claim 1, 13 or 29 characterised in that the weight ratio of the polyhydroxy carboxylate to the phosphonate is from 2:1 to 1:1, in a total proportion the two components of from 0.2 to 1% by weight.

31. A built liquid detergent composition according to claim 1 characterised in that it comprises from 8 to 12% in total of anionic sulphate or sulphonate surfactant and nonionic ethoxylated surfactants; from 9 to 15% builder selected from alkali metal, tetra pyrophosphate or alkali metal citrate; from 3 to 9% alkali metal aryl sulphonate hydrotrope; from 5 to 12%, ethanol; from 5 to 10%, hydrogen peroxide; from 0.2 to 1% in total of a polyhydroxylinear C_6 or C_7 aliphatic carboxylate, and an alkali metal methylene phosphonate complexing agent, up to 5% of detergent adjuvant or adjuvants and the balance, water, %'s being by weight.

32. A composition according to claim 31 characterised by the following features (i) to (v) in combination:—

(i) the composition contains from 3 to 8% anionic surfactant and 2 to 8% nonionic surfactant; and
(ii) the builder is selected from potassium tetrapyrophosphate and sodium citrate; and
(iii) the aliphatic carboxylate is an alkali metal gluconate; and
(iv) the phosphonate complexing agent is an ethylene diamine tetramethylene phosphonate, hexamethylene diamine tetramethylene phosphonate or diethylene triamine pentamethylene phosphonate; and
(v) the aliphatic carboxylate and phosphonate complexing agent are in a weight ratio of 2:1 to 1:1.

33. An unbuilt liquid detergent according to claim 13 characterised in that it comprises from 25 to 40% in total of anionic sulphate or sulphonate surfactant and nonionic ethoxylated surfactants, from 3 to 9% alkali metal aryl sulphonate hydrotrope; from 5 to 12% ethanol; from 5 to 10% hydrogen peroxide; from 0.2 to 1% in total of a polyhydroxy linear C_6 or C_7 aliphatic carboxylate and an alkali metal methylene phosphate complexing agent, up to 5% of detergent adjuvant or adjuvants and the balance, water, %'s being by weight.

34. A composition according to claim 33 characterised by the following features (i) to (v) in combinaton:—

(i) the composition contains from 3 to 8% anionic surfactant and 20 to 35% nonionic surfactant; and
(ii) the aliphatic carboxylate is an alkali metal gluconate; and
(iii) the phosphonate complexing agent is an ethylene diamine tetramethylene phosphonate, hexamethylene diamine tetramethylene phosphonate or diethylene triamine pentamethylene phosphonate; and
(iv) the aliphatic carboxylate and phosphonate complexing agent are in a weight ratio of 2:1 to 1:1.

35. A process for the production of stabilised detergent compositions containing bleach wherein the components are brought into contact with each other and mixed until an homogeneous mixture is obtained, characterised in that the components are as described in any preceding claim and the order of introduction of the components is arranged such that the hydrogen peroxide contacts the builder or surfactants only in the presence of the stabiliser system.

36. A process for washing or laundering comprising the steps of diluting a detergent composition to a desired extent and contacting the article to be washed with the dilute solution at a temperature from ambient to the boiling point of the solution characterised in that the detergent composition employed is as described in any of claims 1 to 34.

Revendications

1. Composition détergente liquide aqueuse stabilisée comprenant un builder, un agnet tensio-actif, de l'eau, un hydrotrope et, éventuellement, un ou plusieurs agents auxiliaires, caractérisée en ce qu'elle contient:

1) au moins 3% d'agent tensio-actif choisi parmi les agents anioniques de la classe des sulfates ou des sulfonates et les agents non ioniques de la classe des éthoxylates,
2) au moins 5% d'un builder choisi parmi les polyphosphates de métal alcalin et les complexants carboxyliques,
3) au moins 2% de peroxide d'hydrogène,
4) un hydrotrope à base d'arylsulfonate de métal alcalin en une quantité suffisante pour maintenir la composition en une phase unique, soit par lui-même soit en conjonction avec d'autres constituants, et
5) une quantité stabilisante d'une combinaison comprenant:
   a) de 0,075 à 1% d'un phophonate d'aminoéthylène ou d'un diphosphonate d'hydroxyalkyle, en même temps que
   b) de 0,08 à 1% d'un carboxylate aliphatique polyhydroxylé en un rapport pondéral vis-à-vis de a) de 3:1 à 1:3 et/ou jusqu'à 15% d'un alcool aliphatique monohydroxylé de bas poids moléculaire en un rapport pondéral vis-à-vis de a) d'au moins 2,5:1,

les pourcentages étant exprimés en poids par rapport à la composition.

2. Composition suivant la revendication 1, caractérisée en ce que la proportion d'agent tensio-actif anionique de la classe des sulfates ou des sulfonates est choisie dans la gamme de 3 à 15% en poids.

3. Composition suivant l'une des revendications 1 ou 2, caractérisée en ce que la proportion d'agent tensio-actif non ionique de la classe des éthoxylates d'alcool est choisie dans la gamme de 3 à 15% en poids.

4. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que la proportion pondérale d'éthoxylate dans l'éthoxylate d'alcool non ionique représente de 60 à 80% de la molécule.

5. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que la proportion totale de tensio-actif anionique de la classe des sulfates ou des sulfonates et de tensio-actifs non ioniques de la classe des éthoxylates d'alcool est de 6 à 15%.

6. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que le rapport pondéral entre le tensio-actif anionique de la classe des sulfates ou des sulfonates et le tensio-actif non ionique de la classe des éthoxylates d'alcool est compris entre 5:2 et 2:5.

7. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que le builder consiste en un polyphosphate ou en un complexant à base d'acide carboxylique hydroxylé.

8. Composition suivant la revendication 7 caractérisée en ce que la proportion de builder est choisie dans la gamme de 9 à 16% en poids.

9. Composition suivant l'une des revendications 7 ou 8 caractérisée en ce que le polyphosphate est du pyrophosphate tétrapotassique.

10. Composition suivant l'une des revendications 7 ou 8 caractérisée en ce que le builder consiste en un citrate de métal alcalin.

11. Compositions suivant l'une quelconque des revendications 1 à 6 caractérisée en que le builder comprend jusqu'à 10% d'un sel de métal alcalin de l'acide nitrilotriacétique ou jusqu'à 8% d'un sel de métal alcalin de l'acide carboxyméthyloxysuccinique.

12. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que la proportion totale de tous les composants autres que l'eau et le peroxyde d'hydrogène est de 30 à 45% en poids.

13. Composition détergente liquide aqueuse stabilisée comprenant un agent tensio-actif, un hydrotrope, de l'eau et, éventuellement, un ou plusieurs agents auxiliaires caractérisée en ce qu'elle contient:

1) au moins 10% d'agent tensio-actif choisi parmi les tensio-actifs anioniques et les agents tensio-actifs non ioniques de la classe des éthoxylates, 5% au moins étant de la classe des non ioniques,
2) au moins 2% de peroxyde d'hydrogène,
3) un hydrotrope à base d'arylsulfonate de métal alcalin en une quantité suffisante pour maintenir la composition en une phase unique, soit par lui-même soit en conjonction avec d'autres constituants, et
4) une quantité stabilisante d'une combinaison comprenant:
    a) de 0,075 à 1% d'un phosphonate d'aminométhylène ou d'un diphosphonate d'hydroxyalkyle, en même temps que
    b) de 0,08 à 1% d'un carboxylate aliphatique polyhydroxylé en un rapport pondéral vis-à-vis de a) de 3:1 à 1:3 et/ou jusqu'à 15% d'un alcool aliphatique monohydroxylé de faible poids moléculaire en un rapport pondéral vis-à-vis de a) d'au moins 2,5:1,

les pourcentages étant exprimés en poids par rapport à la composition.

14. Composition suivant la revendication 13 caractérisée en ce que la proportion d'agent tensio-actif anionique de la classe des sulfates ou des sulfonates est choisie dans la gamme de 3 à 15% en poids.

15. Composition suivant l'une des revendications 13 ou 14 caractérisée en ce que la proportion d'éthoxylate d'alcool non ionique est choisie dans la gamme de 5 à 35% en poids.

16. Composition suivant l'une quelconque des revendications 13 à 15 caractérisée en ce que la proportion pondérale d'éthoxylate dans l'éthoxylate d'alcool non ionique représente de 60 à 80% de la molécule.

17. Composition suivant l'une quelconque des revendications 13 à 16 caractérisée en ce que la proportion totale de tensio-actif anionique de la classe des sulfates ou des sulfonates et de tensio-actif non ionique de la classe des éthoxylates d'alcool est de 25 à 40%.

18. Composition suivant l'une quelconque des revendications 13 à 17 caractérisée en ce que le rapport pondéral entre le tensio-actif anionique de la classe des sulfates ou des sulfonates et le tensio-actif non ionique de la classe des éthoxylates d'alcool est comprise entre 1:3 et 1:6.

19. Composition suivant l'une quelconque des revendications 13 à 18 caractérisée en ce que la proportion totale de tous les composants autres que l'eau et le peroxyde d'hydrogène est de 40 à 65% en poids.

20. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que la proportion de peroxyde d'hydrogène est choisie dans la gamme de 3 à 20% en poids.

21. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que la proportion d'hydrotrope à base de sulfonate est choisie dans la gamme de 3 à 9% en poids.

22. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce qu'elle contient de 1 à 3% en poids d'un ester phosphorique éthoxylé.

23. Composition suivant l'une quelconque des revendications précédentes caractérisé en ce que la proportion d'alcool aliphatique de bas poids moléculaire est choisie dans la gamme de 5 à 15% en poids.

24. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que l'alcool aliphatique de bas poids moléculaire est de l'éthanol.

25. Composition suivant la revendication 24 caractérisée en ce que l'éthanol est introduit sous la forme d'alcool dénaturé.

26. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que la proportion de carboxylate polyhydroxylé est comprise entre 0,1 et 0,4% en poids.

27. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que le carboxylate polyhydroxylé consiste en un gluconate de métal alcalin.

28. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce que le phosphonate consiste en acide éthylènediaminetétra(méthylènephosphonique), en acide hexaméthylènediaminetétra(méthylènephosphonique), en acide diéthylènetriaminepenta(méthylènephosphonique) ou en un sel de métal alcalin de ceux-ci.

29. Composition suivant l'une quelconque des revendications précédentes caractérisée en ce qu'elle contient de 5 à 12% en poids d'éthanol, un carboxylate polyhydroxylé et un phosphonate.

30. Composition suivant l'une des revendications 1, 13 ou 29 caractérisée en ce que le rapport pondéral entre le carboxylate polyhydroxylé et le phosphonate est compris entre 2:1 et 1:1, la proportion totale des deux composants étant comprise entre 0,2 et 1% en poids.

31. Composition détergente liquide contenant un builder suivant la revendication 1 caractérisée en ce qu'elle comprend de 8 à 12% au total de tensio-actif anionique de la classe des sulfates ou des sulfonates et de tensio-actifs non ioniques éthoxylés, de 9 à 15% d'un builder choisi parmi les pyrophosphates tétrasubstitués par un métal alcalin ou les citrates de métal alcalin, de 3 à 9% d'un hydrotrope à base d'arylsulfonate de métal alcalin, de 5 à 12% d'éthanol, de 5 à 10% de peroxyde d'hydrogène, de 0,2 à 1% au total d'un carboxylate aliphatique en C_6 ou C_7 linéaire polyhydroxylé et

d'un agent complexant à base de méthylènephosphonate de métal alcalin, jusqu'à 5% d'un ou plusieurs agents auxiliaires et le complément d'eau, les pourcentages étant exprimés en poids.

32. Composition suivant la revendication 31 caractérisée par les points 1) à 5) ci-après, pris en combinaison:

1) la composition contient de 3 à 8% de tensio-actif anionique et 2 à 8% de tensio-actif non ionique et
2) le builder est choisi parmi le pyrophosphate tétrapotassique et le citrate de sodium et
3) le carboxylate aliphatique est un gluconate de métal alcalin et
4) l'agent complexant à base de phosphonate consiste en un éthylènediaminetétraméthylenephosphonate, un hexaméthylènediaminetétraméthylènephosphonate ou un diéthylènetriaminepentaméthylènephosphonate et
5) le carboxylate aliphatique et l'agent complexant à base de phosphonate sont présents en un rapport pondéral compris entre 2:1 et 1:1.

33. Détergent liquide ne contenant pas de builder suivant la revendication 13 caractérisé en ce qu'il comprend de 25 à 40% au total de tensio-actif anionique du type des sulfates ou des sulfonates et de tensio-actifs non ioniques éthoxylés, de 3 à 9% d'un hydrotrope à base d'arylsulfonate de métal alcalin, de 5 à 12% d'éthanol, de 5 à 10% de peroxyde d'hydrogène, de 0,2 à 1% au total d'un carboxylate aliphatique en C_6 ou C_7 linéaire polyhydroxylé et d'un agent complexant à base de méthylènephosphonate de métal alcalin, jusqu'à 5% d'un ou plusieurs agents auxiliaires et le complément d'eau, les pourcentages étant exprimés en poids.

34. Composition suivant la revendication 33 caractérisée par les points 1) à 4) ci-après, pris en combinaison:

1) la composition contient de 3 à 8% de tensio-actif anionique et 20 à 35% de tensio-actif non ionique, et
2) le carboxylate aliphatique est un gluconate de métal alcalin, et
3) l'agent complexant à base de phosphonate consiste en un éthylènediaminetétraméthylènephosphonate, un hexaméthylènediaminetétraméthylènephosphonate ou un diéthylènetriaminepentaméthylènephosphonate, et
4) le carboxylate aliphatique et l'agent complexant à base de phosphonate sont présents en un rapport pondéral compris entre 2:1 et 1:1.

35. Procédé pour la préparation de compositions détergentes stabilisées contenant un agent de blanchiment dans lequel les composants sont mis en contact entre eux et sont mélangés jusqu'à l'obtention d'un mélange homogène, caractérisé en ce que les composants sont ceux décrits dans l'une quelconque des revendications précédentes et en ce que l'ordre d'introduction des composants est réglé de telle manière que le peroxyde d'hydrogène n'entre en contact avec le builder ou les tensio-actifs qu'en présence du système stabilisant.

36. Procédé de lavage ou de blanchissage comprenant les étapes qui consistent à diluer la composition détergente dans une mesure désirée et à mettre l'article à laver en contact avec la solution diluée à une température comprise entre la température ambiante de le point d'ébullition de la solution, caractérisé en ce que la composition détergente employée est l'une de celles décrites dans l'une quelconque des revendications 1 à 34.

Patentansprüche

1. Stabilisierte wässerigegerüstoffhaltige flüssige Waschmittelzusammensetzung aus einem Tensid, Waschmittelverstärker (Builder), Wasser, Hydrotrop und gegebenenfalls einem oder mehreren Waschmittelhilfsstoffen, dadurch gekennzeichnet, daß sie

(i) mindestens 3% Tenside, ausgewählt aus anionischen Sulfat- oder Sulfonat-Tensiden und nicht-ionischen Äthoxylat-Tensiden;
(ii) mindestens 5% eines Builders, ausgewählt aus Alkalimetallpolyphosphaten und Karbonsäure-Builders;
(iii) mindestens 2% Wasserstoffperoxid;
(iv) ausreichend Alkalimetallarylsulfonat als Hydrotrop, um entweder als solches oder in Verbindung mit anderen Bestandteilen die Zusammensetzung in einer einzigen Phase zu halten; und
(v) eine stabilisierende Menge einer Kombination aus
  (a) 0,075 bis 1% eines Aminomethylenphosphonates oder Hydroxyalkyldiphosphonates, zusammen mit

(b) 0,08 bis 1% eines aliphatischen Polyhydroxycarboxylates in einem Gewichtsverhältnis zu (a) von 3:1 bis 1:3 und/oder bis zu 15% eines niedermolekularen aliphatischen einwertigen Alkohols in einem Gewichtsverhältnis zu (a) von mindestens 2,5:1 wobei % auf das Gewicht der Zusammensetzung bezogen sind,

enthält.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Anteil des anionischen Sulfat- oder Sulfonat-Tensides im Bereich von 3 bis 15 Gew.% liegt.

3. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Anteil des nicht-ionischen Alkohol-äthoxylats im Bereich von 3 bis 15 Gew.% liegt.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Gewichtsanteil des Äthoxylates in dem nicht-ionischen Alkohol-äthoxylat 60 bis 80% des Moleküls beträgt.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Gesamtanteil an anionischem Sulfat oder Sulfonat- und nicht-ionischen Alkohol-äthoxylat-Tensiden 6 bis 15% beträgt.

6. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Gewichtsverhältnis von anionischem Sulfat- oder Sulfonat-Tensid zu nicht-ionischem Alkohol-äthoxylat-Tensid 5:2 bis 2:5 beträgt.

7. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Builder ein Polyphosphat oder ein Hydroxycarbonsäure-Builder ist.

8. Zusammensetzung nach Anspruch 7, dadurch gekennzeichnet, daß der Anteil an Builder im Bereich von 9 bis 16 Gew.% liegt.

9. Zusammensetzung nach Anspruch 7 oder 8, dadurch gekennzeichnet, daß das Polyphosphat Kaliumtetrapyrophosphat ist.

10. Zusammensetzung nach Anspruch 7 oder 8, dadurch gekennzeichnet, daß der Builder ein Alkalimetallcitrat ist.

11. Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der Builder bis zu 10% Nitriloessigsäure als Alkalimetallsalz oder bis zu 8% Carboxymethylsuccinat als Alkalimetallsalz umfaßt.

12. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Gesamtanteil aller Bestandteile mit Ausnahme von Wasser und Wasserstoffperoxid 30 bis 45 Gew.% ausmacht.

13. Stabilisierte wässerige flüssige Waschmittelzusammensetzung aus einem Tensid, Hydrotrop, Wasser und gegebenenfalls einem oder mehreren Waschmittelhilfsstoffen, dadurch gekennzeichnet, daß sie

(i) mindestens 10% Tensid, ausgewählt aus anionischen Tensiden und nicht-ionischen Äthoxylat-Tensiden, wobei mindestens 5% ein nicht-ionisches Tensid ist,
(ii) mindestens 2% Wasserstoffperoxid,
(iii) ausreichend Alkalimetallarylsulfonat als Hydrotrop, um als solches oder in Verbindung mit anderen Bestandteilen die Zusammensetzung in einer einzigen Phase zu halten, und
(iv) eine stabilisierende Menge einer Kombination aus
  (a) 0,075 bis 1% eines Aminomethylenphosphonates oder Hydroxyalkyldiphosphonates zusammen mit
  (b) 0,08 bis 1% eines aliphatischen Polyhydroxycarboxylates in einem Gewichtsverhältnis zu (a) von 3:1 bis 1:3 und/oder bis zu 15% eines niedermolekularen aliphatischen einwertigen Alkohols in einem Gewichtsverhältnis zu (a) von mindestens 2,5:1, wobei % auf das Gewich der Zusammensetzung bezogen sind,

enthält.

14. Zusammensetzung nach Anspruch 13, dadurch gekennzeichnet, daß der Anteil an anionischem Sulfat- oder Sulfonat-Tensid im Bereich von 3 bis 15 Gew.% liegt.

15. Zusammensetzung nach Anspruch 13 oder 14, dadurch gekennzeichnet, daß der Anteil an nicht-ionischem Alkohol-äthoxylat im Bereich von 5 bis 35 Gew.% liegt.

16. Zusammensetzung nach einem der Ansprüche 13 bis 15, dadurch gekennzeichnet, daß der Gewichtsanteil des Äthoxylates im nichtionischen Alkohol-äthoxylat 60 bis 80% des Moleküls ausmacht.

17. Zusammensetzung nach einem der Ansprüche 13 bis 16, dadurch gekennzeichnet, daß der Gesamtanteil an anionischem Sulfat- oder Sulfonat- und nicht-ionischem Alkohol-äthoxylat-Tensiden 25 bis 40% ausmacht.

18. Zusammensetzung nach einem der Ansprüche 13 bis 17, dadurch gekennzeichnet, daß das Gewichtsverhältnis von anionischem Sulfat- oder Sulfonat-Tensid zu nicht-ionischem Alkohol-äthoxylat-Tensid 1:3 bis 1:6 beträgt.

19. Zusammensetzung nach einem der Ansprüche 13 bis 18, dadurch gekennzeichnet, daß der

Gesamtanteil aller Bestandteile mit Ausnahme von Wasser und Wasserstoffperoxid 40 bis 65 Gew.% beträgt.

20. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Anteil an Wasserstoffperoxid im Bereich von 3 bis 20 Gew.% liegt.

21. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Anteil an Sulfonat als Hydrotrop im Bereich von 3 bis 9 Gew.% liegt.

22. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie 1 bis 3 Gew.% eines äthoxylierten Phosphatesters enthält.

23. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Anteil an niedermolekularem aliphatischem Alkohol im Bereich von 5 bis 15 Gew.% liegt.

24. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der niedermolekulare aliphatische Alkohol Äthanol ist.

25. Zusammensetzung nach Anspruch 24, dadurch gekennzeichnet, daß der Äthanol in Form von Brennspiritus vorliegt.

26. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Anteil an Polyhydroxycarboxylat 0,1 bis 0,4 Gew.% beträgt.

27. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polyhydroxycarboxylat ein Alkalimetallgluconat ist.

28. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Phophonat eine Äthylendiamintetra (methylenphosphonsäure) oder Hexamethylendiamintetra (methylenphosphonsäure) oder Diäthylentriaminpenta (methylenphosphonsäure) oder ein Alkalimetallsalz davon ist.

29. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie in einer Menge von 5 bis 12 Gew.% Äthanol, ein Polyhydroxycarboxylat und ein Phosphonat enthält.

30. Zusammensetzung nach Anspruch 1, 13 oder 29, dadurch gekennzeichnet, daß das Gewichtsverhältnis des Polyhydroxycarboxylates zum Phosphonat 2:1 bis 1:1 ist, wobei der Gesamtanteil der zwei Bestandteile 0,2 bis 1 Gew.% ausmacht.

31. Gerüststoffhaltige flüssige Waschmittelzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie aus insgesamt 8 bis 12% an anionischem Sulfat- oder Sulfonat-Tensid und nichtionischem äthoxyliertem Tensid; 9 bis 15% Builder, ausgewählt aus Alkalimetalltetrapyrophosphat oder Alkalimetallcitrat; 3 bis 9% Alkalimetallarylsulfonat als Hydrotrop; 5 bis 12% Äthanol; 5 bis 10% Wasserstoffperoxid; insgesamt 0,2 bis 1% eines aliphatischen linearen C_6- oder C_7-Polyhydroxycarboxylates und eines Alkalimetallmethylenphosphonat- Komplexbildners, bis zu 5% Waschmittelhilfstoff oder-hilfsstoffen und Rest Wasser besteht, wobei % Gew.% sind.

32. Zusammensetzung nach Anspruch 31, gekennzeichnet durch die folgenden Merkmale (i) bis (v) in Kombination:

(i) die Zusammensetzung enthält 3 bis 8% anionisches Tensid und 2 bis 8% nicht-ionisches Tensid; und
(ii) der Builder ist ausgewählt aus Kaliumtetrapyrophosphat und Natriumcitrat; und
(iii) das aliphatische Carboxylat ist ein Alkalimetallgluconat; und
(iv) der Phosphonat-Komplexbildner ist ein Äthylendiamintetramethylenphosphonat, Hexamethylendiamintetramethylenphosphonat oder Diäthylentriaminpentamethylenphosphonat; und
(v) das aliphatische Carboxylat und der Phophonat-Komplexbildner stehen in einem Gewichtsverhältnis von 2:1 bis 1:1.

33. Gerüststoffloses flüssiges Waschmittel nach Anspruch 13, dadurch gekennzeichnet, daß es insgesamt aus 25 bis 40% anionischem Sulfat- oder Sulfonat-Tensid und nicht-ionischem äthoxyliertem Tensid; 3 bis 9% Alkalimetallarylsulfonat als Hydrotrop; 5 bis 12% Äthanol; 5 bis 10% Wasserstoffperoxid; insgesamt 0,2 bis 1% eines aliphatischen linearen C_6- oder C_7-Polyhydroxycarboxylates und eines Alkalimetallmethylenphosphonat-Komplexbildners, bis zu 5% Waschmittelhilfsstoff oder -hilfsstoffen und Rest Wasser besteht, wobei % Gew.% sind.

34. Zusammensetzung nach Anspruch 33, gekennzeichnet durch die folgenden Merkmale (i) bis (v) in Kombination:

(i) die Zusammensetzung enthält 3 bis 8% anionisches Tensid und 20 bis 35% nicht-ionisches Tensid; und
(ii) das aliphatische Carboxylat ist ein Alkalimetallgluconat; und
(iii) der Phosphonat-Komplexbildner ist ein Äthylendiamintetramethylenphosphonat, Hexamethylendiamintetramethylenphosphonat oder Diäthylentriaminpentamethylenphosphonat; und
(iv) das aliphatische Carboxylat und der Phosphonat-Komplexbildner stehen in einem Gewichtsverhältnis von 2:1 bis 1:1.

35. Verfahren zur Herstellung von stabilisierten Bleichmittel enthaltenden Waschmittelzusammensetzungen, bei welchen die Bestandteile zusammengebracht und bis zum Erhalt einer homogenen Mischung gemisch werden, dadurch gekennzeichnet, daß die Bestandteile die in einem der vorhergehenden Ansprüche beschriebenen sind und die Reihenfolge der Einbringung der Bestandteile so vorgenommen wird, daß das Wasserperoxid mit den Buildern oder Tensiden nur in Gegenwart des Stabilisierungssystems zusammengebracht wird.

36. Verfahren zum Waschen oder Reinigen, das die Stufen der Verdünnung einer Waschmittelzusammensetzung auf ein gewünschtes Ausmaß und des Zusammenbringens des zu waschenden Gegenstandes mit der verdünnten Lösung bei einer Temperatur zwischen Raumtemperatur und dem Siedepunkt der Lösung umfaßt, dadurch gekennzeichnet, daß eine Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 34 verwendet wird.