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LIQUID LAUNDRY DETERGENT BLEACH COMPOSITION

This invention relates to liquid laundry detergent compositions. More particularly, this invention relates to liquid detergent compositions containing a stabilised bleaching agent. Preferred non-aqueous liquid laundry detergent compositions are those which are easily pourable and which do not gel when added to water and to the use of these compositions for cleaning soiled fabrics.

Liquid nonaqueous heavy duty laundry detergent compositions are well known in the art. For instance, compositions of that type may comprise a liquid nonionic surfactant in which are dispersed particles of a builder, as shown for instance in the U.S. patents nos. 4,316,812; 3,630,929; 4,264,466, and British patents nos. 1,205,711, 1,270,040 and 1,600,981.

Liquid detergents are often considered to be more convenient to employ than dry powdered or particulate products and, therefore, have found substantial favour with consumers. They are readily measurable, speedily dissolved in the wash water, capable of being easily applied in concentrated solutions or dispersions to soiled areas on garments to be laundered and are non-dusting, and they usually occupy less storage space. Additionally, the liquid detergents may have incorporated in their formulations materials which could not stand drying operations without deterioration, which materials are often desirably employed in the manufacture of particulate detergent products. Although they are possessed of many advantages over unitary or particulate solid

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products, liquid detergents often have certain inherent disadvantages too, which have to be overcome to produce acceptable commercial detergent products. Thus, some such products separate out on storage and others separate out on cooling and are not readily redispersed. In some cases the product viscosity changes and it becomes either too thick to pour or so thin as to appear watery. Some clear products become cloudy and others gel on standing.

Liquid detergent compositions often include, in addition to the detergent active ingredient, one or more detergent additives or adjuvants. One of the more important of these, in terms of consumer appeal and actual cleaning benefit, is the class of bleach agents, especially the oxygen bleaches, of which sodium perborate monohydrate is a particularly preferred example. It is well known in the art that, in solution, the persalt oxygen bleach releases hydrogen peroxide as the active oxidising agent. However, hydrogen peroxide is readily decomposed by catalase, an enzyme always present in natural soils and stains. This decomposition occurs even in the presence of bleach activators, as the rate of reaction between hydrogen peroxide and the activator is slower than the decomposition of hydrogen peroxide by catalase. The activity of catalase is very high, even at room temperature, and a substantial quantity of active oxygen is lost before catalase can be deactivated by increasing the temperature of the washing bath.

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One approach to solving this problem has been to use an excessive amount of perborate or other peroxide bleaching agent, e.g. an amount generally 2 to 4 or more times that which would be required to effectively bleach the soil or stain in the absence of peroxide decomposing enzyme and also 2 to 4 or more times molar excess relative to the number of moles of bleach activator.

It has also been proposed to carry out the bleaching with an aqueous solution of peroxide bleaching agent in the presence of a compound capable of inhibiting enzyme-induced decomposition of the bleaching agent. Thus, U.S. patent 3,606,990 to Gobert and Mouret and assigned to Colgate-Palmolive Company discloses a relatively wide range of inhibitor compounds, including, for example, hydroxylamine salt, hydrazine and phenylhydrazine and their salts, substituted phenols and polyphenols, and others, as well as various detergent compositions incorporating the water soluble inorganic peroxide bleaching agent and the inhibitor compound. However, there is no teaching of liquid detergent compositions which incorporate the inhibitor compounds nor is there a teaching that the inhibitor compounds would be effective in compositions containing a bleach activator in addition to the peroxide bleach.

Furthermore, U.S. patent 3,606,990 states in column 7, lines 25 to 29 that in the case of hydroxylamine sulphate the effective amount of inhibitor compound is from about 0.5 to 2% by weight of the total composition.

It has now been discovered that in the detergent liquid compositions of this invention containing a water soluble inorganic peroxide bleaching agent of the persalt type the incorporation of very limited amounts of less than about 0.5%, for example, 0.01 to about 0.45%, can effectively inhibit enzyme-induced decomposition of the bleaching agent. It has been further discovered that hydroxylamine sulphate is highly stable in the composition and does not at all interfere with activation of the bleaching system by conventional persalt bleach activators.

Therefore, in accordance with the present invention there is provided a nonaqueous liquid laundry detergent composition, comprising a liquid nonionic surfactant, a mono or poly(C₂-C₃)alkylene glycol mono(C₁-C₅)alkylether, a water-soluble inorganic peroxide bleaching agent, a bleach activator to lower the temperature at which the bleaching agent will liberate hydrogen peroxide in aqueous solution, and from about 0.01 to 0.45 percent by weight, based on the total composition, of an hydroxylamine salt capable of inhibiting the enzyme-induced decomposition of the bleaching agent, the enzyme being present in the soiled fabrics.

Other features and specific embodiments of the invention will be apparent and the invention may be more readily understood from the following detailed description.

The nonionic synthetic organic detergents employed in the practice of the invention may be any of a wide variety of such compounds, which are well known and, for example, are described at length in the text Surface Active Agents, Vol. II, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, and in McCutcheon's Detergents and

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10 to 18 carbon atoms and wherein the number of mols of lower alkylene oxide (of 2 to 3 carbon atoms) is from 3 to 12. Of such materials it is preferred to employ those wherein the higher alkanol is a higher fatty alcohol of 10 to 11 or 12 to 15 carbon atoms and which contain from 5 to 8 or 5 to 9 lower alkoxy groups per mol. Preferably, the lower alkoxy is ethoxy, but in some instances, it may be desirably mixed with propoxy, the latter, if present, usually, but not necessarily, being a minor (less than 50%) proportion. Exemplary of such compounds are those wherein the alkanol is of 12 to 15 carbon atoms and which contain about 7 ethylene oxide groups per mol, e.g. Neodol (Registered Trade Mark) 25-7 and Neodol 23-6.5, which products are made by Shell Chemical Company, Inc. The former is a condensation product of a mixture of higher fatty alcohols averaging about 12 to 15 carbon atoms, with about 7 mols of ethylene oxide and the latter is a corresponding mixture wherein the carbon atom content of the higher fatty alcohol is 12 to 13 and the number of ethylene oxide groups present averages about 6.5. The higher alcohols are primary alkanols. Other examples of such detergents include Tergitol (Registered Trade Mark) 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corp. The former is mixed ethoxylation product of 11 to 15 carbon atoms linear secondary alkanol with 7 mols of ethylene oxide and the latter is a similar product, but with 9 mols of ethylene oxide being reacted.

Also useful in the compositions of the present invention as a component of the nonionic detergent are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14 to 15 carbon atoms and the number of ethylene oxide groups per mol being about 11. Such products are also made by Shell Chemical Company. Other useful nonionics are represented by the well-known commercially available Plurafac (Registered Trade Mark) series which are the reaction product of a higher linear alcohol and a mixture of ethylene and propylene oxides, containing a mixed chain of ethylene oxide and propylene oxide, terminated by a hydroxyl group. Examples include Plurafac RA30 (a C₁₃-C₁₅ fatty alcohol condensed with 6 moles ethylene oxide and 3 moles propylene oxide), Plurafac RA40 (a C₁₃-C₁₅ fatty alcohol condensed with 7 moles propylene oxide and 4 moles ethylene oxide), Plurafac D25 (a C₁₃-C₁₅ fatty alcohol condensed with 5 moles propylene oxide and 10 moles ethylene oxide), and Plurafac B26.

Generally, the mixed ethylene oxide-propylene oxide fatty alcohol condensation products can be represented by the general formula $RO(C_2H_4O)_x(C_3H_6O)_yH$, where R is straight or branched primary or secondary aliphatic hydrocarbon, preferably alkyl or alkenyl, of from 6 to 20, preferably 10 to 18, especially preferably 14 to 18 carbon atoms, x is a number of from 2 to 12, preferably 4 to 10, and y is a number of from 2 to 7, preferably 3 to 6.

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Another group of liquid nonionics are available from Shell Chemical Company, Inc. under the Dobanol trade mark: Dobanol 91-5 is an ethoxylated C₉-C₁₁ fatty alcohol with an average of 5 moles ethylene oxide; and Dobanol 25-7 is an ethoxylated C₁₂-C₁₅ fatty alcohol with an average of 7 moles ethylene oxides.

In the preferred poly-lower alkoxyated higher alkanols, to obtain the best balance of hydrophilic and lipophilic moieties the number of lower alkoxies will usually be from 40% to 100% of the number of carbon atoms in the higher alcohol, preferably 40 to 60% thereof and the nonionic detergent will preferably contain at least 50% of such preferred poly-lower alkoxy higher alkanol. Higher molecular weight alkanols and various other normally solid nonionic detergents and surface active agents may be contributory to a gelation of the liquid detergent and consequently, will preferably be omitted or limited in quantity to the compositions of the present invention, although minor proportions thereof may be employed for their cleaning properties, etc. With respect to both preferred and less preferred nonionic detergents the alkyl groups present therein are generally linear although branching may be tolerated, such as at a carbon next to or two carbons removed from the terminal carbon of the straight chain and away from the ethoxy chain, if such branched alkyl is not more than three carbons in length. Normally, the proportion of carbon atoms in such a branched configuration will be minor rarely exceeding 20% of the total carbon atom content of the

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alkyl. Similarly, although linear alkyls which are terminally joined to the ethylene oxide chains are highly preferred and are considered to result in the best combination of detergency, biodegradability and non-gelling characteristics, medial or secondary joiner to the ethylene oxide in the chain may occur. It is usually in only a minor proportion of such alkyls, generally less than 20%, but as is in the cases of the mentioned Tergitols, may be greater. Also, when propylene oxide is present in the lower alkylene oxide chain, it will usually, but not necessarily, be less than 20% thereof and preferably less than 10% thereof.

When greater proportions of non-terminally alkoxyated alkanols, propylene oxide-containing poly-lower alkoxyated alkanols and less hydrophile-lipophile balanced nonionic detergent than mentioned above are employed and when other nonionic detergents are used instead of the preferred nonionics recited herein, the product resulting may not have as good detergency, stability, viscosity and non-gelling properties as the preferred compositions, but use of the viscosity and gel controlling compounds of the present invention can also improve the properties of the detergents based on such nonionics. In some cases, as when a higher molecular weight polylower alkoxyated higher alkanol is employed, often for its detergency, the proportion thereof will be regulated or limited as in the desired detergency and still have the product non-gelling and of desired viscosity. Also, it has

been found that it is only rarely necessary to utilise the higher molecular weight nonionics for their detergent properties since the preferred nonionics described herein are excellent detergents and additionally, permit the attainment of the desired viscosity in the liquid detergent without gelation at low temperatures. Mixtures of two or more of these liquid nonionics can also be used and in some cases advantages can be obtained by the use of such mixtures.

As mentioned above, the structure of the liquid nonionic surfactant may be optimised with regard to their carbon chain length and configuration (e.g. linear versus branched chains, etc.) and their content and distribution of alkylene oxide units. Extensive research has shown that these structural characteristics can and do have a profound effect on such properties of the nonionic as pour point, cloud point, viscosity, gelling tendency, as well, of course, as on detergency.

Preferred examples of mono or poly (C_2-C_3) alkylene glycol mono (C_1-C_5) alkyl ethers include ethylene glycol monoethyl ether ($C_2H_5-O-CH_2CH_2OH$), and diethylene glycol monobutyl ether ($C_4H_9-O-(CH_2CH_2O)_2H$). Diethylene glycol monoethyl ether is especially preferred and, as well be shown below, is uniquely effective to control viscosity.

While the amphiphilic compound, particularly diethylene glycol monobutyl ether, may be the only viscosity control and gel-inhibiting additive in the invention compositions further improvements in the rheological properties of the anhydrous liquid

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nonionic surfactant compositions can be obtained by including in the composition a small amount of a nonionic surfactant which has been modified to convert a free hydroxyl group thereof to a moiety having a free carboxyl group, such as a partial ester of a nonionic surfactant and a polycarboxylic acid and/or an acidic organic phosphorous compound having an acidic - POH group, such as a partial ester of phosphorous acid and an alkanol.

As disclosed in the commonly assigned copending application U.S. Ser. No. 597,948, filed 9 April 1984, corresponding to GB Application No. 8509084, Ser. No. 2158454 the free carboxyl group modified nonionic surfactants, which may be broadly characterised as polyether carboxylic acids, function to lower the temperature at which the liquid nonionic forms a gel with water. The acidic polyether compound can also decrease the yield stress of such dispersion, aiding in their dispensibility, without a corresponding decrease in their stability against settling. Suitable polyether carboxylic acids contain a grouping of the formula

$$(OCH_2-CH_2)_p(CH-CH_2)_q-Y-Z-COOM$$

$$\begin{array}{c} | \\ CH_3 \end{array}$$

where R² represents a hydrogen atom or a methyl group, Y represents oxygen or sulphur, Z represents an organic linkage, p is a positive number of from about 3 to about 50 and q is zero or a positive number of up to 10. Specific examples include the half-ester of Plurafac RA30 with succinic anhydride, the half ester of Dobanol 25-7 with succinic

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anhydride, and the half ester of Dobanol 91-5 with succinic anhydride. Instead of a succinic acid anhydride, other polycarboxylic acids or anhydrides may be used, e.g. maleic acid, maleic anhydride,

5 glutaric acid, malonic acid, succinic acid, phthalic acid, phthalic anhydride, or citric acid.

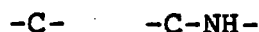
Furthermore, other linkages may be used, such as ether, thioether or urethane linkages, formed by conventional reactions. For instance, to form an

10 ether linkage, the nonionic surfactant may be treated with a strong base (to convert its OH group to an ONa group for instance) and then reacted with a halocarboxylic acid such as chloroacetic acid or chloropropionic acid or the corresponding bromo

15 compound. Thus, the resulting carboxylic acid may have the formula $R-Y-ZCOOH$ where R is the residue of a nonionic surfactant (on removal of a terminal OH), Y represents oxygen or sulphur and Z represents an organic linkage such as a hydrocarbon group of, say,

20 1 to 10 carbon atoms which may be attached to the oxygen (or sulphur) of the formula directly or by means of an intervening linkage such as an oxygen-containing linkage, e.g. a O or O linkage.

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The polyether carboxylic acid may be produced from a polyether which is not a nonionic surfactant, e.g. it may be made by reaction with a polyalkoxy compound such as polyethylene glycol or a monoester

30 or monoether thereof which does not have the long alkyl chain characteristic of the nonionic

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surfactants. Thus, R may have the formula

$$\begin{array}{c} R^2 \\ | \\ R^1(OCH-CH_2)_n- \end{array}$$

5 where R^2 represents a hydrogen atom of a methyl group, R^1 represents an alkylphenyl or alkyl or other chain terminating group and "n" is at least 3 such as 5 to 25. When the alkyl group of R^1 is a higher alkyl group, R is a residue of a nonionic
10 surfactant. As indicated above, R^1 may instead be hydrogen or lower alkyl (e.g. methyl, ethyl, propyl, butyl) or lower acyl (e.g. acetyl). The acidic polyether compound if present in the detergent composition, is preferably added dissolved in the
15 nonionic surfactant.

Another useful class of supplemental anti-gelling agent are the C_6 to C_{14} alkyl or alkenyl dicarboxylic anhydrides, such as, for example, octenylsuccinic anhydride, octenylmaleic anhydride or
20 dodecylsuccinic anhydride. These compounds may be used together with or in place of part or all of the polyether carboxylic acid anti-gelling agents.

As disclosed in the commonly assigned copending application U.S. Ser. No. 597,793, filed 6 April
25 1984, corresponding to GB Application No. 8509083, Serial No. 2158453, the acidic organic phosphorus compound having an acidic - POH group can increase the stability of the suspension of builder, especially polyphosphate builders, in the nonaqueous
30 liquid nonionic surfactant.

The acidic organic phosphorus compound may be, for instance, a partial ester of phosphoric acid and

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an alcohol such as an alkanol which has a lipophilic character, having, for instance, more than 5 carbon atoms, e.g. 8 to 20 carbon atoms.

A specific example is a partial ester of phosphoric acid and a C₁₆ to C₁₈ alkanol (Empiphos 5632 from Marchon); it is made up of about 35% monoester and 65% diester.

The inclusion of quite small amounts, for example from about 0.5 to 0.3% by weight of the composition, of the acidic organic phosphorus compound makes the suspension significantly more stable against settling or standing but remains pourable, presumably, as a result of increasing the yield value of the suspension, but decreases its plastic viscosity. It is believed that the use of the acidic phosphorus compound may result in the formation of a high energy physical bond between the -POH portion of the molecule and the surfaces of the inorganic polyphosphate builder so that these surfaces take on an organic character and become more compatible with the nonionic surfactant.

The acidic organic phosphorus compound may be selected from a wide variety of materials, in addition to the partial esters of phosphoric acid and alkanols mentioned above. Thus, one may employ a partial ester of phosphoric or phosphorous acid with a mono or polyhydric alcohol such as hexylene glycol, ethylene glycol, di- or tri-ethylene glycol or higher polyethylene glycol, polypropylene glycol, glycerol, sorbitol, or mono or diglycerides of fatty acids, in which one, two or more of the alcoholic OH groups of the molecule may be esterified with the phosphorus

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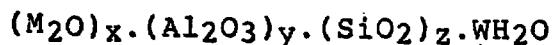
acid. The alcohol may be a nonionic surfactant such as an ethoxylated or ethoxylated propoxylated higher alkanol, higher alkyl phenol, or higher alkyl amide. The -POH group need not be bonded to the organic portion of the molecule through an ester linkage; instead it may be directly bonded to carbon (as in a phosphonic acid, such as a polystyrene in which some of the aromatic rings carry phosphonic acid or phosphinic acid groups; or an alkylphosphonic acid, such as propyl or laurylphosphonic acid) or may be connected to the carbon through other intervening linkage (such as linkages through O, S or N atoms). Preferably, the carbon:phosphorus atomic ratio in the organic phosphorus compound is at least about 3:1, such as 5:1, 10:1, 20:1, 30:1 or 40:1.

The detergent composition of the present invention may also and preferably does include water soluble detergent builder salts. Typical suitable builders include, for example, those disclosed in U.S. Patents 4,316,812; 4,264,466; and 3,630,929. Water-soluble inorganic alkaline builder salts which can be used alone with the detergent compound or in admixture with other builders are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono and diorthophosphate, and potassium bicarbonate. Sodium tripolyphosphate

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(TPP) is especially preferred. The alkali metal silicates are useful builder salts which also function to make the composition anticorrosive to washing machine parts. Sodium silicates of $\text{Na}_2\text{O}/\text{SiO}_2$ ratios of from 1.6/1 to 1/3.2 especially about 1/2 to 1/2.8 are preferred. Potassium silicates of the same ratios can also be used.

Another class of builders useful herein are the water-insoluble aluminosilicates, both of the crystalline and amorphous type. Various crystalline zeolites (i.e. aluminosilicates) are described in British Patent 1,504,168, U.S. Patent 4,409,136 and Canadian Patents 1,072,835 and 1,087,477. An example of amorphous zeolites useful herein can be found in Belgium Patent 835,351. The zeolites generally have the formula



wherein x is 1, y is from 0.8 to 1.2 and preferably 1, z is from 1.5 to 3.5 or higher and preferably 2 to 3 and w is from 0 to 9, preferably 2.5 to 6 and M is preferably sodium. A typical zeolite is type A or similar structure, with type 4A particularly preferred. The preferred aluminosilicates have calcium ion exchange capacities of about 200 milliequivalents per gram or greater, e.g. 400 meq/g.

Other materials such as clays, particularly of the water-insoluble types, may be useful adjuncts in compositions of the present invention. Particularly useful is bentonite. This material is primarily montmorillonite which is a hydrated aluminium

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silicate in which about 1/6th of the aluminium atoms may be replaced by magnesium atoms and with which varying amounts of hydrogen, sodium, potassium, calcium, etc., may be loosely combined. The bentonite in its more purified form (i.e. free from any grit, sand, etc.) suitable for detergents invariably contains at least 50% montmorillonite and thus its cation exchange capacity is at least about 50 to 75 meq. per 100 g of bentonite. Particularly preferred bentonite are the Wyoming or Western U.S. bentonites which have been sold as Thixo-jels 1, 2, 3 and 4 by Georgia Kaolin Co. These bentonites are known to soften textiles as described in British Patent 401,413 to Marriott and British Patent 461,221 to Marriott and Dugan.

Examples of organic alkaline sequestrant builder salts which can be used alone with the detergent or in admixture with other organic and inorganic builders are alkali metal, ammonium or substituted ammonium, aminopolycarboxylates, e.g. sodium and potassium ethylene diaminetetraacetate (EDTA), sodium and potassium nitrilotriacetates (NTA) and triethanol-ammonium N-(2-hydroxyethyl)nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable.

Other suitable builders of the organic type include carboxymethylsuccinates, tartronates and glycollates. Of special value are the polyacetal carboxylates. The polyacetal carboxylates and their use in detergent compositions are described in 4,144,226; 4,315,092 and 4,146,495. Other patents on similar builders include 4,141,676; 4,169,934; 4,201,858; 4,204,852; 4,224,420; 4,225,685;

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4,226,960; 4,233,422; 4,233,423; 4,302,564 and 4,303,777. Also relevant are European Patent Application Nos. 0015024; 0021491 and 0063399.

5 Since the compositions of the present invention are generally highly concentrated, and, therefore, may be used at relatively low dosages, it is desirable to supplement any phosphate builder (such as sodium tripolyphosphate) with an auxiliary builder such as a polymeric carboxylic acid having high
10 calcium binding capacity to inhibit incrustation which could otherwise be caused by formation of an insoluble calcium phosphate. Such auxiliary builders are also well known in the art.

Various other detergent additives or adjuvants
15 may be present in the detergent product to give it additional desired properties, either of functional or aesthetic nature. Thus, there may be included in the formulation, minor amounts of soil suspending or anti-redeposition agents, e.g. polyvinyl alcohol, fatty amides, sodium carboxymethyl cellulose, hydroxy-
20 propyl methyl cellulose; optical brighteners, e.g. cotton, amine and polyester brighteners, for example, stilbene, triazole and benzidine sulphone compositions, especially sulphonated substituted triazinyl
25 stilbene, sulphonated naphthotriazole stilbene or benzidine sulphone, most preferred are stilbene and triazole combinations.

Bluing agents such as ultramarine blue; enzymes, preferably proteolytic enzymes, such as subtilisin,
30 bromelin, papain, trypsin and pepsin, as well as amylase type enzymes, lipase type enzymes, and mixtures thereof; bactericides, e.g. tetrachlorosali-

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cylanilide, hexachlorophene; fungicides; dyes; pigments (water dispersible); preservatives; ultra-violet absorbers; anti-yellowing agents, such as sodium carboxymethyl cellulose, complex of C₁₂ to C₂₂ alkyl alcohol with C₁₂ to C₁₈ alkylsulphate; pH modifiers and pH buffers; colour safe bleaches, perfume, and anti-foam agents or suds-suppressors, e.g. silicon compounds can also be used.

The bleaching agents are classified broadly, for convenience, as chlorine bleaches and oxygen bleaches. Chlorine bleaches are typified by sodium hypochlorite (NaOCl), potassium dichloroisocyanurate (59% available chlorine), and trichloroiso-isocyanuric acid (85% available chlorine). The oxygen bleaches are the subject of the present invention and are represented by percompounds which liberate hydrogen peroxide in solution, i.e. compounds containing hydrogen peroxide or inorganic perhydrates which, when dissolved, liberate hydrogen peroxide enclosed in their crystal lattice. Preferred examples include sodium and potassium perborates, percarbonates, and perphosphates, and potassium monopersulphate. The perborates, particularly sodium perborate monohydrate, is especially preferred.

Hydrogen peroxide and the precursors which liberate it in solution are good oxidizing agents for removing certain stains from cloth, especially stains caused by wine, tea, coffee, cocoa or fruits.

Hydrogen peroxide and its precursors have been found in general to bleach quickly and most effectively at a relatively high temperature, e.g. about 80°C to 100°C. However, such compounds tend to

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decompose and liberate gaseous oxygen at lower temperatures. The liberation of gaseous oxygen, which is not involved in oxidation of dyed goods, needlessly consumes a sizable amount of hydrogen peroxide or precursors liberating it, both of which are expensive products. Moreover, it has been found that the various stains in cloth and the like greatly accelerates decomposition of hydrogen peroxide into gaseous oxygen during washing at ordinary temperature.

5 In general, washing cloth, either in a machine, by hand, or in boiler or tubs, is accomplished by dissolving a bleaching or detergent composition (containing perborate, for example) in cold or lukewarm water, adding to the solution thus formed the
10 soiled cloth (from which some of the stains have often already been removed by soaking or previous washing) and heating, often just to boiling.

 However, it was found that, by a phenomenon similar to that previously mentioned, all or part of
20 the perborate was decomposed during heating and more specifically during the temperature rise, i.e. that all or part of the perborate was decomposed before the really effective temperature is reached.

 It is believed that this rapid decomposition of
25 hydrogen peroxide, perborate, or other precursors of hydrogen peroxide into gaseous oxygen at low temperature is due to the extremely powerful catalytic action of certain enzymes which are always present in stains, which are present on materials to be washed,
30 and particularly on soiled cloth, such as linens, these enzymes coming from secretions or being of bacterial origin. Hydroperoxidases are an especially

active group of enzymes in this respect, particularly catalase, which is well known as a highly effective catalyst for decomposing hydrogen peroxide to gaseous oxygen. Such enzyme substances, whether termed "redox" or otherwise are nevertheless uniformly characterised in exhibiting a pronounced tendency to induce decomposition of peroxide bleaching agent, the decomposition products evolved thereby comprising ineffective bleaching species.

In order to take advantage of the low temperature effective detergents and low temperature washing cycles now commonly used for temperature sensitive fabrics, the peroxygen compound is preferably used in admixture with an activator therefor. Suitable activators which can lower the effective operating temperature of the peroxide bleaching agent to about 40°C (104°F) or less, are disclosed, for example, in U.S. Patent 4,264,466 or in column 1 of U.S. Patent 4,430,244. Polyacylated compounds are preferred activators; among these, compounds such as tetraacetyl ethylene diamine ("TAED") and pentaacetyl glucose are particularly preferred. Other useful activators include for instance acetylsalicylic acid and its salts, ethylidene benzoate acetate (EBA) and its salts, ethylidene carboxylate acetate and its salts, alkyl and alkenyl succinic anhydride, tetraacetylglycouril (TAGU), and the derivatives of these. See also U.S. Patents 4,111,826, 4,422,950 and 3,661,789 for other classes of activators useful herein.

The bleach activator usually interacts with the peroxygen compound to form a peroxyacid bleaching

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agent in the wash water. It is preferred to include a sequestering agent of high complexing power to inhibit any undesired reaction between such peroxy-acid and hydrogen peroxide in the wash solution in the presence of metal ions. Preferred sequestering agents are able to form a complex with Cu^{2+} ions, such that the stability constant (pK) of the complexation is equal to or greater than 6, at 25°C, in water, of an ionic strength of 0.1 mole/litre, pK being conventionally defined by the formula: $\text{pK} = -\log K$ where K represents the equilibrium constant. Thus, for example, the pK values for complexation of copper ion with NTA and EDTA at the stated conditions are 12.7 and 13.8, respectively. Suitable sequestering agents include for example, in addition to those mentioned above, diethylene triamine pentaacetic acid (DETPA); diethylene triamine pentamethylene phosphonic acid (DTPMP); and ethylene diamine tetramethylene phosphonic acid (EDITEMPA).

However, even in the presence of the bleach activators, and even at temperatures as low as room temperature, decomposition of the persalt will occur in the presence of the stained cloth since the rate of reaction between the bleaching agent and the activator is slower than the rate of decomposition of hydrogen peroxide by catalase.

In order to avoid loss of bleaching agent resulting from enzyme-induced decomposition, the compositions of this invention include an effective amount of a compound capable of inhibiting this enzyme-induced decomposition of bleaching agent. Suitable inhibitor compounds are disclosed in U.S.

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Patent 3,606,990.

Of special interest and importance as the inhibitor compound is hydroxylamine sulphate and other water-soluble hydroxylamine salts, including, for example, hydrochloride, hydrobromide. It has now been found that the hydroxylamine salts, especially the sulphate, are effective to inhibit the deleterious effect of catalase even when present in the composition in very limited amounts, for example, less than 0.5%, such as 0.01 to 0.45%, preferably 0.04 to 0.2%, and especially preferably about 0.1%, based on the weight of the total composition.

Furthermore, the hydroxylamine inhibitor is highly stable in the composition: less than 20% loss after aging for 2 months at 43°C. The hydroxylamine salts are very rapidly solubilized in water and can accordingly react with catalase before dissolution of the perborate or other peroxide bleaching agent. Another advantage of the hydroxylamine salts is that they are rapidly destroyed in the washing liquor, and consequently, no nitrosamine derivatives have been detected.

Where the bleaching system is activated by one of the bleach activators, e.g. TAED, the activator is utilized more effectively and, therefore, suitable ratios of persalt bleaching agent/bleach activator can be maintained at levels much closer to the stoichiometric equivalent weights or with only small molar excess of the bleaching agent.

The composition may also contain an inorganic insoluble thickening agent or dispersant of very high

surface area such as finely divided silica of extremely fine particle size (e.g. of 5-100 millimicrons diameters such as sold under the name Aerosil) (Registered Trade Mark) or the other highly voluminous inorganic carrier materials disclosed in U.S. Patent 3,630,929, in proportions of 0.1-10%, e.g. 1 to 5%. It is preferable, however, that compositions which form peroxyacids in the wash bath (e.g. compositions containing peroxygen compound and activator therefor) be substantially free of such compounds and of other silicates; it has been found, for instance, that silica and silicates promote the undesired decomposition of the peroxyacid.

In a preferred form of the invention, the mixture of liquid nonionic surfactant and solid ingredients is subjected to an attrition type of mill in which the particle sizes of the solid ingredients are reduced to less than about 10 microns, e.g. to an average particle size of 2 to 10 microns or even lower (e.g. 1 micron). Compositions whose dispersed particles are of such small size have improved stability against separation or settling on storage.

In the grinding operation, it is preferred that the proportion of solid ingredients be high enough (e.g. at least about 40% such as about 50%) that the solid particles are in contact with each other and are not substantially shielded from one another by the nonionic surfactant liquid. Mills which employ grinding balls (ball mills) or similar mobile grinding elements have given very good results. Thus, one may use a laboratory batch attritor having 8 mm diameter steatite grinding balls. For larger

scale work a continuously operating mill in which there are 1 mm or 1.5 mm diameter grinding balls working in a very small gap between a stator and a rotor operating at a relatively high speed (e.g. a CoBall mill) may be employed; when using such a mill, it is desirable to pass the blend of nonionic surfactant and solids first through a mill which does not effect such fine grinding (e.g. a colloid mill) to reduce the particle size to less than 100 microns (e.g. to about 40 microns) prior to the step of grinding to an average particle diameter below about 10 microns in the continuous ball mill.

In the preferred heavy duty liquid detergent compositions of the present invention, typical proportions (based on the total composition, unless otherwise specified) of the ingredients are as follows:

Suspended detergent builder, within the range of about 10 to 60% such as about 20 to 50%, e.g. about 25 to 40%;

Liquid phase comprising nonionic surfactant and dissolved amphiphilic viscosity-controlling and gel-inhibiting compound, within the range of about 30 to 70%, such as about 40 to 60%; this phase may also include minor amounts of a diluent such as glycol, e.g. polyethylene glycol (e.g. "PEG 400"), or hexylene glycol, such as up to 10%, preferably up to 5%, for example, 0.5 to 2%. The weight ratio of nonionic surfactant to amphiphilic compound is in the range of from about 100:1 to 1:1, preferably from about 50:1 to about 2:1, especially from about 25:1 to about 3:1;

Polyether carboxylic acid gel-inhibiting compound may be present, for example, in an amount to supply in the range of about 0.5 to 10 parts (e.g. about 1 to 6 parts, such as about 2 to 5 parts) of
5 -COOH (M.W. 45) per 100 parts of blend of such acid compound and nonionic surfactant. Typically, the amount of the polyether carboxylic acid compound is in the range of about 0.01 to 1 part per part of nonionic surfactant, such as about 0.05 to 0.6 part,
10 e.g. about 0.2 to 0.5 part;

Acidic organic phosphoric acid compound, as anti-settling agent: up to 5%, for example, in the range of 0.01 to 5%, such as about 0.05 to 2%, e.g. about 0.1 to 1%.

15 Suitable ranges of other optional detergent additives are: enzymes - 0 to 2%, especially 0.7 to 1.3%; corrosion inhibitors - about 0 to 40%, and preferably 5 to 30%; anti-foam agents and suds-suppressors - 0 to 15%, preferably 0 to 5%, for
20 example 0.1 to 3%; thickening agent and dispersants - 0 to 15%, for example 0.1 to 10%, preferably 1 to 5%; soil suspending or anti-redeposition agents and anti-yellowing agents - 0 to 10%, preferably 0.5 to 5%; colourants, perfumes, brighteners and bluing agents
25 total weight 0% to about 2% and preferably 0% to about 1%; pH modifiers and pH buffers - 0 to 5%, preferably 0 to 2%; bleaching agent - 0% to about 40% and preferably 0% to about 25%, for example 2 to 20%; inhibitor compound for inhibiting enzyme-induced
30 decomposition of bleaching agent - up to about 0.5%, preferably 0.01 to 0.4 or 0.5%, more preferably 0.04 to 0.2%; bleach stabilizers and bleach activators 0

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to about 15%, preferably 0 to 10%, for example, 0.1 to 8%; sequestering agent of high complexing power, in the range of up to about 5%, preferably about 1/4 to 3%, such as about 1/2 to 2%. In the selections of the adjuvants, they will be chosen to be compatible with the main constituents of the detergent composition.

The invention may be put into practice in various ways and a number of specific embodiments will be described by way of example.

All proportions and percentages are by weight unless otherwise indicated.

EXAMPLE 1 (comparison Example)

A heavy duty built nonaqueous liquid nonionic cleaning composition having the following formula is prepared:

	<u>Ingredient</u>	<u>Weight%</u>
	Surfactant T7	17.0
	Surfactant T8	17.0
20	Dobanol 91-5 Acid ¹	5.0
	Diethylene glycol monobutyl ether	10.0
	Dequest 20662	1.0
	TPP NW (sodium tripolyphosphate)	29.0925
	Sokolan CPS ³ (Calcium sequestering agent)	4.0
25	Perborate H ₂ O (sodium perborate monohydrate)	9.0
	T.A.E.D. (tetraacetylene diamine)	4.5
	Emphiphos 5632 ⁴	0.3
	Stilbene 4 (optical brightener)	0.5
	Esperase (proteolytic enzyme)	1.0
30	Duet 7875	0.6
	Relatin DM 4050 ⁶ (anti-redeposition agent)	1.0
	Blue Foulan Sandolane (dye)	0.0075

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1) The esterification product of Dobanol 91-5 (a C₉-C₁₁ fatty alcohol ethoxylated with 5 moles ethylene oxide) with succinic anhydride - the half-ester.

5 2) Diethylene triamine pentamethylene phosphoric acid, sodium salt.

3) A copolymer of about equal moles of methacrylic acid and maleic anhydride, completely neutralised to form the sodium salt thereof.

10 4) Partial ester of phosphoric acid and a C₁₆ to C₁₈ alkanol (about 1/3 monoester and 2/3 diester).

5) Fragrance.

6) Mixture of sodium carboxymethyl cellulose and hydroxymethylcellulose.

15 This composition is a stable, free-flowing, built, non-gelling, liquid nonionic cleaning composition in which the polyphosphate builder is stably suspended in the liquid nonionic surfactant phase.

EXAMPLE 2

20 In the same manner as in Example 1, the following heavy duty built non-aqueous liquid nonionic cleaning composition containing an enzyme inhibitor is prepared:

	<u>Ingredient</u>	<u>Weight%</u>
25	Plurafac RA 30	37.5
	Diethyleneglycol monobutyl ether	10.5
	Octenylsuccinic anhydride	2.0
	TPP NW	28.4
	Sokolan CP5	4.0
30	Dequest 2066	1.0
	Perborate H ₂ O	9.0
	TAED	4.5
	Hydroxylamine sulphate	0.1
	Emphiphos 5632	0.3
	ATS-X (optical brightener)	0.2

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<u>Ingredient</u>	<u>Weight%</u>
Esperase	1.0
Perfume	0.6
Relatin DM 4050	1.0
5 TiO ₂	0.4

This composition has the same advantageous features as the composition of Example 1 and, in addition, provides improved bleaching performance.

10 It is understood that the foregoing detailed description is given merely by way of illustration and that variations may be made therein without departing from the spirit of the invention.

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CLAIMS

1. A non-aqueous liquid laundry detergent composition comprising a liquid nonionic surfactant, a mono or poly(C₂ to C₃)alkylene glycol mono(C₁-C₅)alkylether, a water-soluble inorganic peroxide bleaching agent, a bleach activator to lower the temperature at which the bleaching agent will liberate hydrogen peroxide in aqueous solution, and from about 0.01 to 0.45percent by weight, based on the total composition, of an hydroxylamine salt capable of inhibiting the enzyme-induced decomposition of the bleaching agent, the enzyme being present in the soiled fabrics.

2. A composition as claimed in Claim 1 wherein the bleaching agent is a perborate, percarbonate, perphosphate or a persulphate.

3. A composition as claimed in Claim 1 or Claim 2 wherein the hydroxylamine salt is hydroxylamine sulphate, hydroxylamine hydrochloride, or hydroxylamine hydrobromide.

4. A composition as claimed in Claim 1, 2 or 3 wherein the bleach activator is N,N,N',N'-tetraacetyl ethylene diamine.

5. A composition as claimed in any one of Claims 1 to 4 wherein the bleaching agent comprises sodium perborate monohydrate, the bleach activator is N,N,N',N'-tetraacetyl ethylene diamine and the



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hydroxylamine salt is hydroxylamine sulphate or hydroxylamine hydrochloride and is present in an amount of from about 0.02 to 0.2%.

5 6. A composition substantially as herein disclosed with reference to Example 2.

10 7. A method for cleaning and bleaching soiled fabrics which comprises contacting the soiled fabrics with a composition as claimed in any one of Claims 1 to 6.

15 8. The method of Claim 7 wherein the aqueous wash bath has temperature of 40°C or less.

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