

APPLICATION ACCEPTED AND AMENDED UNDER THE PATENTS ACT 1952
COMMONWEALTH OF AUSTRALIA
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Patents Act 1952

LODGED AT SUB-OFFICE
24 MAR 1986
Sydney

PATENT OFFICE
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CONVENTION APPLICATION FOR A STANDARD PATENT

WE, COLGATE-PALMOLIVE COMPANY, a corporation organized and existing under the laws of the State of Delaware, of 300 Park Avenue New York N.Y. 10022 United States of America

hereby apply for the grant of a Standard Patent for an invention entitled

LIQUID LAUNDRY DETERGENT-BLEACH COMPOSITION AND METHOD OF USE

which is described in the accompanying complete specification.

This application is made under the provision of Part XVI of the Patents Act 1952 and is based on an application for a patent or

similar protection made

in United States of America on 29 March 1985
No. (717,726)

in on
No. (

Our address for service is: F.B. RICE & CO.,
28A Montague St,
Balmain N.S.W. 2041

Dated this 21st day of March 1986
COLGATE-PALMOLIVE COMPANY

By: _____
Registered Patent Attorney

TO: The Commissioner of Patents,
COMMONWEALTH OF AUSTRALIA

305

The Patents Act 1952

DECLARATION IN SUPPORT

In support of the (Convention) Application made by: COLGATE PALMOLIVE COMPANY
300 Park Avenue
New York NY 10022
U.S.A.

for a patent for an invention entitled:

"Liquid Laundry Detergent-Bleach Composition and Method of Use"

I (We) ROBERT C. SULLIVAN

of and care of the applicant company do solemnly and sincerely declare as follows:

~~a) I am (We are) the applicant(s) for the patent~~
or

b) I am (We are) authorised by the applicant(s) for the patent to make this declaration on its behalf.

~~Delete the following if not a Convention Application.~~

The basic application(s) as defined by section 141 (142) of the Act was (were) made

on 29 March 1985 in U.S.A. (717,726)

~~on~~ ~~in~~

~~on~~ ~~in~~

by Guy Broze, Leopold Laitem, Danielle Bastin

The basic application(s) referred to in this paragraph is (are) the first application(s) made in a Convention country in respect of the invention the subject of the application.

~~and are (We are) the actual inventor(s) of the invention~~

is	Guy Broze	Leopold Laitem	Danielle Bastin
b)	Rue Claskin, 32 4330 Grace Hollogne, Belgium	Rue de Merdorp 2, 5960 Orp-Jauche BELGIUM	Rue de la Hayoulle, 14 4632 Soumagne Belgium

~~is (are)~~ the actual inventor(s) of the invention and the facts upon which the applicant company

~~is (are)~~ entitled to make the application are as follows:

The applicant is the assignee of the invention from the said actual inventors.

Declared at Piscataway this 29 day of MAR 29 1990 1990
New Jersey U.S.A.

Signed: Robert C. Sullivan Status Vice President & Chief Patent Counsel

Declarant's Name Robert C. Sullivan

F. B. RICE & CO PATENT ATTORNEYS
This form is suitable for any type of Patent Application. No legalisation required.

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LIQUID DETERGENT BLEACH CONTAINING PEROXIDES

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(56) Prior Art Documents
US 4316812
US 3953380
US 3606990

(57) This invention relates to liquid laundry detergent compositions. More particularly, this invention relates to non-aqueous liquid laundry detergent compositions which are easily pourable and which do not gel when added to water and to the use of these compositions for cleaning soiled fabrics.

CLAIM

1. A non-aqueous liquid detergent composition capable of washing and bleaching soiled fabrics at temperatures as low as 40°C or less which comprises a liquid phase comprising nonionic surfactant and a mono or poly (C₂ to C₃) alkylene glycol mono (C₁-C₅) alkyl ether in an amount of 30 to 70%, a water-soluble inorganic peroxide bleaching agent in an effective amount of up to 25%, a bleach activator to lower the temperature at which the bleaching will liberate hydrogen peroxide in aqueous solution in an effective amount of up to 10%, proteolytic

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(10) 599017

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enzyme in an amount of from 0.7 to 2 percent by weight and from 0.01 to 0.4 percent by weight, based on the total composition, of an hydroxylamine salt capable of inhibiting the enzyme-induced decomposition of the bleaching agent, said enzyme being present in the soiled fabrics.

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COMPLETE SPECIFICATION
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Name of Applicant : COLGATE-PALMOLIVE COMPANY

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Complete Specification for the invention entitled:
LIQUID LAUNDRY DETERGENT-BLEACH COMPOSITION AND METHOD OF USE

The following statement is a full description of this invention including the best method of performing it known to us :-

LIQUID LAUNDRY DETERGENT-BLEACH
COMPOSITION AND METHOD OF USE

RECEIVED AT SUB-OFFICE

- 1 MAY 1986

BACKGROUND OF THE INVENTION

(1) Field of Invention

5 This invention relates to liquid laundry detergent compositions. More particularly, this invention relates to non-aqueous liquid laundry detergent compositions which are easily pourable and which do not gel when added to water and to the use of these compositions for cleaning
10 soiled fabrics.

(2) Discussion of Prior Art

Liquid non-aqueous heavy duty laundry detergent compositions are well known in the art. For instance, compositions of that type may comprise a liquid nonionic
15 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.

20 Liquid detergents are often considered to be more convenient to employ than dry powdered or particulate products and, therefore, have found substantial favor with consumers. They are readily measurable, speedily dissolved in the wash water, capable of being easily
25 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
30 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 products, liquid detergents often have certain inherent
35 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
5 thick to pour or so thin as to appear watery. Some clear products become cloudy and others gel on standing.

The present inventors have been extensively involved in studying the rheological behaviour of nonionic liquid surfactant systems with and without particulate matter
10 suspended therein. Of particular interest has been non-aqueous built laundry liquid detergent compositions and the problems of gelling associated with nonionic surfactants as well as settling of the suspended builder and other laundry additives. These considerations have an
15 impact on, for example, product pourability dispersibility and stability.

The rheological behavior of the non-aqueous built liquid laundry detergents can be analogized to the rheological behavior of paints in which the suspended
20 builder particles correspond to the inorganic pigment and the nonionic liquid surfactant corresponds to the non-aqueous paint vehicle. For simplicity, in the following discussion, the suspended particles, e.g. detergent builder, will sometimes be referred to as the
25 "pigment".

It is known that one of the major problems with paints and built liquid laundry detergents is their physical stability. This problem stems from the fact that the density of the solid pigment particles is higher than
30 the density of the liquid matrix. Therefore, the particles tend to sediment according to Stoke's law. Two basic solutions exist to solve the sedimentation problem: liquid matrix viscosity and reducing solid particle size.

For instance, it is known that such suspensions can
35 be stabilized against settling by adding inorganic or

organic thickening agents or dispersants, such as, for example, very high surface area inorganic materials, e.g. finely divided silica, clays, etc., organic thickeners, such as the cellulose ethers, acrylic and acrylamide polymers, polyelectrolytes, etc. However, such increases in suspension viscosity are naturally limited by the requirement that the liquid suspension be readily pourable and flowable, even at low temperature. Furthermore, these additives do not contribute to the cleaning performance of the formulation.

Grinding to reduce the particle size is more advantageous and provides two major consequences:

1. The pigment specific surface area is increased, and, therefore, particle wetting by the non-aqueous vehicle (liquid nonionic) is proportionately improved.
2. The average distance between pigment particles is reduced with a proportionate increase in particle-to-particle interaction. Each of these effects contributes to increase the rest-gel strength and the suspension yield stress while at the same time, significantly reduces plastic viscosity.

The nonaqueous liquid suspensions of the detergent builder-particles, such as the polyphosphate builders, especially sodium tripolyphosphate (TPP) in nonionic surfactant are found to behave, rheologically, substantially according to the Casson equation:

$$\sigma^{1/2} = \sigma_0^{1/2} + n_{\infty}^{1/2} \gamma^{1/2}$$

where γ is the shear rate,

σ is the shear stress,

σ_0 is the yield stress (or yield value),

and n_{∞} is the "plastic viscosity" (apparent viscosity at infinite shear rate).

The yield stress is the minimum stress necessary to induce a plastic deformation (flow) of the suspension. Thus, visualizing the suspension as a loose network of pigment

particles, if the applied stress is lower than the yield stress, the suspension behaves like an elastic gel and no plastic flow will occur. Once the yield stress is overcome, the network breaks at some points and the sample
5 begins to flow, but with a very high apparent viscosity. If the shear stress is much higher than the yield stress, the pigments are partially shear-deflocculate and the apparent viscosity decreases. Finally, if the shear stress is much higher than the yield stress value, the
10 pigment particles are completely shear-deflocculated and the apparent viscosity is very low, as if no particle interaction were present.

Therefore, the higher the yield stress of the suspension, the higher the apparent viscosity at low shear
15 rate and the better is the physical stability of the product.

In addition to the problems of settling or phase separation the non-aqueous liquid laundry detergents based on liquid nonionic surfactants suffer from the drawback
20 that the nonionics tend to gel when added too cold water. This is a particularly important problem in the ordinary use of European household automatic washing machines where the user places the laundry detergent composition in a dispensing unit (e.g. a dispensing drawer) of the
25 machine. During the operation of the machine the detergent in the dispenser is subjected to a stream of cold water to transfer it to the main body of wash solution. Especially during the winter months when the detergent composition and water fed to the dispenser are
30 particularly cold, the detergent viscosity increases markedly and a gel forms. As a result some of the composition is not flushed completely off the dispenser during operation of the machine, and a deposit of the composition builds up with repeated wash cycles, eventually
35 requiring the user to flush the dispenser with hot water.

The gelling phenomenon can also be a problem whenever it is desired to carry out washing using cold water as may be recommended for certain synthetic and delicate fabrics or fabrics which can shrink in warm or hot water.

5 Partial solutions to the gelling problem in aqueous, substantially builder-free compositions have been proposed and include, for example, diluting the liquid nonionic with certain viscosity controlling solvents and gel-inhibiting agents, such as lower alkanols, e.g. ethyl
10 alcohol (see U.S. Patent 3,953,380), alkali metal formates and adipates (see U.S. Patent 4,368,147), hexylene glycol, polyethylene glycol, etc.

In addition, these two patents each disclose the use of up to at most about 2.5% of the lower alkyl (C₁-C₄)
15 etheric derivatives of the lower (C₂-C₃) polyols, e.g. ethylene glycol, in these aqueous liquid builder-free detergents in place of a portion of the lower alkanol, e.g. ethanol, as a viscosity control solvent. To similar effect are U.S. Patents 4,111,855 and 4,201,686. However,
20 there is no disclosure or suggestion in any of these patents that these compounds, some of which are commercially available under the trade name Cellosolve[®], could function effectively as viscosity control and gel-preventing agents for non-aqueous liquid nonionic
25 surfactant compositions, especially such compositions containing suspended builder salts, such as the polyphosphate compounds, and especially particularly such compositions which do not depend on or require the lower alkanol solvents as viscosity control agents.

30 Furthermore, British Patent Specification 1,600,981 mentions that in non-aqueous nonionic detergent compositions containing builders suspended therein with the aid of certain dispersants for the builder, such as finely divided silica and/or polyether group containing
35 compounds having molecular weights of at least 500, it may

be advantageous to use mixtures of nonionic surfactants, one of which fulfills a surfactant function and the other of which both fulfills a surfactant function and reduces the pour point of the compositions. The former is exemplified by C₁₂-C₁₅ fatty alcohols with 5 to 15 moles of ethylene and/or propylene oxide per mole. The other surfactant is exemplified by linear C₆-C₈ or branched C₈-C₁₁ fatty alcohols with 2 to 8 moles ethylene and/or propylene oxide per mole. Again, there is no teaching that these low carbon chain compounds could control the viscosity and prevent gelation of the heavy duty non-aqueous liquid nonionic surfactant compositions with builder suspended in the nonionic liquid surfactant.

It is also known to modify the structure of nonionic surfactants to optimize their resistance to gelling upon contact with water, particularly cold water. As an example of nonionic surfactant modification one particularly successful result has been achieved by acidifying the hydroxyl moiety end group of the nonionic molecule. The advantages of introducing a carboxylic acid at the end of the nonionic include gel inhibition upon dilution; decreasing the nonionic pour point; and formation of an anionic surfactant when neutralized in the washing liquor. Nonionic structure optimization for minimizing gelation is also known, for example, controlling the chain length of the hydrophobic-lipophilic moiety and the number and make-up of alkylene oxide (e.g. ethylene oxide) units of the hydrophilic moiety. For example, it has been found that a C₁₃ fatty alcohol ethoxylated with 8 moles of ethylene oxide presents only a limited tendency to gel formation.

Nevertheless, still further improvements are desired in the stability, viscosity control and gel inhibition of non-aqueous liquid detergent compositions.

Accordingly, it is an object of the invention to

provide non-aqueous liquid laundry detergents which do not gel when contacted with or when added to water, especially cold water.

5 It is a further object of the invention to provide non-aqueous liquid built laundry detergent compositions which are storage stable, easily pourable and dispersible in cold, warm or hot water.

10 Another object of this invention is to formulate highly built heavy duty non-aqueous liquid nonionic surfactant laundry detergent compositions which can be poured at all temperatures and which can be repeatedly dispersed from the dispensing unit of European style automatic laundry washing machines without fouling or plugging of the dispenser even during the winter months.

15 A specific object of this invention is to provide non-gelling, stable, low viscosity suspensions of heavy duty tripolyphosphate built non-aqueous liquid nonionic laundry detergent composition which include an amount of a low molecular weight amphiphilic compound sufficient to
20 decrease the viscosity of the composition in the absence of water and upon contact with cold water.

These and other objects of the invention which will become more apparent from the following detailed description of preferred embodiments are generally
25 provided by adding to the liquid surfactant composition an amount of a low molecular weight amphiphilic compound, particularly, mono-, di- or tri (lower (C_2 to C_3) alkylene) glycol mono(lower (C_1 to C_5) alkyl)ether, effective to inhibit gelation of the nonionic surfactant
30 in the presence of cold water.

Accordingly, in one aspect the present invention provides a liquid heavy duty laundry composition composed of a suspension of a builder salt in a liquid nonionic surfactant wherein the composition includes an amount of a
35 lower (C_2 to C_3) alkylene glycol mono(lower) (C_1 to

C₅) alkyl ether to decrease the viscosity of the composition in the absence of water and upon the contacting of the composition with water.

In a more specific embodiment, the present invention provides a non-aqueous liquid cleaning composition which remains pourable at temperatures below about 5°C and which does not gel when contacted with or added to water at temperatures below about 20°C, the composition being composed of a liquid nonionic surfactant and C₂ to C₃ alkylene glycol mono(C₁ to C₅)alkyl ether and being substantially free of water.

According to another aspect, the invention provides a method of dispensing a liquid nonionic laundry detergent composition into and/or with cold water without undergoing gelation. In particular, a method is provided for filling a container with a non-aqueous liquid laundry detergent composition in which the detergent is composed, at least predominantly, of a liquid nonionic surface active agent and for dispensing the composition from the container into an aqueous wash bath, wherein the dispensing is effected by directing a stream of unheated water onto the composition such that the composition is carried by the stream of water into the wash bath. By including a low molecular weight amphiphilic compound, i.e. a lower C₂ to C₃ alkylene glycol mono(lower) (C₁ to C₅)alkyl ether, the composition can be easily poured into the container even when the composition is at a temperature below room temperature. Furthermore, the composition does not undergo gelation when it is contacted by the stream of water and it readily disperses upon entry into the wash bath.

As will be seen below the 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 oxidizing 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.

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 Cobert and Mouret and assigned to Colgate-Palmolive Company discloses a relatively wide range of inhibitor compounds, including, for example, hydroxyl-amine 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 peroxide bleach. Furthermore, this patent states in column 7, lines 25-29 that in the case of hydroxyl-amine sulfate the effective amount of inhibitor compound is from about 0.5 to about 2 percent by weight of total composition.

10 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 be effectively inhibit enzyme-induced decomposition of the bleaching agent. It has been further discovered that hydroxyl-amine sulfate is highly stable in the composition and does not at all interfere with activation of the bleaching system by conventional persalt bleach activators.

20 Therefore, in accordance with a still further aspect of the present invention there is provided a liquid heavy duty laundry detergent composition which includes a water soluble inorganic peroxide bleaching agent and an effective amount of a compound which can inhibit enzyme-induced decomposition of the bleaching agent, especially in an amount of less than about 0.5% by weight of the composition, and preferably with an activator for activating the bleaching agent.

30 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 Emulsifiers, 1969 Annual, the relevant disclosures of which are hereby incorporated by reference. Usually, the nonionic detergents are poly-lower alkoxyated lipophiles wherein the desired hydrophile-lipophile balance is obtained from addition of a hydrophilic poly-lower alkoxy group to a lipophilic moiety. A preferred class of the nonionic detergent employed is the poly-lower alkoxyated higher alkanol wherein the alkanol is of 10 to 18 carbon atoms and wherein the number of mols of lower alkylene oxide (of 2 or 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 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[®] 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 seven mols of ethylene oxide and

the latter is a similar product but with nine mols of ethylene oxide being reacted.

Also useful in the present compositions 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 a 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 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.

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

of 7 moles ethylene oxide; etc.

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 gelation of the liquid detergent and consequently, will preferably be omitted or limited in quantity in the present compositions, 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 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 joinder 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 Terigtols, 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
5 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
10 preferred compositions but use of the viscosity and gel controlling compounds of the invention can also improve the properties of the detergents based on such nonionics. In some cases, as when a higher molecular weight poly lower alkoxyated higher alkanol is employed, often
15 for its detergency, the proportion thereof will be regulated or limited as in accordance with the results of various experiments, to obtain the desired detergency and still have the product non-gelling and of desired viscosity. Also, it has been found that it is only rarely
20 necessary to utilize 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
25 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 optimized with regard to their
30 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
35 point, cloud point, viscosity, gelling tendency, as well,

of course, as on detergency.

Typically most commercially available nonionics have a relatively large distribution of ethylene oxide (EO) and propylene oxide (PO) units and of the lipophilic hydrocarbon chain length, the reported EO and PO contents and hydrocarbon chain lengths being overall averages. This "polydispersity" of the hydrophilic chains and lipophilic chains can have great importance on the product properties as can the specific values of the average values. The relationship between "poly-dispersity" and specific chain lengths with product properties for a well-defined nonionic can be shown by the following data for the "Surfactant T" series of nonionics available from British Petroleum. The Surfactant T nonionics are obtained by ethoxylation of secondary C₁₃ fatty alcohols having a narrow EO distribution and have the following physical characteristics:

	<u>EO Content</u>	<u>Pour Point (°C)</u>	<u>Cloud Point (1%sol) (°C)</u>	
20				
	Surfactant T5	5	< -2	< 25
	Surfactant T7	7	-2	38
	Surfactant T9	9	6	58
	Surfactant T12	12	20	88

25 To assess the impact of EO distribution, a "Surfactant T8" was artificially prepared in two ways:

- a. 1:1 mixture of T7 and T9 (T8a)
- b. 4:3 mixture of T5 and T12 (T8b).

The following properties were found:

	<u>EO Content (avg)</u>	<u>Pour Point (°C)</u>	<u>Cloud Point (1%sol'n) (°C)</u>	
30				
	Surfactant T8a	8	2	48
35	Surfactant T8b	8	15	< 20

From these results, the following general observations can be made:

1. T8a corresponds closely to an actual surfactant T8 as it interpolates well between T7 and T9 for both pour point and cloud point.
2. T8b which is highly polydisperse and would be generally unsatisfactory in view of its high pour point and low cloud point temperatures.
3. The properties of T8a are basically additive between T7 and T9 whereas for t8b the pour point is close to the long EO chain (T12) while the cloud point is close to the short EO chain (T5).

The viscosities of the Surfactant Tnonionics were measured at 20%, 30%, 40%, 50%, 60%, 80% and 100% nonionic concentrations for T5, T7, T7/T9 (1:1), T9 and T12 at 25°C with the following results (when a gel is obtained, the viscosity is the apparent viscosity) at 100⁻sec:

Nonionic		Viscosity (mPa.s)				
20	type	T5	T7	T7/T9	T9	T12
	100	36	63	61	149	
	80	65		104	112	165
	60	750	78	188	239	32200
	50	4000	123	233	634	89100
25	40	2050	96	149	211	187
	30	630	58		38	27
	20	170	78		28	100

From these results, it may be concluded that Surfactant T7 is less gel-sensitive than T5, and T9 is less gel-sensitive than T12; moreover, the mixture of T7 and T9 (T8) does not gel, and its viscosity does not exceed 225 m Pa.s. T5 and T12 do not form the same gel structure.

Although not wishing to be bound by any particular

theory, it is presumed that these results may be accounted for by the following hypothesis:

For T5: with only 5 EO, the hydrodynamic volume of the EO chain is almost the same as the hydrodynamic volume of the fatty chain. Surfactant molecules can accordingly arrange themselves to form a lamellar structure.

For T12: with 12 EO, the hydrodynamic volume of the EO chain is greater than that of the fatty chain. When molecules try to arrange themselves together, an interface curvature occurs and rods are obtained. The superstructure is then hexagonal; with a longer EO chain, or with a higher hydration, the interface curvature can be such that actual spheres are obtained, and the arrangement of the lowest energy is a face-centered cubic lattice.

From T5 to T7 (and T8), and the interface curvature increases, and the energy of the lamellar structure increases. As the lamellar structure loses stability, its melting temperature is reduced.

From T12 to T9 (and T8), the interface curvature decreases, and the energy of the hexagonal structure increases (rods become bigger and bigger). As the loss in stability occurs, the structure melting temperature is also reduced.

Surfactant T8 appears to be at the critical point at which the lamellar structure is destabilized, i.e. the hexagonal structure is not yet stable enough and no gel is obtained during dilution. In fact, a 50% solution of T8 will finally gel after two days, but the superstructure formation is delayed long enough to allow easy water dispersibility.

The effects of the molecular weight on physical properties of the nonionics were also considered.

Surfactant T8 (1:1 mixture of T7 and T9) exhibits a good compromise between the lipophilic chain (C13) and the

hydrophilic chain (EO8), although the pour point and maximum viscosity on dilution at 25°C are still high.

The equivalent EO compromise for C10 and C8 lipophilic chains was also determined using the Dobanol (91-x series from Shell Chemical Co., which are ethoxylated derivatives of C9-C11 fatty alcohols (average: C10); and Alfonic 610-y series from Conoco which are ethoxylated derivatives of C6-C10 fatty alcohols (average C8); x and y represent the EO weight percentage.

The next table reports the physical characteristics of the Alfonic 610-y and Dobanol 91-x series:

<u>Nonionic</u>	# EO (avg.)	Pour Point (°C)	Cloud Pt. (°C)	Max.n on dilution at 25°C (mPa.s)
Alfonic 610-50R	3	-15		Gel (60%)
Alfonic 610-60	4.4	- 4	41	36 (60%)
Dobanol 91-5	5	- 3	33	Gel (70%)
Dobanol 91-5T	6	+ 2	55	126 (50%)
Dobanol 91-8	8	+ 6	81	Gel (50%)

Dobanol 91-5 and Dobanol 91-8 are commercially available products; Dobanol 91-5 topped (T) is a lab scale product: it is Dobanol 91-5 from which free alcohol has been removed. As the lowest ethoxylation members are also removed, the average EO number is 6. Dobanol 91-5T provides the best results of C10 lipophile chain as it does not gel at 25°C. The 1% cloud point (55°C) is higher than for surfactant T8 (48°C). This is presumably due to the lower molecular weight since the mixture entropy is higher. Alfonic 610-60 provides the best results of the C8 lipophile chain series.

A summary of the best EO contents for each tested lipophilic chain length is provided in the following table:

Nonionic	# C	# EO	Pour Pt. (°C)	Cloud Pt. (1% soln.) (°C)	Pt.Max.n at 25°C (mPa.s)	on dil(%)
.5 Surfactant T8	13	8	+2	48	223	(50%)
Dobanol 91-5T	10	6	+2	55	126	(50%)
Alfonic 610-60	8	4.4	-4	41	36	(60%)

From this data, the following conclusions were reached:

10 Pour points: as the nonionic molecular weight decreases, its pour points decrease too. The relatively high pour point of Dobanol 91-5T can be accounted for by the higher polydispersity. This was also noticed for T8a and T8b, i.e. the chain polydispersity increases the
15 pour point.

Cloud points: theoretically, as the number of molecules increases (if the molecular weight decreases), the mixing entropy is higher, so the cloud point would increase as the molecular weight decreases. It is
20 actually the case from Surfactant T8 to Dobanol 91-5T but it has not been confirmed with Alfonic 610-60. Here it is presumed that the lipophilic hydrocarbon chain polydispersity is responsible for the theoreticall too low cloud point. The relatively large amount of C10-EO
25 present reduces the solubility.

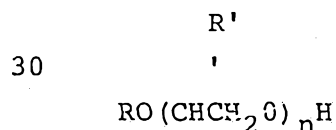
Maximum viscosity on dilution at 25°C: none of these nonionics gel at 25°C when they are diluted with water. The maximum viscosity decreases sharply with the molecular weight. As the nonionic molecular weight
30 decreases, the less efficient becomes the hydrogen bridges. Unfortunately, too low molecular weight nonionics are not suitable for laundry washing: their micellar critical concentration (MCC) is too high, and a true solution, with only a limited detergency would be
35 obtained under practical laundry conditions.

With this information, the present inventors

continued their studies on the effects of the low molecular weight amphiphilic compounds on the rheological properties of liquid nonionic detergent cleaning compositions. These studies revealed that while it is possible to lower the pour point of the composition and obtain some degree of gel inhibition by using a short chain hydrocarbon, e.g. about C₈, with a short chain ethylene oxide substitution, e.g. about 4 moles, as amphiphilic additive, such as Alfonic 610-60, these additives do not significantly contribute to the overall laundry cleaning performance and still do not exhibit overall satisfactory viscosity control over all normal usage conditions.

The present invention is, therefore, based, at least in part, on the discovery that the low molecular weight amphiphilic compounds which can be considered to be analogous in chemical structure to the ethoxylated and/or propoxylated fatty alcohol nonionic surfactants but which have short hydrocarbon chain lengths (C₁-C₅) and a low content of alkylene oxide, i.e. ethylene oxide and/or propylene oxide (about 1 to 4 EO/PO units per molecule) function effectively as viscosity control and gel-inhibiting agents for the liquid nonionic surface active cleaning agents.

The viscosity-controlling and gel-inhibiting amphiphilic compounds used in the present invention can be represented by the following formula



where R is a C₁-C₅, preferably C₂ to C₅, especially preferably C₂ to C₄, and particularly C₄ alkyl group, R' is H or CH₃,

preferably H, and n is a number of from about 1 to 4, preferably 2 to 4 on average.

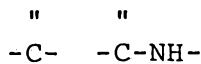
Preferred examples of suitable amphiphilic compounds include ethylene glycol monoethyl ether
5 (C₂H₅-O-CH₂CH₂OH), and diethylene glycol monobutyl ether (C₄H₉-O-)(CH₂CH₂O)₂H).

Diethylene glycol monoethyl ether is especially preferred and, as will be shown below, is uniquely effective to control viscosity.

10 While the amphiphilic compound, particularly diethylene glycol monobutyl ether, can be the only viscosity control and gel inhibiting additive in the invention compositions further improvements in the rheological properties of the anhydrous liquid nonionic
15 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
20 polycarboxylic acid and/or an acidic organic phosphorus 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 Serial No. 597,948, filed April 9, 1984 the disclosure of which is incorporated herein by reference,
25 the free carboxyl group modified nonionic surfactants, which may be broadly characterized as polyether carboxylic acids, function to lower the temperature at which the liquid nonionic forms a gel with water. The
30 acidic polyether compound can also decrease the yield stress of such dispersions, aiding in their dispensability, without a corresponding decrease in their stability against settling. Suitable polyether carboxylic acids contain a grouping of the formula
35 $\{OCH_2-CH_2\}_p \{CH-CH_2\}_q -Y-Z-COOH$ where R² is
CH₃

hydrogen or methyl, Y is oxygen or sulfur, Z is 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 anhydride, the half ester of Dobanol 91-5 with succinic anhydride, etc. Instead of a succinic acid anhydride, other polycarboxylic acids or anhydrides may be used, e.g. maleic acid, maleic anhydride, glutaris acid, malonic acid, succinic acid, phthalic acid, phthalic anhydride, citric acid, etc. Furthermore, other linkages may be used, such as ether, thioether or urethane linkages, formed by conventional reactions. For instance, to form an 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 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 is oxygen or sulfur and Z represents an organic linkage such as a hydrocarbon group of, say, one to ten carbon atoms which may be attached to the oxygen (or sulfur) of the formula directly or by means of an intervening linkage such as an oxygen-containing linkage, e.g. a $\overset{\text{O}}{\parallel}$ or $\overset{\text{O}}{\text{C}}$, etc.



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

of the nonionic surfactants. Thus, R may have the formula

$$R^1 \overset{R^2}{\text{OCH-CH}_2}_n^-$$
 where R^2 is hydrogen or methyl. R^1 is alkylphenyl or alkyl or other chain

5 terminating group and "n" is at least 3 such as 5 to 25. When the alkyl of R^1 is a higher alkyl, R is a residue of a nonionic 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, etc.). The acidic polyether compound if present
10 in the detergent composition, is preferably added dissolved in the nonionic surfactant.

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

20 As disclosed in the commonly assigned copending application Serial No. 597,793, filed April 6, 1984, the disclosure of which is incorporated herein by reference, the acidic organic phosphorus compound having an acidic - POH group can increase the stability of the suspension
25 of builder especially polyphosphate builders, in the nonaqueous liquid nonionic surfactant.

The acidic organic phosphorus compound may be, for instance, a partial ester of phosphoric acid and an alcohol such as an alkanol which has a lipophilic
30 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 C_{16} to C_{18} alkanol (Empiphos 5632 from Marchon); it is made up of about 35% monoester and 65%
35 diester.

The inclusion of quite small amounts, for example, from about 0.05 to 0.3% by weight of the composition, of the acidic organic phosphorus compound makes the suspension significantly more stable against settling on 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.

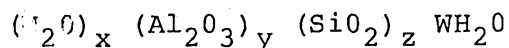
The acidic organic phosphorous compound may be selected from a wide variety of materials, in addition to the partial esters of phosphoric acid and alkanols mentioned above. Thus, one may employ a partial ester of phosphoric or phosphorous acid with a mono or polyhydric alcohol such as hexylene glycol,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

5 The invention detergent composition 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
10 compound or in admixture with other builders are alkali metal carbonate, borates, phosphates, polyphosphates, bicarbonates, and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium tripolyphosphate, sodium
15 carbonate, sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono and diorthophosphate, and potassium bicarbonate. Sodium tripolyphosphate (TPP) is
20 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.
25 Potassium silicates of the same ratios can also be used.

Another class of builders useful herein are the water-insoluble alumino silicates, both of the crystalline and amorphous type. Various crystalline zeolites (i.e. alumino-silicate are described in British
30 Patent 1,504,168, U.S. Patent 4,409,136 and Canadian Patents 1,072,835 and 1,087,477, all of which are hereby incorporated by reference for such descriptions. An example of amorphous zeolites useful herein can be found in Belgium Patent 835,351 and this patent too is
35 incorporated herein by reference. The zeolites

generally have the formula



5 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
10 preferred alumino silicates 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
15 compositions of this invention. Particularly useful is
bentonite. This material is primarily montmorillonite
which is a hydrated aluminum silicate in which about
1/6th of the aluminum atoms may be replaced by magnesium
atoms and with which varying amounts of hydrogen,
20 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
25 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
30 401,413 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
35 alkali metal, ammonium or substituted ammonium,

aminopolycarboxylates, e.g. sodium and potassium ethylene diaminetetraacetate (EDTA), sodium and potassium nitrilotriacetates (NTA) and triethanolammonium N-(2-hydroxyethyl)nitrilodiacetates. 5 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 10 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; 4,226,960; 4,233,422; 4,233,423; 4,302,564 and 4,303,777. Also relevant are 15 European Patent Application Nos. 0015024; 0021491 and 0063399.

Since the compositions of this 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 20 tripolyphosphate) with an auxiliary builder such as a polymeric carboxylic acid having high calcium binding capacity to inhibit incrustation which could otherwise be caused by formation of an insoluble calcium 25 phosphate. Such auxiliary builders are also well known in the art.

Various other detergent additives or adjuvants may be present in the detergent product to give it additional desired properties, either of functional or 30 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-propymethyl cellulose; optical brighteners, e.g. 35 cotton, amine and polyester brighteners, for example,

stilbene, triazole and benzidine sulfone compositions, especially sulfonated substituted triazinyl stilbene, sulfonated naphthotriazole stilbene, benzidene sulfone, etc., most preferred are stilbene and triazole combinations.

Bluing agents such as ultramarine blue; enzymes, preferably proteolytic enzymes, such as subtilisin, bromelin, papain, trypsin and pepsin, as well as amylase type enzymes, lipase type enzymes, and mixtures thereof; bactericides, e.g. tetrachlorosalicylanilide, hexachlorophene; fungicides; dyes; pigments (water dispersible); preservatives; ultraviolet absorbers; anti-yellowing agents, such as sodium carboxymethyl cellulose, complex of C₁₂ to C₂₂ alkyl alcohol with C₁₂ to C₁₈ alkylsulfate; pH modifiers and pH buffers; color 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 preferred 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 monopersulfate. 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, fruits, etc.

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 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.

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 soiled cloth (from which some of the strains 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 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 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, and

particularly on soiled cloth, such as linens, these enzymes coming from secretions or being of bacterial origin. Hydroperoxidas are an especially active group of enzymes in this respect, particularly catalase, which
5 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 characterized in exhibiting a pronounced tendency to induce decomposition of peroxide
10 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
15 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
20 4,264,466 or in column 1 of U.S. Patent 4,430,244, the disclosures of which are incorporated herein by reference. Polyacylated compounds are preferred activators; among these, compounds such as tetraacetyl ethylene diamine ("TAED") and pentaacetyl glucose are
25 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),
30 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 agent
35 in the wash water. It is preferred to include a

sequestering agent of high complexing power to inhibit any undesired reaction between such peroxyacid 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/liter, 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 18.8, respectively. Suitable sequestering agents include for example, in addition to those mentioned above, diethylene triamine pentaacetic acid (DTPA); 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 will preferably additionally include an effective amount of a compound capable of inhibiting this enzyme-induced decomposition of this invention will preferably additionally 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. Patent 3,606,990, the relevant disclosure of which is incorporated herein by

reference.

Of special interest and importance as the inhibitor compound is hydroxylamine sulfate and other water-soluble hydroxylamine salts, including, for example, hydrochloride, hydrobromide, etc. It has now been found that the hydroxylamine salts, especially the sulfate, 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 0.04%, 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) 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 (balls 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.

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

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

15 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 a glycol, e.g. polyethylene glycol (e.g., "PEG 400"), hexylene glycol, etc. 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 20 from about 100:1 to 1:1, preferably from about 50:1 to about 2:1, especiae), hexylrably, from about 25:1 to about 3:1.

25 Polyether carboxylic acid gel-inhibiting compound, 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 -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, e.g. about 30 0.2 to 0.5 part;

35 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%.

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 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%; colorants, perfumes, brighteners and bluing agents 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 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 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.

All proportions and percentages are by weight unless otherwise indicated.

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.

In order to demonstrate the effects of the viscosity control and gel-inhibiting agents, various compositions were prepared using the above Surfactant T8 (C13, E08) (50/50 weight mixture of Surfactant T7 and Surfactant T9) as the non-aqueous liquid nonionic

surface active cleaning agent. Formulations containing 5%, 10%, 15%, or 20% of amphiphilic additive were prepared and were tested at 5°C, 10°C, 15°C, 20°C and 25°C for different dilutions with water, 5 i.e. 100%, 83%, 67%, 50% and 33% total nonionic Surfactant T8 plus additive concentrations, i.e. after dilution in water. The additives tested were Alfonic 610-60 (C8-E04.4). ethylene glycol monoethyl ether (C2-E01), and diethylene glycol monobutyl ether 10 (C4-E02). The results of viscosity behavior on dilution of each tested composition at each temperature is illustrated in the graphs attached as Figures 1-3.

For Alfonic 610-60, 5% addition was sufficient to inhibit gelation at 25°C; however, in the plot of 15 viscosity vs. concentration of nonionic a sharp viscosity maximum was observed at about 67% concentration and a shoulder was observed at about 55% to 35% nonionic concentration. At 5°C, 15% addition was necessary to avoid gel formation. The viscosity 20 decreased to a minimum at a nonionic concentration of about 83% at all levels of additive addition at 5°C whereas at the higher temperatures, viscosity minimums were observed for the non-diluted formulations, i.e. 100% nonionic concentrations. At each temperature and 25 for each tested concentration of additive (except at 20% additive at 25°C) a relatively sharp peak is seen in the viscosity existing between 75 to 50% concentration of nonionic (i.e. 25 to 50% dilution).

For ethylene glycol monoethyl ether 5% additive was 30 capable of inhibiting gel formation even at 5°C. However, sharp peaks and/or maxima of viscosity were again observed at each temperature and additive concentration, although the effects were not as pronounced as for Alfonic 610-60, and for some 35 applications the maximum viscosities, especially at

higher additive concentrations and/or higher temperatures could be acceptable for commercial use.

5 On the other hand, there were no sharp peaks in viscosity observed for diethylene glycol monobutyl ether at any temperature down to 5°C at the 20% additive level. Even at the lower additive levels the viscosity peaks and the viscosity values at substantially all dilutions (concentrations of nonionics) were lower than for either the C8-E04.4 or C2-E01 additive.

10 The following table is representative of the results which were obtained for the different additive concentrations, dilutions, and temperatures, but are given for 20% additive and 5°C temperature:

15

<u>Compositions</u>	<u>Viscosity</u>		<u>Pour Point</u> <u>(°C)</u>
	at 5°C (Pa.sec)		
	<u>No Water</u>	<u>50% Water</u>	
20 Surfactant T8 only	1.140	1.240	5
80% Surfactant T8+20%A	0.086	0.401	-10
80% Surfactant T8+20%B	0.195	0.218	- 2
25 80% Surfactant T8+20%C	0.690	0.936	3

A = ethylene glycol monoethyl ether
B = diethylene glycol monobutyl ether
C = Alfonic 610-60 (C8-4.4EO)

30 Note: 1 PA.sec = 10 poises (e.g. 0.218 Pa.sec = 218 centipoises)

Example 1

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

	<u>Ingredient</u>	<u>Weight %</u>
	Surfactant T7	17.0
5	Surfactant T8	17.0
	Dobanol 91-5 Acid ¹	5.0
	Diethylene glycol monobutyl ether	10.0
	Dequest 2066 ²	1.0
	TPP NW (sodium tripolyphosphate)	29.0925
10	Sokolan CP5 ³ (Calcium sequestering agent)	4.0
	Perborate H ₂ O (sodium perborate monohydrate)	9.0
	T.A.E.D. (tetraacetylene diamine)	4.5
	Emphiphos 5632 ⁴	0.3
15	Stilbene 4 (optical brightener)	0.5
	Esperase (proteolytic enzyme)	1.0
	Duet 787 ⁵	0.6
	Relatin DM 4050 ⁶ (anti-redeposition agent)	1.0
20	Blue Foulan Sandolane (dye)	0.0075

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.

25 2) Diethylene triamine pentamethylene phosphoric acid, sodium salt

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

30 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 hydroxy-methylcellulose.

35 This composition is a stable, free-flowing, built,

non-gelling, liquid nonionic cleaning compositions in which the polyphosphate builder is stably suspended in the liquid nonionic surfactant phase.

5 Example 2

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:

10	<u>Ingredient</u>	<u>Weight %</u>
	Plurafac RA 30	37.5
	Diethyleneglycol monobutyl ether	10.0
	Octenylsuccinic anhydride	2.0
15	TPP NW	28.4
	Sokolan CP5	4.0
	Dequest 2066	1.0
	Perborate H ₂ O	9.0
	TAED	4.5
20	Hydroxylamine sulfate	0.1
	Emphiphos 5632	0.3
	ATS-X (optical brightener)	0.2
	Esperase	1.0
	Perfume	0.6
25	Felatin DM 4050	1.0
	TiO ₂	0.4

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

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOW:

1. A non-aqueous liquid detergent composition capable of washing and bleaching soiled fabrics at temperatures as low as 40°C or less which comprises a liquid phase comprising nonionic surfactant and a mono or poly (C₂ to C₃) alkylene glycol mono (C₁-C₅) alkyl ether in an amount of 30 to 70%, a water-soluble inorganic peroxide bleaching agent in an effective amount of up to 25%, a bleach activator to lower the temperature at which the bleaching will liberate hydrogen peroxide in aqueous solution in an effective amount of up to 10%, proteolytic enzyme in an amount of from 0.7 to 2 percent by weight and from 0.01 to 0.4 percent by weight, based on the total composition, of an hydroxylamine salt capable of inhibiting the enzyme-induced decomposition of the bleaching agent, said enzyme being present in the soiled fabrics.

2. The composition of claim 1 wherein the bleaching agent comprises sodium perborate monohydrate in an effective amount of up to 25%, the bleach activator is N,N,N',N'-tetra-acetyl ethylene diamine in an effective amount of up to 10% and the hydroxylamine salt is hydroxylamine sulfate or hydroxylamine hydrochloride in an amount of 0.02 to 0.2%.

3. The composition of claim 1 which further comprises 20 to 50% of a detergent builder salt suspended in the liquid nonionic surfactant.

4. A non-aqueous liquid laundry detergent composition comprising

30 to 70% by weight of a liquid phase comprising a liquid nonionic surfactant and a mono or poly (C₂ to C₃) alkylene glycol mono (C₁ to C₅) alkyl ether,

20 to 50% by weight of detergent builder salt suspended in the liquid phase,

2 to 20% by weight of an alkali metal perborate bleaching agent,



0.1 to 10% by weight of a bleach activator to lower the temperature at which the bleaching agent will liberate hydrogen peroxide in aqueous solution,

0.7 to 2% by weight of proteolytic enzyme, and

0.01 to 0.4% by weight of hydroxylamine salt capable of inhibiting the enzyme-induced decomposition of the bleaching agent.

5. The detergent composition of claim 4 wherein the hydroxylamine salt is hydroxylamine sulfate or hydroxylamine hydrochloride and is in an amount of 0.04 to 0.2% by weight.

6. The detergent composition of claim 4 wherein the detergent builder salt comprises 25-40% by weight of an alkali metal tripolyphosphate.

7. A non-aqueous liquid laundry detergent-bleaching composition comprising a liquid phase comprising liquid nonionic surfactant and a mono or poly (C₂ to C₃) alkylene glycol mono (C₁ to C₅) alkyl ether, a detergent builder salt suspended in the liquid phase, an effective amount of a water-soluble inorganic peroxide salt bleaching agent selected from the group consisting of perborate, percarbonate, perphosphate and persulfate, an effective amount of a bleach activator compound which will react with the bleaching agent in an aqueous wash bath to form a peroxy bleach agent at a temperature of 40°C, or less, an effective amount of a proteolytic enzyme, and an effective amount in the range of from 0.01 to 0.4% by weight of the composition of an hydroxylamine salt to inhibit enzyme-induced decomposition of the peroxide salt bleaching agent.

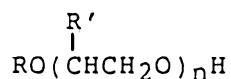
8. The composition of claim 7 wherein the hydroxylamine salt is hydroxylamine sulfate, hydroxylamine hydrochloride, or hydroxylamine hydrobromide.

9. The composition of claim 7 wherein the bleach activator compound comprises N,N,N',N'-tetra-acetylene diamine and is present in an amount of from 0.1 to 8% by weight of the composition.



10. A non-aqueous liquid laundry detergent composition comprising

40 to 60% by weight of a liquid nonionic surfactant and a viscosity-controlling and gel-inhibiting compound of the formula



where R is alkyl of 2 to 5 carbon atoms, R' is hydrogen or methyl, and n is a number from 2 to 4 on average, wherein the weight ratio of nonionic surfactant to said viscosity-controlling and gel-inhibiting compound being from 50:1 to 2:1,

20 to 50% by weight of detergent builder salt suspended in the liquid phase,

2 to 20% by weight of alkali metal perborate bleaching agent

0.1-8% by weight of tetraacetylene diamine bleach activator

0.7 to 2% by weight of proteolytic enzyme, and

0.01 to 0.4% by weight of hydroxylamine salt capable of inhibiting the enzyme induced decomposition of the bleaching agent.

11. The detergent composition of claim 10 wherein the liquid nonionic surfactant is comprised of C₁₀ to C₁₈ fatty alcohol ethoxylated with from 3 to 12 moles of a C₂ to C₃ alkylene oxide per mole of fatty alcohol and the compound of the formula is diethylene glycol monobutylether, and

the detergent builder salt comprises from 25 to 40% by weight of an alkali metal tripolyphosphate.

12. A method for cleaning and bleaching soiled fabrics which comprises contacting the soiled fabrics with the composition of claim 1 in an aqueous wash bath.

13. The method of claim 12 wherein the aqueous wash bath has temperature of 40°C or less.



14. A method for cleaning and bleaching soiled fabrics which comprises contacting the soiled fabrics with the composition of claim 4 in an aqueous wash bath.

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