COMMONWEALTH OF AUSTRALIA

Patents Act 1952

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

LOW PHOSPHATE OR PHOSPHATE FREE LAUNDRY DETERGENTS

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 20 August 1985
No. (767,535).

in United States of America on 20 August 1985
No. (767,570)

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

Dated this 31st day of July 1986.

COLGATE-PALMOLIVE COMPANY

By: Registered Patent Attorney

TO: The Commissioner of Patents,
COMMONWEALTH OF AUSTRALIA
In support of the Convention Application made by

COLGATE-PALMOLIVE COMPANY
300 Park Avenue
New York, New York 10022

for a patent for an invention entitled
LOW PHOSPHATE OR PHOSPHATE FREE LAUNDRY DETERGENTS

I, H.S. Sylvester, Assistant General Counsel Industrial Property, of and on behalf of the applicant company do solemnly and sincerely declare as follows:

(1) I am/we are the applicant(s) for the patent

(2) The basic application was made in the Convention Country in respect of the invention the subject of the application.

(3) I am/we are the first applicant(s) to make the application.

(4) The act of invention was made in the place and country specified below:

Place: New York, New York
Country: United States of America

(5) I am/we are the assignee(s) of the invention and the facts upon which COLGATE-PALMOLIVE COMPANY is/are entitled to make the application are as follows: The applicant is the assignee of the invention from the inventors identified above.

By: H.S. Sylvester
Assistant General Counsel
Industrial Property

To: The Commissioner of Patents
Commonwealth of Australia

F. B. RICE & CO.,
Patent Attorneys,
Sydney.

This Form is suitable for any type of Patent Application. No legalisation required.

*Authorized to Sign This Document by COLGATE-PALMOLIVE COMPANY by Regulations dated Jan. 9, 1984 of the Board of Directors.
Claim

1. A nonaqueous liquid heavy duty laundry detergent composition which comprises
   
   at least one liquid nonionic surfactant detergent,
   
   an hydroxy acrylic acid or acrylic acid salt polymer builder or
   
   an organic polyacetal carboxylate builder salt,
   
   at least one member selected from the group of an acid
   
   terminated nonionic surfactant anti-gel agent and an alkylene glycol
   
   monoalkyl ether, and an
   
   an anti-settling agent.

6. A phosphate detergent builder free nonaqueous liquid heavy duty
   
   laundry detergent composition which comprises
   
   Nonionic surfactant in an amount of about 30-55%
   
   Acid terminated surfactant in an amount of about 1-10%
   
   Alkylene glycol mono alkyl ether in an amount of about 5-15%
   
   Hydroxy acrylate polymer sodium salt builder in an
   
   amount of about 7-22%
C_{16} to C_{18} alkanol ester of phosphoric acid in an amount of about 0.1-0.9%.

Sodium perborate monohydrate bleaching agent in an amount of about 10-22%.

Tetraacetylene diamine bleach activator in an amount of about 4-15%.
COMMONWEALTH OF AUSTRALIA
Patents Act 1952

COMPLETE SPECIFICATION
(ORIGINAL)

Class
Int. Class

Application Number: 6081086
Lodged:

Complete Specification lodged: Accepted: Published:

Priorities: 20 August 1985 and 20 August 1985
Related Art:

Name of Applicant: COLGATE-PALMOLIVE COMPANY

Address of Applicant: 300 Park Avenue, New York, N.Y. 10022, United States of America

Actual Inventors: Guy Broze; Danielle Bastin; Leo Laitem; and Trazollah Ouhadi

Address for Service: F.B. RICE & CO., Patent Attorneys, 28A Montague Street, BALMAIN 2041

Complete Specification for the invention entitled:

LOW PHOSPHATE OR PHOSPHATE FREE LAUNDRY DETERGENTS

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

As disclosed in the commonly assigned copending application Serial No.
LOW PHOSPHATE OR PHOSPHATE FREE LAUNDRY DETERGENTS

BACKGROUND OF THE INVENTION

(1) Field of Invention

This invention relates to nonaqueous liquid fabric treating compositions. More particularly, this invention relates to phosphate free or low phosphate nonaqueous liquid laundry detergent compositions containing a suspension of a hydroxy acrylic acid or salt polymer builder or a polyacetal carboxylate builder salt in nonionic surfactants which compositions are stable against phase separation and gelation and are easily pourable and to the use of these compositions for cleaning soiled fabrics.

(2) Discussion of Prior Art

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.P. Nos. 4,316,812, 3,630,929 and 4,264,466 and British Patent Nos. 1,205,711, 1,270,040 and 1,600,981.

The U.S.P. 4,450,089 discloses a particulate bleaching detergent composition comprising an inorganic peroxygen bleach agent and a hydroxy acrylate polymer to stabilize the bleach agent and U.S.P. 4,445,249 discloses a particulate bleaching detergent composition comprising an organic peroxyacid bleach agent and a hydroxy acrylate polymer to stabilize the bleach agent.

The U.S.P. 3,825,498 discloses the use of polyhydroxy carboxylic acid polymer as a substitute for phosphate or polyphosphate builder salts used in particulate powder or aqueous dishwashing detergent compositions.

The U.S.P. 3,706,672 and U.S.P. 3,922,230 disclose the use of polyacrylate polymers as substitutes for phosphate or polyphosphate builder salts in detergent compositions.

The related pending applications assigned to the common assignee are SN 687,815, filed December 31, 1984;
These applications are directed to liquid nonaqueous nonionic laundry detergent compositions.

The washing power of synthetic nonionic surfactant detergents in laundry detergent compositions can be increased by the addition of builders. Sodium tripolyphosphate is one of the preferred builders. However, the use of sodium polyphosphate in dry powder detergents does involve several disadvantages such as, for example, the tendency of the polyphosphates to hydrolyse into pyro- and ortho-phosphates which represent less valuable builders.

In addition the polyphosphate content of laundry detergents has been blamed for the undesirably high phosphate content of surface water. An increased phosphate content in surface water has been found to contribute towards greater algea growth with the result that the biological equilibrium of the water can be adversely altered.

Recently enacted government legislation has been directed to reducing the amount of polyphosphates present in laundry detergents and in some jurisdictions in which polyphosphates have been a problem to require that the laundry detergents not contain any polyphosphate builders.

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 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 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.

In addition to the problem of settling or phase separation the nonaqueous liquid laundry detergents based on liquid nonionic surfactants suffer from the drawback that the nonionics tend to gel when added to 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 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 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 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.

The tendency of concentrated detergent compositions to gel during storage is aggravated by storing the compositions in unheated storage areas,
or by shipping the compositions during winter months in unheated transportation vehicles.

Partial solutions to the gelling problem have been proposed, for example, by diluting the liquid nonionic with certain viscosity controlling solvents and gel-inhibiting agents, such as lower alkanols, e.g. ethyl alcohol (see U.S.P. 3,953,380), alkali metal formates and adipates (see U.S.P. 4,368,147), hexylene glycol, polyethylene glycol, etc. and nonionic structure modification and optimization. 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 has centered on 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, improvements are desired in both the stability and gel inhibition of low phosphate and phosphate free nonaqueous liquid fabric treating compositions.

BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention a highly concentrated low phosphate, more particularly a polyphosphate detergent builder free, nonaqueous liquid laundry detergent composition is prepared by dispersing hydroxy acrylic acid or salt polymer builder or polyacetal carboxylate builder salt in a liquid nonionic surfactant detergent.

The hydroxy acrylic acid or salt polymer detergent builders used in accordance with an embodiment of the present invention are well known. The method of making the hydroxy acrylic acid and salt polymer and its use...
to stabilize peroxxygen and peroxyacid bleach agents in detergent compositions is disclosed in U.S.P. 4,450,089 and U.S.P. 4,455,249. The disclosure of these two patents is incorporated herein by reference.

The lower molecular weight hydroxy acrylic acid and salt polymers are readily biodegradable. The hydroxy acrylic acid and salt polymers are good bleach stabilizers and function as effective anti incrustation agents. The hydroxy acrylate polymers are particularly good detergent builder salts because of their high sequestering capacity for calcium and magnesium ions in the wash water.

The hydroxy acrylate polymer used as a builder in accordance with the present invention contains monomeric units of the formula

$$\left[ \begin{array}{c} \text{R}_1 \text{COO} \\ \text{C} \\ \text{R}_2 \text{COOM} \end{array} \right]_n$$

wherein $\text{R}_1$ and $\text{R}_2$ are the same or different and represent hydrogen or an alkyl group containing from 1 to 3 carbon atoms, and M represents hydrogen, or an alkali metal, alkaline earth metal or ammonium cation. The degree of polymerization, i.e. the value of n, is generally determined by the limit compatible with the solubility of the polymer in water.

The polyacetal carboxylate salts used in accordance with another embodiment of the present invention are also well known. The method of making the builder salts is described in Crutchfield et al U.S.P. 4,315,092 and 4,144,226 and the use of the polyacetal carboxylates as detergent builder salts is described in Crutchfield et al U.S.P. 4,146,495. The disclosure of these three patents is incorporated herein by reference.

The polyacetal carboxylates are water soluble and will depolymerize rapidly in neutral or nonalkaline medium to form low molecular weight components which are readily biodegradable. The polyacetal carboxylates are accordingly used in formulations which on addition to wash water normally have a pH of above pH7, e.g. about pH8 to 10, such as pH9 to 10. Though the polyacetal carboxylates as used in an alkaline medium are effective
The polyacetal carboxylates are particularly good detergent builder salts because of their high sequestering capacity for calcium and magnesium ions in the wash water. The polyacetal carboxylate detergent builder salts used in the present invention have the general formula:

\[ R_1\text{CHO}R_2\]  

wherein \( PM \) is an alkali or ammonium cation, \( n \) is at least 4, and \( R_1 \) and \( R_2 \) are individually stable groups which stabilize the polymer matrix against depolymerization in alkaline solution and are selected to be compatible with the ingredients of the nonionic liquid detergent composition of the present invention. A commercially available polyacetal carboxylate detergent builder salt is sold by Monsanto Chemical Company under the tradename Builder U and is a sodium salt.

In order to improve the viscosity characteristics of the composition an acid, terminated nonionic surfactant can be added. To further improve the viscosity characteristics of the composition and the storage properties of the composition, viscosity improving and anti-settling agents such as alkylene glycol mono alkyl ethers and phosphoric acid esters and aluminum stearate can be added. In a preferred embodiment of the invention the detergent composition contains an acid, terminated nonionic surfactant and an anti-settling agent.

There can be added to and can be used with the alkali metal hydroxy acrylic acid polymer builder the alkali metal polyacetal carboxylic acid builder.

Though polyacetal carboxylates are effective plant growth regulators, when the aqueous wash waste water is discharged into a sewer or other waste water system and the wash water is neutralized, the polyacetal carboxylates are depolymerized into small fragments which are readily biodegradable.
preferably less than 10 microns to further improve the stability of the suspension of the builder components in the liquid nonionic surfactant detergent.

In addition other ingredients can be added to the composition such as anti-incrustation agents, anti-foam agents, optical brighteners, enzymes, anti-redeposition agents, perfume and dyes.

The presently manufactured washing machines for home use normally operate at washing temperatures of up to 95°C. About ___ gallons (20 liters) of water are used during the wash and rinse cycles.

About 175gms of powder detergent per wash is normally used.

In accordance with the present invention where the highly concentrated liquid detergent is used normally only about 80gms (67ml) or less of the liquid detergent composition is required to wash a full load of dirty laundry.

Accordingly, in one aspect the present invention there is provided a phosphate builder free or substantially phosphate builder free liquid heavy duty laundry composition composed of a suspension of an alkali metal hydroxy acrylate polymer builder or an alkali metal polyacetal carboxylic acid builder salt in liquid nonionic surfactant.

According to another aspect, the invention provides a phosphate free or low phosphate concentrated liquid heavy duty laundry detergent composition which is stable, non-settling in storage and non-gelling in storage and in use. The liquid compositions of the present invention are easily pourable, easily measured and easily put into the washing machine.

According to another aspect, the invention provides a method for dispensing a phosphate free or low phosphate 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 nonaqueous liquid laundry detergent composition in which the detergent is composed, at least predominantly, of a polyphosphate builder free liquid nonionic surface active agent and for dispensing the composition from the container
polymeric hydroxy acid builder 

sodium tripolyphosphate (TPP), sodium pyrophosphate, potassium pyrophosphate, potassium tripolyphosphate and sodium hexametaphosphate.
nonaqueous liquid nonionic laundry detergent composition which include an effective amount of hydroxy acrylate polymer builder or polyacetal carboxylate builder salt.

A further object of this invention is to provide non-gelling, stable suspensions of heavy duty built nonaqueous liquid nonionic laundry detergent composition which include an amount of phosphoric acid alkanol ester and/or aluminum fatty acid salt which is sufficient to increase the stability of the composition, i.e. prevent settling of builder particles, etc., preferably while reducing or at least without increasing the plastic viscosity of the composition.

These and other objects of the invention which will become more apparent from the following detailed description of preferred embodiments are generally provided for by preparing a low polyphosphate or polyphosphate free detergent builder composition by adding to the nonaqueous liquid nonionic surfactant an effective amount of an alkali metal hydroxy acrylate polymer builder or an alkali metal polyacetal carboxylate builder salt and inorganic or organic fabric treating additives, e.g. viscosity improving and anti-gel agents, anti-settling agents, anti-incrustation agents, bleaching agents, bleach activators, anti-foam agents, optical brighteners, enzymes, anti-redeposition agents, perfume and dyes.

Nonionic Surfactant Detergent

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.

As is well known, the nonionic synthetic organic detergents are characterized by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide (hydrophilic in nature). Practically any hydrophobic compound having a carboxy, hydroxy, amido or amino group with a free hydrogen attached to

by magnesium atoms and with which varying amounts of hydrogen, sodium, potassium, calcium, etc., may be loosely combined. The bentonite in its
the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic detergent. The length of the hydrophilic or polyoxyethylene chain can be readily adjusted to achieve the desired balance between the hydrophobic and hydrophilic groups. Typical suitable nonionic surfactants are those disclosed in U.S. patents 4,316,812 and 3,630,929.

Usually, the nonionic detergents are poly-lower alkoxylated lipophiles wherein the desired hydrophilic-lipophilic 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 alkoxylated higher alkanol wherein the alkanol is of 9 to 18 carbon atoms and wherein the number of mols of lower alkyene 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 9 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, often 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 primary alkanols.

Other examples of such detergents include Tergitol 15-8-7 and Tergitol 15-8-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corp. The former is mixed ethoxylate 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 composition 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 commercially well known class of nonionics sold under the trademark Plurafac. The Plurafacs 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 products which are (A) C₁₃₋C₁₅ fatty alcohol condensed with 6 moles ethylene oxide and 3 moles propylene oxide, (B) C₁₃₋C₁₅ fatty alcohol condensed with 7 moles propylene oxide and 4 moles ethylene oxide, (C) C₁₃₋C₁₅ fatty alcohol condensed with 5 moles propylene oxide and 10 moles ethylene oxide, and (D) a 1:1 mixture of (B) and (C).

Another group of liquid nonionics are commercially available from Shell Chemical Company, Inc. under the Dobanol trademark. Dobanol 91-5 is an ethoxylated C₈₋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 oxide per mole of fatty alcohol.

In the preferred poly-lower alkoxyalted higher alkanols, to obtain the best balance of hydrophilic and lipophilic moieties the number of lower alkanes 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 be less than 20% thereof and preferably less than 10% thereof.

When greater proportions of non-terminally alkoxylated alkanols, propylene oxide-containing poly-lower alkoxylated 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 invention can also improve the properties of the detergents based on such nonionics. In some cases, as when a higher molecular weight poly lower alkoxylated higher alkanol is employed, often for its detergency, the proportion thereof will be regulated or limited in accordance with the
results of routine 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 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 temperatures.

Another useful group of nonionic surfactants are the "Surfactant T" series of nonionics available from British Petroleum. The Surfactant T nonionics are obtained by the ethoxylation of secondary C$_{13}$ fatty alcohols having a narrow ethylene oxide distribution. The Surfactant T5 has an average of 5 moles of ethylene oxide; Surfactant T7 an average of 7 moles of ethylene oxide; Surfactant T9 an average of 9 moles of ethylene oxide and Surfactant T12 an average of 12 moles of ethylene oxide per mole of secondary C$_{13}$ fatty alcohol.

In the compositions of this invention, preferred nonionic surfactants include the C$_{13}$-C$_{15}$ secondary fatty alcohols with relatively narrow contents of ethylene oxide in the range of from about 7 to 9 moles, and the C9 to C11 fatty alcohols ethoxylated with about 5-6 moles ethylene oxide.

Mixtures of two or more of the liquid nonionic surfactants can be used and in some cases advantages can be obtained by the use of such mixtures.

Acid Terminated Nonionic Surfactant

The viscosity and gel properties of the liquid detergent compositions can be improved by including in the composition an effective amount an acid terminated liquid nonionic surfactant. The acid terminated nonionic surfactants consist 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 an ester or a partial ester of a nonionic surfactant and a polycarboxylic acid or anhydride.
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, 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 addition of the acid terminated nonionic surfactants to the liquid nonionic surfactant aids in the dispensibility of the composition, i.e. pourability, and lowers the temperature at which the liquid nonionic surfactants form a gel in water without a decrease in their stability against settling. The acid terminated nonionic surfactant reacts in the washing machine water with the alkalinity of the dispersed builder salt phase of the detergent composition and acts as an effective anionic surfactant.

Specific examples include the half-esters of product (A) with succinic anhydride, the ester or half ester of Dobanol 25-7 with succinic anhydride, and the ester or half ester of Dobanol 91-5 with succinic anhydride. Instead of succinic anhydride, other polycarboxylic acids or anhydrides can be used, e.g. maleic acid, maleic acid anhydrided, citric acid and the like.

The acid terminated nonionic surfactants can be prepared as follows:

**Acid Terminated product (A).** 400g of product (A) nonionic surfactant which is a C\textsubscript{13} to C\textsubscript{15} alkanol which has been alkoxylated to introduce 6 ethyleneoxide and 3 propylene oxide units per alkanol unit is mixed with 32g of succinic anhydride and heated for 7 hours at 100°C. The mixture is cooled and filtered to remove unreacted succinic material. Infrared analysis indicated that about one half of the nonionic surfactant has been converted to the acidic half-ester thereof.

**Acid Terminated Dobanol 25-7.** 522g of Dobanol 25-7 nonionic surfactant which is the product of ethoxylation of a C\textsubscript{12} to C\textsubscript{15} alkanol and has about 7 ethyleneoxide units per molecule of alkanol is mixed with 100g of succinic anhydride and 0.1g of pyridine (which acts as an esterification catalyst) and heated at 260°C for 2 hours, cooled and filtered to remove
unreacted succinic material. Infrared analysis indicates that substantially all
the free hydroxyls of the surfactant have reacted.

Acid Terminate Dobanol 91-5. 1000g of Dobanol 91-5 nonionic surfactant
which is the product of ethoxylation of a C₉ to C₁₁ alkanol and has about 5
ethylene oxide units per molecule of alkanol is mixed with 265g of succinic
anhydride and 0.1g of pyridine catalyst and heated at 260°C for 2 hours,
cooled and filtered to remove unreacted succinic material. Infrared analysis
indicates that substantially all the free hydroxyls of the surfactant have
reacted. Other esterification catalysts, such as an alkali metal alkoxide
(e.g. sodium methoxide) may be used in place of, or in admixture with, the
pyridine. The acidic polyether compound, i.e. the acid terminated nonionic
surfactant is preferably added dissolved in the nonionic surfactant.

**BUILDER SALTS**

The liquid nonaqueous nonionic surfactant used in the compositions of
the present invention has dispersed and suspended therein fine particles of
organic and/or inorganic detergent builder salts.

The present invention includes as an essential part of the composition
an organic hydroxy acrylic acid or salt polymer builder or an organic
polyacetal carboxylate acid builder salt.

**Organic Builder Salts**

**Hydroxy Acrylic Acid Polymer Builder**

A preferred organic builder salt comprises alkali metal salts of hydroxy
acrylic acid polymer, preferably the sodium and potassium salts. A
particularly preferred builder is the alpha-hydroxy acrylic acid and sodium
salt polymers.

Briefly, hydroxy acrylic acid and salt polymer detergent builder used
in the present invention contains monomeric units of the formula

\[
\text{\text{R}_{1} OH} \quad \text{C} \quad \text{C} \quad \text{R}_{2} \text{COOM}
\]

wherein R₁ and R₂ can be the same or different and represent hydrogen or
an alkyl group containing from 1 to 3 carbon atoms such as methyl, ethyl
and propyl. The preferred substituents for \( R_1 \) and \( R_2 \) are both hydrogen. \( M \) represents hydrogen, or an alkali metal such as sodium or potassium, or an alkaline earth metal such as calcium, magnesium or barium. The preferred substituent for \( M \) is sodium. The terminal or end groups of the polymer are not critical and can be \( H \), \( OH \), \( CH_3 \) or a hydrocarbon chain.

The degree of polymerization, i.e., the value of \( n \), is generally determined by the limit compatible with the solubility of the polymer in water.

The value of \( n \) can be 10 to 10,000, preferably 10 to 1000 and more preferably 20 to 200. The hydroxy acrylic acid or salt polymer can have a molecular weight of 1000 to \( 10^6 \), preferably 1000 to \( 10^5 \) and more preferably 2000 to 20,000. See for example U.S.P. Nos. 3,920,570 and 4,107,411 which describe methods of making the polymers, the disclosures of which are incorporated herein.

Polyacetal Carboxylic Acid Builder Salts

Other preferred organic builder salts comprises alkali metal salts of polyacetal carboxylic acid, preferably the sodium and potassium salts.

Broadly, however, the polyacetal carboxylate detergent builder salts used in the present invention have the following general formula

\[
\begin{align*}
R_1 & \quad \text{CHO} \quad R_2 \\
\text{COM} \quad n
\end{align*}
\]

wherein \( M \) is selected from the group consisting of alkali metal, ammonium, alkyl groups having 1 to 4 carbon atoms; tetralkyl ammonium groups and alkanol amine groups having from 1 to 4 carbon atoms in the alkyl chain; the alkali metals are preferred, for example sodium and potassium; \( n \) is at least 4; and \( R_1 \) and \( R_2 \) are individually any chemically stable groups. \( R_1 \) and \( R_2 \) may be the same or different groups.

The end groups \( R_1 \) and \( R_2 \) may be selected from a wide range of materials as long as they stabilize the polyacetal carboxylate polymer against rapid depolymerization in an alkaline solution. The \( R_1 \) and \( R_2 \) end groups
are also selected to be compatible with the ingredients used to formulate the nonaqueous liquid nonionic composition of the present invention, particularly the nonionic surfactant and the anti gel and anti settling agents.

The number of the repeating groups, i.e. the value of \( n \), is an important factor since the effectiveness of the polyacetal carboxylate salt as a detergency builder is affected by the polymer chain length. Where \( n = 4 \) the polymer shows effectiveness as a sequestant, chelating agent and builder. The value for \( n \) can be as high as 400. There does not, however, appear to be any advantage for \( n \) to have a greater value than about 200.

When the value for \( n \) exceeds about 100 no significant improvement in sequestering chelating and builder properties is observed. Thus the polyacetal carboxylate can contain between 10 and 400 units, i.e. \( n \) can equal 10 to 400, preferably \( n = 50 \) to 200 and more preferably \( n = 50 \) to 100 repeating units.

Where \( n \) has a value of 50 to 200 there is provided very good sequestration effectiveness for calcium and magnesium ions and very good builder properties.

As an example, suitable chemically stable end groups include stable substituent moieties derived from otherwise stable compounds, such as alkanes, such as methane, ethane, propane and butane; alkenes such as ethylene, propylene and butylene; branched chain hydrocarbons, both saturated and unsatured, such as 2-methyl butane and 2-methyl butene; alcohols such as methanol, ethanol, 2-propanol, cyclohexanol, polyhydric alcohols such as 1,2-ethane diol and 1,4-benzene diol; ethers such as methoxyethane methyl ether, ethyl ether, ethoxypropane and cyclic ethers such as ethylene oxide; epichlorohydrin and tetramethylene oxide; aldehydes and ketones such as ethanal, acetone, propanal and methylethyl ketone; and carboxylate containing compounds such as the alkali metal salts of carboxylic acids, the esters of carboxylic acids and the anhydrides. Particularly suitable end groups include alkyl groups and cyclic alkyl groups containing
oxygeñ such as oxyalkyl groups like methoxy, ethoxy, carboxylic acids; and aldehydes, ethers and other oxygen containing alkyl groups.

The polyacetal carboxylates can contain polymer fragments, and accordingly, the polymer can be a linear homopolymer or copolymer, or it can be branched. Any number of chain extending agents can be copolymerized with the polyacetal carboxylates. It is only necessary that the chain extending agent will provide at least two reactive sites and does not cause the polyacetal carboxylates to depolymerize in alkaline solution and that they be compatible with the nonionic surfactant and the anti-gel and anti settling agents of the present invention. Suitable chain extending agents include: polyhydric alcohols, such as ethylene oxide, propylene oxide and epihalohydin epoxysuccinates; aldehydes, such as formaldehyde and acetaldehyde. It is particularly beneficial when the chain extending agent contains substituent carboxy groups. Aliphatic chain extending agents having from 1 to 4 carbon atoms, such as ethylene oxide or propylene oxide, are especially preferred.

When acetal carboxylate esters are copolymerized with a chain extending agent, the amount of acetal carboxylate should be at least about 50 percent by weight, based on the total weight of the polymer, to insure that the polymer will effectively sequester calcium and magnesium ions and retain its builder properties. It is preferred that the amount of acetal carboxylate is 50 to 80 percent such as about 80 percent by weight, based on the total weight of the polymer, or even higher.

In a preferred embodiment of the invention $R_1$ is a member selected from the group consisting of $\text{-OC}_3\text{H}_3$, $\text{-OC}_2\text{H}_5$, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{1-4}$, and mixtures thereof, and $R_2$ is a member selected from the group consisting of $\text{-CH}_3$, $\text{-C}_2\text{H}_5$, $\text{-}(\text{CH}_2\text{CH}_2\text{O})_{1-4}\text{H}$.
and mixtures thereof, where R is hydrogen or alkyl having 1 to 8 carbon atoms, and M is as defined above.

It is particularly preferred that \( R_1 \) is \( \text{OCH}_2\text{CH}_3 \) or \( \text{COOM} \)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{RC} & \quad \text{H}_2\text{C}_2\text{O} \\
\text{CH}_2-\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{O} & \quad \text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

or mixtures thereof, and \( R_2 \) is \( \text{OCH}_2\text{CH}_3 \)

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

where M is sodium and n is 50 to 200.

Other organic builders that can be used are polymers and copolymers of polyacrylic acid and polymaleic anhydride and the alkali metal salts thereof. More specifically such builder salts can consist of a copolymer which is the reaction product of about equal moles of methacrylic acid and maleic anhydride which has been completely neutralized to form the sodium salt thereof. The builder is commercially available under the tradename of Sokalan CP5. This builder serves when used even in small amounts to inhibit encrustation.

Since the compositions of this invention are generally highly concentrated, and, therefore, may be used at relatively low dosages, it is desirable to supplement the builder with an auxiliary builder such as an alkali metal lower polycarboxylic acid having high calcium and magnesium binding capacity to inhibit incrustation which could otherwise be caused by formation of insoluble calcium and magnesium salts. Suitable alkali metal polycarboxylic acids are alkali metal salts of citric and tartaric acid, e.g. monosodium citrate (anhydrous), trisodium citrate, monosodium and disodium tartarate and dipotassium tartarate.
composition are ground to a particle size of less than 100 microns and to

There can be added to and can be used with the alkali metal hydroxy acrylic acid polymer builder the alkali metal polyacetal carboxylic acid builder salts (e.g. Builder U), that are also disclosed herein.

Examples of organic alkaline sequestrant builder salts which can be used with the hydroxy acrylic acid or salt polymer builder or with the polyacetal carboxylate builder salts of the present invention 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 nitriloacetates (NTA) and triethanolammonium N-(2-hydroxyethyl)nitrilotriacetates. Mixed salts of these aminopolycarboxylates are also suitable. Other suitable builders of the organic type include carboxymethylsuccinates, tartronates and glycolates.

**Inorganic Builder Salts**

The invention detergent compositions can also include inorganic water soluble and/or water insoluble detergent builder salts. Suitable inorganic alkaline builder salts that can be used are alkali metal carbonate, borates, bicarbonates, and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium carbonate, sodium tetraborate, sodium bicarbonate, sodium sesquicarbonate and potassium bicarbonate.

The alkali metal silicates are useful builder salts which also function to adjust or control the pH and to make the composition antifouling to washing machine parts. Sodium silicates of Na$_2$O/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.

Though it is preferred that the detergent composition be phosphate or polyphosphate free or substantially polyphosphate free, small amounts of the conventional polyphosphate builder salts can be added where the local legislation permits such use. Specific examples of such builder salts are
Examples of organic alkaline sequestrant builder salts which can be used with the hydroxy acrylic acid or salt polymer builder or with the polyacetal carboxylate builder salts of the present invention 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 nitriloacetates (NTA) and triethanolammonium N-(2-hydroxyethyl)nitrilodiacetates. Mixed salts of these aminopolycarboxylates are also suitable. Other suitable builders of the organic type include carboxymethylsuccinates, tartronates and glycollates.

Inorganic Builder Salts

The invention detergent compositions can also include inorganic water soluble and/or water insoluble detergent builder salts. Suitable inorganic alkaline builder salts that can be used are alkali metal carbonate, borates, bicarbonates, and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium carbonate, sodium tetraborate, sodium bicarbonate, sodium sesquicarbonate and potassium bicarbonate.

The alkali metal silicates are useful builder salts which also function to adjust or control the pH and to make the composition anticorrosive to washing machine parts. Sodium silicates of Na₂O/SiO₂ 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.

Though it is preferred that the detergent composition be phosphate or polyphosphate free or substantially polyphosphate free, small amounts of the conventional polyphosphate builder salts can be added where the local legislation permits such use. Specific examples of such builder salts are

**EXAMPLE 2**

A concentrated nonaqueous liquid nonionic surfactant detergent...
sodium tripolyphosphate (TPP), sodium pyrophosphate, potassium pyrophosphate, potassium tripolyphosphate and sodium hexametaphosphate. The sodium tripolyphosphate (TPP) is a preferred polyphosphate. In the formulations where the polyphosphate is added it is added in an amount of 0 to 20 or 30%, such as 5 to 15. As mentioned previously, however, it is preferred that the formulations be polyphosphate free or substantially polyphosphate free.

Other typical suitable builders include, for example, those disclosed in U.S. Patents 4,316,812, 4,264466 and 3,630,929. The inorganic alkaline builders can be used with the nonionic surfactant detergent compound or in re with other organic or inorganic builder salts. Water insoluble crystalline and amorphous aluminosilicate zeolites can be used. The zeolites generally have the formula

$$(M_2O)_x·(Al_2O_3)_y·(SiO_2)_z·wH_2O$$

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. 400meq lg.

Various crystalline zeolites (i.e. alumino-silicates) that can be used are described in British Patent 1,504,168, U.S.P. 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 incorporated herein by reference.

Other materials such as clays, particularly of the water-insoluble types, may be useful adjuncts in 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, 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 contains at least 50% montmorillonite and thus its cation exchange capacity is at least about 50 to 75 meq per 100g of bentonite. Particularly preferred bentonites 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 Guan.

Viscosity Control and Anti Gel Agents

The inclusion in the detergent composition of an effective amount of low molecular weight alkylene glycol monoalkyl ether amphiphilic compounds which function as viscosity control and gel-inhibiting agents for the nonionic surfactant substantially improves the storage properties of the composition. The amphiphilic compounds can be considered to be analogous in chemical structure to the ethoxylated and/or propoxylated fatty alcohol liquid nonionic surfactants but have relatively short hydrocarbon chain lengths (C₂ to C₆) and a low content of ethylene oxide (about 2 to 6 ethylene oxide groups per molecule).

Suitable amphiphilic compounds can be represented by the following general formula

$$RO(CH_2CH_2O)_nH$$

where $R$ is a C₂-C₈ alkyl group, and $n$ is a number of from about 1 to 6, on average.

Specifically the compounds are lower (C₂ to C₃) alkylene glycol mono lower (C₂ to C₅) alkyl ethers.

More specifically the compounds are mono di- or tri lower (C₂ to C₃) alkylene glycol mono lower (C₁ to C₅) alkyl ethers.

Specific examples of suitable amphiphilic compounds include ethylene glycol monoethyl ether C₂H₅-O-CH₂CH₂OH,
diethylene glycol monobutyl ether $C_4H_9-O-(CH_2CH_2O)_2\text{H}$, tetraethylene glycol monobutyl ether $C_4H_7-O-(CH_2CH_2O)_4\text{H}$ and dipropylene glycol monomethyl ether $CH_3-O-(CHCH_2O)_2\text{H}$. Diethylene glycol monobutyl ether is especially preferred.

The inclusion in the composition of the low molecular weight lower alkylene glycol mono alkyl ether decreases the viscosity of the composition, such that it is more easily pourable, improves the stability against settling and improves the dispersibility of the composition on the addition to warm water or cold water.

The compositions of the present invention have improved viscosity and stability characteristics and remain stable and pourable at temperatures as low as about $5^\circ\text{C}$ and lower.

**Stabilizing Agents**

In an embodiment of this invention the physical stability of the suspension of the detergent builder compound or compounds and any other suspended additive, such as bleaching agent, etc., in the liquid vehicle is improved by the presence of a stabilizing agent which is an alkanol ester of phosphoric acid or an aluminum salt of a higher fatty acid.

Improvements in stability of the composition may be achieved in certain formulations by incorporation of a small effective amount of an acidic organic phosphorus compound having an acidic $\text{POH}$ group, such as a partial ester of phosphoric 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, the acidic organic phosphorus compound having an acidic $\text{POH}$ group can increase the stability of the suspension of 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
higher alkanol. Higher molecular weight alkanols and various other normally

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 C\textsubscript{16} to C\textsubscript{18} alkanol (Empiphos 5632 from Marchon); it is made up of about 35% monoester and 65% diester.

The inclusion of quite small amounts of the acidic organic phosphorus compound makes the suspension significantly more stable against settling while remaining pourable, while, for the low concentration of stabilizer, e.g. below about 1%, its plastic viscosity will generally decrease.

Further improvements in the stability and anti-settling properties of the composition may be achieved by the addition of a small effective amount of an aluminum salt of a higher fatty acid to the composition.

The aluminum salt stabilizing agents are the subject matter of the commonly assigned copending application Serial No. 725,455, filed April 22, 1985, the disclosure of which is incorporated herein by reference.

The preferred higher aliphatic fatty acids will have from about 8 to about 22 carbon atoms, more preferably from about 10 to 20 carbon atoms, and especially preferably from about 12 to 18 carbon atoms. The aliphatic radical may be saturated or unsaturated and may be straight or branched.

As in the case of the nonionic surfactants, mixtures of fatty acids may also be used, such as those derived from natural sources, such as tallow fatty acid, coco fatty acid, etc.

Examples of the fatty acids from which the aluminum salt stabilizers can be formed include, decanoic acid, dodecanoic acid, palmitic acid, myristic acid, stearic acid, oleic acid, eicosanoic acid, tallow fatty acid, coco fatty acid, mixtures of these acids, etc. The aluminum salts of these acids are generally commercially available, and are preferably used in the triacid form, e.g. aluminum stearate as aluminum tristearate $\text{Al(C}_{17}\text{H}_{35}\text{COO})_3$. The monoacid salts, e.g. aluminum monostearate, $\text{Al(OH)}_2(\text{C}_{17}\text{H}_{35}\text{COO})$ and diacid salts, e.g. aluminum distearate, $\text{Al(OH)}_2(\text{C}_{17}\text{H}_{35}\text{COO})_2$, and mixtures
of two or three of the mono-, di- and triacid aluminum salts can also be used. It is most preferred, however, that the triacid aluminum salt comprises at least 30%, preferably at least 50%, especially preferably at least 80% of the total amount of aluminum fatty acid salt.

The aluminum salts, as mentioned above, are commercially available and can be easily produced by, for example, saponifying a fatty acid, e.g. animal fat, stearic acid, etc., followed by treatment of the resulting soap with alum, alumina, etc.

Although applicants do not wish to be bound by any particular theory of the manner by which the aluminum salt functions to prevent settling of the suspended particles, it is presumed that the aluminum salt increases the wettability of the solid surfaces by the nonionic surfactant. This increase in wettability, therefore, allows the suspended particles to more easily remain in suspension.

Only very small amounts of the aluminum salt stabilizing agent is required to obtain the significant improvements in physical stability.

In addition to its action as a physical stabilizing agent, the aluminum salt has the additional advantage over other physical stabilizing agents that it is non-ionic in character and is compatible with the nonionic surfactant component and does not interfere with the overall detergency of the composition; it exhibits some anti-foaming effect; it can function to boost the activity of fabric softeners, and it confers a longer relaxation time to the suspensions.

Bleaching Agents

The bleaching agents are classified broadly, for instance, as chlorine bleaches and oxygen bleaches. Chlorine bleaches typified by sodium hypochlorite (NaOCl), potassium dichloroisocyanurate (59% available chlorine), and trichloroisocyanuric acid (95% available chlorine). Oxygen bleaches are preferred and are represented by percompounds which liberate hydrogen peroxide in solution. Preferred examples include sodium and
potassium perborates, percarbonates, and perphosphates, and potassium monopersulfate. The perborates, particularly sodium perborate monohydrate, are especially preferred. There can also be used as bleaching agents peroxo acid compounds such as diperoxyazelaic acid, diperoxydodecanedioic acid, monoperoxysuccinic acid, monoperoxyphthalic acid (MPPA) and diperoxyterephthalic acid.

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 are disclosed, for example, in U.S.P. 4,264,466 or in column 1 of U.S.P. 4,430,244, the relevant disclosures of which are incorporated herein by reference. Polyacylated compounds are preferred activators; among these, compounds such as tetracetyl ethylene diamine ("TAED") and pentaacetyl glucose are particularly preferred.

Other useful activators include, for example, acetylsalicylic acid derivatives, ethyldiene benzoate acetate and its salts, ethyldiene carboxylate acetate and its salts, alkyl and alkenyl succinic anhydride, tetracetylglucouril ("TAGU"), and the derivatives of these. Other useful classes of activators are disclosed, for example, in U.S.P. 4,111,826, 4,422,950 and 3,661,789.

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

Suitable sequestering agents for this purpose include sodium salts of nitrilotriacetic acid (NTA), ethylene diamine tetracetic acid (EDTA), diethylenetriamine pentaacetic acid (DTPA), diethylene triamine pentamethylene phosphonic acid (DTPMP) sold under the tradename Dequest.

Nonionic surfactant in an amount of about 30-45%
Acid terminated surfactant in an amount of about 2-18%
2066; and ethylene diamine tetramethylene phosphonic acid (EDITEMPA). The sequestering agents can be used alone or in admixture.

In order to avoid loss of peroxide bleaching agent, e.g. sodium perborate, resulting from enzyme-induced decomposition, such as by catalase enzyme, the compositions may additionally include an enzyme inhibitor compound, i.e. a compound capable of inhibiting enzyme-induced decomposition of the peroxide bleaching agent. Suitable inhibitor compounds are disclosed in U.S.P. 3,606,990, the relevant disclosure of which is incorporated herein by reference.

Of special interest as the inhibitor compound, mention can be made of hydroxylamine sulfate and other water-soluble hydroxylamine salts. In the preferred nonaqueous compositions of this invention, suitable amounts of the hydroxylamine salt inhibitors can be as low as about 0.01 to 0.4%. Generally, however, suitable amounts of enzyme inhibitors are up to about 15%, for example, 0.1 to 10%, by weight of the composition.

In addition to the detergent builders, various other detergent additives or adjuvants 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, hydropropyl methyl cellulose. A preferred anti-redeposition agent is sodium carboxymethyl cellulose having a 2:1 ratio of CM/MC which is sold under the tradename Relatin DM 4050.

Optical brighteners for cotton, polyamide and polyester fabrics can be used. Suitable optical brighteners include stilbene, triazole and benzidine sulfone compositions, especially sulfonated substituted triazinyl stilbene, sulfonated naphthotriazole stilbene, benzidine sulfone, etc.; most preferred are stilbene and triazole combinations. A preferred brightener is Stilbene Brightener N4 which is a dianilinodimorpholino stilbene polysulfonate.
Enzymes, preferably proteolytic enzymes, such as subtilisin, bromelin, papain, trypsin and pepsin, as well as amylase type enzymes; lipase type enzymes, and mixtures thereof can be used. Preferred enzymes include protease slurry, esperase slurry and amylase. A preferred enzyme is Esperse SL8 which is a protease. Anti-foam agents, e.g. silicon compounds, such as Silicane L 7604, which is a polysiloxane can also be added in small effective amounts.

Bactericides, e.g. tetrachlorosalicylanilide and hexachlorophene, fungicides, dyes, pigments (water dispersible), preservatives, ultraviolet absorbers, anti-yellowing agents, such as sodium carboxymethyl cellulose, pH modifiers and pH buffers, color safe bleaches, perfume, and dyes and bluing agents such as ultramarine blue can be used.

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.P. 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 an embodiment of the invention the stability of the builder salts in the composition during storage and the dispersibility of the composition in water is improved by grinding and reducing the particle size of the solid builders to less than 100 microns, preferably less than 40 microns and more preferably to less than 10 microns. The solid builders are generally supplied in particle sizes of about 100, 200 or 400 microns. The nonionic liquid surfactant phase can be mixed with the solid builders prior to or after carrying out the grinding operation.
In a preferred embodiment 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). Preferably less than about 10%, especially less than about 5% of all the suspended particles have particle sizes greater than 10 microns. Compositions whose dispersed particles are of such small size have improved stability against separation or settling on storage. Addition of the acid terminated nonionic surfactant compound aids in the dispersibility of the dispersions without a corresponding decrease in the dispersions stability against settling.

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. After the grinding step any remaining liquid nonionic surfactant can be added to the ground formulation. 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 laundry detergent compositions of the invention, typical proportions (percent based on the total weight of composition, unless otherwise specified) of the ingredients are as follows:
acids, the esters of carboxylic acids and the anhydrides. Particularly suitable end groups include alkyl groups and cyclic alkyl groups containing

Liquid nonionic surfactant detergent in the range of about 20 to 60, such as 25 to 50 percent.

Acid terminated nonionic surfactant may be omitted, it is preferred however that it be added to the composition in an amount in the range of about 2 to 30, such as 2 to 20 or 10 to 25 percent.

Hydroxy acrylic acid or salt polymer builder or polyacetal carboxylate acid builder salt in the range of about 5 to 50, such as 10 to 30 percent.

Polyphosphate detergent builder salt in the range of about 0 to 30 percent, such as 0 to 20 percent and 5 to 15 percent.

Copolymer of polyacrylate and polymaleic anhydride alkali metal salt anti incrustation agent in the range of about 0 to 10, such as 2 to 8 percent.

Alkylene glycol monoalkylether anti-gel agent may be omitted, it is preferred however that it be added to the composition in an amount in the range of about 0 to 20, e.g. 5 to 30, such as 5 to 15 or 20 percent.

Phosphoric acid alkanol ester stabilizing agent in the range of 0 to 2.0 or 0.1 to 2.0, such as 0.10 to 0.5 or 1.0 percent.

Aluminum salt or fatty acid stabilizing agent in the range of about 0 to 3.0, e.g. 0.5 to 2.0, such as 0.1 to 1.0 percent.

It is preferred that at least one of phosphoric acid ester or aluminum salt stabilizing agents be included in the composition.

Bleaching agent in the range of about 0 to 35, e.g. 5 to 40, such as 5 or 10 to 30 percent.

Bleach activator in the range of about 0 to 25, e.g. 2 to 25, such as 5 to 20 percent.

Sequestering agent for bleach in the range of about 0 to 3.0, preferably 0.5 to 2.0 percent.

Anti-redeposition agent in the range of about 0 to 3.0, preferably 0.5 to 2.0 percent.

Optical brightener in the range of about 0 to 2.0, preferably 0.1 to 1.5 percent.
Enzymes in the range of about 0 to 3.0, preferably 0.5 to 2.0 percent can be included.

Perfume in the range of about 0 to 2.0, preferably 0.10 to 1.0 percent can be included.

Various of the previously mentioned additives can optionally be added to achieve the desired function of the added materials.

Mixtures of the acid terminated nonionic surfactant and the alkylene glycol alkyl ether anti-gel agents can be used and in some cases advantages can be obtained by the use of such mixtures alone, or with the addition to the mixture of a stabilizing and anti settling agent.

In the selection of the additives, they will be chosen to be compatible with the main constituents of the detergent composition. In this application, as mentioned above, all proportions and percentages are by weight of the entire formulation or composition unless otherwise indicated.

The concentrated nonaqueous nonionic liquid detergent composition of the present invention dispenses readily in the water in the washing machine. The presently used home washing machines normally use 175gms of powder detergent to wash a full load of laundry. In accordance with the present invention only about 67ml or about 80gms of the concentrated liquid nonionic detergent composition is needed.

In a preferred embodiment of the invention the detergent composition of a typical formulation is formulated using the following named ingredients.
**Alkali Metal Hydroxy Acrylic Acid Polymer Builder**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic surfactant detergent.</td>
<td>30-55</td>
</tr>
<tr>
<td>Acid terminated surfactant.</td>
<td>1-10</td>
</tr>
<tr>
<td>Alkylene glycol monoalkyl ether.</td>
<td>3-15</td>
</tr>
<tr>
<td>Hydroxy acrylate polymer.</td>
<td>7-22</td>
</tr>
<tr>
<td>Alkanol phosphoric acid ester.</td>
<td>0.1-0.9</td>
</tr>
<tr>
<td>Alkali metal perborate bleaching agent.</td>
<td>10-22</td>
</tr>
<tr>
<td>Bleach activator (TAED).</td>
<td>4-15</td>
</tr>
<tr>
<td>Optical brightener.</td>
<td>0.1-0.6</td>
</tr>
<tr>
<td>Enzymes.</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Perfume.</td>
<td>0.1-0.8</td>
</tr>
</tbody>
</table>

In another preferred embodiment of the invention the detergent composition of a typical formulation is formulated using the following named ingredients:

**Alkali Metal Polyacetal Carboxylic Acid Builder Salt**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic surfactant detergent.</td>
<td>30-55</td>
</tr>
<tr>
<td>Acid terminated surfactant.</td>
<td>2-18</td>
</tr>
<tr>
<td>Alkali metal polyacetal carboxylic acid builder salt.</td>
<td>5-22</td>
</tr>
<tr>
<td>Polyphosphate builder salt.</td>
<td>0-20</td>
</tr>
<tr>
<td>Alkanol phosphoric acid ester.</td>
<td>0.1-0.9</td>
</tr>
<tr>
<td>Alkali metal perborate bleaching agent.</td>
<td>7-22</td>
</tr>
<tr>
<td>Bleach activator (TAED).</td>
<td>4-12</td>
</tr>
<tr>
<td>Optical brightener (Stilbene Brightener N4).</td>
<td>0.1-0.8</td>
</tr>
<tr>
<td>Enzymes (Protease-Esperase SL8).</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Perfume.</td>
<td>0.1-0.8</td>
</tr>
</tbody>
</table>
The present invention is further illustrated by the following example.

**EXAMPLE 1**

A concentrated nonaqueous liquid nonionic surfactant detergent composition is formulated from the following ingredients in the amounts specified.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant T9.</td>
<td>20</td>
</tr>
<tr>
<td>Surfactant T7.</td>
<td>20</td>
</tr>
<tr>
<td>Acid terminated Dobanol 91-5 reaction product with succinic anhydride.</td>
<td>4.0</td>
</tr>
<tr>
<td>Diethylene glycol monobutyl ether.</td>
<td>10</td>
</tr>
<tr>
<td>Alpha hydroxy acrylate polymer sodium salt.</td>
<td>17.0</td>
</tr>
<tr>
<td>Alkanol phosphoric acid ester.</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium perborate monohydrate bleaching agent.</td>
<td>17.0</td>
</tr>
<tr>
<td>Tetraacetylene diamine (TAED) bleach activator.</td>
<td>10.0</td>
</tr>
<tr>
<td>Stilbene brightener.</td>
<td>0.4</td>
</tr>
<tr>
<td>Esperase slurry.</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>
EXAMPLE 2

A concentrated nonaqueous liquid nonionic surfactant detergent composition is formulated from the following ingredients in the amounts specified.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product D nonionic surfactant.</td>
<td>40.0</td>
</tr>
<tr>
<td>Acid terminated Dobanol 91-5 reaction product with succinic anhydride.</td>
<td>14.0</td>
</tr>
<tr>
<td>Sodium salt of polyacetal carboxylic acid (Builder U).</td>
<td>17.0</td>
</tr>
<tr>
<td>Alkanol phosphoric acid ester.</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium perborate monohydrate bleaching agent.</td>
<td>17.0</td>
</tr>
<tr>
<td>Tetraacetylethylene diamine (TAED) bleach activator.</td>
<td>10.0</td>
</tr>
<tr>
<td>Stilbene brightener N4.</td>
<td>0.4</td>
</tr>
<tr>
<td>Esperase slurry.</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfume.</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

The formulations of Examples 1 and 2 are or can be ground for about one hour to reduce the particle size of the suspended builder salts to less than 10 microns. The formulated detergent compositions are found to be stable and non-gelling in storage and to have a high detergent capacity.

The formulations can be prepared without grinding the builder salts and suspended solid particles to a small particle size, but best results are obtained by grinding the formulation to reduce the particle size of the suspended solid particles.

The builder salts can be used as provided, or the builder salts and suspended solid particles can be ground or partially ground prior to mixing them with the nonionic surfactant. The grinding can be carried out in part prior to mixing and grinding completed after mixing or the entire grinding operation can be carried out after mixing with the liquid surfactant.

The formulations of the present invention containing an alkali metal hydroxy acrylic acid polymer builder can be thickened with conventional
thickening agents such as Bentonite and Aerosil to form a cream or paste and used as a scourer cleanser.

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.
alkylene glycol mono lower \((C_1\text{ to } C_5)\) alkyl ethers.

Specific examples of suitable amphiphilic compounds include ethylene glycol monoethyl ether \(C_2H_5-O-\text{CH}_2\text{CH}_2\text{OH}\).
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A nonaqueous liquid heavy duty laundry detergent composition which comprises
   
at least one liquid nonionic surfactant detergent,
   an hydroxy acrylic acid or acrylic acid salt polymer builder or an organic polyacetal carboxylate builder salt,
   at least one member selected from the group of an acid terminated nonionic surfactant anti-gel agent and an alkylene glycol monoalkyl ether, and an
   an anti-settling agent.

2. The detergent composition of claim 1 comprising 5 to 50 percent of a hydroxy acrylic acid or hydroxy acrylic acid salt polymer detergent builder or a polyacetal carboxylate detergent builder salt.

3. The detergent composition of claim 1 wherein the hydroxy acrylic acid polymer detergent builder contains monomeric units of the formula
\[
\begin{array}{c}
R_1 \text{OH} \\
C \text{H} \\
R_2 \text{COOH}
\end{array}
\]

wherein \( R_1 \) and \( R_2 \) may be the same or different and are selected from group consisting of hydrogen and alkyl containing 1 to 3 carbon atoms and \( M \) is selected from the group consisting of hydrogen, alkali metal, alkaline earth metal and ammonium cation.

4. The detergent composition of claim 1 comprising
   
at least one liquid nonionic surfactant in an amount of about 25 to 50%,
   an acid-terminated nonionic surfactant in an amount of about 2 to 20%,
   an alkylene glycol mono alkyl ether in an amount of about 5 to 20%,
   hydroxy acrylate polymer builder in an amount of about 10 to 30%, and
an alkanol phosphoric acid ester in an amount of about 0.1 to 1.0%.

5. The detergent composition of claim 4 wherein the hydroxy acrylic acid polymer detergent builder contains monomeric units of the formula

\[ \left( \begin{array}{c} R_1 \\ \text{OH} \\ C \\ C \\ R_2 \\ \text{COOM} \end{array} \right)^n \]

wherein \( R_1 \) and \( R_2 \) may be the same or different and are selected from the group consisting of hydrogen, methyl, ethyl and propyl, \( M \) is selected from the group consisting of sodium and potassium and the value of \( n \) is selected such that the polymer is water soluble.

6. A phosphate detergent bulder free nonaqueous liquid heavy duty laundry detergent composition which comprises

Nonionic surfactant in an amount of about 30-55%

Acid terminated surfactant in an amount of about 1-10%

Alkylene glycol mono alkyl ether in an amount of about 3-15%

Hydroxy acrylate polymer sodium salt builder in an amount of about 7-22%

\( \text{C}_{16} \) to \( \text{C}_{22} \) alkanol ester of phosphoric acid in an amount of about 0.1-0.9%

Sodium perborate monohydrate bleaching agent in an amount of about 10-22%

Tetrasacetylethylene diamine bleach activator in an amount of about 4-15%

7. The detergent composition of claim 6 wherein the hydroxy acrylate polymer has a molecular weight of 2000 to 20,000.

8. The detergent composition of claim 1 wherein the polyacetal carboxylate has the formula:

\[ \begin{array}{c} R_1 \\ \text{CHO} \\ \text{COOM} \end{array} \]

\[ \begin{array}{c} \text{R}_2 \end{array} \]

wherein \( M \) is selected from the group consisting of alkali metal, ammonium, alkyl groups having 1 to 4 carbon atoms, tetraalkyl ammonium groups and alkanol amine groups having from 1 to 4 carbon atoms in the alkyl chain; \( n \)
bleaches are preferred and are represented by percompounds which liberate hydrogen peroxide in solution. Preferred examples include sodium and

is at least 4, and $R_1$ and $R_2$ are selected to be individually stable groups which stabilize the polymer against depolymerization in alkaline solution and are selected to be compatible with the ingredients of the nonionic liquid detergent composition.

9. The laundry detergent composition of claim 1 which is polyphosphate free or low polyphosphate and which comprises

- at least one liquid nonionic surfactant in an amount of about 25 to 50%,
- an acid-terminated nonionic surfactant in an amount of about 10 to 25%,
- a polyacetal carboxylate builder in an amount of about 10 to 30%,
- a polyphosphate detergent builder in an amount of about 0 to 20%, and
- an alkanol phosphoric acid ester in an amount of about 0.1 to 1.0%.

10. The detergent composition of claim 9 wherein the polyacetal carboxylate has the formula: $R_1\left[\begin{array}{c}\text{CHO} \\ \text{GOOM}\end{array}\right]_n R_2$

wherein $M$ is an alkali metal; $n$ is 50 to 200, and $R_1$ and $R_2$ are selected to be individually stable groups which stabilize the polymer against depolymerization in alkaline solution and are selected to be compatible with the ingredients of the nonionic liquid detergent composition.

11. A phosphate detergent builder free nonaqueous liquid heavy duty laundry detergent composition which comprises
Nonionic surfactant in an amount of about 30-45%

Acid terminated surfactant in an amount of about 2-18%

Sodium salt of polyacetal carboxylic acid in an amount of about 5-22%

C_{16} to C_{18} alkanol ester of phosphoric acid in an amount of about 0.1-0.9%

Sodium perborate monohydrate bleaching agent in an amount of about 7-22%

Tetraacetylene diamine (TAED) bleach activator in an amount of about 4-12%

12. The detergent composition of claim 11 wherein the polyacetal carboxylate has the formula:

\[
R_1 \frac{\text{CHO}}{\text{COOM}} R_2
\]

wherein \( M \) is selected from the group consisting of sodium and potassium;

\( n \) is 50 to 200; \( R_1 \) is \( \text{OCH}_2\text{CH}_3 \) or \( \text{COOM} \)

\( \text{CH}_3 \)

or mixtures thereof and \( R_2 \) is \( \text{OCH}_2\text{CH}_3 \)

\( \text{CH}_3 \)

and the polyacetal carboxylate segments comprise 50 to 80 percent by weight of the total polyacetal carboxylate.

13. The detergent composition of claim 12 wherein the polyacetal carboxylate is the sodium salt and the \( R_1 \)'s are stabilizing end groups.

14. The detergent composition of claim 3 or 11 comprising an alkali metal perborate monohydrate bleaching agent in an amount of about 5 to 30%.

tetraacetylene diamine bleach activator in an amount of about 5 to 20%, and
optionally one or more detergent adjuvants selected from the group consisting of optical brighteners, enzymes and perfume.

15. A method for cleaning soiled fabrics which comprises contacting the soiled fabrics with the laundry detergent composition of claim 6.

16. A method for cleaning soiled fabrics which comprises contacting the soiled fabrics with the laundry detergent composition of claim 11.

Dated this 31st day of July 1986.

COLGATE-PALMOLIVE COMPANY

Patent Attorneys for the Applicant
F B RICE & CO.