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LOW SUDSING DETERGENT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Low to medium sudsing heavy duty detergent compositions containing a soap or non-soap synthetic detergent, a detergent builder and a fluoroalkyl suds suppressing agent.

BACKGROUND OF THE INVENTION

This invention relates to heavy duty detergent compositions. More particularly, the present invention relates to low to medium sudsing built detergent compositions containing a soap or non-soap synthetic detergent to impart good cleaning characteristics and a fluoralkyl suds suppressing agent to suppress the suds which are created by the active organic detergent at high wash water temperatures; particularly at wash water temperatures in excess of about 160° F.

By way of background, the ingredients which are combined in the built detergent formulations of this invention are very briefly described below. These ingredients are all known individually but they have not heretofore been utilized in the manner disclosed in this invention to produce low to medium sudsing heavy duty built detergent compositions.

It is well recognized that heavy duty laundry detergents designed for use in tumbler or rotating drum type washing machines must possess a high degree of cleaning power but they must also be relatively low sudsing. Heretofore it has not been possible to formulate low to medium sudsing detergents compositions having good cleaning properties containing only low sudsing detergents, such as certain specific nonionic detergents. When other detergents have been added to one of these low to medium sudsing compositions to increase its cleaning efficiency, the sudsing level has increased to the point at which the composition was no longer useful for tumbler type machines. Furthermore, if a per compound bleaching agent has been added to one of these low to medium sudsing compositions to increase its bleaching efficiency, the suds are greatly accentuated by the oxygen which is released by the per compound at high wash water temperatures.

Tumbler type washing machines differ from the conventional top loading automatic washers which are in general use in the United States. The "tumblers" or rotating drum machines require substantially less water than the top loading automatics. Only about one half to one quarter amount of water is used to operate a tumbler. Most tumblers (particularly those rotating drum machines found throughout Europe) also heat their own water. Cold water is put into the machines from the tap or other water source and is heated either electrically or by gas to the desired temperature. This temperature is generally higher than that of hot water drawn from the faucet. Water used in a tumbler type washing machine is ordinarily heated in the machine to about 160° F. to about 212° F. The hottest hot water tap temperature seldom exceeds about 150° F.

In operating a rotating drum type machine it is essential that the water and suds level be kept down in order to clean the clothes in the machine efficiently and to avoid oversudsing. The common manifestation of oversudsing in a rotating drum machine is suds coming out of the machine and flowing onto the floor.

SUMMARY OF THE INVENTION

The compositions of this invention are low to medium sudsing heavy-duty detergent compositions designed primarily for use in tumbler type washing machines.

The term "soap" as used herein is meant to designate alkali metal soaps and those useful in the present invention are further defined hereinafter.

The non-soap synthetic detergents useful in the present invention can be selected from the group consisting of anionic, nonionic, zwitterionic and amphoteric detergents.

The anionic synthetic detergents can be broadly described as the water-soluble salts, including the alkali metal, ammonium and substituted ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals.

The nonionic synthetic detergents may be broadly defined as compounds produced by condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

The zwitterionic detergents such as betaines and sultaines and similar compounds are compounds wherein the molecule contains both basic and acidic groups which form within the salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of wash water pH values. The amphoteric detergents can be either cationic or anionic depending upon the pH of the system and are further defined hereinafter.

The fluoroalkyl suds suppressors are compounds of the general formula $R_yPO(OM)_{3-y}$, as fully described hereinafter. Certain of the compounds of the above general formula have been suggested for a variety of purposes including use as leveling agents, as oil repellants, as lubricating agents for aqueous systems and as ingredients in rust preventive formulations.

The sudsing propensities of the active synthetic detergents are suppressed by the fluoroalkyl suds suppressing agent. Compositions comprise by weight from about 2% to about 30%, and preferably from about 4% to about 15%, of a detergent selected from the aforementioned group consisting of soap and non-soap synthetic detergents and mixtures thereof; from about 2% to about 65%, and preferably from about 6% to about 45% of a detergent builder and from about 0.1% to about 8%, preferably from about 1% to about 3% of a fluoroalkyl suds suppressing agent of the class described herein.

The compounds comprising the compositions of this invention are fully characterized below:

(1) Natural soaps

The soaps useful in the present invention are the alkali metal soaps such as the sodium and potassium salts of the higher fatty acids of naturally occurring plant or animal

esters, e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease and lard and mixtures thereof. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the fatty acids which are prepared in a separate manufacturing process. Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids (C_{10}–C_{20}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

(2) Synthetic detergents

(a) Anionic detergent (excluding true soaps).—The anionic synthetic detergents of this present invention are as described above. Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the following: as alkali metal (e.g., sodium and potassium) ammonium and substituted ammonium (e.g., lower alkyl ammonium) salts; alkyl sulfates, especially those obtained by sulfating the higher alcohols produced by reducing the glycerides of tallow or coconut oil; random paraffin sulfonates, in which the alkyl group contains from about 8 to about 22 carbon atoms, preferably from about 14 to about 18 carbon atoms, prepared by treating random paraffin hydrocarbons in sulfur dioxide and chlorine in the presence of light followed by treating with a base; branched or linear alkyl benzene sulfonates, in which the alkyl group contains from about 8 to about 18 carbon atoms, preferably from about 10 to about 14 carbon atoms, especially those of the types described in U.S. Pat. Nos. 2,220,099, and 2,477,383; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; coconut oil fatty acid monoglyceride sulfates and sulfonates; sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut alcohols) and from about 1 to about 6, preferably about 3 moles of ethylene oxide; alkyl phenol ethylene oxide ether sulfates with about 4 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; fatty acid amides of the methyl taurine in which the fatty acids, for example, are derived from coconut oil; sulfonated olefins of U.S. Pat. No. 3,332,880; and others known in the art, a number being specifically set forth in U.S. Pat. Nos. 2,486,921; 2,486,922 and 2,396,278.

Preferred anionics include the alkyl sulfates and the random paraffin sulfonates.

(b) Nonionic synthetic deteregnts.—This class of synthetic detergents may be broadly defined as above.

For example, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the products is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine—products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Long chain tertiary amine oxides corresponding to the following general formula, $R_1R_2R_3N\rightarrow O$, wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and R_2 and R_3 contain from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxy ethyl, or hydroxy propyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecyl amine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyldecylamine, oxide dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl) tetradecylamine oxide, 2-dodecoxy ethyl dimethylamine oxide, 3-dodecoxy-2-hydroxy propyl di(3-hydroxypropyl) amine oxide, dimethylhexadecylamine oxide.

(5) Long chain tertiary phosphine oxides corresponding to the following general formula $RR'R''P\rightarrow O$ wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and R′ and R″ are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are:

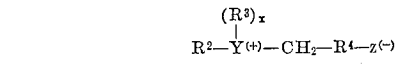
dodecyldimethylphosphine oxide
tetradecyldimethylphosphine oxide
tetradecylmethylethylphosphine oxide
3,6,9-trioxaoctadecyldimethylphosphine oxide
cetyldimethylphosphine oxide
3-dodecoxy-2-hydroxypropyldi (2-hydroxyethyl) phosphine oxide
stearyldimethylphosphine oxide
cetylethylpropylphosphine oxide
oleyldiethylphosphine oxide
dodecyldiethylphosphine oxide
tetradecyldiethylphosphine oxide
dodecyldipropylphosphine oxide
dodecyldi (hydroxymethyl) phosphine oxide
dodecyldi (2-hydroxyethyl) phosphine oxide
tetradecylmethyl-2-hydroxypropyl phosphine oxide
oleyldimethylphosphine oxide
2-hydroxydodecyldimethylphosphine oxide

(6) Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which contains alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20

carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety. Examples include:

octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide
3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide
dodecyl methyl sulfoxide
oleyl 3-hydroxy propyl sulfoxide
tetradecyl methyl sulfoxide
3-methoxytridecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
3-hydroxy-4-dodecoxybutyl methyl sulfoxide

(c) Zwitterionic synthetic detergents.—This group of detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorous, and sulfur atoms; R^3 is an alkyl or monohydroxy alkyl group containing 1 to about 3 carbon atoms; x is 1 when y is a sulfur atom and 2 when Y is a nitrogen or phosphorous atom, R^4 is an alkylene or hydroxy alkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other examples include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
5-[S-3-hydroxypropyl-S-hexadecyl sulfonio]-3-hydroxypentane-1-sulfate;
3-[P,P-diethyl-P-3,6,9-trioxatetracosylphosphonio]-2-hydroxypropane-1-phosphate;
3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;

3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate, 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate, 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate, 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl) sulfonio]-propane-1-phosphate, 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate, and S-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]2-hydroxypentane-1-sulfate.

(d) Amphoteric synthetic detergents.—This group of detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-dodecylaminopropane sulfonate, dodecyl-beta-alamine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Pat. 2,528,378.

(2) Detergent builders

The detergent builders useful in the present invention are water-soluble inorganic alkaline builder salts and organic alkaline sequestering builder salts and mixtures thereof as described and illustrated below.

Examples of water soluble inorganic alkaline builder salts (and mixtures thereof) which are used in the compositions of this invention include the sodium, potassium, ammonium and substituted ammonium salts of the alkali metal carbonates, borates, phosphates, condensed polyphosphates, bicarbonates and silicates. Specific examples of such salts are the sodium and potassium tripolyphosphates, carbonates, tetraborates, pyrophosphates, orthophosphates, bicarbonates and hexametaphosphates.

Examples of organic alkaline builder salts (and mixtures thereof) which can be used are the alkali metal, ammonium or substituted ammonium aminopolycarboxylates; for example: sodium and potassium N-(s-hydroxyethyl)-ethylenediaminetriacetates and sodium and potassium nitrilotriacetates. Other valuable polycarboxylate builders are the sodium and potassium salts of polymaleate, polyitaconate, and polyacrylate. The alkali metal salts of phytic acid are also suitable builders.

The polyphosphonates which can be used as builders for the compositions of this invention include compounds exemplified by the following: sodium and potassium salts of ethane-1-hydroxy-1, 1-diphosphonate, sodium and potassium salts of methylene and ethylenediphosphonates as well as the alkali metal salts of such compounds.

Additional examples of builders useful in the present invention are disclosed by Lyness and O'Connor in U.S. Pat. 3,336,230, said patent being incorporated herein by reference.

(3) Fluoroalkyl suds suppressing agent

The fluoroalkyl compounds useful in the present invention as suds suppressing agents have the following general formula:

$$R_yPO(OM)_{3-y}$$

wherein R is selected from the group consisting of

$$R^1C_mF_{2m}\cdot C_nH_{2n}\cdot O$$

$$R^1C_mF_{2m}\cdot C_nH_{2n}$$

and mixtures thereof; and when $y=2$ one R group can be H; where m is an integer from 1 to about 12, n is an integer from 1 to about 16, the total of $m+n$ equal an integer of from about 2 to about 18, y is a number of average value from 1.0 to 2.5 (The term "average value" is used to show that mixtures are contemplated as part of the present invention.), R^1 is selected from the group consisting of hydrogen and F, and M is selected from the group consisting of hydrogen, alkali metal, ammonium and substituted ammonium.

The fluoroalkyl suds suppressors of the present invention can be utilized alone or in combination and include both the free acid and water soluble salt forms. As used herein and in the accompanying examples "fluoroalkyl suds suppressors" refers to both the acid and water soluble salt forms. Operable salts include the alkali metal (e.g., sodium and potassium), ammonium and substituted ammonium (e.g., mono-, di-, and triethanolammonium) salts. Preferred compounds of this class contain in their alkyl structure a straight chain of at least 2 carbon atoms and not less than 4 fluorine atoms. Examples of such preferred structures include the following:

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

$$H(CF_2)_xCH_2—O—PO(OH)_2$$

x is average of 7

$$[CF_3(CF_2)_5(CH_2)_2—O]_2PO(OM)$$

and

$$H(CF_2)_{10}CH_2—PO(OM)_2$$

wherein M is hydrogen, alkali metal, ammonium or substituted ammonium. Included in the fluoroalkyl suds suppressing agents of the present invention are compounds commercially available from E. I. du Pont de Nemours & Company under the trade name "Zonyl." Additional examples of operable fluoroalkyl suds suppressors and methods for their preparation, are disclosed by Benning in U.S. Pat. 2,559,749 and by Brace and MacKenzie in U.S. Pat. 3,083,224, said patents being incorporated herein by reference.

As hereinbefore stated the fluoroalkyl suds suppressing agents can be used in amounts ranging from about 0.1% to about 8.0% by weight of the total composition. Amounts of less than about 0.1% do not give desirable suds suppressing effects whereas amounts greater than 8% do not appear to produce any greater effect than is attainable with lesser concentrations, thus utilization of such higher amounts is uneconomical and serves no purpose. Preferably the amount is from about 1% to about 3%.

PREFERRED EMBODIMENTS

A preferred embodiment of the present invention contains from about 1% to about 50% by weight of a per compound bleaching agent, such as sodium perborate. The per compound bleaching agent imparts a high level of cleaning and bleaching power to the compositions particularly when used in conjunction with the builder materials described above. Other per compounds which can be used in place of the sodium perborate or in addition thereto include compounds such as sodium percarbonate and sodium persulfate. The potassium and substituted ammonium salts can also be used. The per compounds derive their bleaching power from the release of active oxygen in solution. Sodium perborate is the preferred per compound bleaching agent. From about 15 %to about 35% is the preferred range of usage of the per compound bleaching agent.

A further preferred embodiment includes in the detergent part of the compositions of the present invention from about 0.5% to about 6%, preferably from about 1% to about 3% of a nonionic condensation product. The use of a nonionic condensation product aids in reducing the suds level.

The compounds are the condensation product of aliphatic alcohols having from about 12 to about 22 carbon atoms, in either a straight chain or a branched chain configuration, with ethylene oxide. A typical example is a tallow alcohol-ethylene oxide condensate having from about 5 to about 30 moles (or up to about 45 moles) of ethylene oxide per mole of tallow alcohol. Preferred compounds include tallow alcohol-ethylene oxide condensation product containing 11 moles of ethylene oxide per mole of tallow alcohol. The term "tallow" as used herein and in the accompanying examples indicates a carbon chain length distribution approximately as follows: 2.5% C_{14}, 28%C_{16}, 23%C_{18}, 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids are saturated). The term "coconut" (for example, in a coconut alcohol-ethylene oxide condensation product) applies to a distribution of carbon chain lengths which is approximately as follows: 8%C_8, 7%C_{10}, 48%C_{12}, 17%C_{14}, 9%C_{16}, 2% C_{18}, 7% oleic and 2% linoleic (the first six fatty acids listed are saturated).

In formulating the compositions of this invention, it is essential that the proportion of the ingredients set forth above be observed. Within these proportions the principal object of this invention is observed, i.e., control of the sudsing level attributed in part to sudsing of the organic detergent ingredient which is aggravated by oxygen evolution from any per compound bleaching agent employed in the system.

One of the principal advantages of the present invention is that the suds control mechanism of the fluoroalkyl suds suppressor is not materially affected by the water hardness. It is well known that most prior art suds suppressor agents, such as fatty acids and fatty acid soaps lose some of their effectiveness in hard water.

An additional advantage of the present invention is the excellent whiteness maintenance that the compositions provide. Many suds suppressors are insoluble and deposit on articles washed with compositions containing them leading, to a decrease in the whiteness of the articles. The compositions of this invention containing the fluoroalkyl suds suppressing agents indicate no such deposition problems.

The ingredients of the compositions of this invention are preferably employed in the form of complete detergent formulations. These complete detergent formulations can be prepared in any of several forms including granular, flake, liquid or tablet.

The compositions can contain particulate inorganic salts which are inert to the formula to act as fillers. Examples of such salts include sodium sulfate and sodium chloride.

The compositions of the present invention can also contain adjuvants, diluents, soil suspending agents such as carboxymethylcellulose and additives including germicidal agents, enzymes, anti-tarnishing agents, optical brightners and dyes. Such additional miscellaneous ingredients can be employed in amounts about 10% by weight of the composition.

The compositions of this invention can be prepared in any suitable manner as long as the proportions set forth herein are followed. Numerous methods are known in the art for preparing such compositions; for instance, ingredients can be mechanically admixed, spray-dried or agglomerated according to the stated proportions.

The following examples illustrates in detail the manner in which the invention can be practiced. It will be understood, however, that the invention is not confined to the specific limitations set forth in the individual examples but rather to the scope of the appended claims.

The evaluation procedure to which reference is made in the following examples is a method which was developed to determine the suds profile of low sudsing detergent formulations. These tests are conducted in four smaller than normal (about 1/7 scale), specially designed, horizontally rotating drum washing machines which operate simultaneously and simulate as closely as possible the agitation, temperature control, product concentration, and water conditions of an actual tumbler type washing machine in operation. The machines are so designed (with a transparent front) that the suds heights and water temperatures can be visually observed and recorded throughout any specific test. Cloths to be tested are worn by panelists and distributed so that equal amounts of naturally soiled fabrics are washed in each machine. The load comprises two T-shirts weighing about 200 grams and nine socks weighing about 200 grams. A standard test includes two periods which differ only in temperature and concentration of the detergent compositions. The temperatures are higher and the concentrations greater in the second period. During the first washing period lasting ten minutes, the water temperature is raised from 60° F. to about 120° F. by the heaters which are built into the machine. A portion of the wash solution is then removed from the machines and replaced by an equal quantity of hard water and a weight of detergent composition equal to the amount added for the first period. This represents the "second period" as referred to below and the temperature is raised to about 190° F.

The suds levels and temperatures are recorded at least every two minutes. In this way the actual use and fall, if any, of the suds in response to the soil load, water hardness, product formulation, and increase in temperature can be observed. It takes approximately twenty minutes after the second period is begun for the water in the machines to reach 190° F. The machines are designed to be operated with about three liters of water. Soft water is adjusted to the desired hardness, about 15 grains per gallon, by the

addition of calcium and magnesium salts. The rotators of the machines spin alternatively in the clockwise and counter-clockwise directions throughout the entire washing cycle at 58 r.p.m.

In the following examples unless otherwise stated the proporations are by weight of the complete detergent compositions.

EXAMPLE I

A detergent composition containing the following ingredients was prepared in the manner explained below.

Ingredients:	Parts by wt.
Sodium salt of tallowalkyl sulfate wherein the tallowalkyl is a mixture of chain lengths from 14 to 18 carbon atoms	5.0
Sodium tripolyphosphate	32.0
Sodium silicate solids (SiO_2:Na_2O=2:1)	7.0
Sodium sulfate	19.0
Sodium perborate tetrahydrate	25.0
Water	Balance to 100

The alkyl sulfate was mixed with water to obtain a paste and a 44% water solution of sodium silicate solids was added to the paste. To this mixture was added separately in powdered form the following ingredients: sodium tripolyphosphate, sodium perborate and sodium sulfate. This resulting mixture is utilized in its paste form.

The sudsing characteristics of this composition were determined in the laundry screening test as described above. Temperature and suds heights were taken at two minute intervals during the second period and the results recorded. In conducting the test, 18 grams of the above composition were added to three liters of water containing about 400 grams of naturally soiled cloths. A ten minute first period was followed by replacement of 1.2 liters of the solution with an equal amount of clean hard water and an additional 18 grams of the detergent composition. Heat and agitation were supplied for a second period of 40 minutes. The hardness of the water was adjusted to 15 gr./liter by the addition of calcium chloride.

A similar test was simultaneously run utilizing the same basic detergent composition and testing conditions except that 2.0% by weight of

$$[H(CF_2)_nCH_2—O]_x—PO(OH)_y$$

wherein n is an average of 7, x is an average of 1.5 and $y=3-x$ was added to the composition. The term "average" indicates that a mixture of suds suppressing agents was utilized. This suds suppressing mixture was added to the powdered ingredients of the basic detergent composition in a methanol solution and the methanol allowed to evaporate completely before the testing began.

Table I below shows the effect of the suds suppressing agents of the present invention. (In Table I and subsequent tables, the suds heights are reported at equal temperature intervals rather than the two minute intervals at which they were recorded to permit a more direct comparison of the results.)

TABLE I

	Suds height in centimeters	
Basic detergent composition with	No additive	Suds suppressing agent mixture
Degrees F.:		
130	5.5	0.3
140	10.0	0.6
150	12.7	0
160	15.6	0
170	20.0	0.5
180	24.3	4.3
190	28.8	6.0

Table I shows the suds suppressing effect of the detergent compositions containing the suds suppressing agents over the detergent compositions that do not contain these agents.

When 2% by weight of $H(CF_2)_{10}CH_2—O—PO(OH)_2$ was substituted for the suds suppressing agent mixture of Example I the following results were obtained.

These results of the suds suppressing effect are summarized in Table II. This effect is noticed particularly above 160° F. where oxygen is released by the perborate bleaching agent.

TABLE II

	Suds height in centimeters	
Basic detergent composition with	No additive	Suds suppressing agent
Degrees F.:		
130	5.5	1.5
140	13.0	6.0
150	12.7	7.5
160	15.6	9.3
170	20.0	30.5
380	24.3	12.0
190	28.8	13.8

Table II clearly shows the advantageous effect of the detergent compositions containing the suds suppressing agents.

When about 3.0% by weight of a nonionic condensation product, e.g., tallow alcohol-ethylene oxide condensation product containing an average of 11 moles of ethylene oxide, is added with the fluoroalkyl suds suppressing agents of the present invention to the composition of Example I a further reduction in suds height is noted.

Substantially the same suds suppressing results, i.e., low to medium sudsing, are obtained with the compositions of Example I containing the fluoroalkyl suds suppressing agent when any of the following detergents are substituted on an equal weight basis for the sodium salt of tallow alkyl sulfate in Example I:

sodium dodecyl sulfate;
ammonium tridecyl sulfate;
sodium olefin sulfonate wherein the alkyl chain contains 14 carbon atoms;
sodium salt of randomly sulfonated paraffin containing an average of 15.2 carbon atoms;
potassium coconut alkyl glyceryl ether sulfonate; or
sodium coconut alkyl sulfate.

Substantially the same results are obtained with the compositions of Example I, i.e., low to medium sudsing and good cleaning when the sodium perborate tetrahydrate is replaced on an equal weight basis by sodium percarbonate or sodium persulfate.

EXAMPLE II

The detergent composition set forth below was prepared in the manner described in Example I and the sudsing characteristics evaluated by the same laundry screening test.

Ingredients:	Parts by wt.
Sodium salt of linear alkylbenzene sulfonate having an average chain length of 11.8	9.0
Sodium tripolyphosphate	32.0
Sodium silicate solids (SiO_2:Na_2O=2:1)	7.0
Sodium sulfate	19.0
Sodium perborate tetrahydrate	25.0
Water	Balance to 100

TABLE III

	Suds height in centimeters	
Basic detergent composition with	No additive	Suds suppressing agent
Degrees F.:		
150	31.0	28.5
160	30.0	16.3
170	31.0	23.8
180	29.5	21.7
190	28.0	20.8

The suds suppressing agent utilized was

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

when

$$H(CF_2)_7CH_2—O—PO(OH)_2$$

$$[CF_3(CF_2)_5(CH_2)_2O]_2PO(OM)$$

or

$$H(CF_2)_{10}CH_2—PO(OM)_2$$

are substituted on an equal weight basis for the fluoroalkyl suds suppressing agent

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

of Example II substantially equivalent suds suppressing results are obtained.

Substantially equivalent results, i.e., low to medium sudsing with good cleaning, are obtained when the sodium salt of linear alkylbenzene sulfonate having an average chain length of 11.8 is replaced on an equal weight basis in the compositions of Example II by:

condensation product of octyl phenol with 15 moles of ethylene oxide per mole of octyl phenol;
dimethylhexadecylamine oxide;
dimethyldodecylamine oxide;
dodecyldimethylphosphine oxide;
3,6,9-trioxaoctadecyldimethylphosphine oxide;
dodecyl methyl sulfoxide; or
3-hydroxytridecyl methyl sulfoxide.

EXAMPLE III

The detergent composition described below was prepared in the manner described in Example I.

Ingredients:	Parts by wt.
Coconut alcohol-ethylene oxide condensation product containing 6 moles of ethylene oxide	8.0
Sodium tripolyphosphate	32.0
Sodium silicate solids (SiO_2:Na_2O=2:1)	7.0
Sodium sulfate	19.0
Sodium perborate tetrahydrate	25.0
Water	Balance to 100

The sudsing characteristics of this composition were compared to that of identical compositions containing 2.0% by weight of a suds suppressing agent of the formula

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

The comparisons were run in the laundry screening test previously described with the results given in Table IV. These results show a definite suds suppressing effect with the fluoroalkyl suds suppressing agent of the present invention.

TABLE IV

	Suds height in centimeters	
Basic detergent composition with	No additive	Suds suppressing agent
Degrees F.:		
120	14.5	0.5
130	20.3	0.2
140	23.6	0
150	26.0	0
160	29.0	0
170	31.8	0
180	32.5	0
190	36.0	0

EXAMPLE IV

The detergent composition described below was prepared in the manner described in Example I.

Ingredients:	Parts by wt.
3 - (N,N - dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate	4.0
Sodium tripolyphosphate	32.0
Sodium silicate solids (SiO_2:Na_2O=2:1)	7.0
Sodium sulfate	19.0
Sodium perborate tetrahydrate	25.0
Water	Balance to 100

The sudsing characteristics of this composition were compared to that of identical compositions containing 2% by weight of a suds suppressing agent of the formula

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

The comparisons were run in the laundry screening test previously described and the results in Table V below show the suds suppressing effect of the fluoroalkyl suds suppressing agent of the present invention.

TABLE V

	Suds height in centimeters	
Basic detergent composition with	No additive	Suds suppressing agent
Degrees F.:		
120	13.0	0.5
130	20.5	0.5
140	24.1	0.2
150	26.7	1.0
160	30.0	3.6
170	32.2	6.8
180	33.8	7.3
190	36.0	10.7

Substantially equivalent results are obtained, i.e., low to medium sudsing and good cleaning, when the 3-(N,N-dimethyl-N-hexadecylammonio) - 2 - hydroxypropane-1-sulfonate of Example IV is replaced by:

3-(N,N-dimethyl-N-hexadecylammonio)-2-propane-1-sulfonate;
3-[P,P-dimethyl-P-dodecylphosphonio] propane - 1 - phosphonate;
3-dodecylaminopropionate; or
dodecyl-beta-alanine.

EXAMPLE V

The following detergent composition was prepared:

Ingredients:	Parts by wt.
Sodium tallow-sodium coconut soap (tallow:coconut=4:1)	6.0
Sodium tripolyphosphate	32.0
Sodium silicate solids (SiO_2:Na_2O=2:1)	7.0
Sodium sulfate	19.0
Sodium perborate tetrahydrate	25.0
Water	Balance to 100

The sudsing characteristics of this composition were compared to that of an identical composition containing 2% by weight of a suds suppressing agent of the formula

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

The comparisons were run in the laundry screening test previously described and the results in Table VI below show the suds suppressing effect of the suds suppressing agents of the present invention.

TABLE VI

	Suds height in centimeters	
Basic detergent composition with	No additive	Suds suppressing agent
Degrees F.:		
120	24.1	6.5
130	26.2	10.7
140	27.8	16.0
150	32.5	22.2
160	31.8	25.3
170	33.0	28.1
180	35.0	30.0

The advantages of the present invention, while capable of demonstration with all of the aforementioned detergents, are especially notable with high sudsing detergents which provide exceptionally high levels of cleaning.

A special embodiment of the present invention comprises the use of a non-soap synthetic detergent as the detergent component of the composition.

In addition to the preferred embodiments described herein, other arrangements and variations within the spirit and scope of the invention and the appended claims will occur to those skilled in the art.

What is claimed is:

1. A low to medium-sudsing laundry detergent composition consisting essentially of, by weight, from about 2% to about 30% of a detergent selected from the group consisting of alkali metal soaps; anionic, non-soap synthetic detergents; nonionic, non-soap synthetic detergents; zwitterionic, non-soap synthetic detergents and amphoteric, non-soap synthetic detergents; from about 2% to about 65% of a detergent builder selected from the group consisting of water-soluble inorganic alkaline builder salts, organic alkaline sequestering builder salts and mixtures thereof; and from about 0.1% to about 8% of a fluoroalkyl suds suppressing agent of the general formula

$$R_yPO(OM)_{3-y}$$

wherein R is selected from the group consisting of

$$R^1C_mF_{2m}\cdot C_nH_{2n}\cdot O$$
$$R^1C_mF_{2m}\cdot C_nH_{2n}$$

and mixture thereof; and when $y=2$ one R group can be H; wherein M is an integer from 1 to about 12, n is an integer from 1 to about 16, the total of $m+n$ equal an integer of from about 2 to about 18, y is a number of average value from 1.0 to 2.5 and R^1 is selected from the group consisting of hydrogen, alkali metal, ammonium and substituted ammonium.

2. The composition of claim 1 wherein the fluoroalkyl suds suppressing agent is from about 1% to about 3%.

3. The composition of claim 2 wherein the fluoroalkyl suds suppressing agent is

$$H(CF_2)_{10}CH_2—O—PO(OH)_2$$

4. The composition of claim 2 wherein the fluoroalkyl suds suppressing agent is

$$[H(CF_2)_nCH_2—O]_x—PO(OH)_y$$

wherein n is an average of 7, x is an average of 1.5 and $y=3-x$.

5. The composition of claim 1 wherein the non-soap synthetic detergent is the sodium salt of an alkyl sulfate wherein the alkyl group contains from about 8 to about 18 carbon atoms and mixtures thereof.

6. The composition of claim 1 wherein the non-soap synthetic detergent is the sodium salt of a random paraffin sulfonate containing an average of from about 10 to about 20 carbon atoms.

7. The composition of claim 1 wherein the detergent is a mixture of tallow and coconut soaps in a ratio of about 4:1.

8. The composition of claim 1 containing from about 1% to about 50% by weight of a per compound bleaching agent selected from the group consisting of sodium perborate, sodium percarbonate, sodium persulfate, potassum perborate, potassium percarbonate, potassium persulfate, substituted ammonium perborate, substituted ammonium percarbonate and substituted ammonium persulfate.

9. The composition of claim 10 wherein the per compound bleaching agent is sodium perborate and the builder is sodium tripolyphosphate.

10. The composition of claim 1 wherein the detergent is a mixture of detergents containing from about 0.5% to about 6% by weight of the nonionic condensation product of alcohols having from 8 to 18 carbon atoms with 10–30 moles of ethylene oxide.

References Cited

UNITED STATES PATENTS

3,325,414	6/1967	Inamorato	202—137
3,413,221	11/1968	Gotte et al.	202—99

OTHER REFERENCES

"Zonyl" S–15 Fluorochemical Surfactant Dupont, 1960, pps. 1–5.

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—137; 260—955

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,585,145 **Dated** June 15, 1971

Inventor(s) Walter P. Fethke, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 23, "fluoralkyl" should read -- fluoroalkyl --.

Column 6, line 45, "where" should read -- wherein --.

Column 8, line 33, "illustrates" should read -- illustrate --.

Column 10, line 15, "13.0" should read -- 10.0--; line 17, "9.3" should read -- 9.0 --; line 18, "30.5" should read -- 10.5 --; line 19, "380" should read -- 180 --.

Signed and sealed this 21st day of December 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents