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54 Detergent containing nonionic/cationic surfactant and builder mixture.

57 Described are detergent compositions containing a nonionic/cationic surfactant mixture and, as an improved builder mixture, a combination of aluminosilicate and polycarboxylate builder materials. These compositions contain little or no phosphate materials, yet deliver excellent particulate soil removal performance and greasy/oily soil removal benefits, along with fabric softening, static control and other fabric care benefits.

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DETERGENT CONTAINING NONIONIC/CATIONIC SURFACTANT
AND BUILDER MIXTURE

Technical Field

This invention relates to detergent compositions
5 containing a nonionic/cationic surfactant mixture and,
as an improved builder mixture, a combination of alumino-
silicate and polycarboxylate builder materials. These com-
positions deliver excellent particulate soil removal perfor-
10 mance and greasy/oily soil removal benefits, along with
fabric softening, static control, color fidelity and dye
transfer inhibition benefits. Compositions which utilize
mixtures of selected nonionic and cationic surfactants,
but without the particular builders described herein, are
defined in European Patents No. 0000234, Cockrell, published
15 January 10, 1979, No. 0000235, Murphy, published January 10,
1979, and No. 0004121, Murphy, published September 19, 1979,
all of which are incorporated herein by reference.

Background Art

The property possessed by builder materials of improving
20 detergency levels of soaps and synthetic detergents is
known. Such builders permit the attainment of better cleaning
performance than is possible when so-called unbuilt compo-
sitions are used. However, the behavior and mechanisms by
which builders perform their function are only partially
25 understood. It is known that good builders must be able
to sequester most of the calcium and/or magnesium ions in
the wash water since these ions are detrimental to the
detergency process. However, it is difficult to predict
which compounds possess useful combinations of builder
30 properties because of the complex
nature of detergency and the countless factors which con-
tribute both to overall performance results and the
requirements of environmental acceptability.

Sodium tripolyphosphate (STP) has been found to be a
35 highly efficient cleaning and detergent builder and this
compound has been widely used for decades in cleaning and

detergent formulations. However, because of the recent emphasis on removing phosphates from detergent and cleaning compositions, suitable replacements for phosphate builders, which would deliver effective cleaning performance and be environmentally acceptable, are being sought. Inorganic builders other than STP are generally not satisfactory for use as a builder in detergent formulations because of their poor builder properties. Sodium aluminosilicates, commonly known as zeolites, have been proposed for use in detergent formulations since they are able to soften water by removing calcium ions; but they are not very effective in removing magnesium ions from water.

It has also recently been taught that by combining specific types of cationic surfactants with a narrowly defined range of alcohol ethoxylate type nonionic surfactants, within defined nonionic:cationic ratios, simple, unbuilt detergent compositions which deliver good cleaning performance and fabric care benefits, can be formulated. (see e.g. European Patents No. 0000234, Murphy; No. 0000235, Cockrell; and No. 0004121, Murphy - all of which have been incorporated herein by reference.) These unbuilt detergent compositions, although generally equivalent to fully built phosphate compositions known in the art, still are capable of further improvement.

Thus, it can be seen that there is a need for new detergent compositions with cleaning properties superior or equivalent to phosphate-built detergents, but which do not contain phosphates, and which achieve environmental acceptability by being readily biodegradable. Now, according to the present invention, there is provided new detergent compositions with a cationic/nonionic surfactant mixture and, as an improved builder mixture, a combination of aluminosilicate and polycarboxylate builder materials. These compositions provide cleaning performance superior to that of phosphate-built compositions and also provide other fabric care benefits, such as softening and static control.

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Summary of the Invention

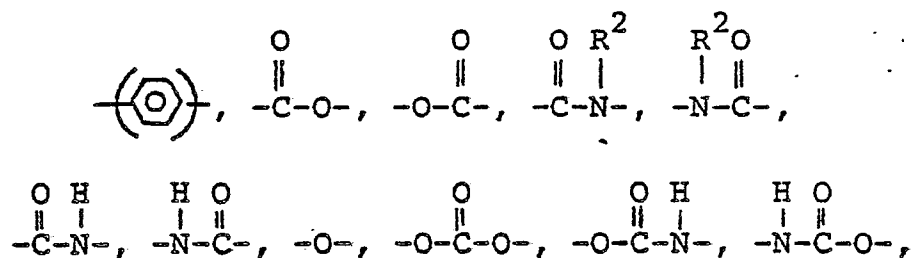
The present invention encompasses a detergent composition, which contains from 0 to about 5% phosphate materials, comprising:

- 5 (a) from about 1% to about 95% of a surfactant mixture consisting essentially of:
- (i) a nonionic surfactant having an HLB of from about 5 to about 17; and
 - (ii) a cationic surfactant, having the formula



wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to 3 phenyl or hydroxy groups and optionally interrupted by up to 4 structures selected from the group consisting of

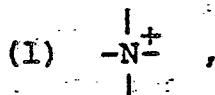
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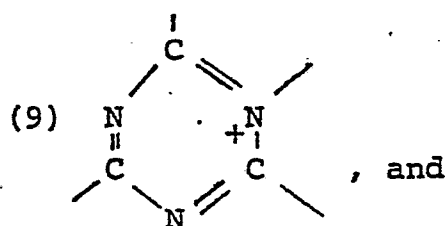
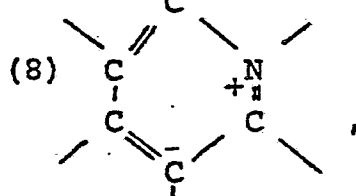
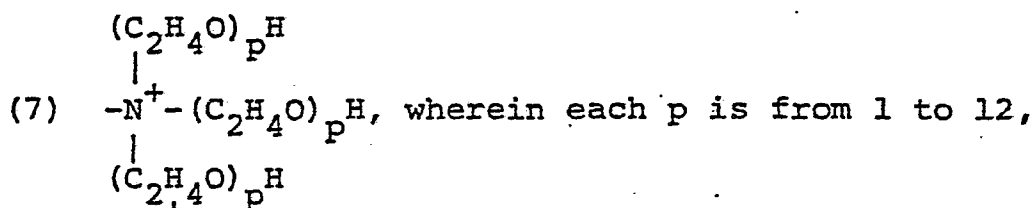
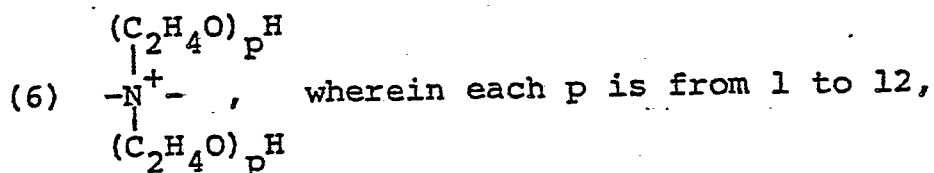
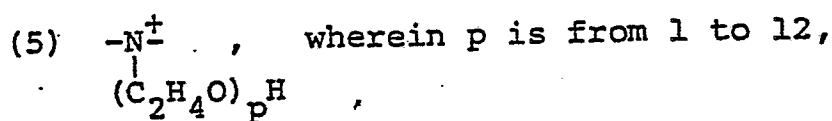
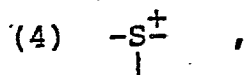
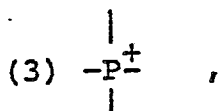
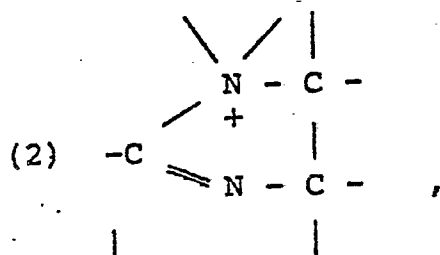


and mixtures thereof, each R^1 containing from about 8 to about 22 carbon atoms, and which may additionally contain up to about 20 ethylene oxide groups; m is a number from 1 to 3; each R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group, with no more than one R^2 in a molecule being benzyl; x is from 0 to 11, the remainder of any carbon atom positions being filled by hydrogens; Y is selected from the group consisting of

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(10) mixtures thereof;

- 10 L is 1 or 2, the Y groups being separated by a moiety selected from the group consisting of R^1 and R^2 analogs having from one to about twenty-two carbon atoms and 2 free carbon single bonds when L is 2; Z is an anion in a number sufficient to give electrical
- 15 neutrality to the molecule; said cationic surfactant being at least water-dispersible in admixture with said

nonionic surfactant;

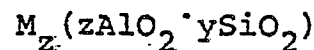
wherein the ratio of said nonionic surfactant to said cationic surfactant is from about 1:1 to about 100:1; and

(b) from about 5% to about 99% of a detergency builder mixture consisting essentially of:

(i) a water-insoluble aluminosilicate material selected from the group consisting of:

(1) Zeolites A, X, or P(B), or mixtures thereof, having a particle size diameter of from about 0.01 microns to about 25 microns and containing at least 10% water of hydration;

(2) amorphous hydrated aluminosilicate material of the empirical formula:



wherein M is sodium, potassium, ammonium, z is from about 0.5 to about 2, y is 1, said material having a particle size diameter of less than about 100 microns, a magnesium ion exchange capacity of at least about 50 milligrams equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate, and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon; and

(3) mixtures thereof; and

(ii) a polycarboxylate builder material;

wherein the weight ratio of the aluminosilicate material to the polycarboxylate material is from about 1:10 to about 10:1.

Disclosure of the Invention

This invention comprises the discovery of an improved builder mixture for use in detergent compositions containing selected nonionic/cationic surfactant mixtures.

The builder mixture, a combination of aluminosilicate and polycarboxylate builder materials, delivers excellent particulate soil removal performance and greasy/oily soil removal benefits. These compositions also provide fabric softening, static control, color fidelity and dye transfer

inhibition benefits. The detergent compositions are particularly good in 10-40°C water, especially when the particle size diameter of the aluminosilicate material is from about 0.5 to about 2 microns.

5. The essential elements in the detergent composition of this invention are: a nonionic/cationic surfactant mixture, and a mixture of aluminosilicate and polycarboxylate builder materials.

Surfactant Mixture

- 10 The compositions of the present invention comprise, by weight, from about 1 to about 95%, preferably from about 15 to about 60%, and most preferably from about 20 to about 50%, of a mixture of particularly defined nonionic and cationic surfactants, defined hereinafter, within ratios
15 of nonionic to cationic surfactant of from about 1:1 to about 100:1, preferably from about 1:1 to about 50:1, and more preferably from about 3:1 to about 40:1. Optimum removal of greasy/oily soils is generally obtained with nonionic:cationic surfactant ratios of from about 5:1 to
20 about 20:1; while optimum removal of particulate soils is obtained with compositions having nonionic:cationic surfactant ratios of from about 2:1 to about 9:1, especially from about 3:1 to about 6.5:1, most especially from about 3.5:1 to about 5.5:1, with these ratios being particularly
25 effective where the cationic surfactant used is of the di-long chain variety disclosed and claimed in European Patent No. 0004121, Murphy, published September 19, 1979, and incorporated herein by reference.

- 30 The compositions of the present invention are preferably formulated so as to have a pH of at least about 7 in the laundry solution, at conventional usage concentrations, in order to optimize their overall cleaning performance, to aid in their manufacturing and processing, and to minimize the possibility of washing machine corrosion. Alkalinity
35 sources, such as potassium hydroxide, potassium carbonate, potassium bicarbonate, sodium hydroxide, sodium carbonate, and sodium bicarbonate, may be included in the compositions for this purpose. Some of the cationic/nonionic systems of

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the present invention may attain optimum removal of greasy/oily soils at higher pHs, while attaining optimum particulate removal at relatively lower pHs. In these systems, overall performance may be enhanced by varying the pH of the wash solution during the laundering process. Particularly preferred compositions have a pH of at least about 8 in the laundry solution in order to optimize the removal of greasy/oily and body soils. In addition to the higher pH in the laundry solution, these preferred compositions should also have the ability to maintain a pH in the laundry solution of from about 8 to 11 throughout the washing operation (reserve alkalinity). Such a reserve alkalinity may be obtained by incorporating compounds which buffer at pHs of from about 8 to 11, such as monoethanolamine, diethanolamine, and triethanolamine.

Preferred compositions of the present invention are also essentially free of oily hydrocarbon materials and solvents, such as mineral oil, paraffin oil and kerosene, since these materials, which are themselves oily by nature, load the washing liquor with excessive oily material, thereby diminishing the cleaning effectiveness of the compositions themselves.

Nonionic Component

Nonionic surfactants, having HLBs of from about 5 to about 17, preferably from about 8.5 to about 14, more preferably from about 10 to about 13.5, which are conventionally used in detergent compositions, may be used in the compositions of the present invention. Such surfactants include the condensation product of 1 mole of a saturated or unsaturated, straight or branched chain carboxylic acid having from about 10 to about 18 carbon atoms with from about 5 to about 50 moles of alkylene (particularly ethylene) oxide; the condensation product of 1 mole of saturated or unsaturated, straight or branched chain alcohol having from about 10 to about 24 carbon atoms with from about 5 to about 50 moles of alkylene (especially ethylene) oxide; polyethylene glycols having a molecular weight of from about 400 to about 30,000; and the condensation product of 1 mole of

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alkyl phenol wherein the alkyl chain contains from about 8 to about 18 carbon atoms with from about 4 to about 50 moles of alkylene (especially ethylene) oxide. Further disclosure of nonionic surfactants useful in the present invention is found in U.S. Patent 3,862,058, Nirschl and Gloss, issued January 21, 1975, incorporated herein by reference.

Preferred nonionic surfactants for use in the compositions of the present invention, because of their excellent biodegradability and performance characteristics, have the formula $R(OC_2H_4)_nOH$, wherein R is a primary or secondary, straight or branched alkyl chain containing an average of from about 8 to about 22, preferably from about 10 to about 20, carbon atoms, and n is an average of from about 2 to about 12, preferably from about 2 to about 9, especially from about 2 to about 7. Where di-long chain cationic materials are used in the compositions of the present invention, it is especially preferred that the R group in the nonionic surfactant contain from about 10 to about 16 carbon atoms. The nonionic surfactants described herein have an HLB (hydrophilic-lipophilic balance) of from about 5 to about 17, preferably from about 8.5 to about 14, and most preferably from about 10 to about 13.5. HLB, an indicator of a surfactants hydrophilic or lipophilic nature, is defined in detail in Nonionic Surfactants, by M. J. Schick, Marcel Dekker, Inc., 1976, pp. 607613, incorporated herein by reference.

Preferred nonionic surfactants for use in the present invention include the condensation product of C_{10} alcohol with 3 moles of ethylene oxide, the condensation product of coconut alcohol with 5 or 7 moles of ethylene oxide, the condensation product of tallow alcohol with 6, 9, or 11 moles of ethylene oxide, the condensation product of secondary C_{15} alcohol with 5 or 9 moles of ethylene oxide, the condensation product of C_{12-13} alcohol with 3, 4, 5, 6.5, or 9 moles of ethylene oxide, the condensation product of C_{12-15} alcohol with 7 or 9 moles of ethylene oxide, the condensation product of C_{12} alcohol with 5 moles of ethylene oxide, the condensation

product of C_{14-15} alcohol with 3, 4, 5, 7, or 9 moles of ethylene oxide, and mixtures thereof.

A preferred class of surfactants utilizes alcohols which contain about 20% of 2-methyl branched isomers, and are commercially available under the trade name Neodol, from the Shell Chemical Company. Particularly preferred nonionic surfactants for use in the compositions of the present invention include the condensation product of C_{10} alcohol with 3 moles of ethylene oxide, the condensation product of C_{12-13} alcohol with about 3 moles of ethylene oxide, and the same product which is stripped to remove substantially all lower ethoxylate and nonethoxylated fractions, the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide, the condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, the condensation product of C_{12} alcohol with 5 moles of ethylene oxide, the condensation product of coconut alcohol with 5 moles of ethylene oxide, the condensation product of C_{12-13} alcohol with 9 moles of ethylene oxide, the condensation product of C_{14-15} alcohol with 3 moles of ethylene oxide, the condensation product of C_{14-15} alcohol with 4 moles of ethylene oxide, the condensation product of C_{14-15} alcohol with 9 moles of ethylene oxide, and mixtures thereof.

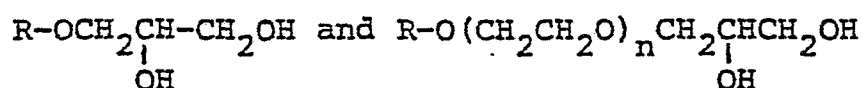
Where optimum particulate soil removal performance is sought, it is preferred that cationic surfactants used are of the di-long chain variety and that the nonionic surfactant be selected from the group consisting of the condensation product of C_{14-15} alcohol with 2.25 moles of ethylene oxide, the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide, the condensation product of C_{12-15} alcohol with 7 moles of ethylene oxide, the condensation product of C_{12-15} alcohol with 9 moles of ethylene oxide, the condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, and the same product which is stripped so as to remove lower ethoxylate and nonethoxylated fractions, the condensation product of C_{9-11} alcohol with 8 moles of ethylene oxide, which is stripped so as to remove

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lower ethoxylate and nonethoxylated fractions, the condensation product of coconut alcohol with 5 moles of ethylene oxide, the condensation product of coconut alcohol with 6 moles of ethylene oxide, the condensation product of tallow alcohol with 9 moles of ethylene oxide, and mixtures thereof.

The compositions of the present invention may contain mixtures of nonionic surfactants falling within the above preferred nonionic surfactant definition, such as a mixture of the condensation product of C₁₂₋₁₃ alcohol with 6.5 moles of ethylene oxide with the condensation product of C₁₄₋₁₅ alcohol with 7 moles of ethylene oxide, in a ratio of from about 4:1 to about 1:4. The present invention may also contain mixtures of nonionic surfactants, some of which do not fall within the above preferred nonionic surfactant definition (such as alcohol ethoxylates having an average of greater than about 12 ethylene oxide groups per molecule), and in such mixtures it is preferred that at least one of the nonionic surfactants contained in the mixture falls within the above preferred nonionic surfactant definition and that this preferred nonionic surfactant (or mixture of surfactants) be included in an amount such that it falls within the nonionic/cationic ratio range required herein. Where the nonionic surfactant mixture contains a nonionic surfactant (or surfactants) which falls outside of the above preferred nonionic surfactant definition, it is preferable that the ratio of the surfactant (or surfactants) within the definition to those outside the definition be within the range of from about 1:1 to about 10:1.

In addition to the required nonionic surfactant, preferred nonionic surfactant mixtures also contain alkyl glyceryl ethers. Particularly preferred are glyceryl ethers having the formulae:



wherein R is an alkyl or alkenyl group of from about 8 to about 18, preferably from about 8 to 12, carbon atoms or an alkaryl group having from about 5 to 14 carbon atoms in the

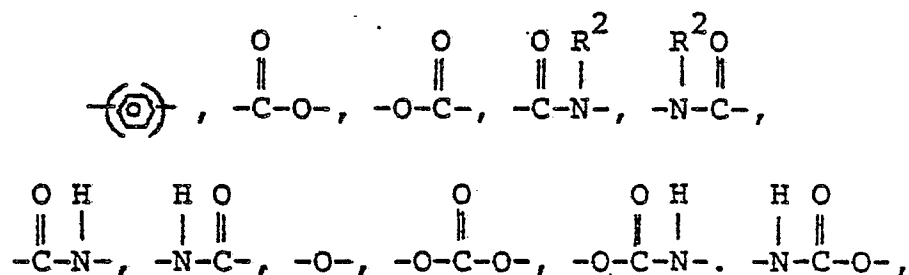
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alkyl chain, and n is from 1 to about 6. These compounds may be used together with the nonionic surfactant component of the present invention, in a ratio of nonionic surfactant to glyceryl ether of from about 1:1 to about 4:1, particularly about 7:3. Glyceryl ethers of the type useful in the present invention are disclosed in U.S. Patent 4,098,713, Jones, issued July 4, 1978, and British Patent No. 1.560.083, Jones, published January 30, 1980, both of which are incorporated herein by reference.

Another preferred group of nonionic surfactants useful herein comprises a mixture of "surfactant" and "co-surfactant", containing at least one nonionic surfactant falling within the definition of the nonionic surfactants preferred herein, as described in British Patent No. 1.462.134, Collins, published on January 19, 1977, the disclosure of which is incorporated herein by reference.

Cationic Component

The cationic surfactants used in the compositions of the present invention have the formula $R_m^1 R_x^2 Y_L Z$ wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to three phenyl or hydroxyl groups, and optionally interrupted by up to four structures selected from the group consisting of:

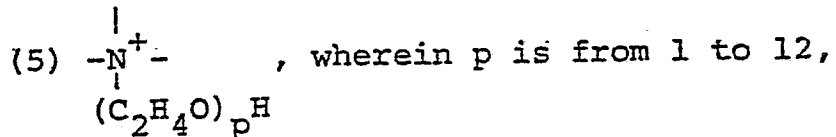
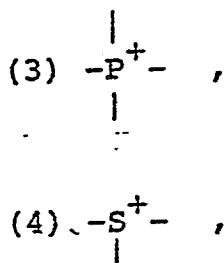
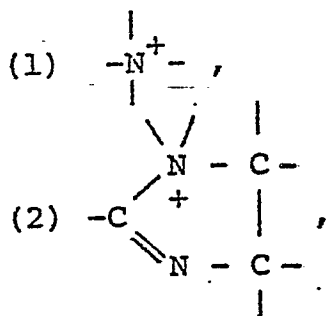


and mixtures thereof, and which contains from about 8 to 22 carbon atoms, and which may additionally contain up to 20 ethylene oxide groups, and m is a number from 1 to 3. R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms, or a benzyl group with no more than one R^2 in

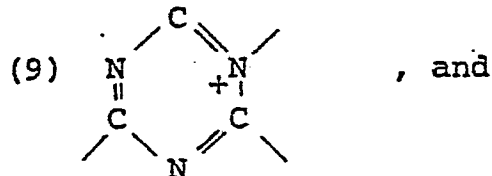
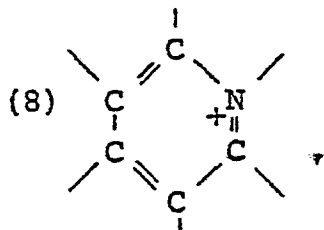
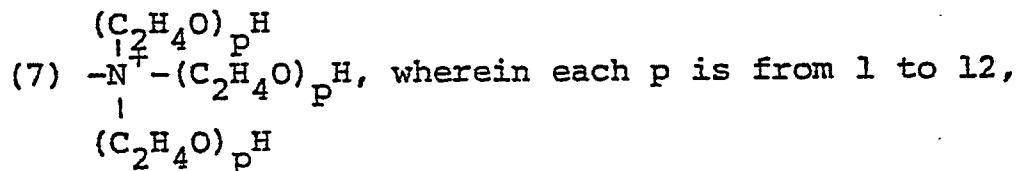
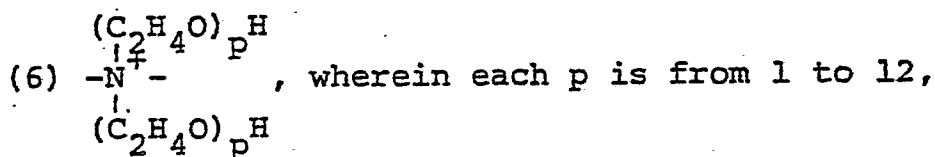
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a molecule being benzyl, and x is a number from 0 to 11, preferably from 0 to 6. The remainder of any carbon positions on the Y group are filled by hydrogens. Y is selected from the group consisting of:

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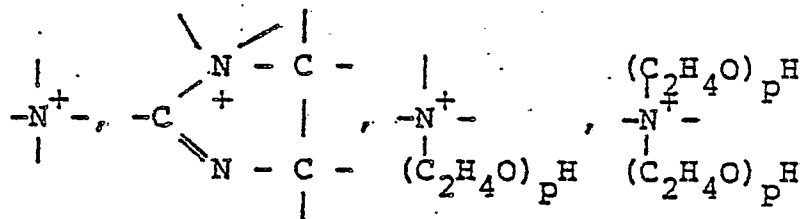


(10) mixtures thereof;

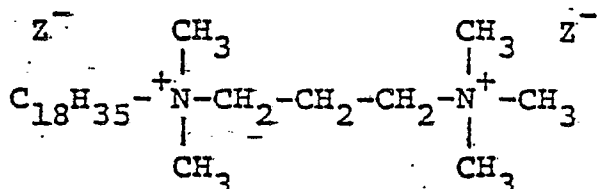
L is 1 or 2, with the Y groups being separated by a moiety selected from the group consisting of R¹ and R² analogs (preferably alkylene or alkenylene) having from one to about twenty-two carbon atoms and 2 free carbon single bonds. when L is 2. Z is a water-soluble anion such as halide, methyl sulfate, sulfate, or nitrate anion, particularly preferred anions being chloride, bromide, iodide, sulfate, or methyl sulfate, in a number to give electrical neutrality of the cationic component.

The particular cationic component to be included in a given system depends to a large extent upon the particular nonionic component to be used; it is selected such that it is at least water-dispersible when mixed with the nonionic surfactant. The cationic surfactant is chosen, in light of the particular nonionic surfactant used, in order to satisfy the cloud point requirements of the detergent composition, discussed below. Mixtures of these cationic materials may also be used in the compositions of the present invention. Preferred cationic surfactants are those having critical micelle concentrations of less than about 500 ppm, especially less than about 100 ppm.

In preferred cationic materials, L is equal to 1, p is from 1 to 12, preferably from 1 to 10, and Y is



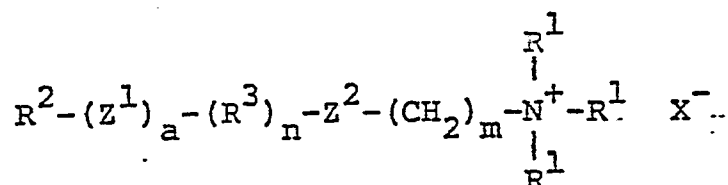
or mixtures thereof. However, L may be equal to two, thereby yielding cationic components containing two cationic charge centers. An example of a di-cationic component is given below:



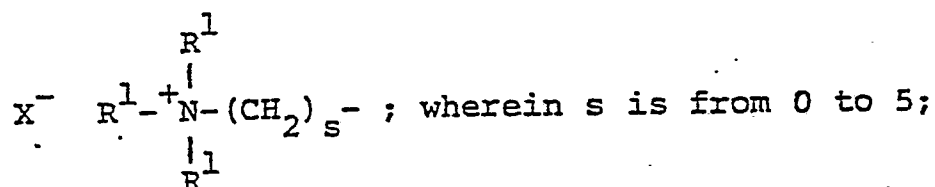
Other cationic materials which are useful in the compositions of the present invention include phosphonium and sulfonium materials.

5 Additional cationic surfactants useful in the compositions herein are disclosed in European Patent No. 0000235, Murphy, published January 10, 1979, incorporated herein by reference.

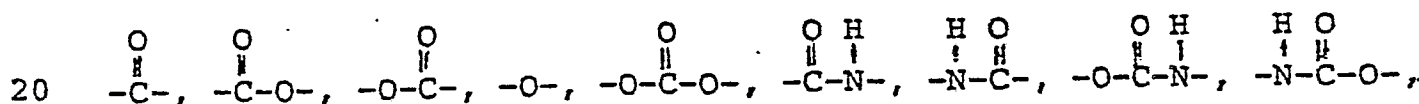
A particularly preferred type of cationic component, which is described in Japan Patent No. 79-39413, 10 Letton, published March 26, 1979, incorporated herein by reference, has the formula



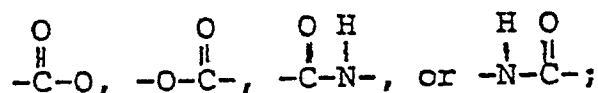
wherein R^1 is C_1 to C_4 alkyl or hydroxyalkyl; R^2 is C_5 to C_{30} straight or branched chain alkyl, alkenyl, alkylbenzyl 15 or alkyl phenyl, or



R^3 is C_1 to C_{20} alkylene or alkenylene; a is 0 or 1, n is 0 or 1, and n is 1 when a is 1; m is from 1 to 5; Z^1 and Z^2 are each selected from the group consisting of



and wherein at least one of said Z^1 or Z^2 groups is

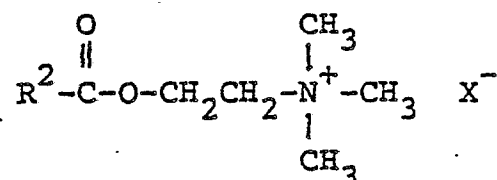


and X is an anion which makes the compound at least water-dispersible, preferably selected from the group consisting

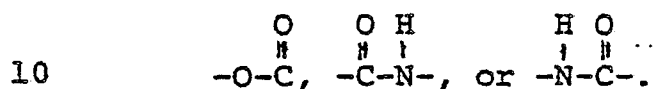
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of halide, methyl sulfate, sulfate, and nitrate, more preferably chloride, bromide, iodide, methyl sulfate and sulfate.

Particularly preferred cationic surfactants of this type are the choline ester derivatives having the following formula:

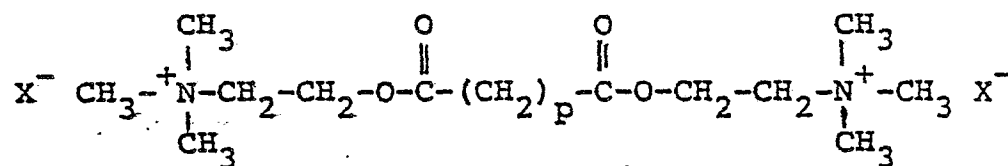
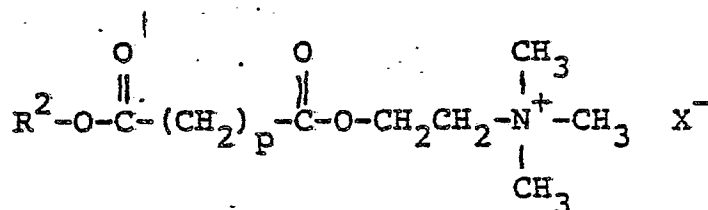


as well as those compounds in which the $\overset{\text{O}}{\parallel}\text{C}-\text{O}-$ linkage in the above formula is replaced with



Particularly preferred examples of this type of cationic surfactant include stearoyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_{17}$ alkyl), palmitoyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_{15}$ alkyl), myristoyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_{11}$ alkyl), and tallowyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_{15}-\text{C}_{17}$ alkyl).

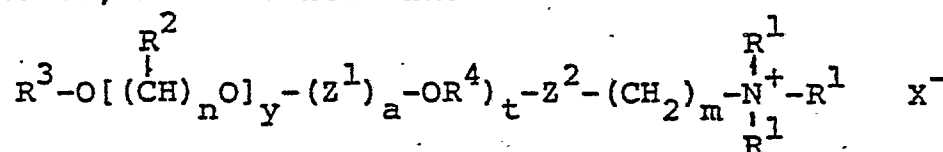
Additional preferred cationic components of the choline ester variety are given by the structural formulas below, wherein p may be from 0 to 20.



The preferred choline-derivative cationic substances, discussed above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst.

5 The reaction product is then quaternized with a methyl halide, forming the desired cationic material. The choline-derived cationic materials may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the
10 presence of an acid catalyst material. The reaction product is then used to quaternize trimethylamine, forming the desired cationic component.

Another type of novel, particularly preferred cationic material, described in Japan Patent No. 79-130509,
15 Letton, published October 9, 1979, incorporated herein by reference, has the formula:

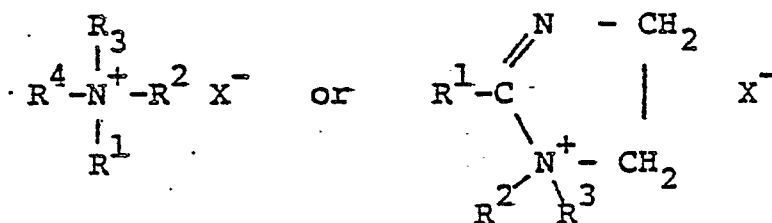


In the above formula, each R^1 is a C_1 to C_4 alkyl or hydroxyalkyl group, preferably a methyl group. Each R^2 is
20 either hydrogen or C_1 to C_3 alkyl, preferably hydrogen. R^3 is a C_4 to C_{30} straight or branched chain alkyl or alkenyl, preferably a C_8 to C_{18} alkyl group, most preferably a C_{12} alkyl group. R^4 is a C_1 to C_{10} alkylene or alkenylene group. n is from 2 to 4, preferably 2; y is from 1 to 20,
25 preferably from about 1 to 10, most preferably about 7; a may be 0 or 1, and t may be 0 or 1, but t is 1 when a is 1; and m is from 1 to 5, preferably 2. Z^2 is selected from the group consisting of

30 $\begin{array}{c} O \\ || \\ -O-C- \end{array}$, $\begin{array}{c} O \\ || \\ -C-O- \end{array}$, $\begin{array}{c} O \\ || \\ -C- \end{array}$, $-O-$, $\begin{array}{c} O \\ || \\ -O-C-O- \end{array}$, $\begin{array}{c} O \ H \\ || \ | \\ -C-N- \end{array}$, $\begin{array}{c} H \ O \\ | \ || \\ -N-C- \end{array}$, $\begin{array}{c} O \ H \\ || \ | \\ -O-C-N- \end{array}$,
 $\begin{array}{c} H \ O \\ | \ || \\ -N-C-O- \end{array}$; Z^1 is $\begin{array}{c} O \\ || \\ -C- \end{array}$ or $\begin{array}{c} O \ H \\ || \ | \\ -C-N- \end{array}$; and at least one of Z^1 and Z^2 groups is selected from the group consisting of

$\begin{array}{cccc} \text{O} & \text{O} & \text{O} & \text{H} & \text{H} & \text{O} \\ \parallel & \parallel & \parallel & | & | & \parallel \\ -\text{O}-\text{C}- & -\text{C}-\text{O}- & -\text{C}-\text{N}- & -\text{N}-\text{C}- & \end{array}$
 X is an anion which makes the compound at least water dispersible, and is selected from the group consisting of halides, methyl sulfate, sulfate, and nitrate, particularly chloride, bromide iodide, methyl sulfate and sulfate. Mixtures of the above structures can also be used.

Where particulate soil removal is to be optimized, it is preferred that the cationic surfactants used are of the di-long chain quaternary ammonium type, having two chains which contain an average of from about 12 to about 22, preferably from about 16 to about 18 carbon atoms. The remaining groups, if any, attach to the quaternary nitrogen atom, are preferably C_1 to C_4 alkyl or hydroxyalkyl groups. Although it is preferred that the long chains be alkyl groups, these chains may contain hetero atoms or other linkages, such as hydroxy groups, double or triple carbon-carbon bonds, and ester, amide, or ether linkages, as long as each chain falls within the preferred carbon atom ranges given above. Cationic surfactants of this type are disclosed in European Patent No. 0004121, Murphy, published September 19, 1979, incorporated herein by reference. Preferred cationic surfactants are those having the formulae:

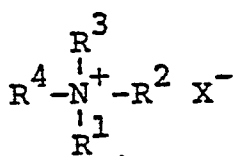


wherein the R^1 and R^2 groups contain an average of from about 16 to about 22 carbon atoms, preferably is alkyl groups, and most preferably contain an average of from about 16 to about 18 carbon atoms, R^3 and R^4 are C_1 to C_4 alkyl or hydroxyalkyl groups, and X is any compatible anion, particularly one selected from the group consisting of halide, hydroxide, methyl sulfate, or acetate anions.

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Preferred cationic surfactants include ditallowalkyl-
 dimethyl (or diethyl or dihydroxyethyl) ammonium chloride,
 ditallowalkyldimethylammonium methyl sulfate, dihexadecyl-
 alkyl (C₁₆) (also known as distearyl), dimethyl (or diethyl,
 5 or dihydroxyethyl) ammonium chloride, dioctadecylalkyl (C₁₈)
 dimethylammonium chloride, dieicosylalkyl (C₂₀) dimethyl-
 ammonium chloride, methyl-(1)-tallowalkylamido ethyl (2)
 tallowalkylimidazolinium methyl sulfate (commercially
 available as Varisoft 475 from Ashland Chemical Company), or
 10 mixtures of those surfactants. Particularly preferred
 cationic surfactants are ditallowalkyldimethylammonium
 chloride, ditallowalkyldimethylammonium methyl sulfate,
 methyl(1)tallowalkylamidoethyl(2)tallowalkylimidazolinium
 methyl sulfate, and mixtures of those surfactants, with
 15 ditallowalkyldimethylammonium chloride being especially
 preferred.

Another particularly useful class of cationic sur-
 factant is that in which the two long chains of the cationic
 surfactant contain a significant amount of unsaturation,
 20 such as where at least about 20%, preferably at least about
 30%, of the long chains contain at least one double bond.
 Compounds of this type have the formula



wherein R¹ and R² contain an average of from about 16 to
 25 about 22 (most preferably from about 16 to about 18) carbon
 atoms, and at least about 20% of these chains contain at
 least one double bond; R³ and R⁴ are C₁ to C₄ alkyl or
 hydroxyalkyl groups, and X is any compatible anion, partic-
 ularly one selected from the group consisting of halide,
 30 hydroxide, methyl sulfate, or acetate anions. Thus, for
 example, a preferred cationic surfactant is di-partially
 hydrogenated tallow dimethylammonium halide (especially
 chloride or methyl sulfate), which is also known as disoftened-
 tallowalkyldimethylammonium halide. A commercially available

compound of this type is Adogen 470, sold by Ashland Chemical Company, wherein about 30% of the tallow chains are oleyl in character. Compositions made with these cationics showed several significant advantages over those made with more conventional cationics (such ditallowalkyldimethylammonium chloride), particularly those compositions show improved particulate soil removal, especially at low wash temperatures, improved static control, and remain in a stable single phase at temperatures down to about 40°F.

Utilizing the nonionic and cationic components, defined above, preferred compositions of the present invention may be formulated using the guidance provided by the reduced monomer concentration of the cationic component (C_R) in the laundry solution. Specifically, the selection of a C_R value for a given nonionic and cationic surfactant pair will determine the ratio in which to combine those surfactants. A given nonionic/cationic surfactant pair will give its best particulate or grease/oil removal performance when it is formulated to have a C_R value which falls within the ranges defined herein. The reduced monomer concentration of a surfactant is obtained by dividing the concentration of the surfactant monomer present in the laundry solution by the critical micelle concentration (CMC) of that surfactant. As used in this application, CMCs are determined at 105°F in water containing 7 grains/gallon of mixed (2:1; Ca:Mg) hardness, unless otherwise stated.

The concept of reduced cationic monomer concentration is explained in detail in European Patent No. 0000235, Murphy, published January 10, 1979; Tamamushi and Tamaki, Proceedings of the Second International Congress of Surface Activity, III, 449, Academic Press, Inc. (1957); and Clint, J. Chem. Soc. Far. Trans., I, 71, 1327 (1975), all of which are incorporated herein by reference. The reduced cationic monomer concentration of the nonionic/ cationic surfactant mixture is defined by equations (a) through (c), below. In systems where grease/oil removal is to be optimized it is preferred that the C_R value of the nonionic/cationic surfactant mixture be in the range of from about 0.002 to about

0.2, especially from about 0.002 to about 0.15, most preferably from about 0.002 to about 0.08. In compositions wherein the particulate soil removal capabilities are to be optimized, it is preferred that the nonionic/cationic surfactant mixture have a C_R of from 0.005 to about 0.2, especially from about 0.008 to about 0.15, most preferably from about 0.01 to about 0.1. It is in the area of overlap (i.e., C_R equals about 0.005 to about 0.2) of these C_R ranges that the compositions of the present invention yield both optimum particulate and greasy/oily soil removal.

In the following equations these abbreviations are used:

C_1^* = critical micelle concentration of nonionic surfactant (moles per liter)

C_2^* = critical micelle concentration of cationic surfactant (moles per liter)

β = a constant based upon the heat of mixing = - 2.8

e = base of Napierian logarithm system = 2.71828

x = mole fraction of the nonionic surfactant in the micelle at concentration C

f_1 = nonionic activity coefficient in the mixed micelle = $e^{\beta(1-x)^2}$

f_2 = cationic activity coefficient in the mixed micelle = $e^{\beta x^2}$

Δ = $f_2 C_2^* - f_1 C_1^*$

M_1 = molecular weight of nonionic surfactant

M_2 = molecular weight of cationic surfactant

W = total analytical surfactant concentration in the solution (ppm) = sum of the cationic and nonionic concentrations

Y = weight fraction of nonionic surfactant in the composition

Where a desired C_R value or range is selected, and β , C_1^* , C_2^* , M_1 and M_2 are known for given nonionic/cationic surfactant pair, the corresponding nonionic:cationic ratios(s) is calculated as follows:

- (a) for a given nonionic surfactant, cationic surfactant, and for each end of the C_R range desired, solve for x using the equation

$$(1-x) e^{\beta x^2} = C_R$$

- 5 by standard numerical iterative techniques to an error in x of less than 0.001;

- (b) find the range of Y from the equation

$$\frac{Y(1-x)}{M_1} - \frac{x(1-Y)}{M_2} = \frac{1000}{W} [x(x-1) \Delta]$$

- 10 using 100 ppm and 10,000 ppm as the boundary values for W , for each end of the desired C_R range;

- (c) the nonionic/cationic ratio(s) (NCR) corresponding to the C_R value or range selected is then obtained by substituting the boundary values for Y into the
15 formula

$$NCR = \frac{Y}{1-Y}$$

- In addition to these reduced cationic monomer concentration criteria, compositions which give the best performance on greasy/oily soils also satisfy specific cloud
20 point requirements, given below, and detailed in European Patent No. 0000235, Murphy, published January 10, 1979, incorporated herein by reference. Thus, these preferred compositions have nonionic/cationic mixtures which exhibit a cloud point between about 10°C and 70°C, more preferably
25 between about 20°C and 70°C, especially between about 30°C and about 50°C. The compositions will exhibit their best grease/oil removal performance when the temperature of the wash solution in which they are used falls within about 20°C, preferably within about 15°C, and most preferably
30 within about 10°C, of the cloud point of the nonionic/cationic surfactant mixture.
- 

As used herein, the term "cloud point" means the temperature at which a graph plotting the light scattering intensity of the composition versus wash solution temperature begins to sharply increase to its maximum value, under the following experimental conditions:

The light scattering intensity is measured using a Model VM-12397 Photogoniometer, manufactured by Societe Francaise d'instruments de controle et d'analyses, France (the instrument being hereinafter referred to as (SOFICA). The SOFICA sample cell and its lid are washed with hot acetone and allowed to dry. The surfactant mixture is made and put into solution with distilled water at a concentration of 1000 ppm. Approximately a 15 ml. sample of the solution is placed into the sample cell, using a syringe with a 0.2 μ nucleopore filter. The syringe needle passes through the sample cell lid, so that the cell interior is not exposed to atmospheric dust. The sample is kept in a variable temperature bath, and both the bath and the sample are subject to constant stirring. The bath temperature is heated using the SOFICA's heater and cooled by the addition of ice (heating rate 1°C/minute); the temperature of the sample is determined by the temperature of the bath. The light scattering (90° angle intensity of the sample is then determined at various temperatures, using a green filter and no polarizer in the SOFICA.

Builder Mixture

The detergent compositions herein contain from about 5% to about 99%, preferably from about 20% to about 60%, by weight of a detergency builder mixture. The builder mixture consists essentially of:

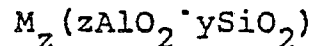
(i) a water-insoluble aluminosilicate material selected from the group consisting of

(1) Zeolites A, X, or P(B), or mixtures thereof, having a particle size diameter of from about 0.01 microns to about 25 microns and containing at least 10% water of hydration, and

(2) amorphous hydrated aluminosilicate material

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of the empirical formula:



wherein M is sodium, potassium, ammonium, z is from about 0.5 to about 2, y is 1, said material having a particle size diameter of less than about 100 microns, a magnesium ion exchange capacity of at least about 50 milligrams equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate, and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon, and

(3) mixtures thereof; and

(ii) a polycarboxylate builder material;

wherein the weight ratio of the aluminosilicate material to the polycarboxylate material is from about 1:10 to about 10:1.

Preferably, the weight ratio of the aluminosilicate material to the polycarboxylate material is from about 1:4 to about 4:1, more preferably from about 1:3 to about 2:1.

Preferably, the aluminosilicate materials for use herein are those commonly known as Zeolites A, X, and P(B). The zeolites should contain at least 10% water of hydration and should have a particle size diameter of from about 0.01 microns to about 25 microns, preferably from about 0.1 microns to about 10 microns, more preferably from about 0.5 microns to about 2 microns. Aluminosilicate materials are more fully described in U.S. Patent 4,096,081, Phenicie et al, issued June 20, 1978, and German Patent No. 27 04 003, Ohren, published on August 18, 1977, the disclosures of which are incorporated herein by reference. The amorphous aluminosilicate materials suitable for use herein are fully described in U.S. Patent Application No. 4,180,485, Llenado, published December 25, 1979, incorporated herein by reference.

Examples of suitable polycarboxylate builder materials for use herein are (I) water-soluble aminopolycarboxylates,

e.g., sodium and potassium ethylenediaminetetraacetates, (2) the water-soluble salts of phytic acid, e.g., sodium and potassium phytates, disclosed in U.S. Patent No. 2,739,942, Eckey, issued March 27, 1956, incorporated herein by
5 reference; (3) the polycarboxylate materials described in U.S. Patent 3,364,103; and (4) water-soluble salts of polycarboxylate polymers and copolymers as described in U.S. Patent No. 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference.

10 A useful detergent builder which may be employed in the present invention comprises a water-soluble salt of a polymeric aliphatic polycarboxylic acid having the following structural relationships as to the position of the carboxy-
late groups and possessing the following prescribed physical
15 characteristics: (a) a minimum molecular weight of about 350 calculated as to the acid form; (b) an equivalent weight of about 50 to about 80 calculated as to acid form; (c) at least 45 mole percent of the monomeric species having at least two carboxyl radicals separated from each other by not
20 more than two carbon atoms; (d) the site of attachment of the polymer chain of any carboxyl-containing radical being separated by not more than three carbon atoms along the polymer chain from the site of attachment of the next carboxyl-containing radical. Specific examples of the
25 above-described builders include polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid and citraconic acid and copolymers with themselves.

In addition, other builders which can be used satis-
30 factorily include water-soluble salts, especially the sodium and potassium salts, of mellitic acid, citric acid, pyromellitic acid, benzene pentacarboxylic acid, oxydiacetic acid, carboxymethyloxysuccinic acid, carboxymethyloxymalonic acid, cis-cyclohexanehexacarboxylic acid, cis-cyclopenta-
35 netetracarboxylic acid and oxydisuccinic acid.

It is to be understood that while the alkali metal salts of the foregoing inorganic and organic polyvalent anionic builder salts are preferred for use herein from an

economic standpoint, the ammonium, alkanolammonium, e.g., triethanolammonium, diethanolammonium, and the like, water-soluble salts of any of the foregoing builder anions are also useful herein.

5 Other suitable polycarboxylates for use herein are the polyacetal carboxylates fully described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,146,495, issued March 27, 1979 to Crutchfield et al, the disclosures of which are incorporated herein by
10 reference.

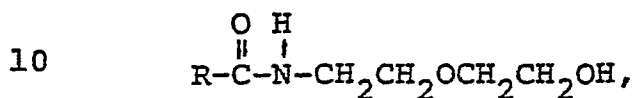
These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to
15 chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant. European Patent No. 80200102.4, Rodriguez et al., filed on February 7, 1980, incorporated
20 herein by reference, discloses a builder system containing these polyacetal carboxylates along with aluminosilicate builder materials, for use in detergent compositions, which preferably contain nonionic/cationic surfactants.

Preferred polycarboxylate builders for use in the
25 present invention are sodium or potassium nitrilotriacetate or citrate, or mixtures thereof. The compositions of this invention contain from 0 to about 5% phosphate materials, and are preferably substantially free of phosphate materials.

Additional Components

30 In particularly preferred embodiments of the present invention, the detergent compositions additionally contain from about 2 to about 25%, preferably from about 2 to about 16%, and most preferably from about 2 to about 10% of a fatty amide surfactant, such as ammonia amides (e.g.,
35 coconutalkyl ammonia amide, diethanol amides, and ethoxylated amides). In relation to the nonionic/ cationic surfactant system, the ratio of the cationic/ nonionic mixture to the amide component in the composition is in the

range of from about 5:1 to about 50:1, preferably from about 8:1 to about 25:1. The addition of the amide component results in a composition which exhibits improved anti-redeposition of both clay and greasy/oily soils. This development is described in greater detail in Japan Patent No. 79-39414; Cambre, published on March 26, 1979, incorporated herein by reference. Preferred amides are C₈-C₂₀ monoethanol amides, C₈-C₂₀ diethanol amides, and amides having the formula



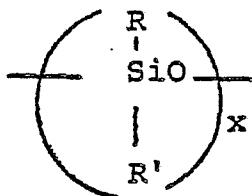
wherein R is a C₈-C₂₀ alkyl group, and mixtures thereof. Particularly preferred amides are those where the alkyl group contains from about 10 to about 16 carbon atoms, such as coconut alkyl monoethanol or diethanol amide. Such compounds are commercially available under the tradenames Superamide GR, from Onyx Chemical Co., Jersey City, N.J., Superamide F-3 from Ryco, Inc., Conshohocken, Pa., and Gafamide CDD-518, available from GAF Corp., New York, N.Y.

20 These amide components may also be added in small amounts, i.e., from about 2% to about 5%, to act as suds modifiers. Specifically, they tend to boost the sudsing in an active system which exhibits relatively low sudsing, and depress the sudsing in an active system which exhibits relatively high sudsing.

25 The compositions of the present invention may also contain additional ingredients generally found in laundry detergent compositions, at their conventional art-established levels, as long as these ingredients are compatible with the nonionic and cationic components required herein. For example, the compositions may contain up to about 15%, preferably up to about 5%, and most preferably from about 0.001 to about 2%, of a suds suppressor component. Typical suds suppressors useful in the compositions of the present invention include, but are not limited to, those described below.

35 Preferred silicone-type suds suppressing additives are described in U.S. Patent 3,933,672, issued January 20, 1976,

Bartolotta et al., incorporated herein by reference. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogels and xerogels and hydrophobic silicas of various types. The silicone material can be described as a siloxane having the formula:



wherein x is from about 20 to about 2,000, and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. Polydimethylsiloxanes (R and R' are methyl, having a molecular weight within the range of from about 200 to about 200,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials wherein the side chain groups R and R' are alkyl, aryl, or mixed alkyl and aryl hydrocarbyl groups exhibit useful suds controlling properties. Examples of such ingredients include diethyl-, dipropyl-, dibutyl-, methyl-ethyl-, phenylmethyl-polysiloxanes and the like. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from about 10 millimicrons to 20 millimicrons and a specific surface area above about 50 m²/gm intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 19:1 to about 1:2. The silicone suds suppressing agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active, detergent-impermeable carrier.

Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in U.S. Patent 4,075,118, Gault et al, issued February 21, 1978, incorporated herein by reference. An example of such a
5 compound is DB-544, commercially available from Dow Corning, which contains a siloxane/glycol copolymer together with solid silica and a siloxane resin.

Microcrystalline waxes having a melting point in the range from 35°C-115°C and a saponification value of less
10 than 100 represent additional examples of a preferred suds regulating component for use in the subject compositions, and are described in detail in U.S. Patent 4,056,481, Tate, issued November 1, 1977, incorporated herein by reference. The microcrystalline waxes are substantially water-insoluble,
15 but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes have a melting point from about 65°C to 100°C, a molecular weight in the range from 400-1,000; and a penetration value of at least 6, measured at 77°F by ASTM-D1321. Suitable examples of the
20 above waxes include: microcrystalline and oxidized microcrystalline petrolatum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax; candelilla; and carnauba wax.

Alkyl phosphate esters represent an additional preferred suds suppressant for use herein. These preferred
25 phosphate esters are predominantly monostearyl phosphate which, in addition thereto, can contain di- and tristearyl phosphates and mono-oleyl phosphates, which can contain di- and trioleyl phosphates.

30 The alkyl phosphate esters frequently contain some trialkyl phosphate. Accordingly, a preferred phosphate ester can contain, in addition to the monoalkyl ester, e.g. monostearyl phosphate, up to about 50 mole percent of dialkyl phosphate and up to about 5 mole percent of trialkyl
35 phosphate.

Other adjunct components which may be included in the compositions of the present invention, in their conventional art-established levels for use (i.e., from about 0 to about

40%), include semi-polar nonionic (such as amine oxides), anionic, zwitterionic and ampholytic cosurfactants; detergency builders; bleaching agents; bleach activators; soil release agents (particularly copolymers of ethylene terephthalate and polyethylene oxide terephthalate, such as Milease T sold by ICI, United States, as disclosed in U.S. Patent 4,132,680, Nicol, issued January 2, 1979, incorporated herein by reference); soil suspending agents; corrosion inhibitors; dyes; fillers; optical brighteners; germicides; pH adjusting agents; alkalinity sources; hydrotropes; enzymes; enzyme-stabilizing agents; perfumes; solvents; carriers; suds modifiers; opacifiers; and the like. However, because of the numerous and diverse performance advantages of the present invention, certain conventional components, such as cosurfactants and other detergency builders, as well as fabric softening and static control agents, will not generally be necessary in a particular formulation, giving the compositions of the present invention a potential cost advantage over conventional detergent/ softener compositions. In fact, because the compositions of the present invention give such outstanding clay removal performance across the range of water hardness conditions, for environmental reasons the compositions of the present invention contain less than about 5% phosphate materials. Preferred compositions are substantially or totally free of such phosphate materials, without decreasing the performance of the compositions. Preferred compositions of the present invention are also substantially free of carboxymethylcellulose in order to optimize the clay removal performance of the system. Finally, while the compositions of the present invention may contain anionic materials, such as anionic surfactants and hydrotropes (e.g., alkali metal toluene sulfonates), it is preferred that particular anionic materials be contained in amounts sufficiently small such that not more than about 10%, preferably not more than about 5%, of the cationic surfactant, contained in the laundry solution, is complexed by the anionic material. Such a complexing of the anionic material with the cationic

- 30 -

surfactant, decreases the overall cleaning and fabric conditioning performance of the composition. Suitable anionic materials may be selected based on their strength of complexation with the cationic material included in the composition (as indicated by their dissociation constant). Thus, when an anionic material has a dissociation constant of at least about 1×10^{-3} (such as sodium toluene sulfonate), it may be contained in an amount up to about 40%, by weight, of the cationic surfactant; where the anionic material has a dissociation constant of at least about 1×10^{-5} , but less than about 1×10^{-3} , it may be contained in an amount up to about 15%, by weight, of the cationic surfactant; and where the anionic material has a dissociation constant of less than about 1×10^{-5} (such as sodium $C_{11.8}$ linear alkylbenzene sulfonate), it may be contained only in amounts up to about 10%, by weight, of the cationic surfactant. Preferred compositions are substantially free of such anionic materials.

Examples of cosurfactants and detergency builders which may be used in the compositions of the present invention are found in U.S. Patent No. 3,717,630, Booth, issued February 20, 1973, and European Patent No. 0000235; Murphy, published January 10, 1979, both of which are incorporated herein by reference. However, these components, particularly the anionic surfactants, should be checked with the particular nonionic/cationic surfactant system chosen, and used in an amount, so as to be certain that they will be compatible with the nonionic/cationic surfactant system.

The compositions of the present invention may be produced in a variety of forms, including liquid, solid, granular, paste, powder or substrate compositions. Preferred substrate articles may be formulated according to U.S. Patent No. 4,170,565, Murphy, published on October 9, 1979, incorporated herein by reference. In a particularly preferred embodiment, the compositions of the present invention are formulated as liquids and contain up to about 20% of a lower alkyl (C_1 to C_4) alcohol, particularly ethanol. Liquid compositions containing lower levels

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of such alcohols (i.e., about 7 to 12%) tend to exhibit less phase separation than compositions containing higher alcohol levels. Granular compositions herein may also contain up to about 15% by weight of alkali metal silicates, especially sodium silicate (2.0 ratio), to increase flowability and physical stability of the granules.

The compositions of the present invention are used in the laundering process by forming an aqueous solution containing from about 0.01 (100 parts per million) to about 0.3% (3,000 parts per million), preferably from about 0.02 to about 0.2%, and most preferably from about 0.03 to about 0.15%, of the detergent compositions defined herein, and agitating the soiled fabrics in that solution. The fabrics are then rinsed and dried. When used in this manner, the compositions of the present invention yield outstanding particulate and greasy/oily soil removal, together with fabric softening, static control, color fidelity, and dye transfer inhibition benefits, without requiring the use of any of the other conventionally used fabric softening and static control laundry additives.

All percentages, parts, and ratios used herein are by weight unless otherwise specified.

The following nonlimiting examples illustrate the compositions of the present invention.

EXAMPLE I

Identical clay-soiled cotton, polyester/cotton, and polyester swatches were washed in aqueous solutions having dissolved therein: 500 parts per million (ppm) of a surfactant mixture containing 4.5 parts of the nonionic surfactant $C_{12-13} E_{6.5}$ (condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, commercially available as Neodol 23-6.5 from Shell Chemical Company) and 1 part of the cationic surfactant (dihydrogenated tallowalkyl dimethylammonium chloride); 600 ppm of the builder or builder mixture listed below; and 87 ppm of monoethanol amine. The swatches were washed for 10 minutes in a miniature agitator containing 1-1/2 gallons of washing liquor at 100°F and artificial water hardness (2 moles Ca^{++} to 1 mole Mg^{++}) at levels of 2, 7 and 12 grains per gallon. The swatches comprised approximately 4% by weight of the washing liquor. After washing, the swatches were spun dry and rinsed with 1-1/2 gallons of water, at 100°F, having the same water hardness as that of the water they were washed in. The swatches were then dried in a miniature electric dryer. A Hunter Reflectometer was used to obtain a reflectance reading (in Hunter Whiteness Units) for each of the laundered swatches. A higher reflectance reading indicates greater cleaning effectiveness. The results were as follows:

<u>Fabric</u>	<u>Water Hardness</u>	<u>Hunter Whiteness Units</u>
<u>Solution Containing 600 ppm Sodium Citrate</u>		
Cotton	2 gr./gal.	20.37 $\pm$ 2.69
"	7 gr./gal.	18.59 $\pm$ 1.40
30 "	12 gr./gal.	11.50 $\pm$ 1.19
Polycotton	2 gr./gal.	63.47 $\pm$ 2.13
"	7 gr./gal.	62.17 $\pm$ 0.31
"	12 gr./gal.	55.85 $\pm$ 0.59
Polyester	2 gr./gal.	74.35 $\pm$ 1.05
35 "	7 gr./gal.	72.65 $\pm$ 1.13
"	12 gr./gal.	70.75 $\pm$ 1.05

Solution Containing 600 ppm Sodium Nitrilotriacetate

	Cotton	2 gr./gal.	27.88 $\pm$ 1.49
	"	7 gr./gal.	24.71 $\pm$ 1.26
	"	12 gr./gal.	15.84 $\pm$ 1.68
5	Polycotton	2 gr./gal.	65.35 $\pm$ 1.91
	"	7 gr./gal.	63.55 $\pm$ 0.42
	"	12 gr./gal.	58.35 $\pm$ 0.84
	Polyester	2 gr./gal.	81.14 $\pm$ 1.34
	"	7 gr./gal.	80.38 $\pm$ 0.48
10	"	12 gr./gal.	75.95 $\pm$ 1.17

Solution Containing 600 ppm Polyacetal Carboxylate*

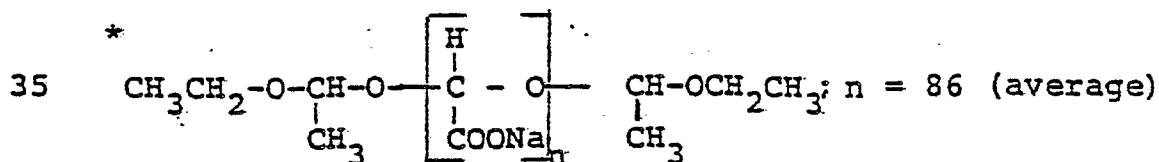
	Cotton	2 gr./gal.	28.60 $\pm$ 0.30
	"	7 gr./gal.	24.98 $\pm$ 0.69
	"	12 gr./gal.	15.94 $\pm$ 0.96
15	Polycotton	2 gr./gal.	59.86 $\pm$ 1.34
	"	7 gr./gal.	56.52 $\pm$ 3.07
	"	12 gr./gal.	50.08 $\pm$ 3.12
	Polyester	2 gr./gal.	70.06 $\pm$ 0.83
	"	7 gr./gal.	61.55 $\pm$ 0.81
20	"	12 gr./gal.	46.45 $\pm$ 2.04

Solution Containing 600 ppm Sodium Mellitate

	Cotton	2 gr./gal.	21.82 $\pm$ 0.39
	"	7 gr./gal.	16.29 $\pm$ 2.63
	"	12 gr./gal.	14.72 $\pm$ 1.17
25	Polycotton	2 gr./gal.	62.43 $\pm$ 0.37
	"	7 gr./gal.	56.50 $\pm$ 0.67
	"	12 gr./gal.	59.41 $\pm$ 1.00
	Polyester	2 gr./gal.	74.00 $\pm$ 1.84
	"	7 gr./gal.	73.64 $\pm$ 0.18
30	"	12 gr./gal.	65.46 $\pm$ 1.23

Solution Containing 600 ppm Zeolite A**

	Cotton	2 gr./gal.	17.85 $\pm$ 2.51
	"	7 gr./gal.	11.43 $\pm$ 1.37
	"	12 gr./gal.	7.57 $\pm$ 1.90



** Hydrated, particle diameter 1-10 microns (same throughout this Example)

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	Polycotton	2 gr./gal.	55.54 $\pm$ 1.34
	"	7 gr./gal.	48.37 $\pm$ 1.43
	"	12 gr./gal.	57.94 $\pm$ 0.75
	Polyester	2 gr./gal.	71.65 $\pm$ 0.86
5	"	7 gr./gal.	71.20 $\pm$ 0.76
	"	12 gr./gal.	69.17 $\pm$ 1.53

Solution Containing 600 ppm Zeolite X***

	Cotton	2 gr./gal.	19.02 $\pm$ 1.50
	"	7 gr./gal.	14.77 $\pm$ 2.04
10	"	12 gr./gal.	14.29 $\pm$ 1.21
	Polycotton	2 gr./gal.	54.73 $\pm$ 1.09
	"	7 gr./gal.	50.89 $\pm$ 4.47
	"	12 gr./gal.	59.41 $\pm$ 1.34
	Polyester	2 gr./gal.	71.98 $\pm$ 0.98
15	"	7 gr./gal.	71.32 $\pm$ 1.36
	"	12 gr./gal.	70.29 $\pm$ 0.72

Solution Containing 300 ppm Zeolite A and
300 ppm Sodium Nitrilotriacetate

	Cotton	2 gr./gal.	31.82 $\pm$ 0.96
20	"	7 gr./gal.	29.40 $\pm$ 0.68
	"	12 gr./gal.	24.84 $\pm$ 1.89
	Polycotton	2 gr./gal.	67.24 $\pm$ 0.47
	"	7 gr./gal.	66.85 $\pm$ 1.57
	"	12 gr./gal.	62.88 $\pm$ 1.07
25	Polyester	2 gr./gal.	82.84 $\pm$ 1.32
	"	7 gr./gal.	80.81 $\pm$ 1.34
	"	12 gr./gal.	77.67 $\pm$ 0.58

Solution Containing 300 ppm Zeolite A and
300 ppm Sodium Citrate

	Cotton	2 gr./gal.	27.66 $\pm$ 0.80
30	"	7 gr./gal.	26.80 $\pm$ 1.41
	"	12 gr./gal.	21.96 $\pm$ 0.47
	Polycotton	2 gr./gal.	64.40 $\pm$ 0.67
	"	7 gr./gal.	62.68 $\pm$ 0.37
	"	12 gr./gal.	61.31 $\pm$ 1.48

35

*** Hydrated, particle diameter 1-10 microns

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Polyester	2 gr./gal.	78.11 $\pm$ 0.55
"	7 gr./gal.	77.65 $\pm$ 2.31
"	12 gr./gal.	74.28 $\pm$ 0.68

Solution Containing 300 ppm Zeolite A and
300 ppm Polyacetal Carboxylate*

5	Cotton	2 gr./gal.	37.57 $\pm$ 1.30
	"	7 gr./gal.	33.48 $\pm$ 0.55
	"	12 gr./gal.	25.66 $\pm$ 1.37
	Polycotton	2 gr./gal.	67.09 $\pm$ 1.20
10	"	7 gr./gal.	63.54 $\pm$ 0.44
	"	12 gr./gal.	58.37 $\pm$ 0.80
	Polyester	2 gr./gal.	70.09 $\pm$ 1.52
	"	7 gr./gal.	68.89 $\pm$ 1.32
	"	12 gr./gal.	64.87 $\pm$ 1.23

15 Solution Containing 300 ppm Zeolite A and
300 ppm Sodium Mellitate

	Cotton	2 gr./gal.	28.04 $\pm$ 2.07
	"	7 gr./gal.	27.26 $\pm$ 0.58
	"	12 gr./gal.	24.78 $\pm$ 0.21
20	Polycotton	2 gr./gal.	63.74 $\pm$ 0.84
	"	7 gr./gal.	60.61 $\pm$ 2.09
	"	12 gr./gal.	59.35 $\pm$ 1.71
	Polyester	2 gr./gal.	74.88 $\pm$ 0.51
	"	7 gr./gal.	71.34 $\pm$ 1.75
25	"	12 gr./gal.	66.55 $\pm$ 3.25

Solution Containing 150 ppm Zeolite A and
450 ppm Sodium Nitrilotriacetate

	Cotton	2 gr./gal.	30.91 $\pm$ 1.49
	"	7 gr./gal.	28.34 $\pm$ 1.33
30	"	12 gr./gal.	13.73 $\pm$ 1.24
	Polycotton	2 gr./gal.	67.80 $\pm$ 0.35
	"	7 gr./gal.	60.98 $\pm$ 1.82
	"	12 gr./gal.	55.23 $\pm$ 1.22
	Polyester	2 gr./gal.	84.22 $\pm$ 0.98
35	"	7 gr./gal.	82.11 $\pm$ 0.68
	"	12 gr./gal.	77.47 $\pm$ 0.43

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Solution Containing 150 ppm Zeolite A and
450 ppm Sodium Citrate

	Cotton	2 gr./gal.	25.22 $\pm$ 3.07
	"	7 gr./gal.	21.15 $\pm$ 0.92
5	"	12 gr./gal.	15.56 $\pm$ 2.12
	Polycotton	2 gr./gal.	63.63 $\pm$ 1.31
	"	7 gr./gal.	62.62 $\pm$ 1.72
	"	12 gr./gal.	57.27 $\pm$ 2.42
	Polyester	2 gr./gal.	81.75 $\pm$ 0.86
10	"	7 gr./gal.	78.11 $\pm$ 1.02
	"	12 gr./gal.	71.82 $\pm$ 1.33

Solution Containing 150 ppm Zeolite A and
450 ppm Polyacetal Carboxylate*

	Cotton	2 gr./gal.	28.44 $\pm$ 0.80
15	"	7 gr./gal.	25.25 $\pm$ 0.08
	"	12 gr./gal.	14.31 $\pm$ 1.18
	Polycotton	2 gr./gal.	60.36 $\pm$ 1.73
	"	7 gr./gal.	57.30 $\pm$ 0.82
	"	12 gr./gal.	50.83 $\pm$ 0.57
20	Polyester	2 gr./gal.	77.51 $\pm$ 1.26
	"	7 gr./gal.	73.85 $\pm$ 0.29
	"	12 gr./gal.	67.35 $\pm$ 1.05

Solution Containing 150 ppm Zeolite A and
450 ppm Sodium Mellitate

25	Cotton	2 gr./gal.	23.65 $\pm$ 0.75
	"	7 gr./gal.	17.28 $\pm$ 1.15
	"	12 gr./gal.	14.52 $\pm$ 2.64
	Polycotton	2 gr./gal.	59.13 $\pm$ 1.92
	"	7 gr./gal.	56.82 $\pm$ 2.96
30	"	12 gr./gal.	54.92 $\pm$ 1.66
	Polyester	2 gr./gal.	76.37 $\pm$ 1.48
	"	7 gr./gal.	75.73 $\pm$ 0.99
	"	12 gr./gal.	76.80 $\pm$ 0.22

These results clearly demonstrate that synergistic
 35 cleaning performance was provided by the combination of
 the aluminosilicate and polycarboxylate builder materials.
 Substantially better overall cleaning was provided, at the

same total builder level in otherwise identical compositions, by the detergent composition containing the builder mixture than was provided by the detergent compositions containing only the individual builders.

5 Substantially similar cleaning results are obtained when the cationic surfactant is replaced, in whole or in part, by ditallowalkyldimethylammonium methyl sulfate, ditallow-
alkyldimethylammonium iodide, dihexadecylalkyldimethyl-
10 ammonium chloride, dihexadecylalkyldihydroxyethylammonium methyl sulfate, dioctadecylalkyldimethylammonium chloride, dieicosylalkyl methyl ethyl ammonium chloride, dieicosyl-
alkyl dimethylammonium bromide, methyl (1) tallowalkyl amido
ethyl (2) tallowalkyl imidazolinium methyl sulfate, or
mixtures of these surfactants.

15 Substantially similar results are also obtained where the nonionic surfactant in Composition A is replaced, in whole or in part, by the condensation product of C_{14-15}
alcohol with 2.25 moles of ethylene oxide; the condensation
product of C_{14-15} alcohol with 7 moles of ethylene oxide;
20 the condensation product of C_{12-15} alcohol with 9 moles of ethylene oxide; the condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, which is stripped so as to
remove lower ethoxylate and nonethoxylated fractions; the
condensation product of coconut alcohol with 5 moles of
25 ethylene oxide; the condensation product of coconut alcohol with 6 moles of ethylene oxide; the condensation product of C_{12-15} alcohol with 7 moles of ethylene oxide; the conden-
sation product of tallow alcohol with 9 moles of ethylene
oxide; a 1:1 by weight mixture of the condensation product
30 of C_{12-15} alcohol with 7 moles of ethylene oxide and the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide; and other mixtures of those surfactants.

Excellent cleaning results are also obtained where
the ratio of nonionic surfactant to cationic surfactant used
35 is about 2:1, 3:1, 3.5:1, 5:1, 6:1 or 9:1.

Cleaning benefits are also obtained when the weight ratio of the aluminosilicate material to the polycarboxylate material is from about 1:10 to about 10:1, especially

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when from about 1:4 to about 4:1. At aluminosilicate/poly-carboxylate ratios above 1, the cleaning advantages are most readily apparent at high water hardness levels, such as above 7 grains/gallon.

5 Similar synergistic cleaning effects are obtained when the aluminosilicate material is any hydrated Zeolite A, X or P(B), having a particle size diameter of from about 0.01 microns to about 25 microns, especially from about 0.1 microns to about 10 microns.

10 Substantially similar cleaning performance is obtained when the number of segments (n) in the polyacetal carboxylate builder averages at least 4, but especially when n averages between 10 and 200.

EXAMPLE II

15 The following detergent composition was produced:

	<u>Component</u>	<u>Wt./%</u>
	Dihydrogenated tallowalkyl dimethylammonium chloride	7.65
	C ₁₂₋₁₃ E _{6.5} ¹	34.45
20	Monoethanol amine	7.3
	Polyacetal carboxylate*	25.25
	Hydrated Zeolite A (particle diameter 1-10 microns)	25.25
25	¹ Condensation product of C ₁₂₋₁₃ alcohol with 6.5 moles of ethylene oxide, commercially available as Neodol 23-6.5 from Shell Chemical Company.	

This composition delivered excellent particulate soil removal performance, as demonstrated in Example I. Further, the composition provided greasy/oily soil removal benefits.

30 EXAMPLE III

The following detergent composition was produced:

	<u>Component</u>	<u>Wt./%</u>
	Dihydrogenated tallowalkyl dimethylammonium chloride	7.65
35	C ₁₂₋₁₃ E _{6.5} ¹	34.45
	Monoethanol amine	7.3
	Sodium nitrilotriacetate	25.25
	Hydrated Zeolite A (particle diameter 1-10 microns)	25.25

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¹Condensation product of C₁₂₋₁₃ alcohol with 6.5 moles of ethylene oxide, commercially available as Neodol 23-6.5 from Shell Chemical Company.

5 This composition delivered excellent particulate soil removal performance, as demonstrated in Example I. Further, the composition provided greasy/oily soil removal benefits.

EXAMPLE IV

The following detergent composition is produced:

	<u>Component</u>	<u>Wt./%</u>
10	C ₁₂₋₁₃ (EO) 6.5	12.0
	C ₁₄₋₁₅ (EO) 7.0	12.0
	Ditallow dimethylammonium chloride	4.8
	Ethanol	10.0
15	Polyacetal carboxylate*	10.0
	Hydrated Zeolite A . (particle diameter 1-10 microns)	10.0
	Miscellaneous (includes perfume, brightener, dye)	0.37
20	Water	Balance

EXAMPLE V

The following detergent composition is produced;

	<u>Component</u>	<u>Wt./%</u>
	C ₁₂₋₁₃ (EO) 6.5	12.0
25	C ₁₄₋₁₅ (EO) 6.5	12.0
	Ditallow dimethylammonium chloride	4.8
	Ethanol	10.0
	Sodium nitrilotriacetate	10.0
30	Hydrated Zeolite A (particle diameter 1-10 microns)	10.0
	Miscellaneous (include perfume, brightener dye)	0.37
	Water	Balance

35

EXAMPLE VI

The following detergent composition is produced:

	<u>Component</u>	<u>Wt./%</u>
	C ₁₂₋₁₃ (EO) 6.5	12.0
	C ₁₄₋₁₅ (EO) 7.0	12.0
40	Ditallow dimethylammonium chloride	4.8



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	Ethanol	10.0
	Sodium citrate	10.0
	Hydrated Zeolite A (particle diameter 1-10 microns)	10.0
5	Miscellaneous (includes perfume, brightener, dye)	0.37
	Water	Balance

EXAMPLE VII

The following detergent composition is produced:

10	<u>Component</u>	<u>Wt./%</u>
	C ₁₂₋₁₃ (EO) 6.5	30.0
	Ditallow dimethylammonium chloride	7.0
	Hydrated Zeolite A (particle diameter 1-10 microns)	25.0
15	Sodium nitrilotriacetate	25.0
	Sodium silicate (2.0 ratio)	8.0
	Miscellaneous (includes perfume, brightener, dye, and moisture)	Balance

EXAMPLE VIII

20 The following detergent composition is produced:

	<u>Component</u>	<u>Wt./%</u>
	C ₁₂₋₁₃ (EO) 6.5	30.0
	Ditallow dimethylammonium chloride	7.0
	Hydrated Zeolite B (particle diameter 1-10 microns)	25.0
25	Sodium citrate	25.0
	Sodium silicate (2.0 ratio)	8.0
	Miscellaneous (includes perfume, brightener, dye, and moisture)	Balance

30 EXAMPLE IX

The following detergent composition is produced:

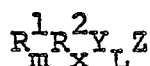
	<u>Component</u>	<u>Wt./%</u>
	C ₁₂₋₁₃ (EO) 6.5	30.0
	Ditallow dimethylammonium chloride	7.0
35	Hydrated Zeolite B (particle diameter 1-10 microns)	25.0
	Polyacetal carboxylate*	25.0
	Sodium silicate (2.0 ratio)	8.0
40	Miscellaneous (includes perfume, brightener, dye, and moisture)	Balance

CLAIMS

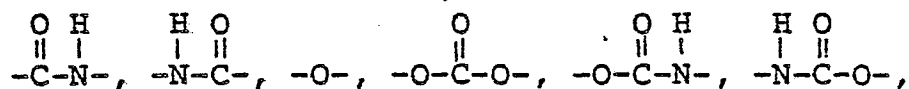
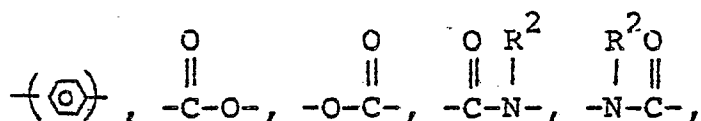
1. A detergent composition, which contains from 0 to about 5% phosphate materials, comprising:

(a) from about 1% to about 95% of a surfactant mixture consisting essentially of:

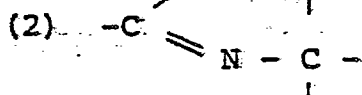
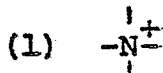
- (i) a nonionic surfactant having an HLB of from about 5 to about 17; and
(ii) a cationic surfactant, having the formula



wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to 3 phenyl or hydroxy groups and optionally interrupted by up to 4 structures selected from the group consisting of



and mixtures thereof, each R^1 containing from about 8 to about 22 carbon atoms, and which may additionally contain up to about 20 ethylene oxide groups; m is a number from 1 to 3; each R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group, with no more than one R^2 in a molecule being benzyl; x is from 0 to 11, the remainder of any carbon atom positions being filled by hydrogens; Y is selected from the group consisting of



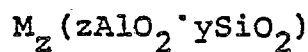
30 (b) from about 5% to about 99% of a detergency builder

mixture consisting essentially of:

(i) a water-insoluble aluminosilicate material selected from the group consisting of:

(1) Zeolites A, X, or P(B), or mixtures thereof, having a particle size diameter of from about 0.01 microns to about 25 microns and containing at least 10% water of hydration,

(2) amorphous hydrated aluminosilicate material of the empirical formula:



wherein M is sodium, potassium, ammonium, z is from about 0.5 to about 2, y is 1, said material having a particle size diameter of less than about 100 microns, a magnesium ion exchange capacity of at least about 50 milligrams equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate, and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/ gram/gallon, and

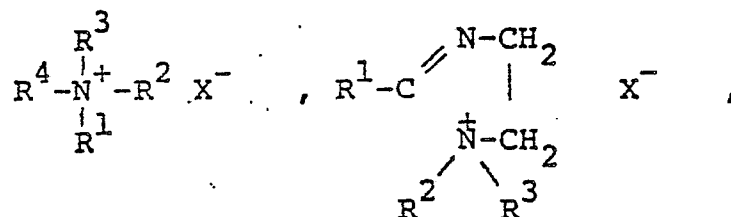
(3) mixtures thereof; and

(ii) a polycarboxylate builder material; wherein the weight ratio of the aluminosilicate material to the polycarboxylate material is from about 1:10 to about 10:1.

2. A composition according to Claim 1 comprising from about 20% to about 50% by weight of the builder mixture.

3. A composition according to Claim 1 wherein the weight ratio of the aluminosilicate material to the polycarboxylate builder material is from about 1:3 to about 2:1.

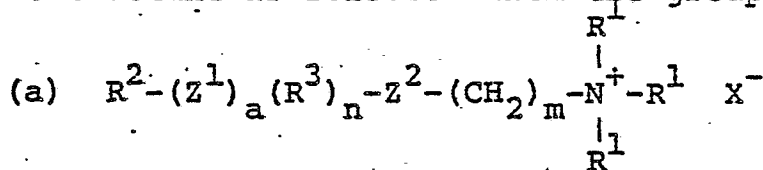
4. A composition according to Claim 1 wherein the polycarboxylate builder material is selected from the group consisting of the water-soluble salts of nitrilotriacetic acid, ethylene diaminetetracetic acid, mellitic acid, citric acid, pyromellitic acid, benzene pentacarboxylic acid, oxydiacetic acid, carboxymethyloxysuccinic acid, carboxymethyloxymalonic acid, cis-cyclohexanehexacarboxylic acid, cis-cyclopentanetetracarboxylic acid and oxydisuccinic acid or mixtures thereof.
5. A composition according to Claim 1 wherein the aluminosilicate material is Zeolite A, X or P(B), or mixtures thereof and has a particle size diameter of from about 0.1 micron to about 10 microns, more preferably from about 0.5 micron to about 2 microns.
6. A composition according to Claim 5 wherein the polycarboxylate builder material is sodium or potassium nitrilotriacetate or citrate, or mixtures thereof.
7. A composition according to Claim 6 which is substantially free of phosphate materials.
8. A composition according to Claim 6 wherein the ratio of said nonionic surfactant to said cationic surfactant is from about 5:1 to about 20:1.
9. A composition according to Claim 6 wherein said nonionic surfactant has the formula $R(OC_2H_4)_nOH$ wherein R is a primary or secondary alkyl chain of from about 8 to about 22 carbon atoms and n is an average of from about 2 to about 12 and wherein the cationic surfactant is selected from the group consisting of



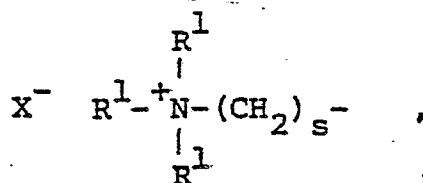
5 or mixtures thereof, wherein the R^1 and R^2 groups contain an
 5 average of from about 16 to about 22 carbon atoms, R^3 and
 R^4 are C_1 to C_4 alkyl or hydroxyalkyl groups, and X is an
 anion selected from the group consisting of halide, hydrox-
 ide, methyl sulfate, sulfate, or acetate.

10 10. A composition according to Claim 9 wherein the cat-
 ionic surfactant is selected from the group consisting of
 ditallowalkyldimethylammonium chloride, ditallowalkyldi-
 methylammonium methyl sulfate, dihexadecylalkyldimethyl-
 ammonium chloride, dioctadecylalkyldimethylammonium chlor-
 15 ide, dieicosylalkyldimethylammonium chloride, methyl (1)
 tallowalkyl amido ethyl (2) tallowalkyl imidazolinium methyl
 sulfate, and mixtures thereof.

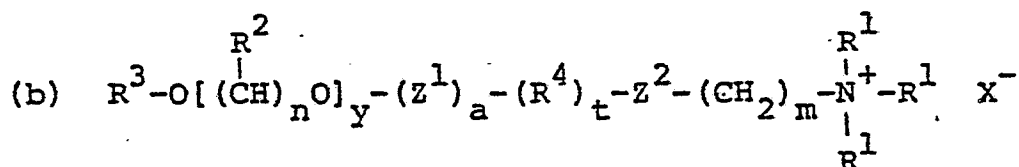
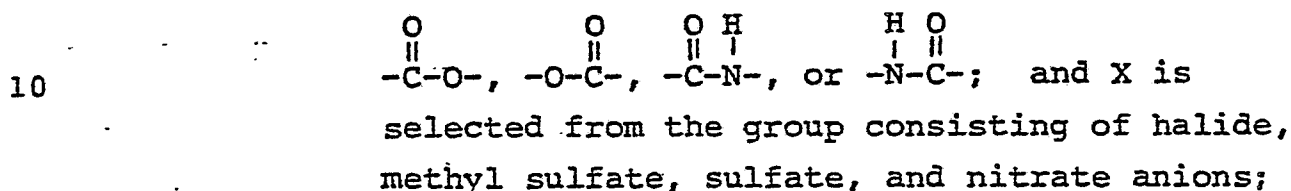
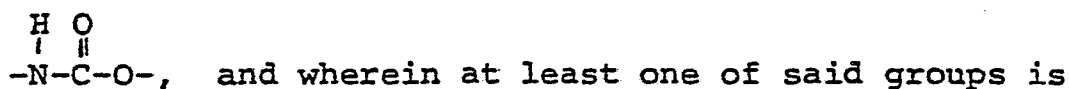
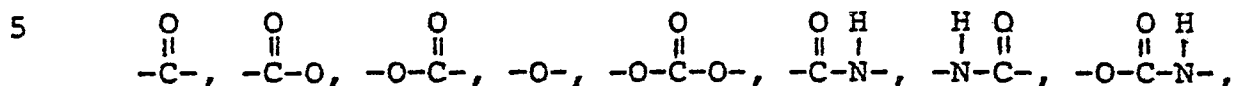
11. A composition according to Claim 9 wherein the cat-
 ionic surfactant is selected from the group consisting of:



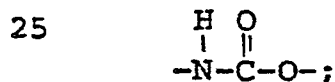
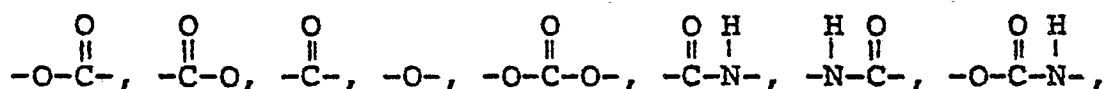
wherein R^1 is C_1 to C_4 alkyl or hydroxyalkyl; R^2
 is C_5 to C_{30} straight or branched chain alkyl,
 alkenyl, alkylbenzyl or alkyl phenyl, or



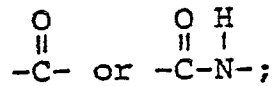
wherein s is from 0 to 5; R^3 is C_1 to C_{20} alkylene or alkenylene; a is 0 or 1; n is 0 or 1, and n is 1 when a is 1; m is from 1 to 5; Z^1 and Z^2 are each selected from the group consisting of



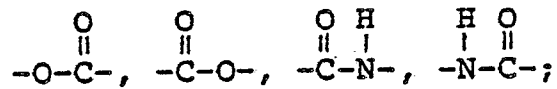
15 wherein each R^1 is a C_1 to C_4 alkyl or hydroxy-alkyl group; each R^2 is a hydrogen or C_1 to C_3 alkyl group; R^3 is a C_4 to C_{30} straight or branched chain alkyl or alkenyl; R^4 is a C_1 to C_{10} alkylene or alkenylene group; n is from 2 to 4; y is from 1 to 20; a may be 0 or 1, and t may be 0 or 1, but t is 1 when a is 1; m is from 1 to 5; Z^2 is selected from the group consisting of



Z^1 is selected from the group consisting of:



and at least one of z^1 or z^2 is selected from the group consisting of



and X is selected from the group consisting of halides, methyl sulfate, sulfate, and nitrate; and

(c) mixtures thereof.



European Patent
Office

EUROPEAN SEARCH REPORT

0021491

Application number

EP 80 20 0524

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	EP - A - 0 000 595 (PROCTER & GAMBLE) * Claims *	1	C 11 D 1/835 3/12 3/33 3/37 3/20
D, A	EP - A - 0 000 235 (PROCTER & GAMBLE) * Claims *	1	
D, A	EP - A - 0 000 234 (PROCTER & GAMBLE) * Claims *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 11 D 1/835 3/12
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
☒ The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search The Hague		Date of completion of the search 11-09-1980	Examiner MALHERBE