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3,537,993

DETERGENT COMPOSITIONS

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1 Claim

ABSTRACT OF THE DISCLOSURE

Detergent compositions, having both satisfactory detergent and fabric softening properties, consisting essentially of: (1) nonionic detergent; (2) detergent selected from the group consisting of certain zwitterionic, amine oxide and amide detergents, and mixtures thereof; (3) detergent builder; and, (4) fabric softener.

This invention relates to detergent compositions having superior detergent and fabric softening properties.

There has been considerable demand for detergent compositions which provide superior detergency under a wide variety of conditions, including cool water conditions, and which have fabric softening properties. In order to obtain superior detergency and effective fabric softening under a wide variety of conditions, many components are needed and the formulation of detergent-softener compositions is very difficult, since individual components may react with each other to the detriment of one or both of said components.

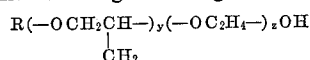
It is an object of this invention to provide a detergent-softener composition which has superior detergency characteristics, including cool water detergency characteristics.

It is a further object of this invention to provide a detergent-softener composition which has superior softening properties.

It is a specific object of this invention to provide a compatible, multi-component, liquid detergent-softener composition in the form of a stable emulsion.

These and other objects can be achieved by providing a detergent-softener composition, consisting essentially of:

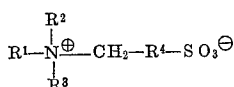
(I) From about 3% to about 9%, preferably about 6%, of a nonionic detergent having the formula



wherein R is selected from the group consisting of alkyl radicals containing from about 8 to about 18 carbon atoms and alkyl phenyl radicals wherein the alkyl groups contain from about 9 to about 15 carbon atoms, wherein Y is an integer from 0 to about 7 and wherein Z is an integer from about 5 to about 50;

(II) From about 4% to about 15%, preferably about 6%, of a detergent selected from the group consisting of

(a) A sultaine detergent having the formula

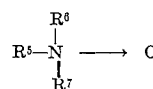


wherein R¹ is an alkyl radical containing from about 10 to about 18 carbon atoms, R² and R³ are each selected from the group consisting of methyl, ethyl and hydroxy ethyl radicals, R⁴ is selected from the group consisting of methylene, ethylene and propylene radicals and X is selected from the group consisting of hydrogen and a hy-

2

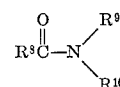
droxyl group wherein said hydroxyl group is attached only to a secondary carbon atom;

(b) A detergent having the formula



wherein R⁵ is an organic radical containing from about 10 to about 24 carbon atoms, containing from 0 to about 3 ether linkages, containing from 0 to 1 hydroxy group, and having one alkyl moiety which contains from about 10 to about 18 carbon atoms and no ether linkages; R⁶ and R⁷ are each selected from the group consisting of methyl, ethyl, hydroxy ethyl, propyl and hydroxy propyl radicals;

(c) Amides having the formula

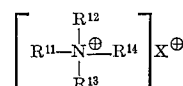


wherein R⁸ is an alkyl group containing from about 9 to about 17 carbon atoms and R⁹ and R¹⁰ are each selected from the group consisting of hydrogen, alkyl radicals containing from 1 to about 3 carbon atoms, and hydroxy alkyl radicals containing from 1 to about 3 carbon atoms and from 1 to 2 hydroxy groups; and

(d) Mixtures thereof.

(III) From about 10% to about 70% of detergency builder; and

(IV) From about 2% to about 8%, preferably 3.5% to 4% of a fabric softener having the formula



wherein each R group is selected from the group consisting of (1) large organic groups containing from about 12 to about 24 carbon atoms, said large organic groups containing from 0 to about 3 ether linkages, from 0 to about 2 amido linkages, from 0 to about 2 ester linkages, from 0 to about 2 hydroxy groups, and from 0 to 1 imino group when the imino group connects two R groups to form an imidazoline ring, there being an alkyl moiety in each such large organic group containing at least 12 carbon atoms without an interruption, and (2) small organic groups selected from the group consisting of alkyl chains containing from 1 to about 3 carbon atoms; hydroxy alkyl groups containing from 1 to about 3 carbon atoms and from 0 to 1 hydroxy group; and benzyl radicals; the R groups being selected so that (a) there are from one to two large, essentially straight chain, alkyl groups, and (b) when there is only one large organic group in the compound it contains a moiety of at least 16 carbon atoms without an interruption, and wherein X is selected from the group consisting of bromide, fluoride, chloride, methosulfate and ethosulfate anions;

The total of (I) and (II) being from about 7% to about 20%, preferably from 10% to about 15%, and the ratio of (I) to (II) being from about 2.5:1 to about 1:4, preferably about 1:1.

The above proportions of these ingredients, in combination, provide the desired product performance characteristics.

It has been discovered that this combination of detergent is required to achieve proper softening with a detergent-softener product, while retaining good whiteness maintenance properties. Within the above ranges, higher ratios of (I):(II) give better whiteness maintenance prop-

erties and poorer softening properties; higher ratios of (II):(I) give poorer whiteness maintenance properties and better softening properties.

Examples of suitable nonionic detergents (Group I) from the class generically defined above include (1) dodecyl phenol condensed with about 11 moles of ethylene oxide per mole of tetrapropylene phenol; (2) coconut alcohol condensed with from about 5 to about 8 moles of propylene oxide per mole of coconut alcohol and this reaction mixture subsequently condensed with from about 7 to about 10 moles of ethylene oxide per mole of reaction mixture; and (3) coconut alcohol condensed with about 20 moles of ethylene oxide. The nonionic detergents impart desirable whiteness maintenance properties to the compositions in their laundering function and provide improved physical stability in built liquid emulsion compositions as described hereinafter.

Specific examples of the detergents of Group II include the following:

(a) Sultaine detergents of particular interest are those in which the long alkyl chain (R^1) is a specific C_{10} - C_{18} alkyl or a mixture of alkyl chains derived from naturally occurring substances, whether hydrogenated or not, and the short alkyl chains are methyl groups. For instance, where R^1 is derived from tallow or coconut oil, R^4 is an ethylene radical with a hydroxyl group substituted on the middle carbon atom of the CH_2 - R^4 grouping, and R^2 and R^3 are methyl groups, the sultaine detergent is of particular interest. Other specific examples of preferred sultaine detergents include

- 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate,
- 2-(N-methyl-N-ethyl-N-decylammonio)-ethane-1-sulfonate,
- 4-(N,N-diethyl-N-tetradecylammonio)butane-1-sulfonate,
- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-2-hydroxy butane-1-sulfonate,
- 2-[N,N-di(2-hydroxyethyl)-N-dodecylammonio]-ethane-1-sulfonate,
- 4-[N-methyl-N-(2-hydroxyethyl)-N-hexadecylammonio]-3-hydroxy-butane-1-sulfonate, and
- 3-(N,N-dimethyl-N-hexadecylammonio)2-hydroxypropane-1-sulfonate.

Other specific examples include compounds wherein different long alkyl chains are used to provide the corresponding decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl homologs of the above compounds such as

- 3-(N,N-dimethyl-N-tetradecylammonio)-propane-1-sulfonate,
- 3-(N,N-dimethyl-N-octadecylammonio)-ethane-1-sulfonate, etc.

Still other specific examples include compounds where the short chains substituted on the nitrogen atom in the above compounds are replaced by the corresponding methyl, ethyl and hydroxy ethyl groups to provide the corresponding homologs of the above compounds.

(b) Specific examples of the amine oxide detergents include

- dimethyldodecylamine oxide
- dimethyltetradecylamine oxide
- ethylmethyltetradecylamine oxide
- cetyldimethylamine oxide
- dimethylstearylamine oxide
- cetyl ethylpropylamine oxide
- diethyldodecylamine oxide
- diethyltetradecylamine oxide
- dipropyldodecylamine oxide
- 3,6,9-trioxaheptacosanyldimethylamine oxide
- bis-(2-hydroxyethyl)dodecylamine oxide
- an amine oxide prepared from an amine containing two 2-hydroxyethyl groups and a long chain group which is derived from the condensation product of coconut alcohol and three moles of ethylene oxide

- bis-(2-hydroxyethyl)-3-dodecoxy-2-hydroxypropylamine oxide
- (2-hydroxypropyl)methyltetradecylamine oxide
- dimethyloleylamine oxide
- dimethyl-(2-hydroxydodecyl)amine oxide

The C_{12} - C_{14} dimethyl or bis-(2-hydroxyethyl) homologs of the above compounds are preferred. Other examples include those compounds wherein the short alkyl chains in the above compounds are each replaced by the methyl, ethyl, hydroxy ethyl, propyl and hydroxy propyl radicals to form homologs of the above compounds. Still other examples include those compounds wherein decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl hydrocarbon groups replace the long alkyl chains in the above compounds to form the corresponding homologs of the above compounds.

Specific examples of the amides include: stearic diethanol amide, lauric diethanol amide, myristic diethanol amide, palmitic diethanol amide, lauric monoethanol amide, lauric glyceryl amide, lauric methyl isopropanol amide, myristic ethyl isopropanol amide, stearic amide, lauric amide, palmitic amide, stearic N-methyl amide, lauric N-ethyl amide, lauric dimethanol amide.

The sultaine, amide, and amine oxide detergents impart superior detergency properties to the compositions of this invention. In particular, the preferred sultaine and amine oxide detergents impart cool, as well as hot, water detergency to the compositions. It is surprising that these surfactants do not detract to any appreciable extent from the excellent whiteness maintenance properties of the nonionic detergent surfactants when used in combination with the nonionic detergent surfactants.

The detergency builder salts are water soluble alkaline detergency builder salts, either of the organic or inorganic types, and should provide a washing solution pH of from about 9 to about 12. The ratio of builder salts to organic detergent is preferably from about 1:4 to about 20:1. Examples of water soluble inorganic alkaline detergency builder salts are alkali metal carbonates, phosphates, polyphosphates and silicates. Specific examples of such salts are sodium and potassium triphosphates, carbonates, pyrophosphates, orthophosphates and hexametaphosphates. Examples of organic alkaline detergency builder salts are (1) alkali metal amino polycarboxylates (e.g., sodium and potassium ethylenediaminetetraacetates, N-(2-hydroxyethyl)-ethylenediaminetriacetates, nitrilo triacetates, and N-(2-hydroxyethyl)-nitrilo diacetates) (2) alkali metal salts of phytic acid (e.g., sodium and potassium phytates—see U.S. Pat. 2,739,942); (3) water soluble salts of ethane-1-hydroxy-1,1-diphosphonate (e.g., the trisodium and tripotassium salts—see U.S. Pat. 3,159,581); (4) water soluble salts of methylene diphosphonic acid (e.g., trisodium and tripotassium methylene diphosphonate and the other salts described in the copending application of Francis L. Diehl, Ser. No. 266,025, filed Mar. 18, 1963); (5) water soluble salts of substituted methylene diphosphonic acids (e.g., trisodium and tripotassium ethylidene, isopropylidene, benzylmethylidene, and halomethylidene diphosphonates and the other substituted methylene diphosphonates disclosed in the copending application of Clarence H. Roy, Ser. No. 266,055, filed Mar. 18, 1963); (6) water soluble salts of polycarboxylate polymers and copolymers as described in the copending application of Francis L. Diehl, Ser. No. 269,359, filed Apr. 1, 1963 (e.g., polymers of itaconic acid, aconitic acid; maleic acid; mesaconic acid; fumaric acid; methylene malonic acid; and citronic acid and copolymers with themselves and other compatible monomers such as ethylene); and (7) mixtures thereof.

Mixtures of organic and/or inorganic builders can be used and are generally desirable. Especially preferred are the mixtures of builders disclosed in the copending application of Burton H. Gedge, Ser. No. 398,705, filed Sept. 23, 1964 (e.g., ternary mixtures of sodium triphospho-

5

phate, sodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate).

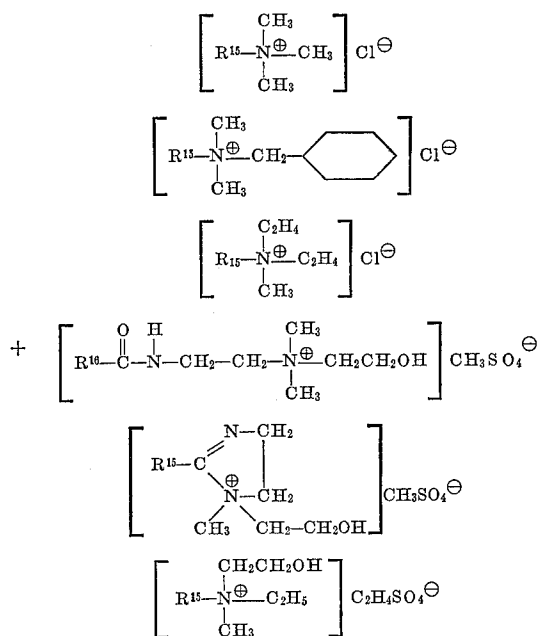
As used herein, "substituted ammonium" salts refer to, for example, monoethanol ammonium, diethanol ammonium, and triethanol ammonium salts.

The above builders tend to be corrosive to aluminum. Therefore, it is desirable that a corrosion inhibitor be included in the composition if the washing solutions will contact aluminum. Sodium and potassium silicates having a ratio of $\text{SiO}_2:\text{M}_2\text{O}$ ("M" refers to sodium or potassium) of from about 1.0 to about 2.6, preferably from about 1.6 to about 2.6 are effective when included at a level of from about 2% to about 6% by weight. Less than 2% of silicate solids does not provide sufficient protection under more extreme conditions and more than 6% has an adverse effect on product stability since the silicate will react with the cationic softener to form an insoluble precipitate.

The detergent-softener compositions of this invention contain from about 2% to about 8% of the fabric softener hereinbefore described. Within this range, the actual amount of fabric softener which the detergent-softener composition contains is dependent upon the desired usage concentration of the detergent-softener composition. It is preferred that the concentration of the fabric softener in the washing solution is from about .006% to about .012%.

Preferred fabric softeners include dialkyl dimethyl ammonium chloride wherein the alkyl groups are derived from tallow or contain 20 carbon atoms and alkyl dimethyl (3-alkoxy-2-hydroxy propyl-1-) ammonium chloride wherein the alkyl and alkoxy groups are derived from tallow.

Other specific examples include softeners having the formulae:

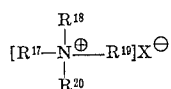


wherein R^{15} and R^{16}



are derived from tallow.

Numerous optional ingredients can be added to the above formula to impart special effects without substantially modifying the basic desirable detergent characteristics of the composition, including from about 0.1% to about 2% of a germicide having the formula



6

wherein R^{17} is an alkyl radical containing from about 8 to about 18 carbon atoms, R^{18} and R^{19} are each selected from the group consisting of methyl, ethyl and propyl radicals, R^{20} is selected from the group consisting of methyl, ethyl and benzyl radicals and X is selected from the group consisting of bromide, fluoride and chlorine anions.

Optional ingredients include optical whitening (brightening) agents. It has been discovered that only a limited number of optical whitening agents are compatible in the compositions of this invention and particularly when the preferred sultaine detergents are used in liquid emulsion compositions as hereinafter described. Suitable optical brightening agents include at least one optical whitening agent selected from the group consisting of:

(1) The reaction product of about one mole of ethylene oxide and one mole of 1,2-bis(benzimidazolyl)ethylene, e.g., N - (2'-hydroxyethyl) - 1,2 - bis(benzimidazolyl)ethylene;

(2) Tetrasodium 4,4' - bis[(4''-bis(2'''-hydroxyethyl)-amino - 6'' - (3''' - sulfophenyl)amino - 1'',3'',5'' - triazin-2''-yl)amino]-2,2'-stilbenedisulfonate;

(3) N - (2-hydroxyethyl)-4,4'-bis(benzimidazolyl)stilbene;

(4) Disodium-4-(6'-sulfonaphtho[1',2'-d]triazol-2-yl)-2-stilbenesulfonate;

(5) Disodium 4,4'-bis[(4''-(2'''-hydroxyethylamine)-6'' - anilino - 1'',3'',5'' - triazin - 2'' - yl)amino] - 2,2'-stilbenedisulfonate;

(6) Disodium 4,4' - bis[(4''-(2'''-hydroxyethoxy)-6'' - anilino - 1'',3'',5'' - triazin - 2'' - yl)amino] - 2,2' - stilbenedisulfonate;

(7) 1,2-bis(5'-methyl-2'-benzoxazolyl)ethylene;

(8) 4-methyl-7-dimethylaminocoumarin;

(9) 2-styrylnaphth[1,2-d]oxazole;

(10) The reaction product of one mole of 4,4'-bis(benzimidazolyl)stilbene with about 0.5 mole of ethylene oxide and 0.5 mole of propylene oxide; and

(11) Mixtures thereof.

Nonionic optical whitening agents are preferred. However, the other named ionic optical whitening agents can be used and are desirable, preferably in combination with nonionic optical whitening agents.

These optical whitening agents are used in a level of from about 0.03% to about 1.0% and preferably at a level of about 0.4% by weight.

The compositions can also contain from about 0.2% to 1.5% of alkali metal, ammonium and substituted ammonium carboxymethylhydroxyethylcellulose.

Other optional ingredients include the germicides hereinbefore mentioned. Specific examples of such germicides include pentadecyl benzyl dimethyl ammonium chloride and tetradecyl diethyl methyl ammonium bromide.

The compositions of this invention are highly effective cleaning and fabric softening compositions. As used herein, cleaning ability is the ability of a solution of a detergent composition to remove soil from cloth. Whiteness maintenance relates to the ability of a detergent solution to prevent suspended soil from depositing on the cloth during the washing operation. The term "detergency" as used herein, is included to embrace both cleaning ability and whiteness maintenance.

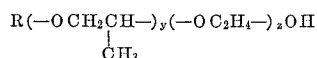
The detergent-softener compositions of this invention are particularly effective insofar as softening is concerned.

The compositions of this invention are particularly effective, as compared to conventional prior art compositions, under cool water washing conditions, e.g., from about 80° F. to about 100° F. This is especially true when the sultaine detergents are present in the compositions of this invention.

A particularly advantageous variation of this invention is a liquid emulsion detergent-softener composition consisting essentially of:

7

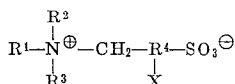
(I) From about 3% to about 9% by weight of a nonionic detergent having the formula



wherein R is selected from the group consisting of alkyl radicals containing from about 8 to about 18 carbon atoms and alkyl phenyl radicals wherein the alkyl groups contain from about 9 to about 15 carbon atoms, wherein Y is an integer from 0 to about 7 and wherein Z is an integer from about 5 to about 50;

(II) From about 4% to about 15%, by weight of a detergent selected from the group consisting of

(a) A sultaine detergent having the formula



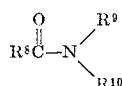
wherein R¹ is an alkyl radical containing from about 10 to about 18 carbon atoms, R² and R³ are each selected from the group consisting of methyl, ethyl and hydroxy ethyl radicals, R⁴ is selected from the group consisting of methylene, ethylene and propylene radicals and X is selected from the group consisting of hydrogen and a hydroxyl group wherein said hydroxyl group is attached only to a secondary carbon atom;

(b) A detergent having the formula



wherein R⁵ is an organic radical containing from about 10 to about 24 carbon atoms, containing from 0 to about 3 ether linkages, containing from 0 to 1 hydroxy group, and having one alkyl moiety which contains from about 10 to about 18 carbon atoms and no ether linkages; R⁶ and R⁷ are each selected from the group consisting of methyl, ethyl, hydroxy ethyl, propyl and hydroxyl propyl radicals.

(c) Amides having the formula



wherein R⁸ is an alkyl group containing from about 9 to about 17 carbon atoms and R⁹ and R¹⁰ are both hydroxy alkyl radicals containing from 1 to about 3 carbon atoms and from 1 to 2 hydroxy groups; and

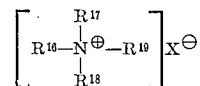
(d) Mixtures thereof.

(III) From about 10% to about 36% of detergency builder selected from the group consisting of alkali metal (e.g., sodium and potassium) pyrophosphates; alkali metal, ammonium and substituted ammonium salts of nitrilo triacetic acid, ethane-1-hydroxy-1,1-diphosphonic acid, and ethylenediaminetetraacetic acid; potassium metal tripolyphosphates; and mixtures thereof; there being no more than about 10% by weight of potassium tripolyphosphate present;

(IV) An emulsion stabilizer selected from the group consisting of ethylene/maleic-anhydride copolymers having a specific viscosity of from about 0.5 to about 1.0, said specific viscosity being determined on a 1% solution of the copolymer in dimethyl formamide at 25° C., and methylvinylether/maleic-anhydride copolymers having a specific viscosity of from about 0.1 to about 0.6, said specific viscosity being determined on a 1% solution of the copolymer in methyl ethyl ketone at 25° C.; when the former emulsion stabilizer is used it is present in the amount from about 1% to about 2% by weight and when the latter emulsion stabilizer is used it is present in an amount from about 0.3% to about 1.5% by weight, and mixtures thereof;

8

(V) From about 3.5% to about 6%, preferably 3.5% to 4%, of a fabric softener having the formula



wherein each R group is selected from the group consisting of (1) large organic groups containing from about 12 to about 24 carbon atoms, said large organic groups containing from 0 to about 3 ether linkages, from 0 to about 2 amido linkages, from 0 to about 2 ester linkages, from 0 to about 2 hydroxy groups, and from 0 to 1 imino group when the imino group connects two R groups to form an imidazoline ring, there being an alkyl moiety in each such large group containing at least 12 carbon atoms without an interruption, and (2) small organic groups selected from the group consisting of alkyl chains containing from 1 to about 3 carbon atoms; hydroxy alkyl groups containing from 1 to about 3 carbon atoms and from 0 to 1 hydroxy group and benzyl radicals; the R groups being selected so that (a) there are from one to two large, essentially straight chain, alkyl groups, and (b) when there is only one large alkyl group in the compound it contains a moiety of at least 16 carbon atoms without an interruption, and wherein X is selected from the group consisting of bromide, fluoride, chloride, methosulfate and ethosulfate anions, and

(VI) The balance water, the pH of the composition being between about 11.7 and about 13.0; the total of (I) and (II) being from about 7% to about 20%, preferably from 10% to about 15%, and the ratio of (I) and (II) being from about 2.5:1 to about 1:4, preferably about 1:1.

The proportions of these ingredients in combination provide both the desired product stability and product performance characteristics.

The pH of the above composition is adjusted to from about 11.7 to about 13.0, if necessary, by the addition of either potassium hydroxide, sodium hydroxide, or the corresponding oxides, for example. All percentages, parts, and ratios herein are by weight unless otherwise specified.

The discrete phase, i.e., the oily phase, in the oil-in-water emulsions of this invention contains the nonionic detergents, at least the major portion of the other detergents (II), and it is believed, the major proportion of the fabric softener (V) and of any minor organic ingredients present, e.g., optical brighteners and pigments. In order for there to be an oily phase, the nonionic detergent must be oily in nature although it need not be an oil (liquid).

The alkali metal pyrophosphates which form a part of the compositions of this invention are the conventional detergent builders found in built liquid detergent compositions. The preferred pyrophosphate is tetrapotassium pyrophosphate.

The preferred organic chelating agents are alkali metal, e.g., sodium or potassium, ammonium, or substituted ammonium salts of nitrilo triacetic acid, or ethane-1-hydroxy-1,1 diphosphonic acid, preferably the potassium salts. The organic chelating (sequestering) agent in admixture with the pyrophosphate provides superior whiteness maintenance characteristics for the detergent composition. Ethylenediaminetetraacetic acid salts are efficient, but care must be taken that the compositions are used with sufficient corrosion inhibitor to prevent this chelating agent from creating excessive corrosion problems.

The emulsion is kept stable by the presence of the aforementioned specific emulsion stabilizers. Apparently the specific compositions described herein, and especially the compositions containing the sultaine detergents hereinbefore described, are extremely sensitive to changes in the stabilizer and therefore the choice of stabilizers is considered to be critical. These stabilizers are described in U.S. Pat. 2,047,398. Preferably these copolymers are linear and the molar ratio of the monomers in these ma-

terials is preferably about 1:1. The copolymers are defined herein in terms of their specific viscosities which is the accepted way of defining this type of compound. Wherever specific viscosities are given herein they are based on the tests hereinbefore described with respect to each type of stabilizer.

The presence of these stabilizers appears to be critical to forming the stable emulsion product of the particularly advantageous variation of this invention. The specific emulsion stabilizers are particularly beneficial with respect to shipment conditions when the compositions are subjected to continuous shocks and agitation.

In order to achieve adequate softening, no less than about 3.5% by weight of the fabric softener should be included in the preferred liquid emulsion detergent-softener compositions of this invention, since the fabric softener and the emulsion stabilizers interact. Also, in the preferred compositions of this invention, it is important to maintain the proper ratio of stabilizer to fabric softener in addition to having the proper amount of stabilizer present, as hereinbefore described. If there is insufficient stabilizer present for the amount of fabric softener, a scum will form on the surface of the washing solution. If too much stabilizer is used, the softness of the cloth which is washed will be appreciably poorer. The ratio of stabilizer to fabric softener should be from about 1:7 to about 1:2.5, preferably from 1:5 to about 1:4.

The pH of the liquid emulsion compositions must be maintained within the range 11.7 to 30.0. Failure to maintain the pH in this range can be disastrous with respect to product stability. As hereinbefore described, the pH can be adjusted to this level, for example, by the addition of sodium hydroxide, potassium hydroxide, or the corresponding sodium, and potassium oxides.

The aforementioned optional ingredients especially the optical brighteners and the silicate corrosion inhibitor can be incorporated in the liquid-emulsion compositions of this invention.

The liquid emulsion compositions are preferably prepared by premixing the nonionic detergent surfactant, from about one-third to all of the other detergent surfactant, any brighteners used, any dyes used, any soil suspending agent employed, and preferably the fabric softener.

The resin is separately hydrolyzed in the presence of from about 2% to about 50%, preferably about 10% by weight of the nonionic detergent surfactant based upon the weight of the resin. The water containing the resin and the small amount of nonionic detergent surfactant is preferably heated to a temperature of from about 170° F. to about 200° F. This reaction takes place at a pH of less than 7. The reaction is very important since the amount of nonionic present determines, to a great extent, the viscosity of the finished composition. The hydrolyzed resin is made alkaline with caustic.

At least a portion of the builder is added to the water before the nonionic premix and/or fabric softener are added to help prevent formation of inverted emulsions.

After the premix has been added, any additional surfactant and/or builder is added and any silicate corrosion inhibitor employed is added last. The pH is then adjusted with sodium or potassium oxide and the composition is subjected to high shear mixing, e.g. mixing with an impeller having high tip speeds of greater than 2000 feet per minute. The last step, involves cooling the composition to approximately room temperature and adding any perfume materials.

The liquid-emulsion compositions of this invention can also be prepared by mixing any optical brightener included, any soil suspending agent, e.g., sodium carboxymethylhydroxyethylcellulose, included, the nonionic detergent surfactant, the sultaine, amide, or amine oxide detergent surfactant, the fabric softener and the pigment, if any. This mixture forms the oily phase of the emul-

sion. This oily phase is added to a solution of the emulsion stabilizer and sodium acid pyrophosphate (or potassium acid pyrophosphate) in water and mixed thoroughly.

Potassium or sodium hydroxide is then added as necessary to neutralize the sodium acid pyrophosphate; the other ingredients, e.g., the potassium nitrilo triacetate, potassium or sodium pyrophosphate, sodium silicate, etc., are added to this mixture.

The practice of this invention is demonstrated by the following examples.

EXAMPLE I

The following formulation is an excellent detergent, in the form of a liquid emulsion, possessing fabric softening properties.

Percent by weight

The condensation product of an alcohol derived from coconut oil and about 20 moles of ethylene oxide per mole of coconut alcohol	6
3-[N-alkyl-N,N-dimethyl ammonio] - 2 - hydroxypropane-1-sulfonate; the alkyl being derived from coconut alcohol and being 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ and 9% C ₁₆	6
Dialkyl dimethyl ammonium chloride, the alkyl being derived from tallow	4
Potassium pyrophosphate	12
Potassium nitrilotriacetate	6
Sodium silicate (2.45:1; SiO ₂ :Na ₂ O)	2.8
Methyl-vinyl - ether/maleic - anhydride copolymer ("Gantrez AN 119") (specific viscosity of about 0.3 being determined on a 1% solution of the copolymer in methyl ethyl ketone at 25° C.)	0.9
Potassium ethane-1-hydroxy-1,1-diphosphonate	6
Disodium 4,4' - bis[4" - (2" - hydroxyethyl) - 6" - anilino - 1",3",5" - triazin - 2" - yl) amino]-2,2'-stilbenedisulfonate	0.3
1,2-bis(5'-methyl-2'-benzoxazolyl)ethylene	0.02
Water	Balance

The pH of the above product is adjusted to about 12 by adding about 0.7% K₂O.

In Examples II-IV the compositions were prepared by:

Premixing all but a small amount of the surfactants and the softeners. A separate mixture was prepared in which the water at a temperature of approximately 190° F.; the acid form of the copolymer; 10% by weight of the nonionic detergent based on the weight of the copolymer; and the detergency builders (except for the silicates) are mixed together and sufficient sodium oxide is added (approximately .4%) to give a pH in the final product of approximately 12. The premix was then dispersed in the second mixture, the silicate was added, and the pH was further adjusted if required. The entire mixture was then subjected to high shear mixing with an impeller having a tip speed greater than 2500 feet per minute and the resulting dispersion was cooled to approximately room temperature.

In Examples II-V, "middle-cut coconut" refers to a mixture of alkyl or acyl groups derived from coconut alcohol and having a chain length distribution as follows: 2%—C₁₀; 66%—C₁₂; 23%—C₁₄; and 9%—C₁₆.

In Examples II-V the compositions were tested by taking approximately five terry cloths and placing them in a simplified, scaled-down, washing machine containing 1 gallon of water having a temperature of 130° F. and a hardness of 7 grains. The product concentration is specified in each example. The cloths were washed, rinsed and dried and washed and rinsed again. After the second cycle the cloths were again dried and comparisons were made between pairs of cloths by skilled graders who graded on the degree of softness and/or whiteness maintenance using a grading scale in which 0 represents no difference and 3 represents a large difference. After the fabrics were graded, the least significant difference at the

95% confidence level (LSD_{95}) was computed for the results given herein and the values reported are in terms

of alcohol ($CNAE_{20}$). They also contained 6% of the indicated surfactants.

Composition:	Surfactant	Softness
1.....	Dodecyl dimethyl phosphine oxide (not part of the invention).....	1.1
2.....	β -Hydroxyundecyl methyl sulfoxide (not part of the invention).....	1.8
3.....	Middle cut coconut diethanol amide.....	3.0
4.....	Middle cut coconut alkyl dimethyl amine oxide.....	3.8
5.....	3-[N-middle cut coconut alkyl-N,N-dimethyl]-2-hydroxypropane-1-sulfonate (HAPS).....	4.0

of the number of LSD_{95} 's between the products, i.e., one LSD_{95} is equal to 1.0 on the grading scale.

EXAMPLE II

The compositions in this example had a formula as follows:

	Percent
Surfactants (noted below)	12
Potassium nitrilotriacetate	6
Ditallowalkyl dimethylammonium chloride	5
Tetrapotassium pyrophosphate	12
Tetrapotassium ethane - 1-hydroxy-1, 1-diphospho- nate	6
Sodium silicate having an $SiO_2:Na_2O$ ratio of about 2.45	2.8
Methyl - vinyl - ether/maleic - anhydride copolymer ("Gantrez AN 119")	0.85
Water	Balance

The compositions of this example contained varying ratios of the following two surfactants: The condensation product of middle cut coconut alcohol and approximately 12 moles of ethylene oxide per mole of alcohol ($CNAE_{12}$) and 3-[N-middle cut coconut alkyl-N,N-dimethyl]-2-hydroxypropane-1-sulfonate (HAPS).

Composition:	$CNAE_{12}/HAPS$	Softness
1.....	8/4	1.5
2.....	7/5	2.2
3.....	6/6	4.0
4.....	3/9	5.4

The above grades of softness are relative to a standard composition which was an anionic detergent composition containing 17.3% of a 55/45 mixture of sodium tallow alkyl sulfate and sodium alkylbenzene sulfonate wherein the alkyl group contains an average of about 12 carbon atoms; 49.4% sodium tripolyphosphate; 5.9% sodium silicate having a $SiO_2:Na_2O$ of about 1.6; 13.7% sodium sulfate; 1.7% middle cut coconut ammonia amide; 0.5% middle cut coconut diethanol amide; 0.21% sodium carboxymethylcellulose; and the balance water. This standard composition was arbitrarily assigned a softness grade of 0.0.

The above compositions were compared at a product concentration of 0.26%.

EXAMPLE III

The compositions in this example had a formula as follows:

	Percent
Surfactants (noted below)	12
Ditallowalkyl dimethylammonium chloride	4
Potassium nitrilotriacetate	6
Tetrapotassium pyrophosphate	12
Tetrapotassium ethane - 1-hydroxy - 1,1-diphospho- nate	6
Sodium silicate having an $SiO_2:Na_2O$ ratio of about 2.45	2.8
Methyl - vinyl-ether/maleic - anhydride copolymer ("Gantrez AN 119")	0.9
Water	Balance

The compositions of this example contained 6% of the composition of the condensation product of middle cut coconut alcohol and 20 moles of ethylene oxide per mole

The above values of softness are relative to a standard composition containing 9% of the condensation product of middle cut coconut alcohol with 20 moles of ethylene oxide per mole of alcohol; 25% tetrapotassium pyrophosphate; 3.2% sodium silicate having a $SiO_2:Na_2O$ ratio of approximately 2.45; 2.0% potassium toluene sulfonate; 0.17% of methyl-vinyl-ether/maleic-anhydride copolymer; 0.7% potassium oxide; 0.3% sodium carboxycellulose; and the balance water. This standard composition was arbitrarily assigned a softness grade of 0.0.

In this example the standard composition of Example II had a softness grade of 1.7. A composition which was similar to the compositions of the example, except that it contained 12% $CNAE_{20}$, had a softness grade of 2.5.

It is clear from the above that the preferred ingredient II surfactants are the sultaine detergents and the amine oxide detergents.

The above compositions were compared at a product concentration of 0.2%.

EXAMPLE IV

The compositions in this example contained 6% of the condensation product of middle cut coconut alcohol and 12 moles of ethylene oxide per mole of alcohol: 6% of 3-[N-middle cut coconut alkyl-N,N-dimethyl]-2-hydroxypropane-1-sulfonate (HAPS); 24% of ethane-1-hydroxy-1,1-diphosphonate; 2.8% sodium silicate having an $SiO_2:Na_2O$ ratio of about 2.45; 0.004% polar brilliant blue; and the following percentages of ditallowalkyl dimethylammonium chloride and methyl-vinyl-ether/maleic-anhydride copolymer ("Gantrez AN 119"); balance water.

	Percent copolymer	Softness
Percent ditallowalkyl dimethylammonium chloride:		
3 ¹	0.6	0.2
3 ¹	0.5	0.9
3 ¹	0.4	1.5
5.....	0.85	3.1

¹ Not part of the invention.

The above softness values are relative to the standard in Example III which was arbitrarily assigned a softness grade of 0.0 and to the standard of Example II, which had a grade of 1.7.

The above compositions were compared at a product concentration of 0.26%.

When any of the specific detergents listed on pages 5, 6 and 7, or mixtures thereof are substituted, either wholly or in part, for the 3-(N-alkyl-N,N-dimethyl ammonio)-2-hydroxy propane-1-sulfonate in the above formula substantially similar results are obtained in that stable emulsion products are obtained having good detergent and fabric softening characteristics. When ethylene/maleic-anhydride linear copolymer having a specific viscosity of approximately 0.7 is substituted for the methyl-vinyl-ether/maleic-anhydride copolymer in the above formula, either wholly or in part, substantially similar results are obtained in that the emulsion is stabilized.

EXAMPLE V

Granular compositions having the following nominal composition are excellent detergent-softener compositions.

	Percent
Surfactants (noted below) -----	12
Tetracosyltrimethylammonium chloride -----	5
Sodium tripolyphosphate -----	60
Sodium silicate having SiO ₂ :Na ₂ O ratio of 2.0 -----	3
Sodium carboxymethylhydroxyethyl cellulose -----	0.4
Water -----	Balance

These compositions are prepared by (1) adding the surfactants, the softeners and water to a crutcher; (2) adding granular anhydrous sodium trimetaphosphate; (3) heating the crutcher mix to 180° F.; (4) and adding sodium hydroxide (38% active) at ambient temperature. The resulting granules which contain sodium tripolyphosphate hexahydrate are then mixed with an agglomerate containing the silicate; the sodium carboxymethylhydroxyethylcellulose; 10.2% of the sodium tripolyphosphate in the finished product; and 3.4% of the water in the finished product. 17% of the agglomerates and 83% of the other granules are mixed to give the indicated compositions.

Composition:	Percent CNAE ¹²	Percent HAPS
1 -----	9	3
2 -----	6	6
3 -----	3	9
4 -----	4	4
5 -----	8	8

The above compositions are used at a product concentration of 0.25%.

When, in the above example, the following builders are substituted either wholly or in part for the sodium tripolyphosphate, substantially equivalent results are obtained in that the composition is built: tripolyphosphates; pyrophosphates; ethylenediaminetetraacetates; N - (2-hydroxyethyl) - ethylenediaminetriacetates; nitrilotriacetates; N - (2 - hydroxyethyl - nitrilotriacetates; phytates; ethane - 1 - hydroxy - 1,1-diphosphonates; methylenediphosphonates; ethylidene diphosphonates; isopropylidene diphosphonates; benzylmethylenediphosphonates; chloromethylidene diphosphonates; salts of polymers of itaconic acid, aconitic acid, maleic acid; mesaconic acid; fumaric acid, methylene maleic acid and citraconic acid; salts of copolymers of the above acids with themselves; salts of copolymers of the above acids with ethylene; salts of copolymers of the above acids with themselves and ethylene (the foregoing named polymers and copolymers have molecular weights of about 10,000; 5,000 and 20,000 and equivalent weights of 50, 65, 70, 76 and 80 based on the acid forms); and mixtures thereof in the form of their sodium, potassium, triethanolammonium, diethanolammonium and monoethanolammonium salts and mixtures thereof.

When, in the above examples, the following brighteners are added in amounts of about 0.3% and/or substituted wholly or in part for the above brighteners substantially equivalent results are obtained in that the compositions are excellent detergents possessing fabric softening properties and having good whitening powers:

(1) The reaction product of about one mole of ethylene oxide and one mole of 1,2 - bis(benzimidazolyl) ethylene, e.g., N - (2'-hydroxyethyl) - 1,2-bis(benzimidazolyl)ethylene;

(2) Tetrasodium 4,4' - bis[(4'' - bis(2'''-hydroxyethyl) - amino - 6'' - (3''' - sulfophenyl)amino - 1'',3'',5''-triazin-2''-yl)amino]-2,2'-stilbenedisulfonate;

(3) N - (2 - hydroxyethyl) - 4,4' - bis(benzimidazolyl) stilbene;

(4) Disodium - 4 - (6' - sulfonaphtho[1',2'-d]triazol-2-yl)-2-stilbenedisulfonate;

(5) Disodium 4,4' - bis[(4'' - (2''' - hydroxyethyl) - amino) - 6'' - anilino - 1'', 3'', 5''-triazin-2''-yl)amino]-2,2'-stilbenedisulfonate;

(6) Disodium 4,4' - bis[(4'' - (2'-hydroxyethoxy)-

6''-anilino-1'',3'',5'' - triazin - 2'' - yl)amino]2,2'-stilbenedisulfonate;

(7) 1,2 - bis(5'-methyl-2'-benzoxazolyl)ethylene;

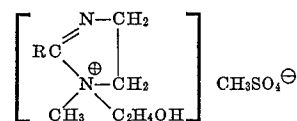
(8) 4-methyl-7-dimethylaminocoumarin;

(9) 2-styrylnaphth[1,2-d]oxazole;

(10) The reaction product of one mole of 4,4'-bis(benzimidazolyl)stilbene with about 0.5 mole of ethylene oxide and 0.5 mole of propylene oxide; and

(11) Mixtures thereof; in e.g., 1:1 ratios by weight.

When in the examples, the following fabric softeners are substituted, either wholly or in part, for the dialkyl dimethyl ammonium chloride, substantially equivalent results are obtained in that the compositions are effective detergents possessing fabric softening properties: tallow alkyl dimethyl (3-tallow alkoxy - 2 - hydroxypropyl-1-) ammonium chloride; dialkyl (C₂₀) dimethyl ammonium chloride; 2-tallow amido - 1 - [N,N' - dimethyl-N''-(2'-hydroxyethyl)ammonio methosulfate]ethane; a softener having the formula



wherein R is derived from tallow; tallow alkyl trimethyl ammonium chloride; the corresponding chloride, fluoride, bromide, ethosulfate and methosulfate quaternary ammonium salts; and mixtures thereof in e.g. 1:1 ratios by weight.

When in the above examples either the sodium, potassium, ammonium, ethanol ammonium, diethanol ammonium, or triethanol ammonium salts of ethane-1-hydroxy-1,1-diphosphonic acid, nitrilotriacetic acid, pyrophosphoric acid, ethylenediaminetetraacetic acid, or mixtures thereof; or potassium ethane-1-hydroxy-1,1-diphosphonate or tripolyphosphates (<10%); or mixtures thereof are substituted either wholly or in part for the potassium pyrophosphate and/or potassium nitrilotriacetate in the above compositions (Examples II-IV), substantially equivalent results are obtained in that calcium ions, etc., are sequestered.

When pentadecyl benzyl dimethyl ammonium chloride and/or tetradecyl diethyl methyl ammonium bromide are added to the compositions of the above examples at levels of about 0.3%, substantially equivalent results are obtained in that the compositions are stable oil-in-water emulsions and are excellent detergent-softener compositions. In addition, the compositions possess germicidal properties.

When, in the above examples, sodium pyrophosphate is substituted for the potassium pyrophosphate and/or ammonium, monoethanol ammonium, diethanol ammonium, triethanol ammonium or potassium carboxymethylhydroxyethylcellulose are substituted for the sodium carboxymethylhydroxyethylcellulose, either wholly or in part, substantially equivalent results are obtained in that the above compositions are excellent detergent-softeners.

When a dodecyl-phenol:ethylene-oxide condensate containing an average of approximately 11 moles of ethylene oxide per mole of phenol is substituted, either wholly or in part, for the coconut-alcohol:ethylene-oxide condensates in the above compositions, and/or any of the detergents listed on pages 5, 6 and 7 are substituted for the HAPS, substantially similar results are obtained in that the compositions still have good whiteness maintenance properties and are excellent detergent-softeners.

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

What is claimed is:

1. A detergent-softener composition, in the form of a liquid emulsion, consisting essentially of:

(I) about 6% by weight of a condensation product of middle cut coconut alcohol and approximately 12 moles of ethylene oxide per mole of alcohol;

(II) about 6% by weight of a detergent selected from the group consisting of:

(a) 3-(N-middle cut coconut alkyl-N, -N,N-dimethyl)-2-hydroxypropane-1-sulfonate;

(b) middle cut coconut alkyl dimethyl amine oxide; 5

(c) middle cut coconut diethanolamide;

(III) from about 10% to about 36% by weight of a detergency builder selected from the group consisting of alkali metal pyrophosphates; alkali metal tripolyphosphates; alkali metal, ammonium, monoethanolammonium, diethanolammonium, and triethanolammonium salts of nitrilo triacetic acid; ethane-1-hydroxy - 1,1 - diphosphonic acid, and ethylenediaminetetraacetic acid; and mixtures thereof; there being no more than about 10% by weight of potassium tripolyphosphate present; 10

(IV) about 4% by weight of ditallowalkyl dimethylammonium chloride; 15

(V) about 0.85% by weight of a methylvinylether/maleicanhydride copolymer having a specific viscosity of from about 0.1 to about 0.6, said specific vis-

cosity being determined on a 1% solution of the copolymer in methyl ethyl ketone at 25° C.; and (VI) the balance water.

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252—8.8, 137, 152

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,537,993 Dated November 3, 1970

Inventor(s) Todd L. Coward and Thomas E. Darling

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

Col. 1, line 46, "CH₂" should read -- CH₃ --. Col. 5, line 43, that portion of the formula reading "C₂H₄" should read -- C₂H₅ --. Col. 5, line 45, that portion of the formula reading "R₁₅" should read -- R¹⁵ --; "C₂H₄" should read -- C₂H₅ --. Col. 5, line 58, "C₂H₄SO₄^θ" should read -- C₂H₅SO₄^θ --. Col. 7, line 66, "25% C" should read -- 25°C --. Col. 9, line 30, "30.0" should read -- 13.0 --. Col. 10, line 35, "[4" - (2"' -" should read -- [4" - 2"' - (2"' --. Col. 12, line 18, "0.17%" should read -- 0.7% --. Col. 13, line 62, "bis(bensimidazolyl)" should read -- bis(benzimidazolyl). Col. 13, line 75, "(2"-hydroxyethoxy)" should read -- (2"'-hydroxyethoxy) --. Col. 15, line 3, "N" should be deleted after "alkyl". Col. 16, line 1, "deterined" should read -- determined --.

Signed and sealed this 17th day of August 1971.

(SEAL)
Attest:

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