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**SOAP COMPOSITIONS HAVING IMPROVED CURD-
 DISPERSING PROPERTIES**

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14 Claims

ABSTRACT OF THE DISCLOSURE

Soap compositions having improved curd-dispersing properties are described which consist essentially of:

- (I) A higher fatty acid soap; and
 (II) At least about 5% by weight of said soap of a synergistic curd-dispersing mixture of (A) at least one synthetic detergent selected from the group consisting of (1) a detergent which contains in its molecular structure a zwitterion or a semi-polar bond; and (2) an amphoteric synthetic detergent; and (B) at least one water-soluble salt of compounds selected from the group consisting of (1) linear polymeric phosphoric acid containing more than 2 phosphorus atoms in the molecule; (2) linear polymeric carboxylic acid which in the acid form has a molecular weight of at least 350 and an equivalent weight of from 50 to 80 and which is derived from a monomeric carboxylic acid containing at least two carboxyl groups in its molecule; and (3) nitrilotriacetic acid; the ratio by weight of (A) to (B) being from about 1:4 to about 4:1. These compositions provide excellent lime soap dispersing power and are particularly adapted to use in hard water.

This invention relates to improved soap compositions particularly suitable for use in hard water.

Soap is an excellent detergent but it has a serious disadvantage. This disadvantage is its tendency to react with the metallic ions which are responsible for the hardness of water, notably calcium and magnesium ions. This reaction forms an insoluble curd known as lime soap. This insoluble lime soap forms undesirable deposits on the inside surfaces of washing machines. It is also deposited on fabrics which are washed in hard water when soap is used as the detergent. These deposits give rise to poor odor and color of the washed fabrics. These deposits also tend to reduce the water-absorbency of fabrics, e.g., towels, which have been washed in hard water using soap.

Attempts have been made to minimize this disadvantage of soap by the use of sequestering agents which prevent formation of lime soap by forming complexes with the metallic ions concerned. Other attempts involved replacing all or part of the soap in the washing composition by synthetic detergents, which do not themselves form insoluble compounds with the metallic ions of hard water. Moreover, synthetic detergents also serve to disperse the lime soap and inhibit its deposition on the washing machine surfaces and on the washed fabrics. However, the proportion of such synthetic detergents which is required to give effective dispersion of lime soap is large and the product is costly.

It is an object of this invention to provide a novel soap detergent composition. It is a further object of this invention to provide a soap detergent composition which is free of the disadvantages described above.

It has now been found that the lime soap dispersing power of certain synthetic detergents can be greatly enhanced if they are used in conjunction with water-soluble salts of certain linear polymeric carboxylic acids, certain linear polymeric phosphoric acids containing more than

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two phosphorus atoms in the molecule, or of nitrilotriacetic acid, or mixtures thereof.

According to the present invention, a soap composition having outstanding curd dispersing characteristics and thereby especially suitable for use in hard water comprises from about 10% to about 95% higher fatty acid soap, and at least about 5%, by weight of the soap, being a curd-dispersing, synergistic mixture consisting essentially of (A) at least one water-soluble amphoteric synthetic detergent; or at least one water-soluble non-soap organic synthetic detergent which contains in its molecular structure a zwitterion or a semipolar bond; or a mixture thereof and (B) at least one water-soluble salt of a linear polymeric carboxylic acid which in the acid form has a molecular weight of at least 350 and an equivalent weight of from 50 to 80 and which is derived from a monomeric carboxylic acid containing at least two carboxyl groups in its molecule; or a water-soluble salt of a linear polymeric phosphoric acid which contains more than 2 phosphorus atoms in the molecule; or a water-soluble salt of nitrilotriacetic acid, or a mixture thereof. The weight ratio of (A) to (B) in the synergistic curd-dispersing mixture should be from about 1:4 to about 4:1 and preferably from about 1:2 to about 2:1. Combinations of the above-mentioned salts are also useful in these combinations.

The synergistic mixture should constitute at least about 5% by weight of the fatty acid soap. It can range up to about 100% by weight of the soap ingredient. Preferably it should be present at a level of from about 20% to about 80% by weight of the fatty acid soap.

The compositions of the invention may also contain up to 20% by weight of the soap, of a low foaming non-ionic synthetic detergent.

The higher fatty acid soaps suitable for use as the present invention are the sodium, potassium, and alkylolammonium salts of higher fatty acids (C_{10} - C_{20}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Similarly palm and palm kernel oil are useful starting materials, as are synthetic fats simulating, for instance, tallow.

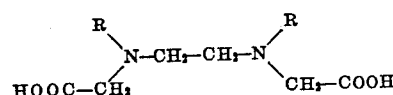
The amphoteric synthetic detergents which are suitable for use in the compositions of the invention are synthetic detergents which contain both an acidic and a basic function in their structure. In the usual amphoteric synthetic detergents, the acidic group is a carboxylic, sulfuric, sulfonic or phosphoric acid group and the basic group contains a non-quaternary nitrogen atom. The following are examples of suitable amphoteric synthetic detergents:

(a) Water-soluble salts of alkylamino alkane carboxylic acids of the general formula:



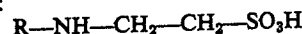
where x is 1 or 2; a specific example is a dodecylaminomethane carboxylic acid sodium salt;

(b) Water-soluble salts of N,N'-dialkylethylenediamine diacetic acids of the general formula:



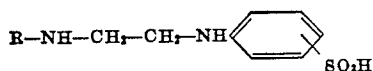
a specific example is a N,N'-dodecylethylenediamine diacetic acid sodium salt;

(c) Water-soluble salts of N-alkyl taurines of the general formula:



a specific example is a N-methyl taurine sodium salt;

(d) Water-soluble salts of N-alkyl-N'-sulfophenyl ethylene diamines of the general formula:



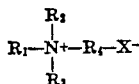
a specific example is an N-methyl-N'-sulfophenyl ethylene diamine sodium salt.

In the above general formulas R represents an alkyl radical of from 10 to 18 carbon atoms.

The preferred amphoteric synthetic detergent is the sodium salt of N-lauryl beta-alanine.

Mixtures of amphoteric detergents are also suitable.

Suitable zwitterionic detergents include aliphatic quaternary ammonium compounds in which one aliphatic substituent contains from 10 to 18 carbon atoms and another aliphatic substituent contains a water solubilizing anionic group. Examples of such compounds are water-soluble alkylated betaines and sultaines of the general formula:



where R_1 is an alkyl group of 10 to 18 carbon atoms, R_2 is an alkyl group of 1 to 3 carbon atoms, R_3 is an alkyl group of 1 to 3 carbon atoms, R_4 is an alkylene or hydroxy alkylene group of 1 to 4 carbon atoms and X^- is a carboxylic acid or sulfonic acid anion. Especially preferred compounds are (N-alkyl-N,N-dimethylammonio) methane carboxylates in which the alkyl group is derived from a mixture of lauryl and myristyl alcohols. Other suitable compounds are 3(N-alkyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate and 3(N-alkyl-N,N-dimethylammonio)-propane-1-sulfonate in which the alkyl group contains from about 10 to about 18 carbon atoms and preferably 12 to 16.

Suitable detergents which contain a semi-polar bond include tertiary amine oxides of the general formula $\text{R}_5\text{R}_6\text{R}_7\text{N}\rightarrow\text{O}$ and tertiary phosphine oxides of the general formula $\text{R}_5\text{R}_6\text{R}_7\text{P}\rightarrow\text{O}$ where R_5 is an alkyl, alkenyl or hydroxyalkyl radical of from 10 to 18 carbon atoms, R_6 and R_7 are each an alkyl or monohydroxyalkyl radical of from 1 to 3 carbon atoms; for example, dodecyldimethylamine oxide, dodecyldiethanolamine oxide, decyldimethylamine oxide, tetradecyldimethylamine oxide, or dodecyl bis(hydroxymethyl) phosphine oxide, tetradecyl dimethyl phosphine oxide, and sulfoxides of the general formula $\text{R}_8\text{R}_9\text{S}\rightarrow\text{O}$ in which R_8 is an alkyl, alkenyl, hydroxy, or alkoxyalkyl radical of 10 to 18 carbon atoms and R_9 is methyl or ethyl. Examples are 3-hydroxytridecylmethyl sulfoxide, or the preferred compound, 3-hydroxy-4-decoxybutylmethyl sulfoxides.

Mixtures of the aforementioned detergents can also be used such as admixtures of equal parts by weight of N-lauryl beta alanine, 3(N-dodecyl-N,N-dimethylammonio)-2-hydroxy propane-1-sulfonate, and dodecyldimethylamine oxide.

Component (B) of the synergistic curd dispersing mixture as mentioned above, is a water-soluble salt of a linear polymeric carboxylic acid which in the acid form has a molecular weight of at least 350 and an equivalent weight of from 50 to 80 and which is derived from a monomeric carboxylic acid containing at least two carboxyl groups in its molecule; or a water-soluble salt of a linear polymeric phosphoric acid which contains more than 2 phosphorus atoms in the molecule; or a water-soluble salt of nitrilotriacetic acid; or a mixture thereof.

Suitable polymeric carboxylic acid salts are water-soluble salts of

(a) Polymers of unsymmetrical polycarboxylic acids e.g., polyitaconic acid, polyaconitic acid and copolymers of itaconic/aconitic acids;

(b) Linear polymers of dicarboxylic acids in which there are no interfering branches between the carboxyl

groups, e.g., polymaleic acid, copolymers of ethylene and maleic anhydride;

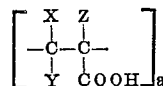
(c) Linear polymers of dicarboxylic acids in which there are interfering branches between the carboxylic acid groups, e.g., copolymers of vinyl methyl ether and maleic anhydride, copolymers of styrene and maleic anhydride, carboxy polystyrene.

In all cases the polymeric carboxylic acid must have a molecular weight of at least 350 and an equivalent weight of 50 to 80. The molecular weight can be as high as 1,500,000. Preferably it should be in the range of 500 to about 175,000. When the polymeric carboxylic acid is a copolymer of a carboxylic acid monomer and a non-carboxylic monomer the proportion of non-carboxylic monomer must be such that the equivalent weight of the polymeric acid is within the range of 50 to 80.

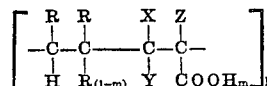
The polymeric carboxylic acid salt can also be a mixture of such salts.

A detailed description of the polymeric carboxylic acid compounds useful in the present invention is contained in a copending patent application, incorporated herein by reference, having Ser. No. 269,359, filed Apr. 1, 1963, by Francis L. Diehl and now U.S. Patent 3,308,067 issued Mar. 7, 1967. Specific examples of suitable polymeric carboxylic acid salts are found on pages 4-9 of the copending patent application.

Suitable polymeric carboxylic acid salts include water-soluble salts of a polymeric aliphatic polycarboxylic acid selected from the group consisting of (a) water-soluble salt of the homopolymer of an aliphatic polycarboxylic acid having the following empirical formula:



wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, carboxyl, and carboxymethyl, at least one of X, Y, and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein only one of X, Y, and Z can be methyl, and wherein n is a whole integer having a value within a range, the lower limit of which is three and the upper limit of which is determined by the solubility characteristics in an aqueous system; (b) a water-soluble salt of a copolymer of at least two of the monomeric species having the empirical formula described in (a); and, (c) a water-soluble salt of a copolymer of a member selected from the group of alkenes and monocarboxylic acids with the aliphatic polycarboxylic compounds described in (a), said copolymers having the general formula:



wherein R is selected from the group consisting of hydrogen, methyl, carboxyl, carboxymethyl, and carboxyethyl; wherein only one R can be methyl; wherein m is at least 45 mole percent of the copolymer; wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, carboxyl, and carboxymethyl, at least one of X, Y, and Z being selected from the group of carboxyl and carboxymethyl provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein only one of X, Y and Z can be methyl; and wherein n is a whole integer within a range, the lower limit of which is three and the upper limit of which is determined primarily by the solubility characteristics in an aqueous system; said material having a minimum molecular weight of 350 calculated as the acid form and an equivalent weight of about 50 to about 80, calculated as the acid form.

It is extremely difficult to accurately determine molecular weights of polymeric compounds. Such figures will

generally vary depending upon the method used to determine them. It is widely recognized, for instance, that any molecular weights of polymeric materials which are given by manufacturers constitute an average of the molecular weights of the molecules present. Moreover, molecular weight ranges are usually given which vary widely depending again upon the method used to measure the molecular weights. Among the several methods frequently used to measure molecular weights of polymeric compounds are osmometric, end-group, cryoscopic, ebullioscopic, light-scattering and ultracentrifuge. Each of these methods are presently in varying degrees of development and each one has special types of polymeric compounds to which it is best adapted.

The minimum molecular weight of 350 mentioned above was arrived at empirically and, to a great extent, is based on the knowledge and experience acquired from working with these polyelectrolytic polycarboxylic polymers.

Viscosity is a property more frequently used by polymer chemists as characterizing polymeric compounds than are molecular weights. This is no doubt due to the comparatively easier and less complicated methods for obtaining viscosity data. To make such data meaningful, it is necessary to also give the test conditions under which the measurements were run. Since there is a recognized correlation between the viscosity of polymeric compounds and their relative molecular weights and since such figures can be more meaningful and can frequently be more available than molecular weights, the polymeric builder compounds used in the examples of this invention are characterized in terms of specific viscosity. In all cases the viscosity characterization corresponds to a molecular weight substantially above 350.

Suitable salts of linear polymeric phosphoric acids are the alkali metal salts of linear polymeric phosphoric acids having more than two phosphorus atoms in the molecule, e.g., triphosphoric acid, $H_5P_3O_{10}$; tetrakisphosphoric acid, $H_6P_4O_{13}$; or hexametaphosphoric acid, $H_6P_6O_{18}$. Salts of pyrophosphoric acid which is linear but has only two phosphorus atoms in the molecule and salts of cyclic polymeric phosphoric acids such as trimetaphosphoric acid are not suitable. The preferred polymeric phosphoric acid salts are sodium tripolyphosphate and sodium hexametaphosphate. In all cases the alkali metal cation can be sodium or potassium or lithium.

The linear polymeric phosphoric acid salt may be a mixture of such salts.

It has been unexpectedly discovered that water-soluble salts of nitrilotriacetic acid also exhibit synergism of lime soap dispersing effect with the organic non-soap detergents described above. Examples include trisodium nitrilotriacetate, and tripotassium nitrilotriacetate. Salts of other amino polycarboxylic acids, for example, ethylenediamine tetraacetic acid, although having a high sequestering power for calcium ions do not exhibit synergism of lime soap dispersing effect in the context of the present invention. Salts of such aminopolycarboxylic acids can, however, be included in the compositions of the invention in small proportions for other purposes, for example, to stabilize peroxy bleaching agents such as sodium perborate, or to protect the soap against oxidative deterioration during storage.

It is also contemplated that the synergistic curd-dispersing mixture can contain mixtures of carboxylic acid salts, phosphoric acid salts and nitrilotriacetic acid salts. Such mixtures can include mixtures within each broad class as well as binary and ternary mixtures selected from all three classes. Thus, one can use mixtures of carboxylic acid salts and phosphoric acid salts, mixtures of carboxylic acid salts and nitrilotriacetates, as well as mixtures of phosphoric acid salts and nitrilotriacetates. The latter binary mixtures are especially valuable; specifically a mixture, on a 4:1 to 1:4 molar basis of sodium tripolyphosphate and sodium nitrilotriacetate.

The water-soluble salts of Component B ingredients can be sodium, potassium, lithium, ammonium or substituted ammonium compounds such as triethanolammonium, and the like.

While the amphoteric, zwitterionic and semi-polar synthetic detergents themselves have some lime soap dispersing power, this is considerably increased by the addition of either the specified polymeric carboxylic acid salts in the specified proportions or by the addition of the specified polymeric phosphoric acid salts or nitrilotriacetic salts in the specified proportions although the polymeric acid salts themselves have very little lime soap dispersing power. This synergism of lime soap dispersing power is illustrated by the following tests.

The sodium salt of polyitaconic acid employed in Test Series I (Table I) and Test Series III (Tables V and VI) has an equivalent weight of 65. It has a specific viscosity at 1% by weight in dimethylformamide of .29 and at .06% in water of .07. (Both the dimethylformamide and the water were at room temperature.)

Test series I

A series of solutions was prepared by dissolving 1 gram of a mixture of the sodium salt of N-lauryl beta alanine (LBA) and a sodium salt of polyitaconic acid (PIA) in 14.4 gr./U.S. gal. hard water at 130° F. The various mixtures used contained 100%, 80%, 60%, 40%, 20% and 0% of LBA with 0%, 20%, 40%, 60%, 80% and 100% PIA respectively. The pH of each solution was adjusted to 10.0.

Into each solution a 1% solution of sodium soap (obtained from a mixture of 20% coconut oil and 80% tallow) was run from a burette with constant agitation of the solution until the solution became cloudy. The number of milliliters of soap solution required to produce a cloud is a measure of the lime soap dispersion power of the mixture. The results are shown in Table I below:

TABLE I

PIA	LBA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	0
80.....	20	42.5
60.....	40	122
40.....	60	100
20.....	80	23
0.....	100	17.5

The above table shows an increase in the lime soap dispersing power of the combination of LBA and PIA compared with that which could be expected from the individual lime soap dispersing powers of the two components of the mixture. Especially remarkable are the performance results obtained at the 60/40 and 40/60 proportions.

Test series II

A series of solutions was prepared by dissolving 2 grams of a mixture of the sodium salt of N-lauryl beta alanine (LBA) and a linear polymeric phosphoric acid salt or nitrilotriacetic acid salt in 400 ml. of 14.4 gr./U.S. gal. hard water at 130° F. The polymeric phosphoric acid salts tested were sodium tripolyphosphate (STPP) and sodium hexametaphosphate (SHMP). The nitrilotriacetic acid salt tested was trisodium-nitrilotriacetate (NTA).

The various mixtures used contained 100%, 80%, 60%, 40%, 20%, and 0% of the LBA with 0%, 20%, 40%, 60%, 80% and 100% of the polymeric phosphate or nitrilotriacetate respectively. The pH of each solution was adjusted to 10.0.

Into each solution a 1% solution of sodium soap (obtained from a mixture of 20% coconut oil and 80% tallow) was run from a burette, with constant agitation of the solution until the solution became cloudy. The number of milliliters of soap solution required to produce a cloud is a measure of the lime soap dispersion power of

the mixture. The results are tabulated in Table II, Table III and Table IV below:

TABLE II

STPP	LBA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	1
80.....	20	35
60.....	40	58
40.....	60	65
20.....	80	45
0.....	100	30

TABLE III

SHMP	LBA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	1
80.....	20	30
60.....	40	60
40.....	60	60
20.....	80	50
0.....	100	30

TABLE IV

NTA	LBA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	5
80.....	20	85
60.....	40	130
40.....	60	130
20.....	80	100
0.....	100	30

The above tables show an increase in the lime soap dispersion power of the combination of LBA with the polymeric phosphate salt (Tables II and III) or nitrilotriacetate (Table IV) compared with that which could be expected from the individual lime soap dispersion powers of the two components of the mixture. The performance of NTA is especially noteworthy at ratios of 60/40 and 40/60.

Test series III

A series of solutions were prepared by dissolving one gram of a mixture of an organic detergent and a sodium salt of polyitaconic acid (PIA) in 14.4 gr./U.S. gal. hard water at 130° F. The various mixtures used contained 100%, 80%, 60%, 40%, 20%, and 0% of organic detergent and 0%, 20%, 40%, 60%, 80% and 100% PIA respectively. The pH of each solution was adjusted to 10.0. Two surface active agents were tested, namely (N-lauryl/myristyl-N,N-dimethylammonio) methane carboxylate (AMC) and N - dodecyl - N,N - dimethylamine oxide (DDMA).

Into each solution a 1% solution of sodium soap (obtained from a mixture of 20% coconut oil and 80% tallow) was run from a burette until the solution became cloudy. The number of milliliters of 1% soap solution required to produce a cloud is a measure of the lime soap dispersion power of the mixture. The results are set out in Tables V and VI below:

TABLE V

AMC	PIA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	20
80.....	20	25
60.....	40	55
40.....	60	60
20.....	80	30
0.....	100	10

TABLE VI

AMC	PIA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	15
80.....	20	25
60.....	40	60
40.....	60	80
20.....	80	60
0.....	100	10

The above tables show a considerable increase in the lime soap dispersion power of the combinations of a zwitterionic (AMC) or a semi-polar (DDMA) organic detergent with a polyitaconate compared with that which could be expected from the individual lime soap dispersion powers of the components of the mixtures.

Test series IV

A series of solutions was prepared by dissolving 2 grams of a mixture of organic detergent and sodium tripolyphosphate (STPP) in 400 ml. of 14.4 gr./U.S. gal. hard water at 130° F. and the pH was adjusted to 10.0. The various solutions used contained 100%, 80%, 60%, 40%, 20% and 0% of the organic surface active agent with 0%, 20%, 40%, 60%, 80% and 100% of the STPP, respectively. The organic detergents tested were dodecyl-dimethylamine oxide (DDMA); 3-(N-dodecyl-N,N-dimethylammonio) - 2-hydroxy - 1 - propane sulfonate (DAHPS); 2-(N-alkyl-N,N-dimethylammonio)-1-ethane carboxylate in which the alkyl radical is a mixture of lauryl and myristyl radicals (LAEC); beta-hydroxy undecylmethyl sulfoxide (HUMS). The pH of each solution was adjusted to 10.0.

Into each solution a 1% solution of sodium soap (obtained from a mixture of 20% coconut oil and 80% tallow) was run from a burette with constant agitation until the solution became cloudy. The number of milliliters of 1% soap solution required to produce a cloud is a measure of the lime soap dispersion power of the mixture. The results are set out in Tables VII to X below:

TABLE VII

DDMA	STPP	No. of mls. of 1% soap solution to produce a cloud
100.....	0	35
80.....	20	45
60.....	40	75
50.....	50	70
40.....	60	65
20.....	80	60
0.....	100	0

TABLE VIII

DAHPS	STPP	No. of mls. of 1% soap solution to produce a cloud
100.....	0	25
80.....	20	45
60.....	40	60
50.....	50	60
40.....	60	55
20.....	80	40
0.....	100	0

TABLE IX

LAEC	STPP	No. of mls. of 1% soap solution to produce a cloud
100.....	0	40
80.....	20	65
60.....	40	80
50.....	50	80
40.....	60	75
20.....	80	45
0.....	100	0

TABLE X

HUMS	STPP	No. of mls. of 1% soap solution to produce a cloud
100.....	0	0
80.....	20	40
60.....	40	50
40.....	60	45
20.....	80	20
0.....	100	0

Similar tests were carried out using mixtures of organic detergents with the sodium salts of nitrilotriacetic acid (NTA), the organic detergents tested being 3-(N,N-dimethyl - N - dodecyl)ammonio - 2 - hydroxy propane-1-sulfonate (DAHPS) and 3-(N,N-dimethyl-N-lauryl/

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myristyl) ammonio methane carboxylate (AMC). The results are set out in Tables XI and XII.

TABLE XI

DAHPS	NTA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	25
80.....	20	120
60.....	40	150
40.....	60	135
20.....	80	90
0.....	100	5

TABLE XII

AMC	NTA	No. of mls. of 1% soap solution to produce a cloud
100.....	0	40
80.....	20	120
60.....	40	140
40.....	60	140
20.....	80	90
0.....	100	5

The above tables show a considerable increase in the lime soap dispersion power of the combinations of the various zwitterionic or semi-polar organic surface active agents with sodium tripolyphosphate or trisodium nitrilotriacetate compared with that which could be expected from the individual lime soap dispersion powers of the components of the mixtures.

The surprisingly marked synergistic curd dispersing power of the mixtures disclosed in Tables XI and XII is especially noteworthy.

The compositions of the invention may be produced in any conventional form such as bars, powders, liquids or pastes. The amounts of soap in the compositions may, of course, be such as are normally found in soap compositions and are known to those skilled in the art. For example, a liquid soap composition can contain from about 10% to about 30% of soap together with from about .5% to about 30% of the novel synergistic curd-dispersing mixture described herein; the balance to 100% being essentially liquid vehicle, e.g., water. Another embodiment of the present invention is a toilet bar comprising essentially of from about 80% to about 95% fatty acid soap (e.g., 80% tallow-20% coconut) and from about 5% to about 20% of a synergistic curd-dispersing mixture of the present invention.

The invention is particularly suitable for granular detergent compositions such as are used in domestic laundry operations. Such compositions preferably comprise from about 40% to about 80% of soap, by weight of the composition, and can contain the usual ingredients of washing compositions such as alkaline builder salts, e.g., sodium carbonate, sodium silicate, sodium sulfate, carboxymethylcellulose, bleaching agents, e.g., peroxy compounds such as sodium perborate, optical whitening agents, color, perfume and the like. Such granular detergent compositions should contain from about 2% to about 50% by weight of the composition of the synergistic curd-dispersing mixture of the present invention.

A further advantage of the compositions of the invention is that they may readily be formulated so that solutions of the compositions in hard water do not foam appreciably until all the hardness of the water has been destroyed and the solution contains sufficient free soap to have effective washing power. This avoids under usage of the composition. When high foaming synthetic detergents are added to soap to inhibit deposition of lime soap, foaming is produced at low concentrations of the product when there is insufficient free soap present for effective washing. There is a tendency for the user to use insufficient product and to obtain poor cleaning performance. This tendency is avoided with the preferred compositions of the invention which do not foam appreciably until sufficient free soap for effective washing is present.

The compositions of the invention give effective lime soap dispersion during the washing stage. If the washed goods are rinsed in hard water, the washing solution

remaining in the fabric is diluted by a large proportion of the added hard water. Under these conditions, some lime soap in undispersed form may be formed. According to a further feature of the invention, the tendency for this to happen can be reduced or entirely eliminated by including in the soap composition a low-sudsing alkylene oxide-containing nonionic detergent of the type described below. Moreover, low-sudsing nonionic detergents are used to avoid the appearance of suds in the rinse water.

Suitable alkylene oxide-containing nonionic synthetic detergents of the type which are useful in this embodiment of the present invention are:

(1) The polyethylene oxide condensates of alkyl phenols and dialkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to about 5 to 30 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, nonene, for example.

(2) Alkylene oxide-containing nonionic detergents derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again a series of compounds are contemplated whose characteristics can be controlled by achieving a desired balance between the hydrophobic and hydrophilic elements. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from about 4 to 30, preferably from 5 to 15, moles of ethylene oxide per mole of coconut alcohol. The coconut alcohol fraction which is preferred is a distilled coconut alcohol having from 10 to 16 carbon atoms, with the approximate chain length distribution being 2% C₁₀, 66% C₁₂, 23% C₁₄ and 9% C₁₆. Another preferred compound is the condensation product of tallow derived alcohol and from about 3 to about 15 moles of ethylene oxide per mole of tallow alcohol; a specific illustration being the condensation reaction product of one mole of tallow alcohol and 4 moles of ethylene oxide (TE₄).

(4) A well known class of alkylene oxide-containing nonionic synthetic detergents of this type is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility, has a molecular weight of from about 1,500 to 1,800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

(5) Specific illustrations of the foregoing classes include the following which are merely illustrative of the type intended: nonylphenol condensed with either about 5 or about 30 moles of ethylene oxide per mole of phenol and the condensation products of coconut alcohol with an average of either about 4 or about 15 moles of ethylene oxide per mole of alcohol and the condensation product of about 15 moles of ethylene oxide with one mole of tridecanol. Other illustrative examples are dodecylphenol

condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; dodecyl mercaptan condensed with 10 moles of ethylene oxide per mole of mercaptan; bis-(N-2-hydroxyethyl) lauramide; nonylphenol condensed with 20 moles of ethylene oxide per mole of nonylphenol; myristyl alcohol condensed with 10 moles of ethylene oxide per mole of myristyl alcohol; lauramide condensed with 15 moles of ethylene oxide per mole of lauramide; and diisooctylphenol condensed with 15 moles of ethylene oxide.

The preferred nonionic detergent is the condensation product of one mole of hydrogenated tallow fatty alcohol with 4 moles of ethylene oxide. The proportion of low sudsing nonionic detergent in the composition may be up to about 20% by weight of the soap content, and preferably from at least about 2% to about 15%, by weight of the soap content, of the composition.

The invention is illustrated by the following examples:

EXAMPLE I

A spray-dried granular soap composition is prepared to the following finished product formula:

	Percent by weight
Sodium soap (20% coconut oil:80% tallow) ----	54
N-lauryl beta-alanine sodium salt ----	6
Sodium poly(itaconate-acrylate) (4:1 on a molar basis; specific viscosity of 1%, by weight, in dimethylformamide at room temperature .40; equivalent weight 65.8) ----	2
Sodium silicate solids (ratio $\text{SiO}_2:\text{Na}_2\text{O}=2.4:1$) --	10.25
Condensation product of 1 mole hydrogenated tallow fatty alcohol and 4 moles ethylene oxide ----	2
Sodium carboxymethyl cellulose ----	0.34
Ethylene diaminetetraacetic acid ----	0.18
Optical whitening agent ----	0.20
Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) --	8.9
Miscellaneous (inorganic salt, glycerine unsaponified fat, etc., associated with soap) ----	1.1
Moisture ----	14.70
Perfume ----	0.33

EXAMPLE II

A spray-dried granular soap composition is prepared to the following finished product formula:

	Percent by weight
Sodium soap (20% coconut oil:80% tallow) ----	52
N-lauryl beta-alanine sodium salt ----	6
Sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) ----	6
Sodium silicate solids (ratio $\text{SiO}_2:\text{Na}_2\text{O}=2.4:1$) --	10.25
Sodium carboxymethyl cellulose ----	0.34
Ethylene diaminetetrasodium tetraacetate ----	0.18
Optical whitening agent ----	0.20
Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) --	8.9
Miscellaneous (inorganic salt, glycerine unsaponified fat, etc., associated with soap) ----	1.1
Moisture ----	14.70
Perfume ----	0.33

EXAMPLE III

A spray-dried granular soap composition is prepared to the following finished product formula:

	Percent by weight
Sodium soap (20% coconut oil:80% tallow) ----	54
3-(N,N - dimethyl-N-dodecyl) ammonio-2-hydroxypropane-1-sulfonate ----	6
Sodium polyitaconate (specific viscosity of 1% by weight in dimethylformamide at room temperature .13; equivalent weight 65) ----	2
Sodium silicate solids (ratio $\text{SiO}_2:\text{Na}_2\text{O}=2.4:1$) --	10.25
Condensation product of 1 mole hydrogenated tallow fatty alcohol and 4 moles ethylene oxide ----	2
Sodium carboxymethyl cellulose ----	0.34
Ethylene diaminetetrasodium tetraacetate ----	0.18

Optical whitening agent ----	0.20
Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) --	8.9
Miscellaneous (inorganic salt, glycerine unsaponified fat, etc., associated with soap) ----	1.1
Moisture ----	14.70
Perfume ----	0.33

EXAMPLE IV

A spray-dried granular soap composition is prepared to the following finished product formula:

	Percent by weight
Sodium soap (20% coconut oil:80% tallow) ----	52
3-(N,N - dimethyl-N-dodecyl) ammonio-2-hydroxypropane-1-sulfonate ----	3
Dodecyldimethylamine oxide ----	3
Sodium tripolyphosphate ----	4
Sodium silicate solids (ratio $\text{SiO}_2:\text{Na}_2\text{O}=2.4:1$) --	10.25
Condensation product of 1 mole hydrogenated tallow fatty alcohol with 4 moles ethylene oxide ----	2
Sodium carboxymethyl cellulose ----	0.34
Ethylene diaminetetrasodium tetraacetate ----	0.18
Optical whitening agent ----	0.20
Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) --	8.9
Miscellaneous (inorganic salt, glycerine unsaponified fat, etc., associated with soap) ----	1.1
Moisture ----	14.70
Perfume ----	0.33

The granular product set forth in Examples I to IV above can be prepared by spray-drying an aqueous slurry of all the ingredients except the sodium perborate and perfume. Perfume is sprayed onto the spray-dried granules which are then mixed with the sodium perborate.

In use in a household washing machine using hard water the products of Examples I through IV give no foam below the point at which all the hardness of the water has been destroyed and the concentration of free soap is sufficient for effective washing. The washing liquor is free from lime soap scum and no deposit of lime soap is left in the washing machine. During the rinsing the water is free from lime soap scum and also free from foam.

Similar results are obtained if N-lauryl beta alanine is replaced by the sodium salt of dodecylaminomethane carboxylic acid, N,N' - dodecylethylenediaminediacetic acid sodium salt, N-methyltaurine sodium salt or N-methyl-N'-sulfophenylethylenediamine sodium salt; if the 3-(N,N - dimethyl-N-dodecyl) ammonio-2-hydroxypropane sulfonate is replaced by 3(N-dodecyl-N,N-dimethylammonio) propane-1-sulfonate; or if the sodium tripolyphosphate is replaced by sodium hexametaphosphate, trisodium nitrilotriacetate or a 1:1 mixture of these two compounds on a weight basis.

Additional illustrative examples are:

EXAMPLE V

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (20% coconut oil:80% tallow) ----	60
Dodecyl - aminomethane carboxylic acid, sodium salt ----	10
Sodium polyitaconate (as in Example III) ----	10
Water ----	17
Miscellaneous ----	3

EXAMPLE IV

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (40% coconut oil:60% tallow) ----	60
Sodium salt of N-lauryl beta-alanine ----	7
Monoethanolammonium polymaleate (specific viscosity of 1% by weight in dimethylformamide at room temperature .21; equivalent weight 58) ----	14
Water ----	17
Miscellaneous ----	2

EXAMPLE VII

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (100% coconut) -----	50
N,N' - dodecylethylenediaminediacetic acid, sodium salt -----	10
Sodium poly(itaconate-aconitate) (1:1 on a molar basis; specific viscosity of 1% by weight in dimethylformamide at room temperature .12; equivalent weight 60.8) -----	30
Water -----	9
Miscellaneous -----	1

EXAMPLE VIII

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (60% coconut:40% tallow) -----	70
N-methyl taurine sodium salt -----	10
Sodium poly(ethylene-maleate) (1:1 on a molar basis; specific viscosity of 1% by weight in dimethylformamide at room temperature 1.58; equivalent weight 72) -----	10
Water -----	8
Miscellaneous -----	2

EXAMPLE IX

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (80% coconut:20% tallow) -----	80
N-methyl - N' - sulfophenylethylenediamine, sodium salt -----	10
Sodium poly(ethylene-maleate) (1:1 on a molar basis; specific viscosity of 1% by weight in dimethylformamide at room temperature 1.58; equivalent weight 72) -----	5
Water -----	4
Miscellaneous -----	1

EXAMPLE X

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (20% coconut:80% tallow) -----	40
Sodium salt of N-lauryl beta-alanine -----	15
70% potassium polymaleate:30% polymaleic acid (1.4:1 on a molar basis, specific viscosity of 1% by weight in dimethylformamide at room temperature .39, equivalent weight 58) -----	15
Sodium silicate solids (ratio $\text{SiO}_2:\text{Na}_2\text{O}=2.4:1$) -----	11
Water -----	6
Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) -----	10
Miscellaneous -----	3

EXAMPLE XI

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (20% coconut:80% tallow) -----	65
Sodium salt of N-lauryl beta-alanine -----	10
Sodium polyitaconate (specific viscosity of 1% by weight in dimethylformamide at room temperature .29; equivalent weight 65) -----	10
Nonylphenol condensed with about 5 moles of ethylene oxide per mole of alcohol -----	10
Water -----	4
Miscellaneous -----	1

EXAMPLE XII

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (20% coconut:80% tallow) -----	60

Percent by weight

(N - lauryl - N,N - dimethylammonio)methane carboxylate -----	10
Sodium salts of polyitaconate (as in Example III) -----	10
Water -----	17
Miscellaneous -----	3

EXAMPLE XIII

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (40% coconut:60% tallow) -----	60
3(N-lauryl-N,N-dimethylammonio)-propane-1 - sulfonate -----	5
Sodium vinylmethylether-maleate polymer; 1:1 on a molar basis; specific viscosity of 1% by weight in dimethylformamide at room temperature .88; equivalent wt. 87) -----	16
Water -----	17
Miscellaneous -----	2

EXAMPLE XIV

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (50% coconut:50% tallow) -----	50
Decyl dimethylamine oxide -----	30
Monoethanolammonium polymaleate (as in Example VI) -----	10
Water -----	9
Miscellaneous -----	1

EXAMPLE XV

A liquid soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (80% coconut:20% tallow) -----	15
Tetradecyldimethylphosphine oxide -----	10
Sodium tripolyphosphate -----	5
Water -----	70

EXAMPLE XVI

A soap bar composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (100% coconut) -----	80
3-hydroxytridecylmethyl sulfoxide -----	10
Sodium hexametaphosphate -----	5
Water -----	5

EXAMPLE XVII

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (20% coconut:80% tallow) -----	45
3-hydroxy-4-decoxy-butylmethyl sulfoxide -----	22.5
Sodium salt of nitrilotriacetic acid -----	22.5
Water -----	7
Miscellaneous -----	3

EXAMPLE XVIII

A soap composition is prepared to give the following product composition:

	Percent by weight
Sodium soap (20% coconut:80% tallow) -----	60
Dodecyl-bis(hydroxymethyl)phosphine oxide -----	16
Sodium tripolyphosphate -----	8
Sodium nitrilotriacetate -----	8
Nonylphenol condensed with about 30 moles of ethylene oxide per mole of alcohol -----	3
Water -----	4
Miscellaneous -----	1

As seen from the tables above, the specifically proportioned combinations of the synthetic detergents and the salts described herein offer superior valuable synergistic curd dispersing properties.

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Germicidal agents can be added to the soap compositions of the present invention especially the bar embodiments to render the products antiseptic in quality.

The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of the invention.

All of the percentages given above are by weight unless otherwise specified.

What is claimed is:

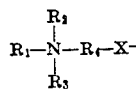
1. A soap composition having improved curd-dispersing properties consisting essentially of:

(I) a higher fatty acid soap and

(II) at least about 5% by weight of said soap of a synergistic curd-dispersing mixture of

(A) at least one synthetic detergent selected from the group consisting of

(1) compounds of the formula



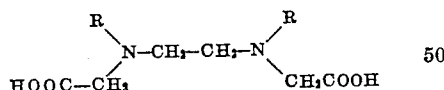
wherein R_1 is alkyl of 10 to 18 carbon atoms, R_2 is alkyl of 1 to 3 carbon atoms, R_3 is alkyl of 1 to 3 carbon atoms, R_4 is alkylene or hydroxyalkylene of 1 to 4 carbon atoms and X^- is a carboxylic acid or sulfonic acid anion;

(2) compounds of the formula $R_5R_6R_7N \rightarrow O$ wherein R_5 is alkyl, alkenyl or hydroxyalkyl of 10 to 18 carbon atoms and R_6 and R_7 are each alkyl or monohydroxyalkyl of 1 to 3 carbon atoms;

(3) compounds of the formula $R_8R_9S \rightarrow O$ wherein R_8 is alkyl, alkenyl, hydroxyalkyl or alkoxyalkyl of 10 to 18 carbon atoms and R_9 is methyl or ethyl;

(4) water-soluble salts of compounds of the formula $R \cdot NH \cdot (CH_2)_x COOH$ wherein R is alkyl of 10 to 18 carbon atoms and x is 1 or 2;

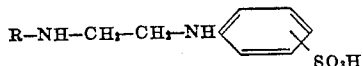
(5) water-soluble salts of compounds of the formula



wherein R is alkyl of 10 to 18 carbon atoms;

(6) water-soluble salts of compounds of the formula $R-NH-CH_2-CH_2-SO_3H$ wherein R is alkyl of 10 to 18 carbon atoms; and

(7) water-soluble salts of compounds of the formula



wherein R is alkyl of 10 to 18 carbon atoms; and

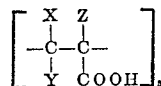
(B) at least one water-soluble salt of compounds selected from the group consisting of

(1) linear polymeric phosphoric acid containing more than 2 phosphorus atoms in the molecule;

(2) water-soluble salts of polymeric aliphatic polycarboxylic acid selected from the group consisting of (a) water-soluble salt of the

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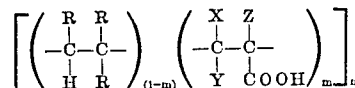
homopolymer of an aliphatic polycarboxylic acid having the following empirical formula



wherein X , Y , and Z are each selected from the group consisting of hydrogen, methyl, carboxyl, and carboxymethyl, at least one of X , Y , and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein only one of X , Y , and Z can be methyl, and wherein n is a whole integer having a value within a range, the lower limit of which is three and the upper limit of which is determined by the solubility characteristics in an aqueous system;

(b) a water-soluble salt of a copolymer of at least two of the monomeric species having the empirical formula described in (a); and,

(c) a water-soluble salt of a copolymer of a member selected from the group of alkenes and monocarboxylic acids with the aliphatic polycarboxylic compounds described in (a), said copolymers having the general formula:



wherein R is selected from the group consisting of hydrogen, methyl, carboxyl, carboxymethyl, and carboxyethyl; wherein only one R can be methyl; wherein m is at least 45 mole percent of the copolymer; wherein X , Y , and Z are each selected from the group consisting of hydrogen, methyl, carboxyl, and carboxymethyl, at least one of X , Y , and Z being selected from the group of carboxyl and carboxymethyl provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein only one of X , Y , and Z can be methyl; and wherein n is a whole integer within a range, the lower limit of which is determined primarily by the solubility characteristics in an aqueous system; said material having a minimum molecular weight of 350 calculated as the acid form and an equivalent weight of about 50 to about 80, calculated as the acid form; and

(3) nitrilotriacetic acid; the ratio by weight of (A) to (B) being from about 1:4 to about 4:1.

2. The soap composition of claim 1 wherein said synergistic curd-dispersing mixture constitutes from about 5% up to about 100% by weight of said higher fatty acid soap.

3. The soap composition of claim 1 in which said synergistic curd-dispersing mixture constitutes from about 20% to about 80% by weight of said higher fatty acid soap.

4. The soap composition of claim 1 in which the ratio by weight of (A) to (B) is from about 1:2 to about 2:1.

5. A soap composition having improved curd-dispersing properties consisting essentially of from about 10% to about 95% by weight of a fatty acid soap containing

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from about 10 to about 20 carbon atoms, and from about 5% to about 100% by weight of said soap of a synergistic curd-dispersing mixture as defined in claim 1.

6. A liquid soap composition having improved curd-dispersing properties consisting essentially of from about 10% to about 30% fatty acid soap containing from about 10 to about 20 carbon atoms, from about .5% to about 30% of the synergistic curd-dispersing mixture described in claim 1, and the balance being water.

7. A soap bar consisting essentially of from about 80% to about 95% by weight of fatty acid soap containing from about 10 to about 20 carbon atoms and from about 5% to about 20% of a synergistic curd-dispersing mixture as defined in claim 1.

8. A granular detergent composition comprising from about 40% to about 80% of a fatty acid soap containing from about 10 to about 20 carbon atoms and from about 2% to about 50% by weight of the composition of a synergistic curd-dispersing mixture defined in claim 1.

9. The composition of claim 5 which also contains up to about 20% by weight of the fatty acid soap of a non-ionic synthetic alkylene oxide-condensate detergent.

10. The composition of claim 9 in which the nonionic synthetic alkylene oxide-condensate detergent is present at a level of from about 2% to about 15% by weight of the higher fatty acid soap.

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11. The composition of claim 1 wherein the detergent II-A is the sodium salt of N-lauryl beta alanine.

12. The composition of claim 1 wherein the water-soluble salt II-B is sodium tripolyphosphate.

13. The composition of claim 1 wherein the water-soluble salt II-B is trisodium nitrilotriacetate.

14. The composition of claim 11 wherein the water-soluble salt II-B is the sodium salt of polyitaconic acid.

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