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Light duty liquid detergent composition

As liquid dishwashing detergent formulations become increasingly popular with the consumer, the performance of such detergent compositions for cleaning kitchen utensils, such as glasses, dishes and other apparatus, becomes more important. Many performance characteristics are associated with this type of detergent formulation, among which are foamability, detergency, soil suspending ability and mildness. In addition, the consumer has become concerned with both the final appearance of the objects that are washed and the ease with which washing, rinsing and the drying of the kitchen utensils can be accomplished.

Spotting may be referred to as resulting from the break-up of a once continuous liquid film followed by the isolation of liquid patches that become stranded on the solid surface. Upon the drying of these isolated liquid patches, spots will form from the solid residue that was dissolved or suspended in the liquid. One of the disadvantages associated with liquid dishwashing detergent compositions, therefore, is the need to dry the washed objects or apparatus with a towel so that spot and film formation from the minerals in the rinse water can be avoided or minimized to a large extent. Moreover, because of the amount of water that remains undrained on the glassware and plates and kitchen utensils, etc., the towel drying process tends to become time-consuming and an additional burden to the consumer, thereby leaving it more desirable to let the washed utensils or apparatus drain and dry by themselves under ambient conditions.

Various attempts have been made to minimize the effect of the water hardness residue and film-forming deposits on washed kitchen utensils by applying various additives in the detergent formulations, either by complexing the water hardness salts, or by formulating special rinsing agents. However, the incorporation of complexing and/or soil suspending agents in the liquid formulations create processing and formulation problems, while any of the special rinsing agents that have been disclosed heretofore must be packed and applied separately in the washing solution.

It has also been proposed e.g. in DE—Al 2,748,800 and 2,650,971, to improve the drainage properties of dishwashing compositions by incorporating an agent, such as gelatin or casein, which allows the rinse water to "sheet-off" the utensil, thereby leaving the surface dry. This rapid "sheeting-off" effect reduces the effort involved in drying the washed objects and also improves their final appearance in terms of minimizing or altogether obviating the spotting and filming associated with suspended soil and water hardness.

Other uses of casein e.g. in conjunction with certain complexing agents for improving the anti-washing properties of detergent compositions have been disclosed in DE—Al 2,607,656.

Applicants have unexpectedly discovered that a liquid detergent composition containing a relatively small amount of a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate, having specific molecular weight limitations, and a small amount of an alkali metal salt of casein, e.g., sodium caseinate, when added to an anionic surfactant, nonionic surfactant, or mixtures thereof, provides an excellent washing and cleaning composition with much improved drainage properties so as to render the cleaned objects virtually free from spotting and/or filming.

The liquid detergent composition will generally contain from 2% to 50% by weight, preferably from 10% to 30% by weight of the total composition of an anionic surfactant compound.

Among the suitable synthetic anionic surface active agents that may be present in the liquid dishwashing detergent composition are the water-soluble hydrocarbon sulfates having the general formula:

$$R_1O(C_2H_4O)_nSO_3M$$

wherein R_1 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 2 to 22 carbon atoms; n is from 0 to 15; and M is a cation, preferably sodium, potassium or ammonium. Important examples which form part of the preferred composition of the present invention are the salts of an organic, sulfuric acid reaction product of a saturated or unsaturated fatty alcohol having 8 to 18 carbon atoms, preferably tallow, or coconut alcohol, reacted with 1.5 to 15, preferably 3 to 13 moles of ethylene oxide per moles of fatty alcohol. Specific examples are

C_{12-14} alkyl —O—$(C_2H_4O)_3$—SO_3Na; C_{14} alkyl —O—$(C_2H_4O)_3SO_3NH_4$;

C_{12-16} alkyl —O—$(C_2H_4O)_6$—SO_3K; and tallow —O—$(C_2H_4O)_9$—$SO_3N(H)_2$ $(C_2H_4OH)_2$.

Important examples of hydrocarbon sulfates as represented by the above formula whereby n is 0, are those obtained by sulfating hydroxylated hydrocarbons, preferably fatty alcohols having 8 to 18, most preferably 12 to 16 carbon atoms, with SO_3, H_2SO_4, etc. followed by hydrolysis and/or bleaching according to processes well known in the art.

Also suitable are the water-soluble salts of the organic sulfuric acid reaction products of the general formula:

$R_2—SO_3M$

wherein R_2 is chosen from the group consisting of a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 24, preferably from 12 to 18 carbon atoms; and an alkylbenzene radical having from 8 to 18, preferably from 12 to 16 carbon atoms in the alkyl group; and M is a cation, preferably sodium, potassium, ammonium, magnesium or calcium. Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the salts of an organic, sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, meso-, and n-paraffins, having 8 to 24 carbon atoms, preferably 11 to 18 carbon atoms, and 1 up to 4 double bonds, and a sulfonating agent, e.g. SO_3, H_2SO_4, oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are sulfonated C_{12-18} n-paraffins, alone or in combination with sulfonated alpha olefins containing an average of 14 carbon atoms. Important examples of alkylbenzene sulfonates in which the alkyl group contains from 9 to 18 carbon atoms are dodecyl-, tetradecyl-, and hexadecylbenzene sulfonates and those which are described in U.S. Patents Nos. 2,220,099, and 2,477,383.

The preferred anionic surface-active agent which can be included in the composition of the present invention, is the water-soluble hydrocarbon sulfate as represented hereinbefore by the general formula $R_1O(C_2H_4O)_nSO_3M$, wherein R_1 is preferably a straight, saturated, aliphatic hydrocarbon radical, having from 8 to 20, desirably 12 to 16 carbon atoms; n is preferably from 3 to 9; and M is preferably sodium, potassium or ammonium. Said preferred ethoxylated hydrocarbon sulfates can be present in amounts up to 50%, but are preferably present between 5 and 35% by weight, based on the total weight of the composition.

In case of combinations of water-soluble, ethoxylated hydrocarbon sulfates, as represented by the aforementioned general formula $R_1O(C_2H_4O)_nSO_3M$, and water-soluble salts of the organic, sulfuric acid reaction product of the general formula R_2SO_3M, wherein R_1, R_2 and M and n have the same meaning recited above; the weight ratio of said water-soluble salts of the organic, sulfuric acid reaction product to the ethoxylated hydrocarbon sulfate will usually be, dependent upon the concentration and type of the metal cations present in the wash solution (i.e. the ionic strength), from 10:1 to 1:10, preferably from 3:1 to 1:1. The most preferred are those compositions whereby the water-soluble ethoxylated hydrocarbon sulfates are C_{12-16} alkyl —O—$(C_2H_4O)_{3-6}SO_3M$, and the water-soluble salts of the organic, sulfuric acid reaction products are C_{11-18} paraffin sulfonates.

The levels of nonionic surface-active detergent in the liquid detergent composition of the present invention will preferably be from 1% to 30% by weight, most preferably from 1% to 10% by weight based on the total weight of the composition.

Suitable, water-soluble, nonionic surface-active agents to be used in the formulation of the liquid dishwashing detergent composition of the present invention are the water-soluble, nonionic, tertiary amine oxides as represented hereinafter by the general formula:

$$R_3R_4R_5N—O$$

whereby R_3 represents a high molecular, straight or branched, saturated or unsaturated, aliphatic hydrocarbon, hydroxyhydrocarbon, or alkyloxyhydrocarbon radical, preferably an alkyl radical having a total of 8 to 24, preferably 12 to 18; R_4 and R_5 which may be the same or different, represent each a methyl, ethyl, hydroxymethyl, and hydroxyethyl radical.

They are generally prepared by direct oxidation of appropriate tertiary amines according to known methods. Specific examples of tertiary amine oxides are: dimethyl dodecyl amine oxide, diethyl tetradecyl amine oxide, bis-(2-hydroxyethyl)-dodecyl amine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropyl amine oxide, dimethyl-2-hydroxydodecyl amine oxide, and diethyl eicosyl amine oxide.

Another group of suitable nonionic surfactant compounds are the water-soluble, tertiary phosphine oxides, represented by the general formula:

$$R_3R_4R_5P—O$$

whereby R_3, R_4 and R_5 have the same meaning as described hereinbefore. They can be prepared by alkylating an alkyl phosphine derivative and oxidizing the resulting reaction product. Specific examples of tertiary phosphine oxides are: dimethyl dodecyl phosphine oxide, diethyl tetradecyl phosphine oxide, bis-(2-hydroxyethyl)- dodecyl phosphine oxide, tetradecyl ethyl 2-hydroxyethyl phosphine oxide, oleyl dimethyl phosphine oxide, and 2-hydroxydodecyl dimethyl phosphine oxide.

Still another group of nonionic surfactant compounds are the water-soluble amides represented by the general formula:

$$R_6—CO—N(H)_{m-1}(R_7OH)_{3-m}$$

wherein R_6 is a saturated or unsaturated, aliphatic hydrocarbon radical having from 7 to 21, preferably from 11 to 17 carbon atoms; R_7 represents a methylene or ethylene group; and m is 1, 2 or 3, prefer-

ably 1. Specific examples of said amides are mono-ethanol coconut fatty acid amide, diethanol dodecyl fatty acid amide, and dimethanol oleyl amide.

Yet another group of nonionic surfactant compounds are the water-soluble condensation products obtained by condensing from 3 to 25 moles of an alkylene oxide, preferably ethylene or propylene oxide, with one moles of an organic hydrophobic compound, aliphatic or alkyl aromatic in nature and having 8 to 24 carbon atoms and at least one reactive hydrogen atom, preferably a reactive hydroxyl, amino, amido or carboxy group. Specific examples of these groups of compounds are:

1. condensation products of ethylene oxide with aliphatic alcohols of more than 8 carbon atoms. The alcohols are usually derived from the naturally occurring fatty acids or from various branched-chain higher alcohols. Among the preferred alcohol-ethylene oxide condensation products are those made from alcohols derived from tallow and coconut fatty acids. Most preferred are the condensation products of 4 to 12 moles of ethylene oxide per mole of an aliphatic alcohol having from 10 to 18 carbon atoms, in particular a middle-cut coconut fatty alcohol condensed with 6 moles of ethylene oxide;

2. condensation products of ethylene oxide with alkylphenols, whereby the phenols may be mono- or polyalkylated and the total number of side-chain carbon atoms may be from 5 to 18 carbon atoms. The aromatic nucleus bearing the phenolic hydroxy may be benzene, naphthalene, or diphenyl, preferably benzene. Specific examples are condensation products of one mole of nonylphenol with 9 to 15 moles of ethylene oxide;

3. condensation products of ethylene oxide with the fatty acid esters, preferably mono-fatty acid esters of the sugar alcohols, sorbitol and manitol, and also of di- and polysaccharides. Specific examples of the polyoxyethylene sorbitanmonolauric acid esters having 20 or more ethylene oxide units; and the polyoxyethylene derivatives of fatty acid partial esters of hexitol anhydrides generally known under the Registered Trade Mark TWEEN, available from ICI America, Inc., Wilmington, Delaware;

4. polyethenoxy esters, or esters formed by reacting ethylene oxide with carboxylic acids. The acids can be natural fatty acids or fatty acids made from oxidized paraffin wax, or mono- or alkylated benzoic and naphthenic acids. Desirable are aliphatic fatty acids having from 10 to 20 carbon atoms, and benzoic acids with 5 to 18 carbon atoms in the alkyl groups. Specific examples and preferred condensation products are tall oil ethylene oxide condensation products having 9 to 15 ethylene oxide units;

5. condensation products of fatty acyl alkanolamides of the type

$$C_{7-17}\ \text{alkyl} —CO—NHC_2H_4OH,$$

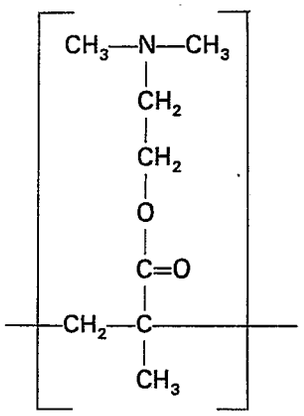
$$C_{7-17}\ \text{alkyl} —CO—N—(C_2H_4OH)_2$$

with ethylene oxide. Those preferred are condensation products of one mole of coconut —CO—NH—C_2H_4OH with 5 to 20 moles of ethylene oxide. Specific examples of polyethenoxy alkanolamides of fatty acids are the commercial products, marked under the Registered Trade Mark ETHOMID, available from Armak Chemical Company, Chicago, Illinois;

6. condensation products of C_{8-18} alkyl-, C_{8-18} alkenyl- and C_{5-18} alkylaryl amines and ethylene oxide. A specific and preferred example is the condensation product of one mole of dodecylamine with 9—12 moles of ethylene oxide.

The maximum level of water-soluble, anionic and nonionic surface-active agents that can be included in the liquid detergent composition of the present invention will usually depend on the level of each of the surfactants present and also to a certain extent on the presence of the drainage modification agents herein. The maximum amount of both nonionic and anionic surface-active agents which can be present in the composition of the present invention is 50% by weight based on the total weight of the composition.

The copolymer used in the present liquid dishwashing detergent composition to provide enhanced drainage properties, is a copolymer of N-vinyl pyrrolidone and dimethylamino-ethylmethacrylate whose monomer structure is represented by the following formula:



The molecular weight of this copolymer is preferably between 40,000 and 1.5 million, and may be present in the composition from 0.1% to 10% by weight of the total composition, preferably between 0.5% and 3.0% by weight. A copolymer that is commercially available may be obtained from the GAF Corporation under the trade name of Gafquat 755, having a molecular weight of about 1 million, and Gafquat 734, having a molecular weight of about 100,000. GAFQUAT is a Registered Trade Mark.

A third ingredient that is used in the dishwashing liquid composition of the invention is an alkali metal salt of the protein, casein, preferably sodium caseinate. The caseinate can be present in an amount of from 0.5% to 5% by weight based on the total weight of the composition, preferably from 1.0% to 3.0% by weight. A commercial grade of sodium caseinate is available from Western Dairy Products under the trade name of Savortone LF having the following analysis:

	% Dry Weight
Protein	95
Fat	1.2
Ash	4.0
Moisture	4.0
pH (5% aqueous solution)	6.7

A more adequate description of casein and its salts may be found in the *"Fundaments of Dairy Chemistry"* by B.H. Webb, A.H. Johnson, and J.A. Alford, Avi Publication Co., Inc., 2d Ed.(1974), pp. 92—111, which is incorporated herein by reference.

Accordingly the invention pertains to a light duty, hand dishwashing liquid detergent composition comprising:

1. 2% to 50% by weight of an anionic surfactant compound, nonionic surfactant compound, or mixtures thereof;

2. 0.1% to 10% by weight of a copolymer of N-vinylpyrrolidone and dimethylaminoethylmethacrylate having a molecular weight from 40,000 to 1,500,000; and

3. From 0.5% to 5% by weight of an alkali metal salt of casein; the percentages expressed being based on the total weight of the composition.

The above liquid detergent composition provides excellent drainage of washed kitchen utensils and apparatus, and prevents water spotting and filming when the utensils are left to dry. Moreover, the utensils are left with a shiny clean appearance and eliminate the necessity for towel drying or wiping.

A preferred embodiment for the dishwashing liquid detergent composition according to the invention is one which contains (a) from 10 to 30% of an anionic surfactant compound, or a mixture of anionic surfactant compounds; (b) from 1% to 10% of a nonionic surfactant compound, or a mixture of nonionic surfactant compounds; (c) from 0.5% to 3.0% of a copolymer of N-vinylpyrrolidone and dimethylamino-ethyl-methacrylate having a molecular weight between 40,000 and 1.5 million, or mixtures thereof; and (d) from 1.0% to 3.0% of sodium caseinate; the percentages expressed being based on the total weight of the composition.

Additional ingredients that can be optionally included in the hand dishwashing liquid composition of the present invention are water-soluble, low molecular weight organic acid, or the water-soluble alkali metal, ammonium, or substituted ammonium salts thereof. Organic acids or their salts are added to enhance the cleaning action of the liquid detergent composition of the present invention and can, in

addition, be used as a source of ions to maintain the pH of the composition at a given pH value. Suitable water-soluble, low molecular weight organic acids include, for example, acetic, citric, malic, gluconic, maleic, lactic, tartaric, propionic, butyric, malonic, polymaleic, polyitaconic, glutaric, citraconic, benzene pentacarboxylic, hexcarboxylic, succinic, ethylene diamine tetra-acetic and nitrilotriacetic acids. Partially and completely neutralized salts of the foregoing acids can also be used. Specific examples of suitable, organic acid salts are mono-, di- and trisodium citrate, diammonium citrate, monopotassium tartrate, disodium succinate, and tetrasodium melletate.

The maximum level of the water-soluble organic acids or salts that can be added to the liquid detergent composition of the present invention should usually not exceed 15 percent by weight of the total weight of the composition, and should preferably be below 10 percent by weight. Some of the organic acid salts can be replaced by inorganic builder salts. The amount of inorganic builder salts, e.g. sodium phosphates and carbonates, should preferably not exceed 5 percent by weight in the composition.

Other suitable ingredients or additional compounds that can optionally be added to improve consumer acceptance of the composition of the present invention are: perfume, dyes, fluorescers, tarnish inhibitors, such as benzotriazole or ethylene thio-urea; shine improvers, such as boric acid or its salts in amounts of up to 3 percent by weight; bactericides such as 2-bromo-2-nitro-1, 3-propanediol, substituted benziodolium compounds, diphenyl ethers substituted with Cl, Br or —CF_3, e.g. 3,4-dichloro-4'-trifluoromethyldiphenyl ether; organic solvents, and hydrotropes; in amount of up to about 15 percent by weight to improve the pourability of the composition and to enhance the compatibility of the different components. Examples of the organic solvents are the mono- and dialcohols containing 2 to 8 carbon atoms such as ethanol, butanol, methylpropanol-1 and -2, amylol (pentanol), 1,2-, 1,3- and 1,4-butanediol, toluol, benzyl carbinol, ethyleneglycol monobutyl ether, propyleneglycol propyl ether and diethyleneglycol dimethyl ether. Examples of hydrotropes are sodium, potassium or ammonium xylene sulfonate, and sodium, potassium or ammonium isethionate.

The benefits and advantages of the instant liquid dishwashing detergent composition are illustrated in the examples and tests set forth below.

Example 1

The substrates used to judge the effectiveness of the foregoing agents in the drainage modification in a liquid dishwashing detergent composition of all of the examples herein were either 310 ml drinking glasses, glass dinner plates (23 cm diameter), ceramic dinner plates (23 cm diameter), or plastic dinner plates (23 cm diameter), Boontonware. The substrates were washed with various detergent compositions at a use level of 0.15% and 0.20% for 1 minute and 3 minutes at a temperature of 40—45°C. Edgewater, New Jersey tap water was used in all of the experiments. The substrates were then rinsed either under running tap water or in a dishpan filled with clean tap water. In both cases, the temperature of the rinse water was approximately 45°C. The duration of the rinse was varied between 10 seconds and 2 minutes.

After the rinse, the substrate was placed on a rack to dry. The time at which drainage began and the percentage of the surface area of the substrate that dried due to this drainage were recorded. The degree of benefit arising from the agent is directly related to the time at which drainage begins and the percentage of the area dried by this drainage. The benefit produced by drainage modification increases with increasing drainage rate and increasing percentage area dried by the enhanced drainage, provided that the rinse water film drains as a uniform sheet, and does not break up into water droplets which produce objectionable spotting.

The drainage agents used in the following tests are listed in Table 1 below.

TABLE 1

Drainage Modification Agent	Composition
PVP—K90*	Polyvinylpyrrolidone, MW ≅ 360,000
PVP—K30*	Polyvinylpyrrolidone, MW ≅ 40,000
Gafquat 755*	Copolymer of N-vinylpyrrolidone and dimethyl-amino-ethylmethacrylate, MW ≅ 1,000,000
Gafquat 734*	Copolymer of N-vinylpyrrolidone and methyl-amino-ethylmethacrylate, MW ≅ 100,000
Gelatin**	Type B, Bloom Strength 225
Savortone LF***	Sodium Caseinate

* Available from the GAF Corporation.
** Available from General Foods, Inc.; also described in USP 3,963,649.
*** Available from Western Dairy Products. SAVORTONE is a Registered Trade Mark.

The influence of polyvinylpyrrolidone and the copolymer of N-vinylpyrrolidone and dimethyl-amino-ethylmethacrylate on the drainage of rinse water from several substrates after washing with a liquid dishwashing composition is set forth in Table 3. The surfactant system used in these formulations is given in Table 2 below:

TABLE 2

Surfactant System	% by weight
Secondary alkane ($C_{15.3}$ avg.) sulfonate (SAS—6 0)****	17
Ammonium C_{12}—C_{15}(3 ethylene oxide) sulfate	12
Lauryl diethanolamide	5
Ethanol	5
Water	to 100

**** Available from American Hoechst Corporation.

All of the results shown in Table 3 are compared with the base surfactant system given in Table 2 without the inclusion of a drainage modification agent.

TABLE 3

Effect of Drainage Modification Agents on Substrates

Agent	Concentration in Formulation	Time for Effect To Begin (seconds)			% Area Dried By Evaporation		
		Glasses	Glass Plates	Plastic Plates	Glasses	Glass Plates	Plastic Plates
No agent	—	—	—	—	100	100	100
PVP K—90	10%	9	—	—	<10	—	—
PVP K—90	5%	4	5	10	30	25	25
PVP K—90	2%	10	—	—	10—15	—	—
PVP K—90	1%	12	—	—	20	—	—
PVP K—30	10%	10	—	—	20—30	—	—
Gafquat—755	10%	8	—	—	10—20	—	—
Gafquat—734	10%	4	—	—	<10	—	—
Gafquat—734	5%	3	3	10	<10	10	25
Gafquat—734	2.5%	—	3	3	—	23	70
Gafquat—734	2.0%	10	—	—	15	—	—
Gafquat—734	1.0%	15	—	—	30	—	—
Gafquat—734	0.35%	12	—	—	50	—	—
Gafquat—734	0.21%	10	—	—	55	—	—
Na Caseinate	2.5%	12	3	4	70	75	76
Na Caseinate	2.0%	20	—	—	85	—	—
Na Caseinate	1.0%	—	—	—	100	—	—
Gelatin**	2.0%	10	—	—	85	—	—
Gelatin**	1.0%	12	—	—	85	—	—

Example 2

Mixtures of the copolymer of the present invention with sodium caseinate shows enhanced drainage modification on various substrates as compared with sodium caseinate used alone. This is demonstrated by the results shown in Table 4 with a surfactant system used according to Example 1.

TABLE 4
Drainage Modification Produced by Combination of Copolymer and Sodium Caseinate

Agent	Wt.% in Formulation	Cermic Plates Time (sec),	% Area	Plastic Plates Time (sec),	% Area	Glass Plates Time (sec),	% Area
Na Caseinate	2.5%	—	100	3	76	3	75
Gafquat—734	2.5%	4	40	3	70	3	23
Na-Caseinate-plus Gafquat—734	2.5% } 2.5% }	2	2.5	3	73	2.5	1
Gafquat—734	5.0%	—	—	10	25	3	1

It will be seen that the sodium caseinate used alone is not as effective as when it is used in combination with the drainage modification agent according to the invention herein.

Example 3

The results described thus far in the foregoing tables have concerned the extent to which drainage modification agents according to the invention decrease the surface area that dries by evaporation for a given substrate, e.g. glassware. This rapid drainage not only facilitates the drying process but also significantly improves the final appearance of the glassware with respect to liquid dishwashing formulations. The following test illustrates the extent of this improvement in appearance.

Ten drinking glasses were soiled with milk. Five of the glasses were washed in a formulation containing 2.5% by weight of Gafquat—734 copolymer and 2.5% by weight of sodium caseinate in combination with the Surfactant Formulation described in Table 2. The remaining five glasses were washed in a solution of a commercial hand dishwashing liquid composition at an identical concentration of 0.20%. The commercial liquid composition is set forth below in Table 5. A panel of 12 people then compared the two sets of glasses with respect to spotting, filming and general appearance under normal laboratory lighting. The panel unanimously selected glasses washed in the copolymer Gafquat—734/sodium caseinate formulation as having less spotting and filming and as having an overall "cleaner" appearance compared with glasses washed with the commercial product.

TABLE 5

Component	% by weight
Ammonium fatty (C_{12-14}) alcohol (3 E.O.) sulfate	25.0
Potassium alkyl (C_{12-14}) oxyhydroxypropane sulfonate	3.8
Dimethyl alkyl amine oxide	6.0
Ethanol	5.6
Nonionic by-product (C_{12-14} fatty alcohol + C_{12-14} fatty alcohol (3 E.O.) ethoxylate)	2.5
KCl	2.5
NaCl	0.9
K_2SO_4	0.2
Water	to 100

Example 4

Samples of a surfactant system as used in Example 1 comprising the mixture according to the invention were compared with those containing only the copolymer or sodium caseinate alone.

The samples were examined on drinking glasses with respect to drain-dry performance and end

result following rinsing. The washing tests were carried out at 42°C using precleaned glasses for each test at 0.2% product concentration under various water hardness conditions. Wash and rinse times were prolonged to optimise drain-dry effect; the treated glasses which had been rinsed were drained in an inverted position following the normal procedure.

The results are shown in the following Table 6.

TABLE 6

Effect of 2.5% Gafquat-734 and/or 2.5% sodium caseinate incorporated in base formulation
D.D.=Drain-dry

	6—6.5°H Water		11.4—12.3°H Water		18°H Water	
Agent	D.D. performance	End result	D.D. performance	End result	D.D. performance	End result
2.5% Gafquat-734 + 2.5% Na-caseinate	Unidirectionally D.D., wavy; tends to break from rim; acceptable	very good; negligible spotting	Unidirectionally D.D., slightly uneven; breaking slightly from rim later; acceptable	very good; negligible spotting	Unidirectionally D.D., slightly uneven; breaking slightly from rim; acceptable	good; some spots near rim
2.5% Gafquat-734	Multi-directionally D.D., leaving spots & trails; unacceptable	very good; negligible spotting	initially uni-directionally D.D., but later breaks all over from rim; unacceptable	fair; some considerable spotting near rim	unidirectionally D.D., slightly uneven inside; acceptable	fairly good; some spots and trails
2.5% Na-caseinate	mainly hydro-phylic; unacceptable	good; faint film; trace spots	mainly hydro-phylic; unacceptable	poor; extensive spotting and some film	slightly uneven and slightly slower on in-side, other-wise OK	some spotting

The above results show that the composition of the invention is clearly superior in performance to the compositions outside the invention.

The results also indicate that there is a synergistic effect of sodium caseinate and Gafquat—734, a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate.

Claims

1. A light duty, hand dishwashing, liquid detergent composition comprising

(a) from 2% to 50% by weight of an anionic surfactant compound, nonionic surfactant compound, or mixtures thereof;

(b) from 0.1% to 10% by weight of a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate having a molecular weight from 40,000 to 1,500,000, or mixtures thereof; and

(c) from 0.5% to 5% by weight of an alkali metal salt of casein; the percentages expressed being based on the total weight of the composition.

2. A liquid detergent composition according to claim 1 wherein component (c) is sodium caseinate.

3. A liquid detergent composition according to claim 1 wherein the anionic surfactant is a water-soluble hydrocarbon sulphate having the formula $R_1O(C_2H_4O)_nSO_3M$ wherein R_1 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 22 carbon atoms; n is an integer from 0 to 15; and M is a cation of sodium, potassium or ammonium.

4. A liquid detergent composition according to claim 1 wherein the anionic surfactant is a compound of the formula

$$R_2—SO_3M$$

wherein R_2 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 24 carbon atoms, or an alkyl benzene radical having from 8 to 18 carbon atoms in the alkyl group; and M is a cation of sodium, potassium, ammonium, magnesium or calcium.

5. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a water-soluble tertiary amine oxide having the general formula $R_3R_4R_5N—O$ wherein R_3 represents a high molecular straight or branched, saturated or unsaturated, aliphatic hydrocarbon, hydroxyhydrocarbon, or alkoxyhydrocarbon radical, having a total of 8 to 24 carbon atoms, and R_4 and R_5, which may be the same or different, represent each a methyl, ethyl, hydroxymethyl or hydroxyethyl radical.

6. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a compound of the formula

$$R_3R_4R_5P—O$$

wherein R_3 represents a high molecular, straight or branched, saturated or unsaturated, aliphatic hydrocarbon, hydroxyhydrocarbon, or alkoxyhydrocarbon radical, having a total of from 8 to 24 carbon atoms; and R_4 and R_5, which may be the same or different, represent each a methyl, ethyl, hydroxymethyl or hydroxyethyl radical.

7. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a compound of the formula

$$R_6—CO—N(H)_{m-1}(R_7OH)_{3-m}$$

wherein R_6 is a saturated or unsaturated, aliphatic hydrocarbon radical having from 7 to 21 carbon atoms; R_7 is a methylene or ethylene group; and m is an integer from 1 to 3.

8. A liquid detergent composition according to claim 7 wherein the nonionic surfactant is lauryl diethanolamide.

9. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a water-soluble condensation product of from 3 to 25 moles of an alkylene oxide and 1 mole of an organic, hydrophobic aliphatic or alkyl aromatic compound having 8 to 24 carbon atoms and at least one reactive hydrogen atom.

10. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a water-soluble condensation product of ethylene oxide with (a) an aliphatic alcohol having from 10 to 18 carbon atoms; (b) an alkylphenol; (c) a fatty acid ester; (d) a polyethenoxy ester or an ester formed by reacting ethylene oxide with a carboxylic acid; (e) a fatty acyl alkanolamide of the type C_{7-17} alkyl —CO—NHC_2H_4OH or C_{7-17} alkyl —CO—$N(C_2H_4OH)_2$ or (f) a C_8—C_{18} alkyl-, C_{8-18} alkenyl-, or C_{5-18} alkylaryl amine.

11. A liquid detergent composition according to claim 1, comprising:

(a) from 10% to 30% of an anionic surfactant compound, or a mixture of anionic surfactant compounds;

(b) from 1% to 10% of a nonionic surfactant compound, or a mixture of nonionic surfactant compounds;

(c) from 0.5% to 3.0% of a copolymer of N-vinylpyrrolidone and dimethylamino-ethyl-methacrylate having a molecular weight between 40,000 and 1.5 million; and

(d) from 1.0% to 3.0% of sodium caseinate; the percentages expressed being based on the total weight of the composition.

Revendications

1. Une composition détergente liquide douce pour le lavage de la vaisselle à la main, comprenant:

a) de 2 à 50% en poids d'un composé tensio-actif anionique, d'un composé tensio-actif non-ionique ou de leurs mélanges;

b) de 0,1% à 10% en poids d'un copolymère de la N-vinylpyrrolidone et du méthacrylate de diméthylaminoéthyle, ayant un poids moléculaire de 40.000 à 1.500.000, ou de leurs mélanges; et

c) de 0,5% à environ 5% en poids d'un sel de métal alcalin de la caséine; les pourcentages exprimés se rapportant au poids total de la composition.

2. Une composition détergente liquide selon la revendication 1, dans laquelle le composant c) est le caséinate de sodium.

3. Une composition détergente liquide selon la revendication 1, dans laquelle l'agent tensio-actif anionique est un hydrocarbure sulfaté hydrosoluble répondant à la formule $R_1O(C_2H_4O)_nSO_3M$ dans laquelle R_1 est un radical hydrocarboné aliphatique à chaîne droite ou ramifiée, saturé ou insaturé, contenant de 8 à 22 atomes de carbone, n est un nombre allant de 0 à 15 et M est un cation de sodium, de potassium ou d'ammonium.

4. Une composition détergente liquide selon la revendication 1, dans laquelle l'agent tensio-actif anionique est un composé de formule

$$R_2—SO_3M$$

dans laquelle R_2 est un radical hydrocarboné aliphatique à chaîne droite ou ramifiée, saturé ou insaturé, contenant de 8 à 24 atomes de carbone, ou un radical d'alkylbenzène contenant de 8 à 18 atomes de carbone dans le groupe alkyle; et M est un cation de sodium, de potassium, d'ammonium, de magnésium ou de calcium.

5. Une composition détergente liquide selon la revendication 1, dans laquelle l'agent tensio-actif non-ionique est un oxyde d'amine tertiaire hydrosoluble répondant à la formule générale $R_3R_4R_5N—O$ dans laquelle R_3 représente un radical hydrocarboné, hydroxyhydrocarboné ou alkyloxyhydrocarboné à haut poids moléculaire, à chaîne droite ou ramifiée, saturé ou insaturé, contenant au total 8 à 24 atomes de carbone, et R_4 et R_5, qui peuvent être identiques ou différents, représentent chacun un radical méthyle, éthyle, hydroxyméthyle ou hydroxyéthyle.

6. Une composition détergente liquide selon la revendication 1, dans laquelle l'agent tensio-actif non-ionique est un composé de formule

$$R_3R_4R_5P—O$$

dans laquelle R_3 représente un radical aliphatique hydrocarboné, hydroxyhydrocarboné ou alkyloxyhydrocarboné à haut poids moléculaire, à chaîne droite ou ramifiée, saturé ou insaturé, contenant au total de 8 à 24 atomes de carbone; et R_4 et R_5, qui peuvent être identiques ou différents, représentent chacun un radical méthyle, éthyle, hydroxyméthyle ou hydroxyéthyle.

7. Une composition détergente liquide selon la revendication 1, dans laquelle l'agent tensio-actif non-ionique est un composé de formule

$$R_6—CO—N(H)_{m-1}(R_7OH)_{3-m}$$

dans laquelle R_6 est un radical hydrocarboné aliphatique saturé ou insaturé contenant de 7 à 21 atomes de carbone; R_7 est un groupe méthylène ou éthylène; et m est un nombre allant de 1 à 3.

8. Une composition détergente liquide selon la revendication 7, dans laquelle l'agent tensio-actif non-ionique est le lauryldiéthanolamide.

9. Une composition détergente liquide selon la revendication 1, dans laquelle l'agent tensio-actif non-ionique est un produit de condensation hydrosoluble de 3 à 25 moles d'un oxyde d'alkylène et d'une mole d'un composé organique aliphatique ou alkylaromatique hydrophobe contenant de 8 à 24 atomes de carbone et au moins au atome d'hydrogène réactif.

10. Une composition détergente liquide selon la revendication 1 dans laquelle l'agent tensio-actif non-ionique est un produit de condensation hydrosoluble de l'oxyde d'éthylène avec a) un alcool aliphatique contenant de 10 à 18 atomes de carbone; b) un alkylphénol; c) un ester d'acide gras; d) un polyéthénoxyester ou un ester formé par réaction de l'oxyde d'éthylène avec un acide carboxylique; e) un acylalcanolamide gras du type (alkyle en C7—C17)—CO—NHC_2H_4OH ou (alkyle en

C7—C17)—CO—N($C_2H_4OH)_2$; ou f) une (alkyle en C8—C18)—, (alcényle en C8—C18)— ou [(alkyle en C5—C8)-aryl]-amine.

11. Une composition détergente liquide selon la revendication 1, comprenant:

a) de 10% à 30% d'un composé tensio-actif anionique ou d'un mélange de composés tensio-actifs anioniques;

b) de 1% à 10% d'un composé tensio-actif non-ionique ou d'un mélange de composés tensio-actifs non-ioniques;

c) de 0,5% à 3,0% d'un copolymère de la N-vinylpyrrolidone et du méthacrylate de diméthylamino-éthyle à un poids moléculaire de 40.000 à 1,5 million; et

d) de 1,0% à 3,0% de caséinate de sodium; les pourcentages exprimés se rapportant au poids total de la composition.

Patentansprüche

1. Flüssiges Reinigungsmittel für das Geschirrspülen von Hand für geringe Beanspruchung, umfassend

a) 2 bis 50 Gew.-% einer anionischen Tensidverbindung, nichtionischen Tensidverbindung oder deren Gemischen,

b) 0,1 bis 10 Gew.-% eines Copolymeren von N-Vinylpyrrolidon und Dimethylaminoethylmethacrylat mit einem Molekulargewicht von 40 000 bis 1 500 000 oder deren Gemischen und

c) 0,5 bis etwa 5 Gew.-% eines Alkalimetallsalzes von Casein, wobei die genannten Prozentsätze auf das Gesamtgewicht des Mittels bezogen sind.

2. Flüssiges Reinigungsmittel nach Anspruch 1, worin die Komponente c) Natriumcaseinat ist.

3. Flüssiges Reinigungsmittel nach Anspruch 1, worin das anionische Tensid ein wasserlösliches Kohlenwasserstoffsulfat der Formel $R_1O(C_2H_4O)_nSO_3M$ ist, worin R_1 ein geradkettiger oder verzweigter, gesättigter oder ungesättigter aliphatischer Kohlenwasserstoffrest mit 8 bis 22 Kohlenstoffatomen ist, n eine ganze Zahl von 0 bis 15 ist und M ein Kation von Natrium, Kalium oder Ammonium ist.

4. Flüssiges Reinigungsmittel nach Anspruch 1, worin das anionische Tensid eine Verbindung der Formel

$$R_2—SO_3M$$

ist, worin R_2 ein geradkettiger oder verzweigter, gesättigter oder ungesättigter aliphatischer Kohlenwasserstoffrest mit 8 bis 24 Kohlenstoffatomen oder ein Alkylbenzolrest mit 8 bis 18 Kohlenstoffatomen in der Alkylgruppe ist und M ein Kation von Natrium, Kalium, Ammonium, Magnesium oder Calcium ist.

5. Flüssiges Reinigungsmittel nach Anspruch 1, worin das nichtionische Tensid ein wasserlösliches tertiäres Aminoxid der allgemeinen Formel $R_3R_4R_5N—O$ ist, worin R_3 ein hochmolekularer, geradkettiger oder verzweigter, gesättigter oder ungesättigter aliphatischer Kohlenwasserstoff-, Hydroxykohlenwasserstoff- oder Alkyloxykohlenwasserstoffrest mit, insgesamt 8 bis 24 Kohlenstoffatomen ist und R_4 und R_5, die gleich oder verschieden sein können, jeweils einen Methyl-, Ethyl-, Hydroxymethyl- oder Hydroxyethylrest bedeuten.

6. Flüssiges Reinigungsmittel nach Anspruch 1, worin das nichtionische Tensid eine Verbindung der Formel

$$R_3R_4R_5P—O$$

ist, worin R_3 einen hochmolekularen geradkettigen oder verzweigten, gesättigten oder ungesättigten aliphatischen Kohlenwasserstoff-, Hydroxykohlenwasserstoff; oder Alkyloxykohlenwasserstoffrest mit insgesamt 8 bis 24 Kohlenstoffatomen bedeutet und R_4 und R_5, die gleich oder verschieden sein können, jeweils einen Methyl-, Ethyl-, Hydroxymethyl- oder Hydroxyethylrest bedeutetn.

7. Flüssiges Reinigungsmittel nach Anspruch 1, worin das nichtionische Tensid eine Verbindung der Formel

$$R_6—CO—N(H)_{m-1}(R_7OH)_{3-m}$$

ist, worin R_6 ein gesättigter oder ungesättigter aliphatischer Kohlenwasserstoffrest mit 7 bis 21 Kohlenstoffatomen ist, R_7 eine Methylen- oder Ethylengruppe und m eine ganze Zahl von 1 bis 3 ist.

8. Flüssiges Reinigungsmittel nach Anspruch 7, worin das nichtionische Tensid Lauryldiethanolamid ist.

9. Flüssiges Reinigungsmittel nach Anspruch 1, worin das nichtionische Tensid ein wasserlösliches Kondensationsprodukt von 3 bis 25 Mol eines Alkylenoxids und 1 Mol einer organischen hydrophoben aliphatischen oder alkylaromatischen Verbindung mit 8 bis 24 Kohlenstoffatomen und wenigstens einem reaktiven Wasserstoffatom ist.

10. Flüssiges Reinigungsmittel nach Anspruch 1, worin das nichtionische Tensid ein wasserlös-

liches Kondensationsprodukt von Ethylenoxid mit (a) einem aliphatischen Alkohol mit 10 bis 18 Kohlenstoffatomen, (b) einem Alkylphenol, (c) einem Fettsäureester, (d) einem Polyethenoxyester oder einem durch Umsetzen von Ethylenoxid mit einer Carbonsäure gebildeten Ester, (e) einem Fettacylalkanolamid des Typs C_{7-17}-Alkyl—CO—NHC_2H_4OH oder C_{7-17}-Alkyl—CO—$N(C_2H_4OH)_2$ oder (f) einem C_{-18}-Alkyl-, C_{8-18}-Alkenyl- oder C_{5-8}-Alkylarylamin ist.

11. Flüssiges Reinigungsmittel nach Anspruch 1, umfassend

(a) 10 bis 30% einer anionischen Tensidverbindung oder eines Gemisches anionischer Tensidverbindungen,

(b) 1 bis 10% einer nichtionischen Tensidverbindung oder eines Gemischs nichtionischer Tensidverbindungen,

(c) 0,5 bis 3,0% eines Copolymeren von N-Vinylpyrrolidon und Dimethylamino-ethylmethacrylat mit einem Molekulargewicht zwischen 40 000 und 1 500 000 und

(d) 1,0 bis 3,0% Natriumcaseinat, wobei die genannten Prozentsätze auf das Gesamtgewicht des Mittels bezogen sind.