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LOW-FOAMING DETERGENT COMPOSITIONS
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18 Claims

ABSTRACT OF THE DISCLOSURE

Low-foaming detergent composition comprising a synthetic organic detergent, alkaline builder salts, and a 1,1 dialkyl urea as a foam suppressing agent.

BACKGROUND OF THE INVENTION

The present invention relates to new synthetic detergent compositions and more particularly to compositions based on anionic detergents, nonionic detergents, and mixtures thereof having improved properties. Aqueous solutions of these detergent compositions are characterized by a very low degree of foam formation under conditions of vigorous and continuous agitation.

Although the formation of abundant foam has been considered a desirable property of a washing agent as an indication of lasting detergent power, it is also recognized that copious suds formation is not necessarily a measure of detergent effectiveness. In fact, with certain household and commercial appliances and apparatus, production of copious suds is a handicap rather than an advantage. Compositions of the present invention not only do not foam excessively, but they also have superior detergent properties.

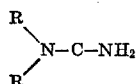
SUMMARY OF THE INVENTION

Urea and certain lower alkyl derivatives thereof have heretofore been used with certain surface-active agents chiefly in large proportions as cheap and innocuous fillers and as solubilizing agents. It has now been discovered that the presence of a 1,1 dialkyl urea in detergent compositions consisting essentially of anionic sulfated and sulfonated and nonionic surfactants is effective to achieve a significant enhancement in surface-active properties and a reduction in foaming. More particularly, the improved detergent compositions consist essentially of water-soluble anionic surfactants, nonionic surfactants, alkaline builder salts, and a minor proportion of a 1,1 dialkyl urea effective to suppress the formation of foam in the detergent compositions.

The new detergent compositions generate less foam than current available products, and prevent over-foaming in soft water areas. In addition, the new detergent compositions permit the consumer to use higher levels of detergent before over-foaming occurs.

Illustrative of the foam suppressing additives of the present invention are the higher dialkyl substituted urea compounds wherein the alkyl substituents have 8 to 18 carbon atoms. Suitable examples of such compounds are 1,1 di (2 ethyl hexyl) urea; 1,1 dihydrogenated tallow urea; and 1,1 dicoco urea.

These 1,1 dialkyl ureas may be prepared by reacting secondary amines with urea. They are represented by the formula



wherein R is an alkyl group of between 8 and 18 carbon atoms.

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The novel compositions of the present invention contain as the active ingredient the anionic sulfated and sulfonated detergents, and nonionic detergents including suitable mixtures thereof. Included therein are the aliphatic sulfated or sulfonated compounds, such as the aliphatic acyl-containing compounds wherein the acyl radical has between 8 and 22 carbon atoms, and, more particularly, the aliphatic carboxylic ester type, containing at least about 10 and preferably between 12 and 26 carbon atoms to the molecule. Among the aliphatic detergent compounds, it is preferred to use the sulfated aliphatic compounds having between 12 and 22 carbon atoms. As suitable examples of aliphatic detergents, there may be mentioned the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g., coconut oil monoglyceride monosulfate, tallow-di-glyceride monosulfate; the long chain pure or mixed higher alkyl-sulfates, e.g., lauryl sulfate, cetyl sulfate, higher fatty alcohol sulfates derived from coconut oil; the hydroxy sulfonated higher fatty acid esters, e.g., higher fatty acid esters of 2,3 dihydroxy propane sulfonic acid; the higher fatty acid esters of low molecular weight alkylol sulfonic acids, e.g., oleic ester of isethionic acid; the higher fatty acid ethanolamide sulfates; the higher fatty acid amides of amino alkyl sulfonic acids, e.g., lauric amide of taurine, and the like.

It is a feature of this invention that the effects are particularly enhanced with the alkyl aryl sulfonate detergents. These aromatic sulfonate detergents are also known in the art. They may be mononuclear or polynuclear in structure. More particularly, the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresols, naphthalene, etc. The alkyl substituent on the aromatic nucleus may vary widely, as long as the desired detergent power of the active ingredient is preserved.

More specific examples of suitable alkyl aromatic sulfonate detergents are the higher alkyl aromatic sulfonates. The higher alkyl substituent may be branched or straight-chain in structure; it comprises such groups as octyl, decyl, dodecyl, tridecyl, keryl, pentadecyl, and hexadecyl, mixed long-chain alkyls derived from long-chain fatty materials, cracked paraffin wax olefins, polymers of mono olefins, etc. Preferred examples of this class are the higher alkyl mononuclear aryl sulfonates wherein the alkyl group has about 8 to about 22, and preferably between 12 and 18 carbon atoms. More particularly, it is preferred to use the higher alkyl benzene sulfonates wherein the higher alkyl group averages between 12 and 16 carbon atoms. For example, propylene may be polymerized to the tetramer and condensed with benzene in the presence of a Friedel-Crafts catalyst to yield essentially the dodecyl benzene derivative which is suitable for sulfonation to the desired sulfonate compounds.

These various anionic detergents are generally used in the form of their water-soluble salts, such as the alkali metal, alkaline earth metal, ammonium, amine, and alkylolamine salts. While the sodium, potassium, ammonium, and alkylolamine (e.g., mono-, di-, and tri-ethanol-amine) salts are preferred ordinarily, other salts such as the lithium, calcium, and magnesium salts may be used if desired. For general use, it is ordinarily preferred to use the sodium and potassium salts. For certain specialized uses, it may be preferred to select the ammonium and alkylolamine salts in view of their generally greater solubility in aqueous solution. The concentration of these water-soluble salts (including suitable mixtures thereof) in the detergent compositions of the present invention is generally at least 5% by weight of total solids, and preferably from about 5-50%. With built compositions, particularly in particulate form, an active ingredient content of 5-50%, and preferably about 10-40%, yields highly

satisfactory results. Compositions with very high concentrations of these active ingredients are prepared for specialized use generally. Thus in liquid detergent compositions, any suitable concentrations may be employed, e.g., from about 5 to about 50% of the weight of the total liquid detergent composition.

Nonionic surfactants are also suitable in the practice of the present invention. One class of compounds comprises surfactants having alkylene oxide groups which are hydrophilic in nature combined with an organic hydrophobic group. The preferred class includes the ethoxylation products of hydrophobic hydroxyl compounds such as long chain aliphatic compounds and alkylaromatic compounds. Among such materials are the poly (ethylene oxide) condensates of aliphatic alcohols having, for example, 8 to 18 carbon atoms, such as lauryl or tallow alcohols, combined with, for example, 3-30 moles of ethylene oxide for each mole of the long chain alcohol. The corresponding alkyl mercaptans, when condensed with ethylene oxide, are also admirably suitable in the compositions of the present invention.

Other non-ionic detergents are the polyethylene oxide condensates of alkyl phenols, having, for example, an alkyl group of about 6 to 12 carbon atoms (e.g., nonyl phenol) in which there are a plurality of ethylene oxide units (e.g., up to 30) per mole of alkyl phenol. Another class of non-ionic detergents includes the polyethylene oxide condensates of higher glycols, which may be made, for example, by condensing ethylene oxide with a polypropylene glycol made by reacting propylene oxide and propylene glycol, said polypropylene glycol having a molecular weight of 1500-1800. Again, the non-ionic detergent may be made by condensing ethylene oxide with a water-insoluble reaction product (e.g., of molecular weight about 3000) of a diamine (e.g., ethylene diamine) and excess propylene oxide, to incorporate about 40-80% of ethylene oxide in the final condensation product. Ethoxylation products of compounds containing mercapto-, rather than hydroxyl, groups may also be used.

Other suitable nonionic compounds are the polyoxyalkylene esters of the organic acids such as the higher fatty acids, the rosin acids, tall oil acids, acids from petroleum oxidation products, etc. These esters will usually contain from about 10 to 22 carbon atoms in the acid moiety and from about 12 to about 30 moles of ethylene oxide or its equivalent.

Still other nonionic surfactants are the alkylene oxide condensates with higher fatty acid amides. The fatty acid group will generally contain from about 8 to 22 carbon atoms, and this will be condensed with about 10 to about 50 moles of ethylene oxide as the preferred illustration. The corresponding carboxamides and sulfonamides may also be used as substantial equivalents.

In liquid detergents, the active ingredient (surfactant) should preferably be in the form of a highly water soluble salt, e.g., ammonium, mono-, di-, and triethanol amine salts. The liquid detergent composition may be prepared in dilute or concentrated aqueous solution with or without the presence of a lower molecular weight aliphatic alcohol such as ethyl alcohol, propylene glycol, etc.

The amount of nonionic surfactant that can be present in compositions of the present invention ranges from about 2% to 40%, preferably from about 5% to about 15%, by weight, based on the final composition.

The presence of conventional amounts of inorganic salt detergent builders, such as various water-soluble inorganic polyphosphates, sulfates, silicates, borates, and carbonates, does not adversely affect the foaming and detergent properties of the present composition. These builders, the total amount of which may range by weight based on finished composition, from about 40% to about 90%, but more usually between 45% to about 85%, contribute their different specific effect toward a more satisfactory washing treatment of soiled clothing, dishes, etc.

The most common alkaline builder salts are the phosphates, which inhibit the precipitation of alkaline earth materials, such as calcium and magnesium compounds, in aqueous media. The alkali metal salts, and, most particularly, the potassium salts, of the chain polyphosphates are usually employed. Examples of such compounds include: potassium tripolyphosphate, potassium acid tripolyphosphate, tetrapotassium pyrophosphate, potassium hexametaphosphate, potassium tetraphosphate, and the like. The phosphates are either crystalline substances or glassy, amorphous products. Any water-soluble glassy polyphosphate with mole ratios of alkali oxide to phosphorous oxide of between about 5:3 and about 1:1, and an average chain length of from 3 to several thousands, is suitable for use as a builder in the compositions of the present invention. These phosphates may be the sole builder salts or may be used in combination with any of the aforementioned builder salts.

Where a phosphate free detergent composition is desired, the principal builder salts used are the soluble alkali-metal silicates. Suitable silicates are those having an alkali oxide to silica ratio within a range of about 1:1 to about 1:4, and preferably from about 1:2 to about 1:3. Other builder salts which may be combined with the silicates in phosphate-free compositions include water-soluble alkali metal salts of borates, carbonates, and sulfates.

Other functional materials which optionally may be present in the compositions of the present invention include soil suspending agents, brighteners, thickening agents, coloring materials, and perfumes. These additives are generally present in amounts of less than 5% of the total detergent composition.

The soil suspending agents are generally water-soluble or hydrophilic polymeric substances such as the lower alkyl cellulose esters, e.g., methyl cellulose and ethyl cellulose; hydroxyalkyl cellulose esters, e.g., hydroxyethyl cellulose, cellulose ethane sulfonic acid, cellulose glycolic acid; carboxy lower alkyl cellulose compounds, e.g., sodium carboxy methyl cellulose, potassium carboxy methyl cellulose, sodium carboxy propyl cellulose, and the like; water-soluble or dispersible synthetic polymeric materials which may be homopolymers, copolymers, graft copolymers, terpolymers, interpolymers, and the like and are illustrated by polyvinyl pyrrolidone, polyvinyl alcohol, hydrolyzed polyvinyl acetate, polyacrylic acid, polyacrylamide; maleic anhydride copolymers with alkyl vinyl esters, e.g., methyl vinyl ester; natural products such as starch, and the like.

The brighteners that can be used include various well known types of the more commonly used products. Such types, which are by no means limiting, include the coumarin types, the triazolyl stilbene types, the stilbene cyanuric types, the acylamino stilbene types, and the like.

The amount of the substituted urea foam suppressing additives is generally minor in proportion to the total detergent composition. Particularly effective results have been achieved wherein the 1,1 dialkyl urea is present in amounts between ½% and 15% of the total detergent composition, although it is preferred generally to use from about 1% to about 5% additive. The optimum amount of additive and its ratio to the active ingredients will vary according to the specific materials, the contemplated field of application, and manner of use.

The additives may be incorporated with the active ingredient at any point during the manufacturing process at which subsequent operations will not adversely modify the properties of the detergent compositions. A variety of procedures which have proved to be convenient, economical, and productive of best results are: the additives may be added to a hot aqueous slurry of about 40-50% solids concentration comprising the active ingredient with vigorous stirring to form a smooth, uniform, and homo-

geneous paste; the additives may be dissolved in a suitable solvent and added to the slurry of the active ingredient; a mixture or emulsion of the additives in water with a minor proportion of the active ingredient may be incorporated into the slurry; or the additives may be incorporated in the detergent composition by a post treatment of spray-dried detergent particles, etc.

Thereafter, these compositions may be prepared in the form of solutions, pastes, or as dry or partially hydrated solid products, preferably in a finely divided condition. It is preferred to prepare the products in particulate form. Accordingly, the slurry of the detergent composition may be subjected to any suitable drying operations and converted to particle form. The mixture may thus be subjected to conventional spray-drying, roll-drying, or drum-drying operations utilizing temperatures above about 212° F. to obtain homogeneous deterative particles.

In the foam height tests tabulated *infra*, detergent compositions A, B, and C were prepared by mixing the synthetic control detergent and a 1,1 dialkyl urea in the specified amounts.

To determine the degree of foam inhibition, foam heights were measured under simulated household-use conditions in a tumbler-type washing machine test. The washing machine test was conducted in the following manner:

To a tumbler-type washing machine was charged 26 liters of water (150 p.p.m. hardness) at 120° F. containing 0.15% by weight of the test formulation. Then three pounds of clean terry towels were added. The foam height, in inches, as viewed through the door window, is measured periodically over a 10-minute wash cycle.

The results of the tests are tabulated below.

In the tables, identification of the 1,1 dialkyl urea used as foam suppressors is as follows:

- A is 1,1 di (2 ethyl hexyl) urea
- B is 1,1 dicoco urea
- C is 1,1 dihydrogenated tallow urea

TABLE I.—FOAM SUPPRESSANT EFFECTS OF ANIONIC-DIALKYL UREA SYSTEMS

Time	Control	1% A	1% B	1% C
0.....	3	¾	½	2
1.....	3½	1	¾	2½
2.....	4½	1	¾	2½
3.....	6½	1	¾	3
4.....	8	1¼	1	3½
5.....	10	1½	1	4
7½.....	10	1½	1½	4½
10.....	10	1½	1½	5½

TABLE II.—FOAM SUPPRESSANT EFFECTS OF NONIONIC-DIALKYL UREA SYSTEMS

Time	Control	1% A	1% B	1% C
0.....	2½	½	½	½
1.....	3½	½	½	½
2.....	4½	½	½	½
3.....	6	½	½	½
4.....	6½	¾	½	½
5.....	8	¾	½	½
7½.....	10	1	¾	1
10.....	10	1	¾	1½

The anionic detergent control composition of Table I, consists of the following:

	Percent
Tridecyl benzene sulfonate	10
Neodol 4511 ¹	2
CB soap ²	2
Sodium tripolyphosphate	45
Sodium silicate	7.5
Water	10
Sodium carboxymethyl cellulose	0.5
Sodium sulfate	23

¹ Ac₁₄-C₁₅ linear primary alcohol with 11 ethoxy groups, made by Shell Chemical Co.

² A mixture of coco and tallow soaps.

The nonionic detergent control composition of Table II, consists of the following:

	Percent
Neodol 4511	10
Sodium tripolyphosphate	45
Sodium silicate	7.5
Water	10
Polyvinyl alcohol	0.2
Sodium carboxy methyl cellulose	0.5
Optical brighteners	0.3
Sodium sulfate	27

Table III shows a comparison of the anionic detergent of Table I containing the foam suppressors of the instant invention with a commercial low foaming detergent. The washing machine test was conducted as above. In this table, A is the anionic detergent composition containing 1% 1,1 di (2 ethyl hexyl) urea, B is the anionic detergent composition containing 1% 1,1 di coco urea, and C is the anionic detergent composition containing 1% 1,1 di hydrogenated tallow urea. D is the commercial low foaming detergent.

TABLE III.—FOAM SUPPRESSANT EFFECTS OF 1,1 DIALKYL UREAS COMPARED TO COMMERCIAL LOW-FOAMING DETERGENT

Time (min.)	Foam heights (inches)			
	A	B	C	D
0.....	¾	½	½	3
1.....	1	½	½	4½
2.....	1	¾	½	6
3.....	1	¾	½	6½
4.....	1½	1	½	7½
5.....	1½	1	½	10
7½.....	1½	1½	1	10
10.....	1½	1½	1½	10

The results of this foam test indicate that detergent compositions of the present invention are much lower foamers than the current commercially available low foaming detergent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate compositions of the present invention:

Example I

A detergent composition is prepared by forming about a 60% solids slurry containing on a solids basis about 10% sodium tridecylbenzene sulfonate, about 4% Neodol 4511, about 45% sodium tripolyphosphate, about 1% 1,1 di (2 ethyl hexyl) urea, about 7.5% sodium silicate, 0.5% sodium carboxymethyl cellulose, and about 32% sodium sulfate. This slurry is agitated at about 140° F. in a conventional soap crutcher to form a homogeneous mixture. The slurry is submitted to spray drying with heated air at a temperature of about 350° F. with a resultant moisture loss of about 40%. The resulting composition is recovered in the form of beads, and possesses a high degree of deterative properties and a low degree of foaming properties in both hard and soft water.

Example II

Using the procedure of Example I, an improved phosphate free detergent composition is prepared from the following components:

	Percent
Sodium dodecyl benzene sulfonate	35
Sodium silicate	40
Sodium sulfate	22
1,1 dihydrogenated tallow urea	2
Sodium carboxy methyl cellulose	1

Example III

An improved liquid detergent composition is prepared from the following components:

	Percent	
Neodol 4511	10	5
Potassium tetrapyrophosphate	25	
Sodium silicate	7.5	
Optical brighteners	0.2	
Sodium carboxy methyl cellulose	0.3	
Resin stabilizer (ethylene-maleic anhydride polymer)	1.0	10
1,1 dicoco urea	0.5	
Water	Q.s.	100

The improved detergent formulations of this invention are suitable for use in dilute aqueous solutions in a variety of washing appliances, such as rotary drum or tumbler-types washers, top-loading agitator washers, bottle washers, etc. When so employed, little or no foam is formed, with no adverse effect on the detergency characteristics, in operating at temperatures from about 65 to 140° F., as commonly used in washing practice. This suppression of suds in accordance with the invention permits employing a larger concentration of the active detergent in the preparation of washing solutions, as compared with the concentrations heretofore considered permissible maxima for tumbler-washer operations. Furthermore, the tendency to froth upon rinsing is substantially obviated.

The low foaming detergent formulations of the present invention can be used in tumbler-type washers, as well as in any other washing equipment which utilizes conventional high foaming organic detergent materials. In fact, these formulations can be used to reduce foaming in a number of solutions and emulsions which, upon agitation, produce unduly high suds levels; causing spillage and pumping difficulties, and interfering with a satisfactory filling of containers.

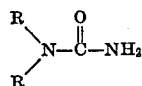
What is claimed is:

1. A low-foaming detergent composition consisting essentially of:

(A) a synthetic organic detergent selected from the group consisting of anionic and nonionic detergents and mixtures thereof;

(B) about 40 to about 90% by weight of inorganic water-soluble alkaline builder salts; and

(C) about 0.5 to about 15% by weight of a foam suppressing agent represented by the formula:



wherein R is an alkyl group of between 8 and 18 carbon atoms.

2. The detergent composition of claim 1 wherein the synthetic organic detergent is a nonionic detergent.

3. The detergent composition of claim 1 wherein the foam suppressing agent is 1,1 di (2 ethyl hexyl) urea.

4. The detergent composition of claim 1 wherein the foam suppressing agent is 1,1 di coco urea.

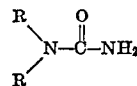
5. The detergent composition of claim 1 wherein the foam suppressing agent is 1,1 dihydrogenated tallow urea.

6. A low-foaming detergent composition consisting essentially of:

(A) a synthetic organic detergent selected from the group consisting of anionic and nonionic detergents and mixtures thereof;

(B) about 40 to about 90% by weight of inorganic water-soluble alkaline builder salt selected from the group consisting of water-soluble alkali metal borates, carbonates, silicates, sulfates, and mixtures thereof; and

(C) about 0.5 to about 15% by weight of a foam suppressing agent represented by the formula:



wherein R is an alkyl group of between 8 and 18 carbon atoms.

7. The detergent composition of claim 6 wherein the foam suppressing agent is 1,1 di (2 ethyl hexyl) urea.

8. The detergent composition of claim 6 wherein the foam suppressing agent is 1,1 dicoco urea.

9. The detergent composition of claim 6 wherein the foam suppressing agent is 1,1 dihydrogenated tallow amine.

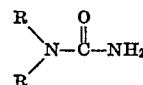
10. The detergent composition of claim 6 wherein the inorganic alkaline builder is sodium silicate.

11. A low-foaming detergent composition consisting essentially of:

(A) from about 10 to about 40% of a synthetic organic detergent selected from the group consisting of anionic and nonionic detergents and mixtures thereof;

(B) from about 50 to about 90% of inorganic water-soluble alkaline builder salts; and

(C) from about 1/2 % to about 10% of a foam suppressing agent represented by the formula:



wherein R is an alkyl group of between 8 and 18 carbon atoms.

12. The detergent composition of claim 11 wherein the inorganic water-soluble alkaline builder salt is a water-soluble potassium polyphosphate.

13. The detergent composition of claim 12 wherein the water-soluble potassium polyphosphate is potassium triphosphate.

14. The detergent composition of claim 11 wherein the foam suppressing agent is 1,1 di (2 ethyl hexyl) urea.

15. The detergent composition of claim 11 wherein the foam suppressing agent is 1,1 dicoco urea.

16. The detergent composition of claim 11 wherein the foam suppressing agent is 1,1 dihydrogenated tallow area.

17. The detergent composition of claim 11 wherein the inorganic, water-soluble alkaline builder is a mixture of sodium silicate and sodium sulfate.

18. The detergent composition of claim 11 wherein the inorganic, water-soluble alkaline builder is sodium silicate.

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