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3,320,172

## DETERGENT COMPOSITION

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The present application is a continuation-in-part of patent application No. 162,276, filed Dec. 26, 1961, now abandoned.

The present invention relates to synthetic detergent compositions and, more particularly to anionic detergent compositions having improved properties.

In formulating detergent compositions, it is now customary to add to the synthetic detergents which form the basic active ingredient, a variety of additives or builders, the purpose of which is to impart to the formulations some particularly desirable properties or to enhance those they already possess. Thus, heavy and medium duty commercial detergent compositions, e.g. those designed for the laundering of heavily soiled linens and cottons, will generally contain certain amounts of alkali metal polyphosphates, the effect of which is generally to enhance the deterative power of the anionic detergents in the formulation. Light duty detergents, e.g. those used for dishwashing and for the laundering of lightly soiled garments, have generally been formulated in the liquid form and without the benefit of builders of the type of the aforementioned phosphates; but it is generally desirable that these, too, contain additives directed toward increasing the foaming and deterative properties, the stability, colour, clarity, etc., of the solution. It is well known that it has been difficult to include builders of the phosphate type in liquid detergents, primarily because the large quantities of phosphates required for heavy duty performance tend to separate out of solution and thereby to endanger the stability of the liquid detergent mixture.

We have found that by incorporating with anionic detergents exceedingly small quantities of certain inorganic additives, we can enhance the detergency and foaming properties of synthetic detergent compositions to a level where the addition of builders, particularly polyphosphate builders, can be partially or completely dispensed with.

Accordingly, the present invention provides synthetic detergent compositions containing anionic organic detergents and a foaming and detergency enhancing additive selected from the group of compounds consisting of water-soluble compounds of cerium, molybdenum and tungsten.

The anionic detergents used as the active ingredient in the compositions of the present invention include the water-soluble anionic sulphonated and sulphated detergent compounds and suitable mixtures thereof. Included therein are, in the first place, the alkyl aryl sulphonate detergents represented by the general formula  $R-Ar-SO_3M$ , wherein R is a higher alkyl chain containing from 8 to 20 carbon atoms, Ar represents an aromatic group, and M represents a cation of the group consisting of hydrogen, an alkali metal, an alkaline earth metal, and the ammonium and amine radicals. The aromatic nucleus may have one or several substituents on the ring and may be derived from benzene, toluene, xylene, phenol or cresols; it may be poly-nuclear and be derived, e.g. from naphthalene. Included therein are also petroleum sulphonates obtained by sulphonating certain petroleum fractions. Preferred use, however, is made of monosulphonated alkyl benzenes containing in their chain from 10 to 16 carbons, e.g. dodecyl benzene sulphonate, and particularly the sodium, ammonium, amine and alkylolamine salts thereof.

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The sulphated detergents suitable for use in the present invention include the higher aliphatic alcohol sulphates, such as the half esters of sulphuric acid with higher aliphatic alcohols having 10 to 20 carbon atoms in their molecule, e.g. lauryl sulphate; also, sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, such as coconut oil glyceride monosulphate; they include further the sulphuric acid esters of higher alkyl ethers of polyethylene glycol, the sulphated alkyl phenol ethers of polyethylene glycol and the like.

These various detergents may be used singly or in combination, but the preferred practice, particularly in formulating detergent compositions in liquid form, is to employ a mixture of an alkyl aryl sulphonate detergent and a sulphated detergent compound in any desirable proportions, such mixtures being generally more stable in concentrated solutions than are single components. To these basic ingredients may be further added one or more of a number of well-known agents which contribute to the enhancement of certain valuable properties of the composition. Thus, it may be desirable to incorporate with the anionic detergent a fatty acid dialkylolamide, which material is known to enhance the detergency and to contribute to a very rich and stable form of foam. Certain non-ionic types of detergent compounds, such as the polyoxyethylene ethers of alkyl phenols and polyoxyethylene ethers of higher fatty alcohols, may be further added, such compounds being known to contribute to foam stability, to the solubilizing of the anionic detergent materials, and to the free rinsing qualities of the formulation. Also, the already-mentioned alkali metal polyphosphates may be added in an amount between 2% and 40% to increase further the deterative power of the formulation; as may also soil suspending agents, such as methyl cellulose or the sodium salt of carboxymethyl cellulose and the like; and optical brighteners such as the 1,2,3-triazole derivatives of 4,4'-diamino stilbene 2,2-disulphonic acid and the like.

The additive to be incorporated with the anionic detergents in accordance with this invention is a compound of the group consisting of water-soluble salts of cerium, molybdenum and tungsten. The term water-soluble will be construed in relation to the concentration of said compound in the detergent composition of this invention, which concentration will be generally exceedingly low. Among the compounds of cerium, those preferred are the compounds of tetravalent cerium, such as ceric ammonium nitrate and ceric sulphate. The tendency of molybdenum and tungsten to form complex compounds is well known. Only those compounds will be of use in the present invention which have the desirable properties of solubility, colour, non-staining, etc. While various compounds of molybdenum and tungsten may thus be useful, it is preferred to use the water-soluble salts of molybdic and tungstic acids, such as the molybdates or tungstates of alkali-metal and ammonium.

Effective amounts of the additive in the detergent compositions of this invention will vary between 0.00001% and 0.5%, but preferably between 0.0001% and 0.1% of the weight of active ingredients.

To prepare a liquid detergent composition, first a solution of the anionic detergents is prepared in a mixture of alcohol and water, and to this is added with gentle stirring a dilute solution (approximately 0.1 molar) of the additive material in dilute acid, or alkali, or water. The two solutions are then thoroughly mixed, and subsequently other ingredients, if desired, such as the above-mentioned non-ionic detergent compounds, polyphosphates, soil suspending agent, and the like, are added to the concentrated solution of the anionic compounds to produce the required formulation. The concentration

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of the anionic detergents in the formulation may vary, but will be preferably between 5% and 50% by weight of the total solution.

The following data and examples will illustrate the nature and advantages of this invention. It will be understood that the invention is not limited to the examples given hereinbelow.

The compositions of the present invention are characterized by increased foam formation, improved suds stability, and greater detergency, and also less irritancy on the skin. While the three properties first enumerated are interrelated, the precise relationship between them is not yet clear to researchers and evaluation has to be made separately by a number of practical tests. It is possible to measure directly the foam height, and a procedure which is now standard in the industry is the Ross Miles procedure in which 1 ml. of detergent solution and 99 mls. of water at 100° F. are mixed in a 500 ml. measuring cylinder by inverting 10 times and the foam height measured at 1, 3, etc. minutes. Foam persistence or stability is another measurable property. The consumer likes to see a blanket of foam which will remain to the end of the wash no matter how heavily loaded the solution is with fat and soils. In a test devised to simulate conditions encountered in practice, consistent quantitative results were obtained by introducing, by means of a burette, a fat or oil into an agitated dilute solution of a detergent, the introduction being effected below the foam blanket.

The compositions of the present invention have shown superior foaming properties when submitted to the above test as well as to the standard practical plate washing test. In this latter test, standard plates are soiled with a given weight (e.g. 5 gm.) of a standard soil, such as a coloured fat or grease, and washed by hand in a standard detergent solution, e.g. a standard weight of detergent dissolved in a standard volume of water, under controlled conditions of time, temperature, etc. The rate of foam decrease is slower with solutions containing compositions of the present invention compared with corresponding solutions of the prior art, and the number of standard plates washed accordingly higher. Moreover, the emulsification power exhibited by the compositions of this invention is visibly increased, as evidenced by another test designed to measure the speed of grease removal by various detergent compositions. In this latter test, standard microscope slides are covered with a film of hard fat, weighed and immersed in a standard detergent solution under controlled conditions, then removed, dried and reweighed, the percentage weight loss per unit time providing a measure of the speed of emulsification and removal of fat under given conditions.

Comparative results obtained in the above-outlined tests and showing the superior performance of compositions containing the additive material of the present invention are given below.

Composition	Foam Height (inches)		Fat Removed from Slides (percent)			
	Initial	Final	Minutes			
0.1% solution of sodium dodecyl benzene sulfonate.....	0.5	0.25	16	19	33	76
0.1% solution of sodium dodecyl benzene sulfonate containing 0.0001% calcium chloride.....	1.1	0.35	22	29	40	78
0.1% solution of sodium dodecyl benzene sulfonate containing 0.000006% ceric ammonium nitrate.....	2.0	1.75	31	39	63	85

The following comparison is between formulated detergent compositions with and without the additive of this invention. Compositions A, B, C and D are respec-

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tively the ones described in Examples 1, 2, 3 and 4 below:

Composition:	Number of dishes washed before foam broke	
	Formulation without additive	Formulation with additive
A.....	9	13
B.....	10	12
C.....	9	15
D.....	9	12

It will be apparent that the incorporation of the additives of this invention in detergent compositions containing anionic organic detergents results in a synergistic increase in foam formation and endurance, in the speed of emulsification and the detergency power of the anionic detergent compositions, compared with corresponding compositions which do not contain the said additive.

#### EXAMPLE 1

A detergent composition was prepared consisting of 18% of a water-soluble salt of dodecyl benzene sulphonate, 12% of the ammonium salt of the sulphate ester of nonyl-phenoxy-polyethoxyethanol ("ALIPAL" 436), together with 2% of nonyl-phenoxy-polyethoxyethanol ("IGEPAL" CO 630), 6% of lauric diethanolamide, and 0.002% of ceric ammonium nitrate. These materials were mixed together with some 62% water to form a stable liquid detergent composition of high detergency value.

#### EXAMPLE 2

A composition was prepared by mixing together 10% of a water-soluble salt of dodecyl benzene sulphonate, 15% of the ammonium salt of the sulphate ester of nonyl-phenoxy-polyethoxyethanol ("ALIPAL" 436), together with 3% of nonyl-phenoxy-polyethoxyethanol ("IGEPAL" CO 630), 3% of lauric diethanolamide, 6% of potassium tetraphosphosphate, 0.0001% of molybdic acid H<sub>2</sub>MoO<sub>4</sub>, and about 63% of water. The composition formed a stable liquid medium-duty detergent of high detergency power.

#### EXAMPLE 3

A stable heavy-duty liquid detergent was produced by mixing together some 15% of a water-soluble salt of dodecyl benzene sulphonate, some 10% of the sodium salt of the sulphate ester of nonyl-phenoxy-polyethoxyethanol, together with 2% of nonyl-phenoxy-polyethoxyethanol, 2% of lauric diethanolamide, 6% of potassium tripolyphosphate, 0.3% of carboxy-methylcellulose, 0.0003% of orthotungstic acid (H<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O), and some 65% water.

#### EXAMPLE 4

By mixing together 14% of sodium dodecyl benzene sulphonate, 10% of nonyl-phenoxy-polyethoxy-ammonium sulphate, 2% of triethanolamide dodecyl benzene sulphonate, 3% of lauric diethanolamide, 2% of ethoxylated nonyl-phenol and 15% alcohol together with 2% sodium tripolyphosphate and 0.00002% ceric ammonium nitrate and some water, a detergent of superior performance was obtained.

#### EXAMPLE 5

To a 35% dispersion in alcohol-water of sodium dodecyl benzene sulphonate is added 0.0002% of ceric ammonium nitrate.

This material subsequently showed, singly or formulated, enhanced detergency.

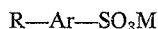
#### EXAMPLE 6

A powder of superior detergent activity was produced by spray drying a slurry of sodium dodecyl benzene sul-

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phonate (8 parts by weight), sodium dodecyl benzene sulphate (6 parts), lauric acid (2 parts), lauric diethanolamide (3 parts), sodium tripolyphosphate (30 parts), sodium sulphate (50 parts), carboxymethyl cellulose (1 part), ceric ammonium nitrate (0.0002 parts), to produce granules of some 10% moisture content.

It will be understood that the foregoing examples are only illustrative of the compositions of the present invention, and that various modifications that may be made therein will suggest themselves to those skilled in the art. While the sodium and ammonium salts of dodecyl benzene sulphonate have been employed and illustrated in these examples, it will be apparent that other specific alkyl aryl sulphonates, of the general formula



given above, may be substituted therefor. Likewise, in place of the ammonium or sodium salt of the sulphated nonyl-phenol condensates with 3 to 5 moles of ethylene oxide used in the foregoing examples, there may be used other sulphated detergents of the type previously indicated, such as lauryl sulphate, tallow fatty alcohol sulphates, and the like. There may be used the sulphated higher alkyl ethers of polyethylene glycol, e.g. sulphuric acid esters of 3 to 5 mole ethylene oxide condensates with lauryl alcohol, tridecyl alcohol and the like; or the sulphated higher alkylphenol ethers of polyethylene glycol, e.g. the 3 to 5 mole ethylene oxide condensates with such alkyl-phenols as iso-octylphenol, diamylphenol, dodecylphenol, 2-ethyl-hexylphenol, and the like. Likewise, in place of the specific ingredients of the foregoing formulations, other non-ionic detergent additives (e.g. ethylene oxide condensates of fatty alcohols, such as lauryl alcohol), other soil suspending agents (such as methyl cellulose), varying proportions of polyphosphates, optical brighteners, and the like, may be employed.

While the invention is primarily concerned with liquid detergent compositions, and mainly liquid detergent compositions have been described and illustrated, it will be apparent that the invention is not limited to liquid formulations, but can be effectively applied to the formulation of dry detergent compositions.

What we claim is:

1. A detergent composition consisting essentially of an aqueous solution of an anionic detergent selected from the group consisting of an alkyl aryl sulphonate detergent, an alkyl sulphate detergent and mixtures thereof, in an amount between 5% and 50% by weight of total solution, and as a foaming and detergency enhancing additive a water-soluble compound selected from the group consisting of an alkali-metal and ammonium molybdate, an alkali-metal and ammonium tungstate and ceric ammonium nitrate, in an amount between 0.00001% and 0.5% by weight of detergent.

2. A detergent composition as claimed in claim 1 wherein the additive is in an amount between 0.0001% and 0.1% by weight of detergent.

3. A detergent composition as claimed in claim 1 wherein the additive is ceric ammonium nitrate.

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4. A detergent composition as claimed in claim 1 wherein the additive is an alkali-metal or ammonium molybdate.

5. A detergent composition as claimed in claim 1 wherein the additive is an alkali-metal or ammonium tungstate.

6. A detergent composition consisting essentially of an aqueous solution of an anionic detergent selected from the group consisting of

an alkyl aryl sulphonate detergent wherein the alkyl chain contains from 8 to 20 carbon atoms,

an alkyl sulphate detergent selected from the group consisting of half esters of sulphuric acid with higher aliphatic alcohols containing 10 to 20 carbon atoms, sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, sulphuric acid esters of condensates of 1 mole of a higher aliphatic alcohol containing 10 to 20 carbon atoms with 3 to 5 moles of ethylene oxide and sulphuric acid esters of condensates of 1 mole of an alkyl phenol with 3 to 5 moles of ethylene oxide, and mixtures thereof,

in an amount of between 5% and 50% by weight of total solution, and as a foaming and detergency enhancing additive a water-soluble compound selected from the group consisting of an alkali-metal and ammonium molybdate, an alkali-metal and ammonium tungstate and ceric ammonium nitrate, in an amount between 0.00001% to 0.5% by weight of detergent.

7. A detergent composition as claimed in claim 6 wherein the additive is an alkali-metal or ammonium molybdate.

8. A detergent composition as claimed in claim 6 wherein the additive is an alkali-metal or ammonium tungstate.

9. A detergent composition according to claim 6 wherein the additive is in an amount between 0.0001% and 0.1% by weight of detergent.

10. A detergent composition according to claim 6 wherein the additive is ceric ammonium nitrate.

11. A detergent composition consisting essentially of an aqueous solution of a water-soluble salt of an alkyl benzene mono-sulphonate detergent having 10 to 16 carbon atoms in the alkyl group, a water-soluble salt of the sulphuric acid ester of a condensate of one mole of nonylphenol with 3 to 5 moles of ethylene oxide, said sulphonate and sulphate being present in an amount between 5% and 50% by weight of total solution, a water-soluble alkali-metal polyphosphate builder in an amount between 2% and 40% by weight of total solution, and as a foaming and detergency enhancing additive ceric ammonium nitrate in an amount of between 0.0001% and 0.1% by weight of active ingredients.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

2,766,212 10/1956 Grifo ----- 252—161 X  
2,920,045 1/1960 Hearn et al. ----- 252—137

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