United States Patent Office 2,733,214 Patented Jan. 31, 1956

2,733,214

SYNTHETIC DETERGENT COMPOSITIONS

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No Drawing. Application October 29, 1949, Serial No. 124,512

9 Claims. (Cl. 252—137)

The present invention relates to new synthetic detergent compositions and, more particularly, to compositions of the type of alkyl aromatic sulfonate detergents having improved detersive characteristics, and to a process for preparation of the same.

Various additives have been incorporated in a wide range of concentrations to modify the properties of synthetic detergent compositions in a desired manner. These additives individually may affect one or more of the following properties or mechanisms including dispersion, suspension, interfacial tension, sequestration of harmful ions, modification of micellar structure, etc. In view of the varied nature of the synthetic detergents, these additives exhibit a certain degree of specificity of action. Thus, for example, it is not uncommon to find that a particular additive may be beneficial for the detersive efficiency of a detergent composition in soft water, but prove to be an undesirable constituent in such compositions designed for use in hard water. Accordingly, there has been considerable experimentation toward the formulation of detergent compositions suitable for general use both in hard and soft water areas.

It has been suggested that the higher fatty acid amide type compounds may be useful as additives in synthetic detergent compositions. With alkyl aryl sulfonate detergent compositions though no apparent significant improvement in detergency in hard water is effected generally, by the addition of these compounds, as set forth more fully hereinafter.

It has now been discovered, however, that the simultaneous presence of higher aliphatic amide type compounds and tripolyphosphates in synthetic detergent compositions of the alkyl aryl sulfonate type yield valuable detersive characteristics to such compositions in both hard and soft water. It is significant moreover that the improvement in detergency, particularly in hard water, may even be of a synergistic order.

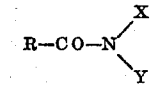
The alkyl aromatic sulfonate detergents referred to are well known in the art. They may be mononuclear or polynuclear in structure. More particularly, the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresols, phenol ethers, naphthalene, derivatives of phenanthrene nuclei, etc. It has also been found that the alkyl group may vary similarly. Thus, for example, the alkyl group may consist of such radicals as propyl, hexyl, octyl, nonyl, decyl, keryl, mixed alkyls derived from fatty materials, cracked paraffin wax olefins, and polymers of lower mono olefins, etc. While the number of sulfonic acid groups present on the nucleus may vary, it is usual to have only one such group present in order to preserve as much as possible a balance between hydrophilic and hydrophobic portions of the molecule.

More specific examples of suitable alkyl aromatic sulfonate detergents are the propylated naphthalene sulfonates, the mixed butyl naphthalene sulfonates, tetrahydronaphthalene sulfonates, the various butylated diphenyl sulfonates and phenyl-phenol sulfonates. It

is preferred, however, to use the higher alkyl aromatic sulfonates rather than the lower alkyl substituted detergents. Typical examples of this preferred class are the sulfonated and alkylated benzene type compounds wherein the alkyl group contains about 8–18 and preferably about 10 to about 16 carbon atoms. The benzene ring may possess other substituents including lower alkyl and hydroxy groups.

These detergents are commonly used in the form of their water soluble salts. Of these, the alkali metal (e. g. sodium, potassium) and ammonium salts are preferred though other salts such as the amine, alkylolamine, calcium, and magnesium salts may be used if desired. Their concentration in the detergent compositions of the present invention is generally at least about 10 and preferably at least about 20% by weight of total solids. Compositions with very high concentrations of active ingredient of the order of up to about 90% are prepared for specialized uses generally. With built compositions however, it is preferred to use an active ingredient content of about 20 to about 50% concentration.

The amides to be used in conjunction with the polyphosphates are preferably the surface-active higher amides having the formula:



wherein R—CO— is an aliphatic acyl radical, preferably of a higher fatty acid, having from about 10 to 20, and preferably about 12 to 16 carbon atoms, and X and Y may each be selected from the group consisting of hydrogen, and alkyl and alkylol radicals of 1 to about 5 carbon atoms each, and preferably about 2 carbon atoms. With the non-alkylol containing amides, it is preferred that the acyl radical be about 10–14 carbon atoms. With the monoalkylolamides, it is generally preferred that the acyl radical be about 10 to 16 carbons, whereas with the dialkylolamides, acyl radicals of slightly longer chain length of about 12 to 20 carbon atoms are preferred generally. Specific examples of amides which come within the scope of the invention are: palmitylethanolamide, myristylethanolamide, laurylethanolamide, oleylethanolamide, myristamide, lauramide, stearamide, lauric diethanolamide, and amide type mixtures prepared from mixtures of higher fatty acids derived from various fats, oils, and waxes of animal, vegetable or marine origin.

The polyphosphate additives in the alkyl aryl sulfonate detergent compositions are preferably the water soluble inorganic tri-polyphosphates of the formula:

$$M_5P_3O_{10}$$

M representing an alkali metal (e. g. sodium, potassium) or ammonium group.

These additives may be incorporated either together or separately with the active ingredient at any point during the manufacturing process at which subsequent operations will not adversely modify the properties of the detergent composition. In general, this addition may be accomplished by wet-mixing the solid polyphosphates and the amides with the active ingredient, or by dry-mixing those materials which are solid under normal conditions in comminuted form. The best results are not achieved by mechanically intermixing the comminuted solid components. A variety of procedures, which have proven to be convenient, economical, and productive of the best results are:

(1) The addition of the solid polyphosphates and molten amides to a hot aqueous slurry of the active ingredient of about 40 to 50% concentration with vigorous stirring to form a smooth, uniform and homogeneous paste.

(2) The amides may be dissolved in a suitable solvent, e. g. ethanol, and added to a slurry of the active ingredient, before, during, or after addition of the polyphosphates.

3. A cream emulsion of the polyphosphates and amides in water with a minor proportion of the active ingredient may be prepared and incorporated into the slurry of the active ingredent in the manner set forth above.

Thereafter, these compositions may be made up in the form of solutions, pastes, or as dry or partially hydrated solid products, preferably in a finely divided condition.

The amount of the mixed additives is sufficient to produce a beneficial action on the detersive power of the detergent compositions referred to herein. The amount of amides is minor in proportion to the weight of total solids, and generally varies within rather definite proportions of the order of about 1 to about 10% and preferably from about 1 to about 5%. The tripolyphosphates, however, may be used in any desired proportion. To some extent, the degree of improvement appears to be proportional to its content in the composition. In general, the greater the percentage of tripolyphosphate, the better the result where the active ingredient has been maintained constant. For best results, the proportion of phosphate should be at least 20% by weight, and preferably within the range of about 20 to about 50%. An amount of active ingredient of about 20 to about 50% with about 1–10% amides, and about 20–50% polyphosphates produces sufficient detering properties in an aqueous solution for even heavily soiled laundry; and such composition is economical to prepare and convenient for use in the home or commercially.

It may be noted that the total washing efficiency of a detergent composition is the result of both the amount of soil removed and the amount redeposited. It has been ascertained that the mixed additives in the relationship set forth perform the dual function of both increasing the soil removal power and of inhibiting the soil redeposition power generally of the detergent compositions referred to herein in both hard and soft water. In addition, the mixed additives may effect a synergistic increase in detergency, particularly in hard water, such that these alkyl aryl sulfonate detergent compositions possess a high level of detersive efficiency in both hard and soft water.

These results are evident from a consideration of the following data and examples which are merely illustrative of the present invention and it will be understood that the invention is not limited thereto.

The effect of these mixed additives may be determined by standard soil removal and soil redeposition tests. Briefly, these tests involve the addition of a large number of standard soiled cotton swatches and unsoiled cotton swatches to a detergent solution at 120° F. The system is agitated in a standard manner and the swatches are then rinsed, dried and examined under a Hunter reflectometer. The increase in reflectance of the soiled swatches is an indication of the soil removal value and the decrease in reflectance of the unsoiled cloths is the redeposition value. The values in the tables are expressed in Hunter units$\times 10^3$. A higher value in the soil removal column is an indication of better washing power, and lower values in the soil redeposition column are more desirable.

Using a standard 0.25% concentration of a detergent composition comprising 40% sodium salts of higher alkyl benzene sulfonates wherein the alkyl group averages 9–14 carbon atoms and 60% sodium sulphate in hard water of 300 parts per million (p. p. m.) hardness, calculated as calcium carbonate, and varying the additive content as disclosed in Table I, the following results are obtained. Where it is indicated that polyphosphates are present, they have been substituted for an equivalent quantity of sodium sulphate. The amide has been added in percent of total solids in the standard composition.

TABLE I

Additive	Soil Removal	Soil Redeposition
None	108	102
Sodium tri-polyphosphate (25%)	136	138
Palmitylethanolamide (5%)	86	90
Sodium tri-polyphosphate (25%)+Palmitylethanolamide (5%)	169	60

The synergistic improvement in hard water using the mixed additives is evident from the data.

Using a detergent composition of 40% higher alkyl benzene sulfonate salts and 60% sodium sulphate, and varying the palmitylethanolamide content, the following results are obtained in hard water of 300 p. p. m. hardness at 0.25% concentrations:

TABLE II

Percent Alkylolamide	Soil Removal	Soil Redeposition
0	108	102
1	109	88
3	93	85
5	86	90
7	82	70
9	81	85

Repeating the tests with a composition of 40% active ingredient, 25% sodium tri-polyphosphates, and 35% sodium sulphate yields the following values:

TABLE III

Percent Alkylolamide	Soil Removal	Soil Redeposition
0	136	138
1.5	171	122
3	185	108
5	169	60
7	155	50

Comparison of the values in the soil removal columns of Tables II and III discloses the consistently improved soil removal power of the detergent composition in the presence of the mixed additives. Without the presence of the polyphosphates (Table II), increasing amounts of the alkylolamide yield decreasing soil removal efficiency. With the combination of the mixed additives (Table III), a high level of soil removal power is maintained, with an optimum concentration of 3% alkylolamide for this particular composition.

Referring to the soil redeposition values, the use of the alkylolamide as the sole additive (Table II) in the relationship set forth appears to inhibit the amount of redeposited soil. The mixed additives (Table III) however exert their most beneficial influence starting at 3% alkylolamide in the above composition. Since the total detersive efficient is necessarily the combined result achieved from the two factors of soil removal and redeposition, it will be recognized that in any of the above compositions, improved detergency is achieved with the use of the mixed additives.

Similarly to the effects achieved in hard water, a high degree of detersive efficiency in soft water is obtained with the use of the alkyl aryl sulfonate detergent compositions containing the mixed additives. A standard detergent composition of 40% active ingredient and 60% sodium sulphate at 0.25% concentration in distilled water gives soil removal and redeposition values of 109 and 138 respectively. With the substitution of 25% sodium tripolyphosphate for an equivalent amount of sodium sul-

phate, the addition of varying amounts of palmitylethanolamide gives the following results.

TABLE IV

Percent Alkylolamide	Soil Removal	Soil Redeposition
0	114	118
5	142	105
7	161	114
9	183	110
11	183	96
13	184	82

It is evident that in all cases the soil removal and redeposition values were desirably higher and lower respectively than the results attained without the mixed additives.

From the viewpoint of foaming generally, the novel compositions of the present invention may exhibit a high level of foam stability in washing operations. The fact that the mixed additives may produce foam and suds which are more stable, creamier and of good consistency do not readily break down by evaporation and have in general a longer drainage time in comparison to the effects of the organic additive alone is significant as these characteristics are desirable generally for a detergent composition. The effect on the foaming properties by the mixed additives however appears to be highly specific and may vary markedly with the specific detergent composition and additives. In general, the alkylolamides in conjunction with the polyphosphates exert a more beneficial action on the detergent compositions than the non-alkylolamide compounds in a similar relationship.

These effects on the foaming characteristics can be studied quantitatively for a given composition. A pour foam test designed for comparative study of the relative foam stability of liquids and an appropriate apparatus for carrying out the test is set forth in United States Patent No. 2,315,983 to Ross and Miles. The foam height in millimeters of solutions tested in accordance with the Ross and Miles patent is read at various time intervals and is an indication of foam stability.

To 0.25% concentrations of a detergent composition comprising 35% salts of higher alkyl benzene sulfonates, 40% sodium tri-polyphosphate, 3% sodium silicate, and 22% sodium sulfate, amide compounds are added in 2% and 3 amounts on the basis of total solids. The results of pour foam tests at 110° F. in distilled water are:

TABLE V

Organic Additive	0 min.	10 min.	15 min.
2% Palmitylethanolamide	230	230	225
3% Palmitylethanolamide	225	225	220
2% Myristamide	225	70	35
3% Myristamide	220	60	35

It may be noted from the results above that the alkylolamides with the polyphosphates give a high level of foam stability in distilled water in contradistinction to the marked foam breakdown that occurs using the non-alkylolamide additives in the same relationship. Similar results may be observed in hard water where the mixtures containing the alkylolamide had a foam height above 200 millimeters at 15 minutes whereas marked foam breakdown (reading about 40–45 mm.) occurs at the 10 minute interval using the amide. The superior desirable effects of the mixed alkylolamide and polyphosphate additives are rendered more unique by the fact that both the amide and alkylolamide have a marked general adverse effect in such detergent compositions when they are compounded without the tri-polyphosphates.

Though the alkyl aryl sulfonated detergents containing the alkylolamides and polyphosphates may be used as a relatively pure mixture of these components, it is common to employ various adjuvant materials in synthetic detergent compositions. These other builders or additives may be inorganic or organic in structure and may be mixed with the active ingredient in any suitable manner. Such adjuvant materials may include any of the substances employed by the art in admixture with these detergents generally, provided the use of any such materials does not completely neutralize or remove the effect of the mixed amide and polyphosphate additives. It has been found that these added materials may vary greatly both in structure and in concentration without impairing the improved results attained by the compositions of the present invention. Thus, such conventional inorganic builders or additives as the silicates, other alkali metal phosphates (e. g. hexametaphosphate, tetrapyrophosphate), the sulfates, carbonates, etc. may be employed in these compositions. Organic materials such as carboxymethylcellulose salts, esters (e. g. ethylene glycol monostearate, methyl palmitate), and the like may also be used under suitable conditions.

The following formulations are additional examples of compositions containing the mixed amides and polyphosphates productive of a high level of detersive efficiency.

Example I

	Percent
Higher alkyl aryl sulfonate salt	32
Sodium tri-polyphosphate	50
55:45 mix of stearylethanolamide and palmitylethanolamide	3
Sodium sulfate	15

Example II

	Percent
Higher alkyl aryl sulfonate salt	35
Sodium tri-polyphosphate	40
Myristylethanolamide	2
Sodium sulfate	23

Example III

	Percent
Higher alkyl aryl sulfonate salt	25
Sodium tri-polyphosphate	50
Coconut oil fatty acid amides	3
Sodium silicate	3
Sodium carbonate	3
Sodium sulfate	16

Example IV

	Percent
Higher alkyl aryl sulfonate salt	20
Sodium tri-polyphosphate	50
Myristamide	2.5
Sodium silicate	3
Sodium carboxymethylcellulose	0.5
Sodium sulfate	24

Certain general conclusions are apparent from the many tests which have been conducted to determine the effect of the mixed additives in the alkyl aryl sulphonate detergent compositions. The most appropriate mixture of the additives, their proportion to each other, and their concentration in each detergent composition may be suitably determined by routine controls since the beneficial results vary to some degree of course with changes in formulations. In each case, the proper washing conditions and the intended use of the composition (e. g. hard or soft water, general home or commercial use, shampoos, machine washing, etc.) should be taken into consideration in order to derive the maximum beneficial results.

The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other ma-

terials in such amounts as not substantially to affect said properties and characteristics adversely.

Although the present invention has been described with reference to particular embodiments and examples it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

Having described the invention, what is desired to be secured by Letters Patent is:

1. A detergent composition consisting essentially of about 10 to about 50% of water-soluble higher alkyl mononuclear aryl sulfonate detergent, in minor proportion to said detergent and from about 1 to about 10% of an amide compound having the formula:

$$R—CO—NH_2$$

wherein R—CO— is an acyl group of a saturated higher fatty acid of about 10 to 14 carbon atoms, and the balance being primarily water-soluble inorganic builder salts with about 20% of about 50% alkali metal tripolyphosphate, the above amounts being by weight of total solids of said detergent composition.

2. A detergent composition consisting essentially of about 10 to about 50% of water-soluble higher alkyl mononuclear aryl sulfonate detergent, in minor proportion to said detergent and from about 1 to about 10% of a higher saturated fatty acyl monoalkylolamide, said fatty acyl group having about 10 to 16 carbon atoms and said alkylol group having up to about 5 carbon atoms, and the balance being primarily water-soluble inorganic builder salts with about 20% of about 50% alkali metal tripolyphosphate, the above amounts being by weight of total solids of said detergent composition.

3. A detergent composition consisting essentially of about 10 to about 50% of water-soluble higher alkyl benzene sulfonate detergent, in minor proportion to said detergent and from about 1 to about 10% of an amide compound having the formula:

$$R—CO—NH_2$$

wherein R—CO— is an acyl group of a saturated higher fatty acid of about 10 to 14 carbon atoms, and the balance being primarily water-soluble inorganic builder salts with about 20% to about 50% sodium tripolyphosphate, the above amounts being by weight of total solids of said detergent composition.

4. A detergent composition consisting essentially of about 10 to about 50% of water-soluble higher alkyl benzene sulfonate detergent, in minor proportion to said detergent and from about 1 to about 10% of a higher saturated fatty acyl monoalkylolamide, said fatty acyl group having about 10 to 16 carbon atoms and said alkylol group having up to about 5 carbon atoms, and the balance being

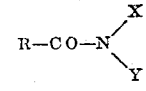
primarily water-soluble inorganic builder salts with about 20% to about 50% sodium tripolyphosphate, the above amounts being by weight of total solids of said detergent composition.

5. A detergent composition in accordance with claim 3 wherein said amide is lauramide.

6. A detergent composition in accordance with claim 4 wherein said amide is palmitoylmonoethanolamide.

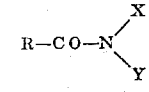
7. A detergent composition in accordance with claim 4 wherein said amide is lauroylmonoethanolamide.

8. A detergent composition consisting essentially of about 10 to about 50% of sodium higher alkyl benzene sulfonate detergent, in minor proportion to said detergent and from about 1 to about 10% of a higher aliphatic amide compound having the formula:



wherein R—CO— is an aliphatic acyl radical of about 10 to 20 carbon atoms, and X is hydrogen and Y is selected from the group consisting of hydrogen, and alkylol radicals having up to about 5 carbon atoms, and the balance being primarily water-soluble inorganic builder salts with about 20% to about 50% sodium tripolyphosphate, the above amounts being by weight of total solids of said detergent composition.

9. A detergent composition comprising about 10 to about 50% of water-soluble higher alkyl mononuclear aryl sulfonate detergent, in minor proportion to said detergent and from about 1 to about 13% of a higher aliphatic amide compound having the formula:



wherein R—CO— is an aliphatic acyl radical of about 10 to 20 carbon atoms, and X is hydrogen and Y is selected from the group consisting of hydrogen and alkylol radicals having up to about 5 carbon atoms, and the balance being primarily water-soluble inorganic builder salts with about 20% to about 50% tripolyphosphate salt selected from the group consisting of alkali metal and ammonium tripolyphosphate, the above amounts being by weight of total solids of said detergent composition.

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