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NON-SOAP DETERGENT COMPOSITIONS

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The present invention relates to new synthetic detergent compositions, and more particularly to compositions of the type of sulfated and sulfonated aliphatic acyl-containing detergents wherein the acyl radical has about 8 to 22 carbon atoms, having improved properties, and to a process for preparing 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 effect one or more of the following properties or mechanisms involved in the action of the detergent composition including foam volume, foam stability, dispersion, interfacial tension, modification of micellar structure, etc. In view of the varied nature of many synthetic detergents, additives in general exhibit a certain degree of specificity of action.

While the exact relationship, if any, between detergency and foam is not known, it is preferred that the detergent composition should exhibit excellent foaming properties, particularly for consumer appeal and certain home and industrial uses. Accordingly, additives which improve foam and/or detergency efficiency of a detergent composition are highly desirable. In general, most testing conditions to determine the suitability of additives in synthetic detergents have revolved around the use of concentrations of detergent compositions of the order of 0.15, 0.2 and 0.25%.

It has now been discovered that the incorporation of minor amounts of fatty alcohols of about 10 to about 22, and preferably about 12 to about 18 carbon atoms in synthetic water-soluble sulfated and sulfonated aliphatic acyl-containing detergents having an acyl radical of about 8-22 carbon atoms, give improved foam stability and detergency power at certain selected washing concentrations.

The novel compositions of the present invention containing the selected fatty alcohols as additives do not show any significant increase in detergency and may even exhibit decreased detergency when employed in certain concentrations, in comparison to the use of these detergent compositions without the alcohol additives. It has been found, however, that within certain selected washing concentrations a marked and synergistic increase in detergency results from the use of the alcohol additives. It may be noted that the total washing power of any composition is necessarily the result of the amount of soil removal and soil suspension or redeposition. Additives in general may increase both soil removal and redeposition, or may change one such factor. It has been found, however, that the fatty alcohol additives in the compositions referred to herein have the desirable properties of both increasing soil removal and inhibiting soil redeposition, though the improvement in the former factor appears to be more pronounced.

With respect to the foaming properties, it has been de-

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termined that the saturated fatty alcohols of about 14 to about 18 carbon atoms exert a highly beneficial and synergistic action on the foam stability of the compositions referred to herein, in comparison to the use of other alcohols as additives. The reason for this specificity of action is not known at this time.

The synthetic detergent compositions comprised by the invention contain as the active ingredient the surface active synthetic sulfated or sulfonated aliphatic acyl-containing compounds wherein the acyl radical has about 8-22 carbon atoms. Within the scope of such definition are the higher fatty acid ethanolamide sulfates; the sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e. g. coconut oil monoglyceride monosulfate, tallow diglyceride monosulfate; 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 acid ester of isethionic acid; and the like. More particularly, it is preferred to use the sulfated and sulfonated aliphatic carboxylic esters containing at least about 10 carbon atoms, especially those having about twelve to about twenty-six carbon atoms to the molecule, which may be derived from fatty oils, mono and di-glycerides, partial fatty acid esters and ethers of polyglycols, etc.

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, alkaline earth metal (e. g. calcium, 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 these active ingredients 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%.

The fatty alcohols used as additives in the present invention are those of about 10 to 22, and preferably of about 12 to 18 carbon atoms. These essentially aliphatic alcohols may be primary or secondary; and saturated or unsaturated in character. It is preferred however to use the saturated straight-chain primary alcohols of about 14 to about 18 carbon atoms. Examples of suitable alcohols falling within the broad classification are lauryl, myristyl, cetyl, stearyl, oleyl, palmityl, etc. It is not necessary to use the pure substances themselves as the commercial mixtures of these substances are also operable and may be preferred from the viewpoint of economy. Thus, commercial mixtures of fatty alcohols containing predominantly the desired fatty alcohols are included within the scope of this invention, even though such mixtures may contain minor amounts of fatty alcohols of different chain length.

The fatty alcohols may be derived either from natural or synthetic sources. Many naturally occurring wax esters are an important source of higher aliphatic alcohols. Certain animal oils, chiefly those of marine origin such as sperm oil, also contain a high proportion of recoverable alcohols occurring as esters. The most plentiful and economic sources for their production, however, are their preparation from fatty acids or aldehydes by reduction, or their recovery from oxidized petroleum stocks, etc., by processes known in the art.

These additives may be incorporated with the active ingredient at any point during the manufacturing process at which subsequent operations will not adversely modify

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the properties of the detergent composition. In general, this addition may be accomplished by adding the alcohols to the active ingredient either in liquid form, or by 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 proved to be convenient, economical, and productive of the best results are:

1. The addition of the fatty alcohols in a molten state 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 fatty alcohols may be dissolved in a suitable solvent, e. g. ethanol, and added to a slurry of the active ingredient.

3. A cream emulsion of the fatty alcohols in water with a minor proportion of the active ingredient may be prepared and incorporated into the slurry of active ingredient 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 these added long chain alcohols is generally minor in proportion to the weight of the total detergent composition and sufficient to produce a marked effect on its foaming and detergency properties. Generally, the amount of each additive varies within rather definite proportions of the order of about 1 to about 10% by weight since it has been determined that within these somewhat critical limits the desirable effects appear to be attained to a maximum degree. With built compositions, it is preferred to use about a 1 to about 5% concentration of alcohols.

With respect to detergency, it has been found that the fatty alcohol additives perform the dual function of increasing the soil removal power and of inhibiting the soil redeposition factor of the detergent compositions referred to herein. The unitary effect on detergency resulting from a concurrent activation of one factor and repression of another is of a synergistic character, since the fatty alcohols per se have no deterging power. One of the most significant aspects of this improvement however is the fact that it may be noted only when used in a particular manner. The compositions of the present invention containing the free alcohols in general do not show any significant increase in detergency and even may exhibit decreased detergency when employed in washing concentrations of the order of 0.15–0.25%. It has been found, however, that under washing concentrations such as 0.4–0.75% a marked increase in detergency results from the use of these alcohols as additives.

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

Tables I and II indicate the changes in washing power at various bath concentrations in soft and hard water of a detergent composition containing 23% sodium salt of coconut oil monoglyceride sulfate as the active ingredient, 2% of a 90:10 mixture of cetyl and stearyl alcohol, 50% tetrasodium pyrophosphate, 3% sodium silicate and 22% sodium sulfate.

The washing procedure involves the uniform soiling, washing at $110^{\circ}\text{F} \pm 2^{\circ}\text{F}$, and drying of a large number of cotton swatches. The whiteness of the various test swatches are measured by a Hunter reflectometer. The units of soil removed may be calculated by subtracting the average reflectivity of the unwashed control samples from the washed swatches. The effect on redeposition of soil in the fabric is determined by placing unsoiled samples in the detergent bath together with the soiled samples and measuring the brightness after wash-

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ing. The numbers in the tables represent the change in units of soil removed and redeposited with the use of the above detergent composition with and without the fatty alcohol additives. A + value indicates an increase in soil removal and redeposition; a - value indicates a decrease in soil removal and lesser redeposition of soil.

Table I.—Soft water solutions

Percent Concentration	Soil Removal	Soil Rede-position
0.15	0	-2.1
0.25	0	-3.4
0.5	+10	-3.5
0.75	+12	-4.4

Table II.—Hard water (300) p. p. m.) solutions

Percent Concentration	Soil Removal	Soil Rede-position
0.15	-3	-1.7
0.25	+1	-2.2
0.4	+7	-2.7
0.75	+8	-1.9

It may be noted from the above data that no significant improvement in total washing power is attained either in hard or soft water using concentrations of 0.15 and 0.25%. In fact, at low concentrations in hard water decreased detergency may result from the use of the alcohol additives. At higher concentrations however, a marked and synergistic increase in detergency results from the use of the fatty alcohol additives, particularly due to improved soil removal power. It is not completely understood why these additives in the relationship set forth should exhibit this unique specificity of action.

Though the sulfonated and sulfated detergent compositions referred to herein containing the alcohol additives may be used as a relatively pure mixture of these components, it is common however to employ various adjuvant materials in synthetic detergent compositions. These builders or additives may be inorganic or organic in structure, and may be admixed with the active ingredient in any suitable manner. Such adjuvant materials may include any of the substances employed by the art in admixture with sulfonated organic detergents generally, provided the use of any such materials do not neutralize or remove the effectiveness of the fatty alcohols. It has been found that these added materials may vary greatly both in structure and in concentration without impairing the improved results of the compositions referred to herein.

Thus, such convenient inorganic builders or additives as the silicates, various alkali metal phosphates (e. g. hexametaphosphate, tetrapyrophosphate), the alkali metal sulfates, carbonates, etc., may be employed in these compositions. Organic materials such as carboxymethylcellulose, esters (e. g. ethylene glycol monostearate, methyl palmitate), and the like may also be used under suitable conditions.

Of the indicated vast variety of known builders and additives which may be employed in detergent compositions, it has been found that the water soluble polyphosphates in conjunction with the mixed organic additives have remarkable effects on the sulphonated and sulphated acyl-containing detergent compositions. The polyphosphates are preferably the water soluble inorganic tri-polyphosphates of the formula:



M representing an alkali metal or ammonium group.

The actions of the tri-polyphosphate and the fatty

alcohol additives in these detergent compositions are not only not antagonistic, but mutually contribute to a balanced detergency system such that a unitary result of vastly improved detergency is achieved thereby.

As previously indicated, the effect of the alcohol is primarily one of activation of the soil removal power of the detergent compositions referred to herein with a more moderate inhibition of the amount of soil redeposition. It has been determined however, that the tri-polyphosphates appear to exert beneficial results in an opposite direction in these detergency systems. The tri-polyphosphates exhibit their greatest effect on soil suspension or prevention of soil redeposition, and only to a minor extent on the soil removal factor. Since the total washing efficiency is due to a combination of both soil removal and soil suspension, it is apparent that the mixed additives of the organic fatty alcohols and the inorganic water soluble tri-polyphosphates mutually contribute to produce a somewhat balanced effect since both the two factors of improved soil removal and lessened soil redeposition are activated concurrently to a significant degree.

These unexpected results are not achieved to the same degree when other phosphate compounds, such as tetrasodiumpyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) or tri-sodiumphosphate (Na_3PO_4) are substituted for the tri-polyphosphates. It is not known at this time why the indicated washing mixtures with the tripolyphosphate should yield a markedly superior cleaning performance compared to mixtures with other phosphates in the detergent systems referred to herein.

These tri-polyphosphates 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 tri-polyphosphate, the better the result where the active ingredient has been maintained constant. It has been found that best results are attainable when the ratio of tri-polyphosphate to the active ingredient is at least about 1:1. For maximum efficiency of these compositions, the active ingredient should be present in an amount at least about 20% by weight of the total composition. A proportion of active ingredient from about 20% to up to about 50% with a similar proportion of the tri-polyphosphates and a minor amount of the higher fatty alcohols produces sufficient deterging properties for even heavily-soiled laundry; and such compositions are economical to prepare and convenient for use in the home or commercially.

The tri-polyphosphates may be incorporated with the active ingredient in any suitable manner. It is possible to mechanically intermix these constituents in the form of small solid particles. It is preferred, however, to apply the techniques set forth above for the introduction of the higher alcohols. Thus the tri-polyphosphates may be added to a slurry of the active ingredients before, during or after incorporation of the alcohols. The resulting mixtures may be dried in any convenient manner e. g. roll or spray dried. Excessively high temperatures during drying should be avoided however to prevent substantial decomposition of the polyphosphates.

It is a significant feature of this invention that the long chain saturated primary alcohols of at least about 14 carbon atoms exert a beneficial effect on the foaming properties of the synthetic non-soap aliphatic acyl-containing sulfated and sulfonated detergents wherein the acyl group has 8 to 22 carbon atoms. The desirable effect of these fatty alcohols on the foam of such detergents as the fatty acid monoglyceride sulfates, fatty acid ethanolamide sulfates, etc., is unique and in marked contrast to the general adverse effect on foam produced by these alcohols on other sulfonated and sulfated detergents.

These fatty acyl-containing detergent compositions containing the fatty alcohol additives are characterized by increased stability of the foam produced in washing operations in comparison to the foam effects produced by

these compositions without the fatty alcohol additives. The fact that these alcohol adducts in the particular relationship set forth produce foams and suds which are more stable, do not readily break down by evaporation, have in general longer drainage time and contain more liquid, are significant and desirable properties for a detergent composition.

Moreover, it has been found that in general, the alcohol adducts in these compositions tend to increase the tolerance of these detergent compositions in the assimilation or holding in suspension of a maximum amount of dirt, grease, etc., with less foam loss than is found without the use of these additives.

The effects on the foaming characteristics can be studied quantitatively for a given composition by means of a foam consistency test. Briefly, this test consists of the formation of a foam by standardized agitation of 500 cc. of a detergent at 110° F. in a two quart unsilvered Dewar flask. The foam formed after a 10 minute agitation period is then measured with a consistometer after standing for 5, 10 and 15 minutes. The readings are an indication of the foam consistency or bodying effect. It has been arbitrarily determined using a standard consistometer that a value below about 275 units represents relatively low viscosity, a value of 275-350 units intermediate consistency, and above 350 units is high consistency.

This consistometer is a means for measuring the minimum torque necessary for rotation of a paddle of any standard size through a foam. This device applies the torque by means of a coil spring which has its inner end attached to a paddle shaft and the outer end attached to a circular plate which can be rotated. The degrees through which the spring may be twisted before the paddle starts to move in the foam may be readily determined. An indicator needle is attached to the top of the paddle shaft and a circular scale divided into 360° is set on the plate which holds the outer end of the spring. The paddle shaft is held in place by a pair of ball bearing races in such a way that it can turn freely.

A foam consistency test is conducted in distilled and in hard water using a detergent composition comprising essentially 30.9% coconut oil monoglyceride sulfate salts, 7.5% sodium phosphates, and the remainder sodium sulfate with and without alcohol additives. The results using 0.25% concentration of the detergent composition are set forth in the tables below. The values given therein represent the averages of the three readings at 5, 10 and 15 minute intervals.

TABLE I

Alcohol	Percent Added	Consistency in Distilled Water
1. None.....		220
2. Dodecanol-1.....	5	200
3. Tetradecanol-1.....	1	280
	5	385
4. Hexadecanol-1.....	1	390
	5	430
5. Octadecanol-1.....	1	270
6. (1:1) Tetradecanol+Octadecanol.....	2	290
7. (1:1) Hexadecanol+Octadecanol.....	1	420
	1	390

The data in the table above indicate the remarkable effectiveness of the saturated straight-chain primary alcohols of 14 to 18 carbon atoms as foam stabilizers on such detergent compositions. It may be noted that dodecanol containing 12 carbon atoms is ineffective to increase the foam consistency. Tetradecanol and octadecanol give intermediate to high foam consistency. The hexadecanol appears to represent an optimum in regard to chain length. It is also evident moreover, that combinations of fatty alcohols consisting essentially of C_{14} to C_{18} are effective in improving the foam stability of the detergent composition.

The improved results are also observable in hard water as disclosed in Table II below:

TABLE II

Alcohol	Percent Added	Consistency in Hard Water (300 p. p. m.)
1. None.....	2	150
2. Hexadecanol.....	2	450
3. (1:1) Tetradecanol+Octadecanol.....	5	430
4. (1:1) Hexadecanol+Octadecanol.....	2	450
5. Chinese Tallow Alcohols ¹	2	240
6. Palm Oil Alcohols ¹	2	340
7. 2:1 mix of hydrogenated ¹ tallow and coconut oil alcohols.....	4	370
	4	360
	5	420
	5	330
	5	310-330

¹ Synthetic mixtures of fatty alcohols corresponding to fatty acid compositions of the indicated fats and oils.

It is evident that the fatty alcohols containing essentially C₁₄-C₁₈ alcohols are highly effective to improve the foam consistency in hard water. It may be noted that synthetic mixtures of these alcohols corresponding to the fatty acid composition of various fats and oils which predominate in fatty acids of 14 to 18 carbon atoms are also highly effective in the relationship set forth. In number 7 of Table II, a 2:1 mix of hydrogenated tallow and coconut oil alcohols is used to determine if the presence of minor amounts of coconut oil alcohols predominating in C₁₂ alcohols would neutralize the effectiveness of the higher homologues. It may be noted that such a mixture maintains relatively high consistency in hard water, thereby indicating that minor but significant amounts of alcohols of less than 14 carbon atoms may be incorporated in the fatty alcohol mixtures used to give improved results.

The beneficial results derived using the organic additives referred to herein are exhibited with varying concentrations of active ingredients as set forth in Table III.

TABLE III

Composition	Foam Consistency
10 A. I., 4 Cetyl alcohol, 86 Na ₂ SO ₄	380
15 A. I., 4 Cetyl alcohol, 81 Na ₂ SO ₄	440
20 A. I., 4 Cetyl alcohol, 76 Na ₂ SO ₄	420
40 A. I., 4 Cetyl alcohol, 56 Na ₂ SO ₄	440
60 A. I., 4 Cetyl alcohol, 36 Na ₂ SO ₄	430
80 A. I., 4 Cetyl alcohol, 16 Na ₂ SO ₄	430

It is evident that high consistency is maintained throughout a wide range of concentrations of active ingredients with best results attained using a concentration of 15-80% active ingredients.

A detergent composition comprising 30% sodium salts of the sulfated condensation product of coconut oil fatty acids and monothanolamine as the active ingredients with and without alcohol additives is examined in 0.25% concentration in distilled water by means of the foam consistency test. The results are set forth in Table IV below:

TABLE IV

Additive	Percent	Consistency in Distilled Water
1. None.....		220
2. Lorol ¹	5	225
3. Tetradecanol.....	2	430
4. Hexadecanol.....	2	410
5. Octadecanol.....	2	370
6. Oleyl alcohol.....	5	220

¹ Fatty alcohol mixture derived from coconut oil.

It is evident from the data in the table above that the

saturated fatty alcohols of 14 to 18 carbon atoms are superior foam stabilizing agents.

EXAMPLE I

- 5 The foam consistency test is repeated on a detergent composition comprising 40% of the condensate of coconut oil fatty acids with isethionic acid as the active ingredient and 2% lauryl alcohol as the organic additive. This detergent composition exhibits a foam consistency of 230. With the substitution of 2% cetyl alcohol as the organic additive, however, there is obtained a foam consistency value of 360.

EXAMPLE II

- 15 Using a 0.25% concentration in distilled water of a detergent composition comprising 40% of the condensate of coconut oil fatty acids with methyl taurine and 60% sodium sulfate, there is obtained a foam consistency value of 220. With the addition of 5% lauryl alcohol a consistency value of 220 is also obtained. Using 2% cetyl alcohol as the organic additive, improved foam stability is obtained since the detergent composition has a consistency value of 390.

EXAMPLE III

- 25 Using an 0.25% concentration in distilled water of a detergent composition comprising 30% magnesium coconut oil monoglyceride monosulfate as the active ingredient, there is obtained a foam consistency value of 230. With the addition of 2% cetyl alcohol, a foam consistency value of 410 is obtained thereby indicating improved foam stability due to the presence of the alcohol additive.

- Certain general conclusions are apparent from the many tests which have been conducted to determine the effectiveness of the long chain fatty alcohols in the relationship set forth. The most appropriate fatty alcohol and its most effective concentration for each particular sulfonated or sulphated carbonyl-containing detergent composition may suitably be determined by routine controls. In each case the intended use (e. g. hard or soft water, hair shampoos or machine washing compositions, etc.) and the proper washing conditions should be taken into consideration in order to derive the maximum beneficial effects.

- 45 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 significant amounts of other synthetic detergents and 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 materials 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.

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

1. A detergent composition consisting essentially of a water-soluble higher fatty acid monoglyceride monosulfate detergent having about 8-22 carbons in the fatty acyl group, and in minor proportion thereto and from about 1 to about 10% by weight of a primary saturated monohydric fatty alcohol of about 14 to 18 carbon atoms.

2. A detergent composition consisting essentially of a water-soluble higher fatty acid monoglyceride monosulfate detergent having about 8-22 carbons in the fatty aryl group, and in minor proportion thereto and from about 1 to about 10% by weight of cetyl alcohol.

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