

UNITED STATES PATENT OFFICE

2,156,996

DETERGENT AND WETTING COMPOSITIONS

Wilfred S. Martin, Norwood, Ohio, assignor to
The Procter & Gamble Company, Cincinnati,
Ohio, a corporation of Ohio

No Drawing. Application June 13, 1935,
Serial No. 26,519

13 Claims. (Cl. 87-5)

My invention relates to new and improved laundering preparations which have excellent wetting, sudsing and detergent properties especially in hard water.

Essentially my invention comprises, as a detergent, a mixture of water-soluble salts of the product of the reaction of a sulfating agent on higher molecular weight normal primary aliphatic alcohols under conditions favoring the formation of the sulfuric acid ester and water-soluble salts of true sulfonic acids described below, and also comprises the process of producing said detergents. Reference in the specification and claims to "sulfonate promoters" is to be interpreted to mean the salts of the true sulfonic acids more specifically set forth hereinafter, and reference to "alkyl sulfates" is to be interpreted to mean the salts of the above noted reaction products derived either from individual higher molecular weight alcohols or from a mixture of such alcohols, such as may be obtained by the reduction of natural fats and fatty oils. It should be noted that the term "alkyl sulfate" as above defined includes those sulfuric acid ester salts containing small amounts of salts of true sulfonic acids unavoidably formed under the conditions of sulfation of the alcohols.

It is an object of my invention to improve sudsing and detergent properties of the water-soluble salts of primary alkyl sulfuric acids having eight or more, especially eight to eighteen, carbon atoms in the molecule. These alkyl sulfuric acids have the general formula $RHSO_4$ where R is an alkyl radical containing preferably eight to eighteen carbon atoms. The most commonly used water-soluble salts of these alkyl sulfuric acids are those of the alkali metals, ammonia, substituted ammonia, and organic bases, but other water-soluble salts come within the scope of my invention. Further objects and advantages will become apparent in the course of the following description.

I have noted that alkyl sulfates, although good sudsing agents in distilled water, are somewhat less efficient in these respects when used in the average type of hard water, especially in the presence of soiled fabrics. I have found, for example, that in natural hard water equivalent in hardness to 21 grains $CaCO_3$ per U. S. gallon, especially when the calcium compounds predominate over the magnesium the detergent power is less than in soft water and the sudsing power, particularly the suds stability, is markedly reduced, especially in the presence of soiled fabrics. Since detergent and sudsing power and suds stability are properties of primary consideration in the choice of an efficient detergent in common laundering operations, I have directed efforts to improve said properties.

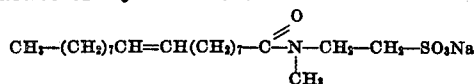
I have found that the above difficulties in suds-

ing and detergent properties may be overcome and that wetting, sudsing and detergent agents of improved efficiency, in various forms, such as for example flaked, spray or drum dried, puffed, powdered, shredded, paste, liquid, or other form, may be obtained by adding to or incorporating with known water-soluble alkyl sulfate detergents, a small amount of a water-soluble salt of a true alkyl sulfonic acid corresponding to the general formula $R-CO-X-R_1-SO_2-OH$, in which R denotes an aliphatic radical having at least eight carbon atoms, especially eight to eighteen carbon atoms, $-X-R_1-$ denotes an oxy-alkylene ($-O-R_1-$) or an amino alkylene radical. (The term "alkylene radical" is used herein with its accepted meaning: an aliphatic radical having two unattached valences.)

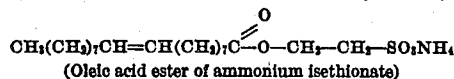
The alkyl sulfate detergents may be obtained by neutralization, with a suitable base such as sodium or potassium hydroxide, ammonia, an amine or an organic base, of the reaction product of normal primary alcohols, such as those obtainable by reduction of fatty acids, or oils and fats of vegetable or animal origin, with a sulfating agent such as sulfuric acid, chlorosulfonic acid and the like in the customary manner wherein the alcohol is substantially completely sulfated.

The true sulfonates, which act as promoters for improved sudsing and detergent power, are obtainable, for example, by the condensation of fatty acids of vegetable or animal origin, or their synthetic equivalents, or their derivatives, with hydroxylated or halogenated derivatives of ethyl sulfonic acid or of ethionic acid, carbyl sulfate or amino sulfonic acid, or corresponding derivatives prepared from glycerin, such as 1,2 dihydroxy propyl 3 sulfonic acid or salts of these sulfonated compounds.

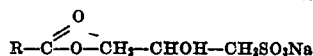
The following materials are illustrative of the types of sulfonate promoters operative in the practice of my invention.



(Sodium salt of the oleyl acid amide of methyl taurine)



(Oleic acid ester of ammonium isethionate)



wherein R denotes an aliphatic radical such as that present in lauric, oleic, myristic, stearic acids or the mixed acids obtainable from coconut or palm kernel oils or talow. (Coconut oil fatty acid ester of sodium glyceryl sulfonate, for example.)

Thus it will be seen that in the general formulas, the R_1 grouping may have either two or three carbon atoms in the molecule. Of course,

other soluble salts of these types of compounds, in addition to those specifically given above, may be used in the practice of my invention.

The sulfonate promoters themselves in aqueous solution possess sudsing and cleansing power, even in hard water, but their value as promoters lies in the remarkable fact that when such a compound is added to a water-soluble salt of a sulfated higher alcohol the mixture possesses sudsing and detergent power far in excess of expectations based upon the behavior of the components of the mixture when used separately. In other words, the sulfonate promoter is much more than additive in its effect.

The amount of sulfonate promoter which is to be used, as well as the magnitude of the effect produced thereby, depends upon many factors, such as the nature of the sulfonate promoter, the nature of the alkyl sulfate, and the conditions under which the product is used. Even small additions of any of the sulfonate promoters mentioned produce an effect which is greater than can be predicted from the properties of the sulfonate promoter alone. The optimum effect is generally obtained by the replacement of about five to about thirty per cent of the alkyl sulfate with a sulfonate promoter. I have found that in excess of thirty per cent, for example sixty percent, may be used and that the effect will still be beneficial but not much greater than would be predicted upon the basis of the behavior of the constituents when used alone.

The method of adding the sulfonate promoter to the alkyl sulfate to improve and stabilize sudsing and to improve detergency may vary considerably. For example, the sulfonate promoter may be added in dry form to alkyl sulfate paste and incorporated therein by any of a number of well known methods. The mixture may be used in paste form or may be dried in any manner such as for example spray drying or drum drying to give it a variety of forms. In the improvement of liquid detergents, the sulfonate promoter may be dissolved therein before use.

In the preparation of products of solid or extruded form, the sulfonate promoter may be added to the solid alkyl sulfate and incorporated

The relative sudsing power of certain mixtures was determined by shaking a definite quantity of solution containing the detergent mixture under standardized conditions for a definite period of time and noting the volume of suds formed. The stability of the suds formed was also noted. The detergency tests were made on uniformly soiled fabric according to a standardized procedure known to give comparative results.

Example 1.—In this example, commercial sodium alkyl sulfate, prepared from the alcohols obtained from coconut oil by high pressure hydrogenation, and having the following approximate analysis, was employed: 48 per cent actual sodium alkyl sulfate, 48 per cent sodium sulfate, 2 per cent unsulfated material, 1 per cent moisture and 1 per cent sodium chloride. The sulfonate promoter consisted of commercial sodium salt of oleic acid amide of methyl taurine containing approximately 33 per cent actual sulfonate, 64 per cent sodium chloride, and 3 per cent sodium sulfate. A mixture containing the dry active ingredients in the ratio of 9 parts actual alkyl sulfate to 1 part of actual oleic acid amide of methyl taurine was prepared. Likewise, mixtures were prepared containing the active detergents in the ratio of 8:2 and 7:3. Separate solutions were prepared from each of the above mixtures and the individual constituents thereof. The water used contained compounds of calcium and magnesium in the molar ratio of 2.9 calcium to 1 magnesium, the total hardness of the water being equivalent to 21 grains of CaCO_3 per U. S. gallon. The concentration of actual detergent was the same, and equal to that of a 0.10 per cent solution of the alkyl sulfate (per cent solids basis). It will be noted that the amount of active ingredients present was approximately 0.048 per cent. 100 c. c. of the solutions at 85°–90° F. were poured into suitable 500 c. c. graduated cylinders and were shaken for 20 seconds in a shaking rig, after which the volume of the suds formed was noted. The cylinders were allowed to stand for 5 minutes, after which period the volume of suds was again noted. The data obtained are given in the following table.

Table I

Description of sample	Percent actual detergent in solution	Experimental		Predicted result	
		Cc. suds after shaking 20 sec.	Cc. suds after standing 5 min.	Suds formation	Suds stability
Sodium alkyl sulfate (48% actual) (A).....	0.048	110	30	-----	-----
Sulfonate promoter (33% actual) (B).....	.048	200	185	-----	-----
Mixture of A+B contg. the actual detergents in the proportion of 9:1.....	.048	120	120	115	33
Mixture of A+B contg. the actual detergents in the proportion of 8:2.....	.048	150	150	121	36
Mixture of A+B contg. the actual detergents in the proportion of 7:3.....	.048	250	250	127	40

therein by any process for accomplishing the desired homogenization, such as the well known milling process in the soap industry. The mixture of detergents may then be formed into a product having any desired physical shape.

The sudsing and detergent power of mixtures coming within the scope of my invention are illustrated in the following examples which include data taken from actual tests carried out both in the absence and presence of standard soiled fabrics.

The exceptionally useful and unpredictable more-than-additive effect of the sulfonated promoter on the sudsing of the alkyl sulfate in hard water is thus shown. Even more remarkable is the improvement in the stability of the suds noted under identical testing conditions. Other primary alkyl sulfate detergents and sulfonate promoters described herein may be substituted in the above test with similar results.

The results of other experimental work carried out under comparable conditions indicated that

the amounts of inorganic salts such as sodium sulfate or sodium chloride commonly occurring in commercial products, within rather wide variations, had but little effect on either the amount and stability of the suds or the detergent of the products, provided of course equal quantities of actual detergents were used. A certain amount of the inorganic sulfate salt naturally and unavoidably occurs in the neutralized product as made commercially.

Example 2.—Separate solutions of commercial sodium alkyl sulfate produced from the alcohols obtainable from coconut oil by sodium reduction and containing about 48 per cent actual detergent, and of commercial oleic acid ester of ammonium isethionate containing approximately 49 per cent actual sulfonate promoter, were prepared. These solutions were mixed in the necessary proportion to yield a solution containing the active ingredients in the proportion 80 parts of actual sodium alkyl sulfate to 20 parts actual sulfonate promoter. Test solutions containing 0.10 per cent solid material or about 0.048 per cent actual detergent were then prepared from the sulfonate promoter, the alkyl sulfate, and the mixture of alkyl sulfate and sulfonate promoter detergents. Sudsing tests were carried out as above, the temperature of the test being 85°–90° F. and the hardness of the water being 21 grains per gallon as described above. It will be seen that the mixture of detergents was markedly superior to either of the individual constituents both in amount of suds and in the stability of suds.

Table II

Description of sample	Percent actual detergent in solution	Experimental		Predicted result	
		Cc. suds after shaking 20 sec.	Cc. suds after standing 5 min.	Suds formation	Suds stability
Alkyl sulfate (48% actual) (A).....	0.048	110	35	-----	-----
Sulfonate promoter (49% actual) (B).....	.049	120	110	-----	-----
Mixture of A+B contg. the actual detergents in the proportion of 8:2.....	.048	350	325	112	41

Example 3.—The coconut oil fatty acid ester of sodium glyceryl sulfonate used as promoter in this example contained about 85 percent actual sulfonate promoter and the alkyl sulfate detergent was similar in composition to that used in the previous examples. Sudsing tests were carried out as in the case of Example 2. The improvement both in sudsing and in the stability of suds is convincingly demonstrated in the following table.

Table III

Description of sample	Percent actual detergent in solution	Experimental		Predicted result	
		Cc. suds after shaking 20 sec.	Cc. suds after standing 5 min.	Suds formation	Suds stability
Alkyl sulfate (48% actual) (A).....	0.048	110	25	-----	-----
Sulfonate promoter (85% actual) (B).....	.051	125	125	-----	-----
Mixture of A+B contg. the actual detergents in the proportion of 9:1.....	.048	140	115	111	27
Mixture of A+B contg. the actual detergents in the proportion of 8:2.....	.048	260	250	113	30

In all of the above examples it will be noted that the amount of suds and the stability of the suds obtained by shaking a solution of the mixed detergents is not predictable. One detergent,

it will be noted, is slightly better than the other in sudsing characteristics. It is clearly shown, however, that the mixing of the alkyl sulfate and sulfonate promoter produces a particularly new and exceptionally useful more-than-additive effect not predictable from the properties of the individual ingredients themselves. In fact, in general effect, the mixture was superior to either of the individual constituents.

It is understood, of course, that it is not necessary to form an intimate mixture of the materials such as would be obtained by thoroughly mixing pastes or concentrated solutions of the respective constituents. A mechanical mixture of the dry ingredients in proper proportion may be used with identical results. Similarly, the materials may be added individually to the water in the correct proportion to effect similar improvements in the sudsing qualities of the alkyl sulfate. The manner of mixing is not a limitation of my invention.

The sudsing properties of alkyl sulfates of other alcohols can be similarly improved by the addition of any of the above mentioned sulfonate promoters, but obviously because of the variable solubility of the alkyl sulfates of the various alcohols the optimum results will vary according to the conditions of use.

In the determination of the suitability of materials as washing agents, it is found that volume of suds produced, stability or lasting quality of the suds, and cleansing or detergent power, are three different properties which are not neces-

sarily associated with each other, but which are all desirable in a good washing agent. Good sudsing or stability of suds in clear water, furthermore, is not necessarily followed by good sudsing, or especially by good stability of suds, in the presence of soiled fabrics.

The improvement in sudsing properties of the alkyl sulfate detergents in the presence of standard soiled fabric and the improvement in the detergent properties of same by the addition of

the above sulfonate promoters is illustrated in the following example.

Example 4.—The materials used were as follows: (A), a commercial detergent product hav-

ing the following approximate analysis: 46.5 per cent of the sodium salt of alkyl sulfuric acid prepared from the alcohols obtainable from coconut oil, 52.2 per cent sodium sulfate and 1.3 per cent petroleum ether extract; (B), a commercial form of the sodium salt of oleyl acid amide of methyl taurine, and consisting approximately of 33 per cent of actual sulfonate, 64 per cent sodium chloride and 3 per cent sodium sulfate.

- 10 Mixtures of the above compounds containing: first, 90 per cent of (A) and 10 per cent of (B), and second, 80 per cent (A) and 20 per cent (B) were prepared by mechanically mixing the correctly proportioned ingredients. It will be noted
15 that in these two mixtures the actual detergent ingredients were in the ratio of 12.7:1 and 5.6:1, respectively. Solutions of 21 grain water as previously described containing various percentages of the mixtures were prepared and used in
20 the washing of uniformly soiled fabric at 100° F. according to a standardized procedure known to give comparative results, to show the amount of detergent required to obtain a given degree of
25 whiteness. Sudsing data were also collected during the washing tests. Concentrations of the respective actual detergents necessary to wash the fabric under identical conditions to a given degree of whiteness as measured by an electrical
30 grading apparatus not dependent on human eye comparisons were as follows.

Table IV

35 Description of sample	Experimental—	Predicted result—
	Percent actual detergent in solution to give same whiteness	Percent actual detergent in solution to give same whiteness
Alkyl sulfate (46.5% actual) (A).....	0.033	-----
10 Sulfonate promoter (33.0% actual) (B).....	0.012	-----
Mixture of A+B contg. the actual detergents in ratio of 12.7:1.....	0.020	.029
15 Mixture of A+B contg. the actual detergents in ratio of 5.6:1.....	0.020	.026

A comparison of the experimental and predicted data will readily show the marked improvement in detergency and especially the more-than-additive effect obtained by the addition of the sulfonate promoter to the alkyl sulfate in that less of the mixture is required to give a definite degree of whiteness than that predictable from the properties of the individual constituents of the mixture.

15 The concentrations of the respective actual detergents necessary to yield a given amount of suds in the presence of soiled fabrics were as follows.

Table V

10 Description of sample	Experimental—			Predicted result		
	200 cc. suds	100 cc. suds	50 cc. suds	200 cc. suds	100 cc. suds	50 cc. suds
15 Alkyl sulfate (46.5% actual) (A).....	.035	.030	.028	-----	-----	-----
Sulfonate promoter (33% actual) (B).....	.026	.020	.013	-----	-----	-----
20 Mixture of A+B contg. the actual detergents in the proportion of 12.7:1.....	.029	.025	.018	.034	.029	.026
25 Mixture of A+B contg. the actual detergents in the proportion of 5.6:1.....	.024	.017	.013	.033	.028	.024

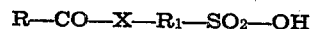
The results in Table V show clearly the more-than-additive sudsing effect produced by the addition of a sulfonate detergent of the character above described to a sulfate detergent, and demonstrates that a smaller quantity of the mixture is required to give a definite volume of suds than that predictable from the properties of the individual constituents of the mixture. Similar results are obtained if other sulfonate promoters such as the oleic acid ester of ammonium isethionate or the esters of sodium glyceryl sulfonate are used.

In the tabulated data above, I have presented what I term "experimental" and "predicted" results to show the marked more-than-additive effect in sudsing and detergent power noted when the respective detergents are mixed with each other as herein described. The experimental data are the results of actual tests, while the predicted results on the mixtures are calculated mathematically from the experimental data obtained on the individual constituents.

In the claims, reference to coconut oil is meant to include that group of tropical nut oils which are of similar chemical constitution, in general, and for use in my products are substantially interchangeable and of which coconut oil and palm kernel oil are the best known members.

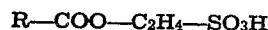
Having thus described my invention, what I claim as new and useful and desire to secure by Letters Patent is:

1. A wetting, sudsing and detergent agent comprising a mixture of a water soluble alkyl sulfate having eight to eighteen carbon atoms in the alkyl radical and a water-soluble salt of a true sulfonic acid corresponding to the general formula



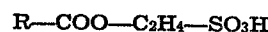
in which R denotes an aliphatic radical having eight to eighteen carbon atoms, and $-X-R_1-$ denotes an oxyalkylene or an amino alkylene radical, the ratio of true sulfonate to alkyl sulfate being not greater than three to two but such that water solutions of said mixture are characterized by sudsing and detergent power greater than that predictable from the corresponding characteristics of the respective ingredients.

2. A wetting, sudsing and detergent agent comprising a mixture of sodium alkyl sulfates derived from the higher alcohols obtainable from coconut oil, and a water-soluble salt of a true sulfonic acid corresponding to the formula



in which $R-COO-$ is the radical of a fatty acid having eight to eighteen carbon atoms, the ratio of true sulfonate to alkyl sulfonate being not greater than three to two but such that water solutions of said mixture are characterized by sudsing and detergent power greater than that predictable from the corresponding characteristics of the respective ingredients.

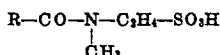
3. A wetting, sudsing and detergent agent comprising a mixture of sodium alkyl sulfates derived from the higher alcohols obtainable from coconut oil, and a water-soluble salt of a true sulfonic acid corresponding to the formula



in which $R-COO-$ is the radical of oleic acid, the ratio of true sulfonate to alkyl sulfonate being not greater than three to two but such that water solutions of said mixture are characterized by sudsing and detergent power greater than that

predictable from the corresponding characteristics of the respective ingredients.

4. A wetting, sudsing and detergent agent comprising a mixture of alkali metal alkyl sulfates derived from the higher alcohols obtainable from coconut oil, and a water-soluble salt of a true sulfonic acid corresponding to the formula



- in which R— is the alkyl radical contained in oleic acid, the ratio of true sulfonate to alkyl sulfonate being not greater than three to two but such that water solutions of said mixture are characterized by sudsing and detergent power greater than that predictable from the corresponding characteristics of the respective ingredients.

5. A wetting, sudsing and detergent agent comprising a mixture of alkali metal alkyl sulfates derived from the higher alcohols obtainable from coconut oil, and a water-soluble salt of a true sulfonic acid corresponding to the formula



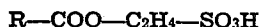
- in which R—COO— represents the mixed acid radicals contained in coconut oil, the ratio of true sulfonate to alkyl sulfonate being not greater than three to two but such that water solutions of said mixture are characterized by sudsing and detergent power greater than that predictable from the corresponding characteristics of the respective ingredients.

6. The process of preparing a spray dried laundering agent, the active ingredient of which consists in part of primary alkyl sulfate having eight to eighteen carbon atoms in the alkyl radical, which comprises incorporating with two parts of the primary alkyl sulfate prior to spray drying not more than three parts of a water-soluble salt of a true sulfonic acid corresponding to the general formula



- in which R denotes an aliphatic radical having eight to eighteen carbon atoms and —X—R₁— denotes an oxyalkylene or an amino alkylene radical, said salts being substantially non-volatile at the temperature of spray drying, whereby the sudsing and detergent power of said primary alkyl sulfate in water solution is improved to a greater extent than that predictable from the characteristics of the true sulfonic acid salt added.

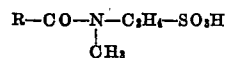
7. The process of preparing a spray dried laundering agent, the active ingredient of which consists in part of the higher primary alkyl sulfates obtainable from coconut oil which comprises adding to and incorporating with two parts of the primary alkyl sulfate prior to spray drying not more than three parts of a water-soluble salt of a true sulfonic acid corresponding to the formula



- in which R—COO— is the radical of oleic acid, whereby the sudsing and detergent power of said primary alkyl sulfate is improved to a greater extent than that predictable from the characteristics of the true sulfonic acid salt added.

8. The process of preparing a spray dried laundering agent, the active ingredient of which consists in part of the higher primary alkyl sulfates obtainable from coconut oil which comprises adding to and incorporating with two parts of the primary alkyl sulfate prior to spray drying

not more than three parts of a water-soluble salt of a true sulfonic acid corresponding to the formula



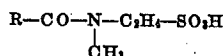
in which R— is the alkyl radical contained in oleic acid, whereby the sudsing and detergent power of said primary alkyl sulfate is improved to a greater extent than that predictable from the characteristics of the true sulfonic acid salt added.

9. The process of preparing a spray dried laundering agent, the active ingredient of which consists in part of the higher primary alkyl sulfates obtainable from coconut oil which comprises adding to and incorporating with two parts of the primary alkyl sulfate prior to spray drying not more than three parts of a water-soluble salt of a true sulfonic acid corresponding to the formula



in which R—COO— represents the mixed acid radicals contained in coconut oil, whereby the sudsing and detergent power of said primary alkyl sulfate is improved to a greater extent than that predictable from the characteristics of the true sulfonic acid salt added.

10. A detergent preparation having greater sudsing power in water solution from that predictable from the corresponding characteristics of the respective ingredients and containing as the active detergent a mixture consisting essentially of about 70–95 per cent of the sodium salt of alkyl sulfuric acids obtained by the sulfation of the higher alcohols derived from coconut oil and about 5–30 per cent of the sodium salt of the true sulfonic acid corresponding to the general formula



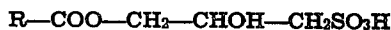
in which R— is the alkyl radical contained in oleic acid.

11. A detergent preparation having greater sudsing power in water solution than that predictable from the corresponding characteristics of the respective ingredients and containing as the active detergent a sudsing mixture consisting essentially of about 70–95 per cent of the sodium salt of alkyl sulfuric acids obtained by the sulfation of the higher alcohols derived from coconut oil and about 5–30 per cent of the ammonium salt of a true sulfonic acid corresponding to the general formula



in which R—COO is the radical of oleic acid.

12. A detergent preparation having greater sudsing power in water solution than that predictable from the corresponding characteristics of the respective ingredients and containing as the active detergent a mixture consisting essentially of about 70–95 per cent of the sodium salt of alkyl sulfuric acids obtained by the sulfation of the higher alcohols derived from coconut oil and about 5–30 per cent of the sodium salt of the true sulfonic acid corresponding to the general formula



in which R—COO represents the mixed acid radicals contained in coconut oil.

13. A detergent composition containing as the active constituent a mixture consisting essentially of about seventy per cent to about ninety-five

per cent of a water soluble alkyl sulfate derived from a mixture of alcohols obtainable from a natural fatty substance, and about five per cent to about thirty per cent of a water-soluble salt of a true sulfonic acid having the formula



in which R denotes an aliphatic radical having

eight to eighteen carbon atoms and $-X-R_1$ denotes an oxyalkylene or an amino alkylene radical, said composition having greater detergent and lathering power in water solution than that predictable from the corresponding characteristics of the respective constituents.

WILFRED S. MARTIN.

DISCLAIMER

2,156,996.—*Wilfred S. Martin*, Norwood, Ohio. DETERGENT AND WETTING COMPOSITIONS. Patent dated May 2, 1939. Disclaimer filed June 4, 1940, by the assignee, *The Procter & Gamble Company*.

Hereby disclaims from claims 1 and 6 wetting, sudsing and detergent agents other than those in which the alkyl sulfates of the mixture are obtained by reaction of the sulfating agent on higher molecular weight normal primary aliphatic alcohols.

[*Official Gazette July 2, 1940.*]