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G. O. FUNDERBURK ET AL

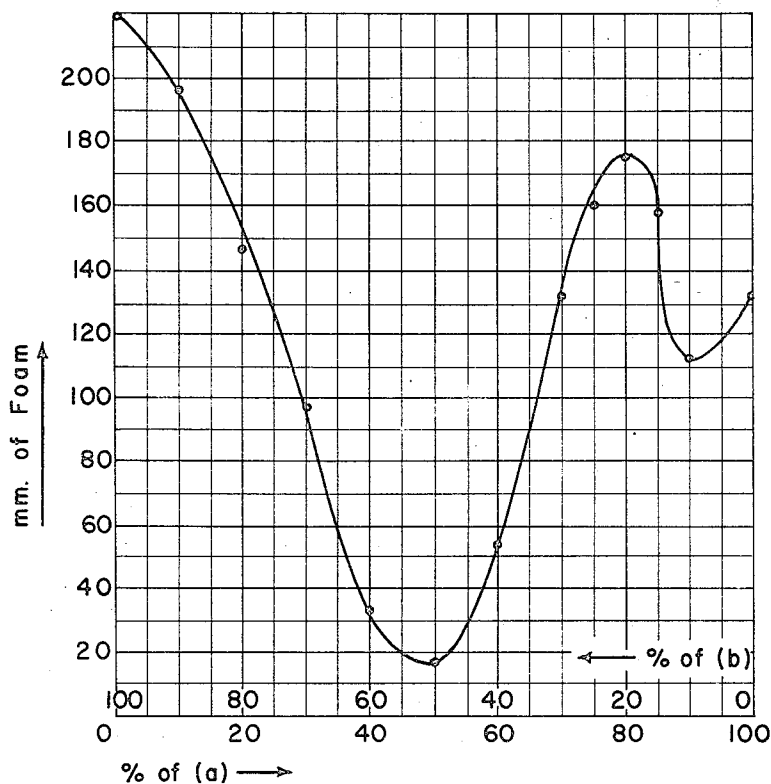
2,833,722

DETERGENT COMPOSITIONS

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(a) = $C_{12}H_{25}-O-SO_3Na$

(b) = $C_{12}H_{25}-NH-CH_2CH_2-COONa$



INVENTORS
GEORGE O. FUNDERBURK
ROBERT C. JOHNSON
RUSSELL H. SMITH

BY

David Katz

ATTORNEY

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2,833,722

DETERGENT COMPOSITIONS

George O. Funderburk, Upper Penn's Neck, N. J., Robert C. Johnson, Wilmington, Del., and Russell H. Smith, Western Springs, Ill., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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6 Claims. (Cl. 252—152)

This invention relates to detergent compositions of matter. It is an object of this invention to provide improved detergents, characterized by their ability to produce and maintain copious foam in the presence of greasy soil and by improved ability to emulsify such soil and hold it in suspension. Additional important objects and effects of this invention will appear as the description proceeds.

Detergent compositions such as soap and synthetic detergents have for many years been admixed with various other chemical materials, which enhance the detergent power of the former. Common examples of such materials are sodium sulfate, sodium carbonate, and various polyphosphates and silicates. These materials are generally referred to in the art as builders, and their principal effect is to improve the cleansing power of the detergent in so far as the power to remove solid particles from textile fiber is concerned. Thus, the test commonly applied to detergents containing such adjuvants is generally a measurement of the degree of whiteness imparted to (or light reflected by) a white piece of fabric which has been darkened by a standard soil prior to testing and which has then been washed for a standard length of time by a standard bath containing the detergent being tested.

Our invention differs from the foregoing field in that we are interested primarily in improving the capacity of a detergent to remove greasy soil from various articles, not necessarily textiles. Typical examples of the field in which we are interested are the washing of dishes by hand or in a dishwashing machine and the shampooing of human hair.

The power of a detergent to emulsify greasy soil is generally related to its power to produce and maintain foam in the presence of greasy soil. The two practically go hand-in-hand, and the one may be taken as a convenient yard stick for the other. Thus, in household use, the housewife is accustomed to adding more detergent when foam disappears from the dishwasher or washing machine. To the detergent manufacturer, this persistence of foam in the presence of grease constitutes "mileage" per unit of active component.

Our invention is also not to be confused with the problem of preparing a composition of matter adapted to produce copious foam for its own value, as for instance in fire extinguishers. Such foams are frequently made from non-detergent materials and have no detergent power whatever in the usual sense. Also, in their field of application grease is not ordinarily present; and the problem, generally, is how to produce a maximum volume of foam from a given weight of the composition or in a given time limit, or how to produce a foam of certain qualities for instance as to bubble size, stability in time, etc.

We are not concerned with such problems. Our problem is to endow the composition with the power to emulsify a maximum quantity of grease, and in so far as foaming is an index to this power, our problem is to produce a detergent which will continue to produce foam

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until a great many greasy dishes have passed through the washing bath containing the detergent.

Our present invention is based on the observation that the foaming powers in the presence of grease of salts of mono-n-dodecyl sulfuric acid such as the sodium, potassium, ammonium, diethanolammonium and triethanolammonium salts, are increased considerably, in some cases practically doubled, if these salts are admixed with a minor quantity (say 10 to 30% by weight of the combination) of an auxiliary agent as defined below.

The auxiliary agent above referred to may be defined as an N-alkyl-beta-amino propionate of the general formula



wherein R is a normal alkyl radical of 10 to 12 C-atoms, while X is a water-solubilizing cation and may be exemplified by sodium, potassium, ammonium, diethanolammonium and triethanolammonium.

Compounds of the latter type are not novel. Convenient methods for producing them have been described in U. S. Patents 2,195,974 and 2,468,012. These compounds have also been recognized in the art as having detergent, emulsifying and surface active powers. Such action, however, is not definably related to the power of a given substance to emulsify and hold greasy soil and to produce persistent foam in the presence of such soil. As a matter of fact, the salts of monododecyl sulfuric acid aforementioned are per se well established on the market as detergents for various purposes, but nevertheless fall short when the soil to be removed is characterized by copious proportions of grease or oil.

In U. S. Patent 2,619,467, compositions of matter are described and claimed wherein alkylamino-propionate agents of the same general type as above but having longer alkyl chains are admixed with a small quantity of other surface-active agents which have a more predominantly hydrophilic character, for the purpose of improving the detergent properties of said propionates. Now, although the patent embraces broadly in its list of hydrophilic auxiliary agents "soluble salts of sulfates of a large variety of hydroxy compounds, including the fatty alcohols of intermediate molecular weight," its specific examples fail to include compositions of this type.

We have investigated this subject, and have found that as a matter of fact salts of monododecyl sulfuric acid decrease the foaming powers of decyl and dodecyl beta alanine salts ("alanine" being here used as a short name for amino-propionic acid). The impairment of the foaming qualities continues to increase as the concentration of the dodecyl sulfate increases until, when the proportion of the two agents is about 50:50 by weight, the foam breaks down altogether.

In spite of the above detrimental effect of the specified admixture, we have found, nevertheless and to our great surprise, that when water-soluble salts of decyl or dodecyl beta alanine are added to water-soluble monododecyl sulfates, but in such quantities that the alanine compound is present only in minor proportions (10 to 30% of the weight of the mixtures), the composition again acquires high foaming qualities, and the grease suspending powers of the dodecyl sulfate component become greatly increased.

The entire subject is made clearer by the accompanying drawing, wherein the sole figure constitutes a graph showing the behavior of mixtures of sodium dodecyl sulfate and N-dodecyl-beta-amino-sodium propionate, ranging in composition from 0 to 100% for each component. The ordinates represent millimeters of foam measured by the standard Ross-Miles method (Oil and Soap, vol. 18, page 99; 1941). The abscissas represent %-compo-

sition by weight of the sulfate and propionate components.

It will be noted that whereas the pure alanine compound produces about 220 mm. of foam in the above test, the height of the foam drops rapidly as quantities of sodium dodecyl sulfate are admixed therewith, until at about 50%, the foam has reached a minimum of such low value as to put the admixture practically in the classification of non-foamers. However, as the proportion of sodium dodecyl sulfate is increased still further, the foaming qualities of the mixture begin to rise and reach a maximum at about the 80:20 point by weight. The optimum for practical purposes lies somewhere in the region of 10 to 30% of the alanine compound and 90 to 70% of the alkyl sulfate salt.

Such a behavior of the mixture is very surprising as a matter of knowledge and constitutes a most valuable contribution to the practical field, inasmuch as it enables us to provide for practical use a relatively inexpensive but highly effective cleansing agent for greasy articles and for hair shampoos.

The compositions of matter prepared according to this invention may be dry mixtures, aqueous pastes or aqueous solutions of the two components. In all cases, any of the conventional detergent builders and fillers may also be present. These are chosen by the formulator, depending on the color, odor, consistency and performance he desires. The mode of compounding may follow ordinary practice such as milling together the dry substances or pastes, or simply mixing together the solutions.

The requisite dodecyl sulfate component may be 100% material or a commercial grade of this agent. A common commercial form of this agent is obtained by sulfation of an alcohol mixture resulting from the catalytic hydrogenation or sodium-alcohol reduction of coconut oil. This hydrogenation or reduction gives mixed higher, normal, straight-chain alcohols, which usually are fractionated to give a mixture having the desired properties. One of the common commercial grades of this mixture has the following approximate composition by weight: C₁₀, 3%; C₁₂, 61%; C₁₄, 23%; C₁₆, 11% and C₁₈, 2%.

For the alanine component, likewise, commercially available grades thereof may be employed.

For the purpose of testing our novel compositions we have adopted the following procedure as a standard:

One liter of 0.1% solution, in water of 300 p. p. m. hardness, of the composition to be tested is placed in a relatively wide and shallow, circular enameled pan. Then 55 g. of a standard greasy soil are added, and the mixture is agitated moderately for 5 minutes at 24° to 26° C. If a voluminous foam is produced, the detergent mixture meets the strict requirements of this invention for operability; i. e., it has the capacity to emulsify a heavy load of greasy soil in hard water and simultaneously foam copiously.

The concentration index above (0.1%) refers to total per cent of active ingredient. That is, if either component is diluted with builders, fillers or water, the weight thereof employed for the test is proportionately increased.

The standard greasy soil above referred to may be made up at will, but in our tests it was made up essentially as in U. S. P. 2,702,278 issued to Cupery and Funderburk, except that the last two ingredients there mentioned (salicylanilide and ammonium hydroxide) were omitted.

Water of 300 p. p. m. hardness was employed to make the conditions of the test more drastic, inasmuch as grease-emulsification and foaming are more difficult to attain in hard water.

Without limiting our invention, the following examples will illustrate our preferred mode of procedure. Parts mentioned are by weight. All alkyl radicals named are normal.

Example 1

267 parts of a commercial aqueous paste of sodium

monoalkyl sulfate (of a composition as above indicated, the C₁₂ component predominating, and the total active ingredient of the mixture being 30% by weight) are mixed with 66.7 parts of a commercial aqueous paste of N-decyl-beta-amino-sodium propionate (30% active ingredient). The active ingredient of the resulting mixture is thus likewise equal to 30% by weight, and contains 80 parts of the sodium monoalkyl sulfate and 20 parts of the mentioned propionate.

The product is an essentially odorless, stiff, white paste. At 0.1% active ingredient concentration in water, it gives voluminous foam when subjected to the above standard test. In contrast, neither the sulfate salt nor the propionate alone, produces any foam whatsoever under the same conditions. Only greasy curds are formed.

If the above product is drum-dried, a dry white solid results which has the same good grease-emulsifying and foaming properties as the paste, when tested at the same active ingredient concentration.

Example 2

A liquid detergent composition of 40% total A. I. (active ingredient) is prepared by mixing 80 parts of the triethanolamine salt of mono-dodecyl sulfate (as a 40% A. I. aqueous solution), 20 parts of the triethanolamine salt of N-decyl-beta-amino propionic acid and 30 parts of water. The product is a slightly viscous, amber liquid. It emulsifies a heavy load of greasy soil and foams copiously at the same time, whereas its components give only greasy curds when used singly under the same conditions.

In a similar manner, the following additional compositions were prepared, tested and found to give excellent performance for the purposes of this invention. In this table, the two components (a) and (b) were mixed in each example in the proportions indicated.

(a) represents a dodecyl sulfate salt of the formula C₁₂H₂₅-OSO₃M, wherein M is a cation as indicated.

(b) represents a beta-alkyl alanine salt of the formula R-NH-CH₂CH₂-CO-OX, wherein R is decyl or dodecyl, as indicated, while X is a cation as named in the respective column.

Example	M	R	X	Weight-ratio of (a):(b)
3	Sodium	Decyl	Sodium	9:1
4	do	do	do	7:3
5	do	Dodecyl	do	8:2
6	Potassium	Decyl	do	8:2
7	Ammonium	do	do	8:2
8	Diethanol-ammonium	do	do	9:1
9	do	do	do	7:3
10	Triethanol-ammonium	do	do	9:1
11	do	do	do	7:3
12	Sodium	Dodecyl	Potassium	8:2
13	do	do	Ammonium	8:2
14	Diethanolammonium	Decyl	do	8:2
15	Triethanolammonium	do	do	8:2
16	do	do	Diethanolammonium	8:2
17	Sodium	do	do	8:2
18	Diethanolammonium	Dodecyl	do	8:2
19	do	Decyl	do	8:2
20	do	do	Triethanolammonium	8:2
21	Sodium	do	do	8:2

In all the examples above, essentially the same results are obtained when the named decyl or dodecyl alanine salts are replaced respectively by the corresponding dodecyl or decyl homologs. Also, in all the examples above, greasy curds and no foam are obtained when either ingredient (a) or (b) is used alone to the same total A. I. concentration (0.1%), in the above standard tests.

Example 22

30 parts of the 80:20 detergent composition prepared in Example 5 above and 65 parts of tetrasodium pyrophosphate were mixed together intimately to produce a dry detergent product. When made up at 0.1% A. I. concentration (based on 80:20 mixture) in hard water of 300 p. p. m. and then tested in the manner previously described, this detergent solution foamed voluminously in the presence of the heavy load of greasy soil.

Control solutions containing respectively sodium dodecyl sulfate alone and beta-decylamino-sodium propionate alone, but each containing the same proportion of tetrasodium pyrophosphate as the foregoing dry detergent product, produced no foam when treated under the same condition at 0.1% A. I. concentration.

Example 23

30 parts of the 80:20 detergent composition prepared in Example 5 above were mixed intimately with 15 parts of sodium sesquisilicate ($\text{Na}_3\text{HSiO}_4 \cdot 5\text{H}_2\text{O}$) and 50 parts of sodium sulfate to produce a dry detergent product. When tested as above at 0.1% A. I. in hard water containing a heavy load of greasy soil, this product produced voluminous foam, while control solutions containing the same builders but only one or the other of the named principal ingredients (in the same total weight), produced no foam under the same conditions.

The practical merits of this invention will now be readily appreciated.

The compositions of this invention possess an excellent combination of properties. They are light colored, odorless, non-toxic, reasonably cheap, capable of emulsifying heavy loads of greasy soil and of foaming copiously in the presence of it. They can be used both in soft water and in hard water.

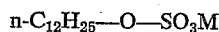
These properties make them eminently suited for the detergent in formulations designed for several important household uses. One such use is dishwashing, where heavy grease loads of widely varying compositions must be emulsified. Simultaneous foaming is also required.

Another very important household use is the washing of hair. In addition to cleansing the hair and scalp free from natural skin oils and greasy materials, shampoos must also be capable of emulsifying large amounts of mineral oil and similar materials derived from the use of hair oils. The novel compositions of this invention are excellently adapted to achieve this result.

We claim as our invention:

1. A detergent composition adapted for emulsifying

greasy soil, comprising as active ingredient a mixture of a water-soluble sulfate of the formula



- 5 and a water-soluble propionate of the formula



wherein X and M represent cations selected from the group consisting of sodium, potassium, ammonium, diethanolammonium and triethanolammonium, and R is a normal alkyl radical of the group consisting of decyl and dodecyl, the proportion of the propionate being not less than 10% and not more than 30% of the combined weight of said propionate and sulfate.

- 15 2. A detergent composition adapted for emulsifying greasy soil, comprising as active ingredient a mixture of sodium n-dodecyl sulfate and sodium beta-N-n-decylamino-propionate, the proportion of the two in the order named being 80:20 by weight.

- 20 3. A detergent composition adapted for emulsifying greasy soil, comprising as active ingredient a mixture of sodium n-dodecyl sulfate and sodium beta-N-n-dodecylamino-propionate, the proportion of the two in the order named being 80:20 by weight.

- 25 4. A detergent composition adapted for emulsifying greasy soil, comprising as active ingredient a mixture of diethanolammonium-n-dodecyl sulfate and diethanolammonium beta-N-n-decylamino-propionate, the proportion of the two in the order named being 80:20 by weight.

- 30 5. A detergent composition adapted for emulsifying greasy soil, comprising as active ingredient a mixture of diethanolammonium-n-dodecyl sulfate and diethanolammonium beta-N-n-dodecylamino-propionate, the proportion of the two in the order named being 80:20 by weight.

- 35 6. A detergent composition adapted for emulsifying greasy soil, comprising as active ingredient a mixture of triethanolammonium-n-dodecyl sulfate and triethanolammonium beta-N-n-decylamino-propionate, the proportion of the two in the order named being 80:20 by weight.

References Cited in the file of this patent

UNITED STATES PATENTS

2,619,467 Isbell ----- Nov. 25, 1952

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,833,722

May 6, 1958

George O. Funderburk et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 30, for "solid solid" read -- solid soil --; column 3, line 8, for "admixture" read -- mixture --.

Signed and sealed this 22nd day of July 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

UNITED STATES PATENT OFFICE
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