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SYNTHETIC DETERGENT COMPOSITIONS

John David Malkemus, Allendale, N. J., assignor to Colgate-Palmolive-Peet Company, Jersey City, N. J., a corporation of Delaware

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The present invention relates to new synthetic detergent compositions and, more particularly, to new compositions of the type of modified sulphated and sulphonated organic materials having improved wetting, emulsifying and detergent characteristics, and to a process for preparing the same.

Various inorganic builders, such as phosphates, carbonates, etc., have been added to fatty acid soaps for the purpose of modifying the characteristics of the soaps, and certain of these inorganic builders have also been employed with synthetic detergents. In the latter field, however, while useful for some purposes, such inorganic materials have not been found fully adequate for improving synthetic detergents because of the entirely different chemical nature of synthetic detergents and their different properties in aqueous solution as compared with soaps. For example, while certain built soaps will normally form a relatively stable foam capable of retaining a large amount of water therein for several minutes, the use of the same inorganic builders in synthetic detergents does not provide appreciably improved foaming characteristics under similar conditions.

The foaming characteristics of a wetting agent or detergent are important for a number of reasons and are largely determinative of the manner in which said composition may be used. Thus, a poorly foaming detergent has very little consumer appeal for household use. The non-industrial consumer insists upon a detergent which foams readily and thereby provides an indication of the amount of detergent added to the wash solution, although the actual relationship between foaming and detergency is still to be understood.

The amount of solution held in a foam and the stability of the foam formed are very important in certain uses, particularly when the detergent is employed outside of a container. For example, the success of a hair shampoo is believed to depend largely upon whether, when agitated in aqueous solution, it can form a strong and wet foam which will keep enough of the detergent solution in the hair so that thorough washing can be effected before the solution runs off.

Superior foaming characteristics are also desirable in a shaving cream. A good shaving foam or lather is believed to serve two notable functions: (1) the wetting agent solution in the foam softens the hairs and makes them more easily cut by the razor; and (2) a "stiff" foam holds the hairs upright on the skin and permits the blade to cut them at a right angle to their length, thus providing a close shave. A stable foam capable of retaining a large amount of the wetting agent in solution around the hairs for a sufficient length of time for the shaving operation is thus highly desirable.

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Foams are of great industrial importance in flotation operations, particularly in the concentrating of mineral ores. A froth or foam is produced capable of carrying the richer portion of a crushed ore, and this foam rises to the top of the liquid body and is either skimmed off or caused to flow to a collecting point. Stability and control of foam are the essence of such flotation procedures, for the foam must be stable throughout the operation and must be adaptable to control by the operator in selective carrying power.

It is an object of the present invention to provide novel wetting and detergent compositions capable of foaming relatively stable foams in aqueous solution and capable of forming foams which carry a large amount of liquid.

It is also an object of this invention to provide a method for preparing new wetting and detergent compositions of improved foaming characteristics.

Other objects and advantages of the invention will be apparent from the following description.

According to this invention, it has been found that the incorporation of a small proportion of an aliphatic surface-active compound of the class consisting of fatty acids and their monohydric alcohol and glycol esters with non-soap detergents, emulsifiers and wetting agents of the type of sulphated or sulphonated organic materials provides a composition which in aqueous solution has markedly improved foaming and sudsing properties. A suggested theory of operation is that the presence of such polar and at most only slightly ionized compounds having a hydrophylic carboxylic group or derivative thereof, relatively stable to hydrolysis, at or near the end of a moderately long carbon chain, when dissolved in water with the detergent material, alters the surface-active properties of the air-liquid interface. The interface thereby gets the properties of the active detergent, emulsifying and/or wetting ingredient plus those of the organic builder or perhaps the properties of the organic builder alone by its entirely displacing the active ingredient. It will be understood that the foregoing discussion of theoretical principles and considerations is intended solely as a suitable explanation of this invention for the benefit of those skilled in the art, and it is in no wise to be considered a limitation of the invention herein described.

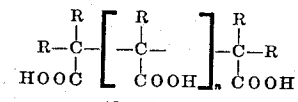
The synthetic organic non-soap water-soluble

detergents from the class consisting of sulphates and sulphonates comprised by the novel compositions of the invention may be prepared from organic materials which are applicable for sulphonation ("true" sulphonation and/or sulphation), especially those having about eight to about twenty-six (and preferably about twelve to about twenty) carbon atoms to the molecule, including fatty oils, unsaturated fatty acids, mineral oils, mineral oil extracts, mono- and di-glycerides, partial esters or ethers of polyglycols, esters or ethers of glycols, polyglycols and polyalcohols, aromatic and alkylated aromatic compounds, alcohols and olefines, coal tar distillates, and numerous other organic compounds and mixtures of compounds. Such compounds can be sulphonated by any of several methods and may form any of several products, depending upon the method of sulphonation employed. The sulphonated or sulphated organic compounds include sulphonated mineral oil; conventional mineral oil refinery sludges; sulphonated mineral oil extracts; sulphonated fatty acids and oils, including sulphonated castor oil, sulphoricinoleic acid, sulphonated olive oil, and sulpho-oleic acid, aliphatic sulphonates and sulphates, including cetyl sulphuric acid, dodecyl acid sulphate, and tetradecanehydroxy sulphonic acid-1,2; aliphatic ether and ester sulphonates including the dodecyl ether of hydroxy ethyl sulphonic acid, the cetyl ether of glyceryl sulphonic acid, and coconut oil monoglyceride monosulphate; sulphonates prepared by treatment of organic materials with sulphur dioxide and chlorine in the presence of light followed by hydrolysis of the product; sulphonates prepared by treatment of organic bodies with sulphuryl chloride and an activating agent in the presence of light followed by hydrolysis of the product; fatty acid amides of amino alkyl sulphonic acids, including lauric amide of taurine and tall oil acid amide of amino glyceryl sulphonic acid; sulphonic acids of naphthenes and naphthenic acids; lignin sulphonic acids; aromatic and alkylated aromatic sulphonic acids, including naphthalene sulphonic acid, octadecyl benzene sulphonic acid, and dodecyl naphthalene sulphonic acid; the product of a mineral oil extract sulphonated while dissolved in liquid sulphur dioxide; and innumerable other organic sulphonic and sulphuric acid derivatives or mixtures thereof. These organic sulphate and true sulphonate compounds include those in which the organic radicals of the molecule are unsubstituted or those which contain substituents, such as halogens, halogenoids, hydroxyls, nitrogen-containing groups, acyl groups, acyloxy groups, alkoxy groups, etc. Of these sulphated and sulphonated materials, the most suitable for inclusion in the novel compositions of the present invention are normally non-alkaline (having a pH below 7.0), and especially those having carboxylic ester linkages, including the sodium salts of the sulphuric acid esters of coconut oil fatty acid monoglycerides, tallow diglyceride monosulphate, etc.

The aliphatic surface-active compounds, which may be added to sulphated and/or sulphonated compounds to serve as organic builders and to achieve the desirable results described, are the slightly water-soluble carboxylic acids, especially fatty acids, having carbon chains of about eight to about twenty-six, and preferably about eight to about eighteen, carbon atoms per molecule and their monohydric alcohol and glycol esters. The fatty acid carbon chains may be straight or branched, saturated or unsaturated, and may be either unsubstituted or substituted by substituents such as halogens, hydroxyls, acyl groups acyloxy groups, alkoxy groups, nitrogen-containing groups, heterocyclic groups, alicyclic groups aryl groups, etc., although it is generally preferred that substituent groups of hydrophilic character be located near or adjacent to the carboxylic group or derivative.

Where esters are employed, the alcohol or glycol with which the fatty acid is esterified is preferably a lower member of the respective series, having about one to about three carbon atoms per molecule. Diesters of glycols may also be used where the glycol residue is attached to a fatty acid residue, as aforesaid, of about eight to about twenty-six, preferably about eight to about eighteen, carbon atoms per molecule and the other hydroxyl of the glycol is esterified with a short-chain acid containing one to about three carbon atoms per molecule. This serves the purpose of providing compounds having a hydrophylic group at or near the end of a moderately long carbon chain rather than near the middle of a carbon chain.

Similarly, certain dibasic and polybasic acids may be employed, such as those of the type:



where only one of the R's is a moderately long carbon chain and the other R's are, respectively, hydrogen atoms or short carbon chains (one to about three carbons) and where n is zero or a small whole number, say, 1 to 3. Mono- or diesters or glycol esters of these acids also form suitable builders in accordance with the present invention.

Any one or more of the foregoing compounds may be incorporated in the compositions of this invention, and/or other compounds which break down or react with the sulphonated materials or other constituents of the compositions to provide said organic builders may be employed.

Suitable carboxylic acids employed as builders include lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid, lauryl succinic acid, isocaprylic acid, α-aminocapric acid, undecylenic acid, undecanoic acid, linoleic acid, hexacosanoic acid, chloropalmitic acid, mixed coconut oil fatty acids, mixed tallow fatty acids, mixtures of any of these acids, etc. Similarly, esters of any of these acids with methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, etc., such as methyl laurate, ethyl oleate, ethylene glycol ricinoleate monoester, the acetic acid ester of ethylene glycol monolaurate, propylene glycol stearate monoester and the like, are suitable organic builders for incorporation in the novel compositions of this invention.

While a proportion of the organic builder ranging from about 0.01% to about 50% of the weight of active ingredient may be used, it is preferred to incorporate about 0.1% to about 20%, and more preferably about 1% to about 10%, of organic builder based upon the weight of active ingredient. The optimum proportion employed will vary with the particular active ingredient or mixture of active ingredients used; with the proportion of other ingredients present, if any; and to some degree with the strength or concentration of solution to be formed in use.

The organic builder may be incorporated with the active ingredient to form the novel composi-

tion of this invention at any point during the manufacturing process at which subsequent operations will not destroy or objectionably modify the builder or cause a deleterious reaction between the builder and any other material in the composition. In general, it is preferred to add the builder at a point in the manufacturing subsequent to the hydrolyzing and/or neutralizing step. This may be accomplished by adding the organic builder to solutions containing the active ingredient, by mixing the builder with the solid active ingredient in comminuted form, or by adding the builder to a solution of the active ingredient and thereafter subjecting the solution containing active ingredient and organic builder to spray-drying, roll-drying, etc., to form a solid composition.

Thus, the novel compositions provided may be made up in solutions, preferably concentrated, or a dry or partially hydrated solid product may be formed. The product may be made in a more or less finely divided condition, which permits its ready transformation into flakes or other physical forms, for example by passing between a pair of properly spaced rolls, or by pressing into cakes, or by other means, with or without addition or modifying agents.

Adjuvant materials may be admixed with the sulphonate salts by mixing the adjuvant materials with the sulphonated organic compounds and/or the neutralizing agents before neutralization or flashing, by simultaneously flashing a second solution containing such adjuvant materials, and/or by mixing the final product therewith. When added after neutralization, the adjuvant materials may be added before, after, or simultaneously with the organic builder. Such adjuvant material may include any of the substances employed by the art in admixture with sulphonated organic detergents generally, care being exercised to avoid the use of any material which would remove or otherwise substantially diminish the effectiveness of the particular organic builder incorporated. The type of addition agent will depend upon the ultimate use of the new composition.

The novel and improved synthetic detergents, emulsifiers and/or wetting agents of this invention, comprising sulphated and/or sulphonated organic compounds (with or without adjuvant materials) and a proportion of the organic builder described, produce foams and suds which are more stable, contain more liquid, drain more slowly, are formed of smaller bubbles, and do not so readily break due to evaporation as the foams and suds of similar compositions without the builder. From the point of view of foaming characteristics, it would be difficult to over-emphasize the importance of stability of the foam. As pointed out in United States Patent No. 2,315,983 to Ross and Miles, detergent solutions differ, not in their capacity to form foam, but in the stability of the foam produced. Thus, in the present case, solutions of the novel detergents of this invention, whether they produce an increased suds volume or a decreased suds volume, are characterized by increased stability of the foam produced. According to a suggested theory, it is not that more foam is produced but that, possibly due to decreased surface tension, less foam is destroyed. The low rates of drainage and of evaporation of foam produced in solutions of the improved compositions of this invention, as well as the smaller bubbles formed and the higher content of liquid, may also presumably be due in large measure to the lowered surface tension resulting from the presence of the organic builder.

Another advantageous characteristic of the novel detergent compositions of this invention lies in the ability of their aqueous solutions to assimilate a "load" (of dirt, grease, etc.) with greatly decreased foam loss. Many prior art detergent solutions foam very well until a load is added, after which volume and stability of foam are markedly reduced. This effect is largely overcome when employing the built detergents of the present invention.

It is a feature of the new compositions that aqueous solutions thereof have decreased wetting times as compared with "unbuilt" compositions which are otherwise quite similar. As will be appreciated, this reduction in time for wetting is of considerable commercial importance.

The effect, on the foaming characteristics of synthetic detergents and wetting agents, of the various organic builders described can be studied quantitatively for any given composition. The Ross and Miles patent (U. S. 2,315,983) referred to supra disclosed a pour foam test designed for comparative study of the relative foam stability of liquids and an apparatus for carrying out the test.

The liquid retained in the foam may be ascertained by shaking a measured volume of the solution under test in a graduated container under standardized conditions, and then measuring the amount of liquid drained at set time intervals. For example, 100 milliliters of the solution to be studied is placed in a 250 milliliter graduated cylinder having a total volume of 330 milliliters, and the cylinder is put in a thermostatic bath of desired temperature. After the solution reaches this temperature, the cylinder is shaken in an inverted position fifty times in thirteen seconds, held upside down for two seconds longer, then quickly righted and placed in the bath. The liquid drained from the foam at ten, twenty, thirty, forty-five and sixty seconds is recorded.

This cylinder foam drainage test clearly shows the greatly improved liquid-retentive properties of detergent solutions containing organic builders according to this invention. A 1% aqueous solution of the ether-extracted sodium salts of the sulphuric acid esters of coconut oil fatty acid monoglycerides shows about 16% of liquid held in the foam at 20° C. after thirty seconds. The improved liquid-retention of the foam formed upon addition to the solution of 0.05% of builder is shown in the following table:

Table I

Organic Builder	Per cent Liquid Held
Blank	16
Lauric Acid	36
Myristic Acid	35
Palmitic Acid	33
Stearic Acid	38
Methyl Myristate	26
Methyl Palmitate	25
Ethylene Glycol Stearate	28

The improvement in foam stability of detergent solutions by incorporating these organic builders therewith is demonstrated by the pour foam test described by Ross and Miles. Using a 0.25% solution of ether-extracted sodium salts of the sulphuric acid esters of coconut oil fatty acid monoglycerides, the solution being made alkaline to a pH of about 9 and containing 300 parts per million of hardness (calculated as calcium car-

bonate) and 0.004% of coconut oil acids soap, a pour foam test at 115° F. shows 155 millimeters of pour foam initially, 80 millimeters at the end of five minutes, and 25 millimeters in fifteen minutes. The improvement obtained upon adding 0.005% of a builder is shown in the following table:

Table II

Organic Builder	Mm. Pour Foam		
	Initial	5-min.	15-min.
Blank	155	80	25
Methyl Laurate	185	165	
Ethylene Glycol Laurate	195	185	80

This is far from a theoretical consideration, as synthetic detergents frequently find their greatest usefulness and advantage over fatty acid soaps in alkaline hard water areas. In such localities conditions quite similar to those described above are met, especially in non-industrial use, where the synthetic detergent is often employed in a container or with a utensil which has been in contact with a fatty acid soap solution. Small amounts of fatty acid soaps are normally quite destructive of foams in alkaline hard-water solutions of synthetic detergents, especially detergents of the non-alkaline type, and it has formerly been desirable to buffer such detergents on the acid side to minimize the effect on the foam. The addition of the buffer, usually in proportions of 10% and more, adds nothing to the value of the detergent in other areas but instead actually reduces the content of active ingredient. A far smaller proportion of the organic builder of this invention acts as a foam stabilizer, and the effectiveness of the organic builder in protecting foams against the calcium soaps formed is shown by the above table. When protecting the foam under such conditions of a solution of coconut oil monoglyceride monosulphate with ethylene glycol monolaurate, for example, a proportion of 5% to 15% of the monolaurate (based on the active ingredient) is a suitable one.

The following examples, described hereinafter, are merely illustrative of the present invention, and it will be understood that the invention is not limited thereto.

EXAMPLE I

The monosulphate of monoglycerides of coconut oil fatty acids, as prepared, is purified by extraction with ether and is dissolved in water to form an aqueous solution containing about 40% by weight of solids. Propylene glycol laurate monoester in an amount equivalent to about 2% by weight of said active ingredient is added to the solution. The solution is then roll-dried to produce a detersive material having excellent foaming characteristics in aqueous solution. A 0.25% solution is made up in water having 300 P. P. M. calcium hardness and 0.004% coconut oil acids soap, and sufficient alkali is added to raise the pH to about 9.0. The 5-minute pour foam at 115° F. is 130 millimeters as compared with a blank (without propylene glycol laurate) of 80 millimeters.

EXAMPLE II

About 20 parts by weight of coconut oil monoglyceride monosulphate sodium salt and about 1 part of stearic acid are thoroughly mixed together. The resulting detergent is stirred into 179 parts of water, and a cylinder foam drainage test is run on the resulting solution. About 23% of liquid is retained after thirty seconds at 40° C., as compared with a blank (without stearic acid) of 6% retained.

EXAMPLE III

One part by weight of methyl myristate is added to about 50 parts of a sulphonate prepared by treating a Pennsylvania white mineral oil of paraffin base and having an average molecular weight of 235 with sulphur dioxide and chlorine in the presence of light and neutralizing the product with sodium hydroxide. Sodium sulphate is added, and the ingredients are thoroughly mixed, the resulting detergent composition providing solutions of fine foaming characteristics.

EXAMPLE IV

The Edeleanu extract of a naphthene base mineral oil is dissolved in about twice its volume of liquid sulphur dioxide and sulphonated with oleum. A dry, fluffy powder containing about 96% of active ingredient is obtained, and this is dissolved in water to form an aqueous solution. A comparative test is made by dividing the solution among eight vessels and diluting with water to provide various concentrations of the active sulphonated mineral oil extract, as shown in the following table. Two solutions at each of the four concentrations are made up, and an amount of propylene glycol monolaurate equivalent to about 5% of the weight of the total solids present is stirred into one solution of each concentration. The solutions thus provided are compared as to wetting time at concentrations, respectively, of 1.00%, 0.50%, 0.25% and 0.125% with the unbuilt solutions (without propylene glycol monolaurate) at the same concentrations, a standard canvas disc being employed in a uniform manner in each test and at a temperature of about 30° C. A very large reduction in wetting time for the built detergent, particularly at the lower concentrations, is observed:

Table III

Per cent Concentration	Wetting Time in Seconds	
	Blank	Built Detergent
1.00	8	2.5
0.50	30	4
0.25	170	8
0.125	525	17

A comparison of the surface tension at each concentration is shown by the following table and indicates the depressive effect on surface tension of the presence of propylene glycol monolaurate:

Table IV

Per cent Concentration	Surface Tension in dynes per centimeter	
	Blank	Built Detergent
1.00	34.0	29.8
0.50	33.8	28.3
0.25	33.0	27.9
0.125	32.8	27.5

EXAMPLE V

Ether-extracted coconut oil monoglyceride monosulphate sodium salt is mixed with ethylene glycol monolaurate in the proportion of about twenty parts by weight to one to form a novel detergent according to this invention. Comparative tests for wetting times of aqueous solutions containing various concentrations of detergent indicate greatly decreased times for the novel detersive material produced over "unbuilt" blanks. Solution containing, respectively, 1.00%, 0.50%, 0.20% and 0.10% of the new detergent containing ethylene glycol monolaurate are compared in the following table with blanks ("unbuilt") of the same concentrations, all being at about 30° C.

Table V

Per cent Concentration	Wetting Time in Seconds	
	Blank	Built Detergent
1.00	21	9
0.50	31	13
0.20	99	47
0.10	710	114

The surface tension at each concentration and at the same temperature, both for blanks and the built detergents, is tabulated below:

Table VI

Per cent Concentration	Surface Tension in dynes per centimeter	
	Blank	Built Detergent
1.00	34.7	31.3
0.50	33.8	31.3
0.20	33.6	29.9
0.10	33.1	28.9
0.05	34.8	28.8

A 0.25% aqueous solution is then prepared and a cylinder foam drainage test is run. The new detergent holds 34% of liquid in the foam after thirty seconds at 20° C., as compared with a blank (without ethylene glycol monolaurate) of 18% retained.

EXAMPLE VI

The active ingredient of Example V is mixed with a "builder" in the same proportions as there described, substituting diethylene glycol monolaurate for ethylene glycol monolaurate. Similar tests of wetting time and surface tension are carried out on this novel detergent, and the results obtained are tabulated below and compared with the blanks at various concentrations:

Table VII

Per cent Concentration	Wetting Time in Seconds	
	Blank	Built Detergent
1.00	21	9
0.50	31	14
0.20	99	51
0.10	710	280

Table VIII

Per cent Concentration	Surface Tension in dynes per centimeter	
	Blank	Built Detergent
1.00	34.7	31.7
0.50	33.8	31.6
0.20	33.6	31.4
0.10	33.1	30.4
0.05	34.8	29.7

EXAMPLE VII

A built detergent similar to that described in Example III is prepared, but replacing the methyl myristate by one part by weight of ethylene glycol monolaurate for each twenty parts of the sulphonate present. Wetting time and surface tension for the new detergent thus produced are studied at various concentrations, the temperature being maintained at 30° C., and the following figures are obtained, comparison with blanks at the same concentrations being afforded:

Table IX

Per cent Concentration	Wetting Time in Seconds	
	Blank	Built Detergent
1.00	5	2
0.50	19	3.5
0.25	77	7
0.125	210	18

Table X

Per cent Concentration	Surface Tension in dynes per centimeter	
	Blank	Built Detergent
1.00	29.1	26.9
0.50	29.7	26.9
0.25	30.3	26.7
0.125	31.3	26.4

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 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.

I claim:

1. A solid detergent composition in the form of dried particles consisting essentially of synthetic organic non-soap water-soluble detergent from the class consisting of sulphates and sulphonates and an amount of organic builder sufficient markedly to improve the foaming properties in aqueous solutions but not over 50% by weight of said synthetic detergent, said builder being se-

lected from the group consisting of the lower monohydric alcohol and glycol esters of higher aliphatic fatty acids.

2. A cleansing and laundering composition having improved foaming characteristics in aqueous solution consisting essentially of synthetic organic non-soap water-soluble detergent from the class consisting of sulphates and sulphonates, and about 0.01% to about 50% by weight of said synthetic detergent of organic builder from the group consisting of the lower monohydric alcohol and glycol esters of higher aliphatic fatty acids wherein the fatty acid radical contains 8 to 18 carbon atoms.

3. A cleansing and laundering composition having improved foaming characteristics in aqueous solution consisting essentially of alkali metal salts of the sulphuric acid esters of coconut oil fatty acid monoglycerides, and about 0.1% to 20% by weight of said salts of organic builder selected from the class consisting of the lower monohydric alcohol and glycol esters of higher aliphatic fatty acids wherein the fatty acid radical contains from 8 to 18 carbon atoms.

4. A cleansing and laundering composition having improved foaming characteristics in aqueous solution consisting essentially of a mineral oil sulphonate produced by treating a mineral oil with sulphur dioxide and chlorine in the presence of actinic light and substantially neutralizing the product of said treatment and about 0.01% to 20% by weight of said sulphonate of an aliphatic

surface active compound of the group consisting of lower monohydric alcohol and glycol esters of higher aliphatic fatty acids wherein the fatty acid radicals contain 8 to 18 carbon atoms.

5. A cleansing and laundering composition having improved foaming characteristics in aqueous solution consisting essentially of a mineral oil sulphonate produced by treating a mineral oil with sulphur dioxide and chlorine in the presence of actinic light and substantially neutralizing the product of said treatment, and about 1% to 10% by weight of said mineral oil sulphonate of ethylene glycol mono-laurate.

JOHN DAVID MALKEMUS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,990,009	Stiles	Feb. 5, 1935
2,024,981	Reddish	Dec. 17, 1935
2,134,666	Kritchevsky	Oct. 25, 1938
2,144,884	Kritchevsky	June 24, 1939
2,164,717	Kritchevsky	July 4, 1939
2,169,344	Kimball	Aug. 15, 1939
2,184,952	Zimmer et al.	Dec. 26, 1939
2,356,903	Wood	Aug. 29, 1944
2,383,738	Richardson	Aug. 28, 1945
2,391,087	Donlan	Dec. 18, 1945