Patented Oct. 24, 1950 2,527,077

UNITED STATES PATENT OFFICE

2,527,077

DETERGENT COMPOSITION

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No Drawing. Application June 2, 1947, Serial No. 752,007

16 Claims. (Cl. 252—121)

1

The present invention relates to detergent compositions, and more particularly to soap-containing compositions which are highly resistant to curd-forming ingredients of hard water.

It is well known that the use of ordinary toilet or household soap in hard water results in the formation and precipitation of insoluble fatty acid salts, more commonly referred to as "lime soaps." It is also known that such precipitated lime soaps have a tendency to coagulate and form a sticky curd. This curd is commonly observed in the washstand and bath tub and also in the laundry rinse tube where it rises to the surface of the water as a scum, adheres to the walls of the tub as a ring, and sticks to the clothes during the rinsing operation, thereby giving to the clothes an unsightly dingy appearance, producing spots upon subsequent ironing, and often causing the development of a rancid odor. When soap is used for shampooing the hair, rinsing with hard water results in deposition of the lime soaps on the hair. In applications as divergent as the dyeing of textile fabrics and the plating of metals, the formation of lime soaps has undesirable effects.

In fact, if soap is used in hard water, insoluble lime soap curd forms during the rinsing process or whenever the soap dilution becomes sufficiently great to destroy the foaming and dispersing power of the soap.

The coagulation of the lime soaps to form soap curd is dependent not only on the degree of dilution of the soap in the hard water, but also on the age of the solution and on the degree of violence of agitation to which it is subjected, increasing age and increasing agitation both being important factors in promoting coagulation.

The primary object of the present invention is to provide a soap composition which forms little or no lime soap curd when used with hard water.

Another object is to provide a detergent composition which will not form a sticky lime soap curd which will cling to clothes or form the unsightly, difficultly removable soap ring in the washstand or bath tub.

A further object is to increase the resistance of soap-containing detergent compositions to precipitation of lime soap and the coagulation thereof to form curd when such compositions are used in hard water under conditions involving prolonged standing or agitation.

It is known that synthetic detergents such as the various organic sulfonates and sulfates, when

2

mixed or used with soap in hard water, are capable of reducing the formation of lime soap curd. Several such mixtures have been proposed. Some have been commercially produced and designated as "hard water soaps," allegedly free of curd forming characteristics when used in hard water. However, according to my investigations and experience, products prepared in accordance with prior art practices, even those which contain more synthetic detergent than soap, frequently form objectionable curd in hard water under normal conditions of use. As the proportion of synthetic detergent increases, the trouble with such hard-water curd may decrease in seriousness, but at the same time the cost of the product increases and some of the desirable physical properties found in soap are adversely affected.

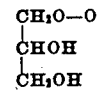
As more fully hereinafter described, I have discovered that polyhydric alcohols partially esterified with aliphatic carboxylic acids of high molecular weight (although possessing no power to inhibit curd formation when used with soap alone) have a marked power to inhibit lime soap precipitation and curd formation in the case of curd-forming detergent compositions comprising essentially a mixture of soap and synthetic detergent in proportions more fully hereinafter described. This power exists even when the compositions are used under conditions wherein the solution is subjected to prolonged standing or to mild or vigorous agitation.

I am aware that prior workers in the art have suggested the combination of soap with synthetic detergents (Patents 1,906,484, 2,026,816 and 2,088,308). None of these patents, however, suggests the use of partially esterified polyhydric alcohols for inhibiting the curd formation when compositions comprising soap and synthetic detergent are employed in hard water.

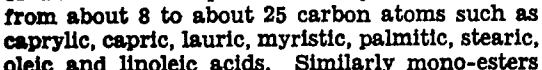
Partially esterified polyhydric alcohol esters which come within the scope of the invention are those mono-esters of polyhydric alcohols having not more than 6 carbon atoms, such as glycerol, diglycerol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, trimethylene glycol, sorbitol, mannitol and the hexitans and hexides obtainable from sorbitol and mannitol by partial anhydrization, partially esterified with saturated and unsaturated aliphatic monocarboxylic acids having from 8 to 25 carbon atoms in the molecule. Of especial interest are the monoglycerides of saturated fatty acids having from 10 to 14 carbon atoms, and par-

ticularly of those acids from oils of the coconut oil group.

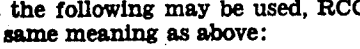
Some specific esters which may be used in the practice of the present invention are monoglycerides such as



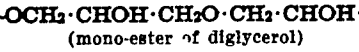
where RCO— is the acyl radical of a saturated or unsaturated aliphatic carboxylic acid having from about 8 to about 25 carbon atoms such as caprylic, capric, lauric, myristic, palmitic, stearic, oleic and linoleic acids. Similarly mono-esters such as the following may be used, RCO— having the same meaning as above:



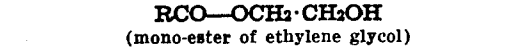
(mono-ester of diglycerol)



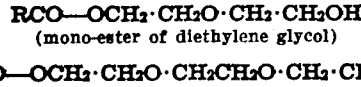
(mono-ester of ethylene glycol)



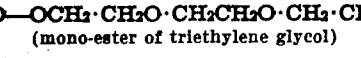
(mono-ester of diethylene glycol)



(mono-ester of triethylene glycol)

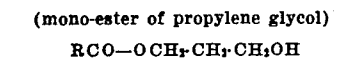


(mono-ester of propylene glycol)

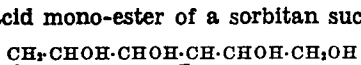


(mono-ester of trimethylene glycol)

Fatty acid mono-ester of a sorbitan such as:



Fatty acid mono-ester of a sorbide such as:



Fatty acid mono-esters of mannitans and mannides.

Fatty acid mono-esters of an inner ether of a hexitol.

Instead of employing esters of single fatty acids as above indicated, corresponding mono-esters of mixtures of fatty acids, especially those mixtures obtainable from oils, fats, and waxes of animal and vegetable origin, may be employed without departing from the spirit of the invention. For example, those mono-esters of a mixture of fatty acids derived from oils of the coconut oil group (a group of tropical nut oils characterized by their high content of lauric and myristic acids) such as coconut oil, palm kernel oil, and babassu oil are of particular value, but those mono-esters of fatty acids derived from other oils and fats such as palm oil, tallow, cottonseed oil, sunflower seed oil, fish oils such as menhaden oil and the like, as well as hydrogenated and partially hydrogenated fats and oils in general, may also be employed. Corresponding mono-esters of synthetic aliphatic carboxylic acids having 10 to 25 carbon atoms may also be used. Such acids may be obtained, for example, by oxidation of paraffin hydrocarbons or petroleum, or they may be obtained directly by hydrogenation of carbon monoxide (sometimes called the Fischer-Tropsch process) or indirectly by oxidation of the saturated or unsaturated

hydrocarbons or oxygenated hydrocarbons resulting from this process.

The kind of soap which is used in preparing my improved detergent compositions is not a limitation of the invention. Any of the water-soluble soaps formulated for industrial, household, and toilet use may be employed. Thus the character of the soap constituent may vary widely in its composition depending on whether the final ternary composition is to be in powdered, spray dried, flake, bar, paste, thread, liquid or other form, and it is to be understood that the specific soaps referred to in the examples given below and prepared from tallow and coconut oil are not to be construed as limiting in nature. Water-soluble soaps such as the sodium soaps and other suitable alkali metal or ammonium soaps derived from other fats and oils such as cottonseed oil, soybean oil, corn oil, olive oil, palm oil, peanut oil, palm kernel oil, lard, greases, fish oils and the like as well as their hydrogenated derivatives, and mixtures thereof, properly blended to yield the desired soap quality, may be used in compounding the ternary mixtures herein contemplated.

The synthetic detergent constituent of the present detergent compositions may be broadly designated as a detergent of the class consisting of water-soluble salts of organic sulfonic acids and water-soluble salts of aliphatic sulfuric acid esters, that is, water-soluble salts of organic sulfuric reaction products having in the molecular structure a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. As indicated above in the designation of the soaps which may be used in compounding the compositions of my invention, the choice of synthetic detergent will depend inter alia on the physical characteristics of the final product, that is, whether the composition is to be in flake, bar, paste, or other form. Obviously if a detergent composition in bar form is desired, it will be impractical to combine ingredients which are too soft to retain their shaped form in use.

Synthetic detergents of special interest and particular value are the water-soluble salts of higher alkyl sulfuric acids containing from 8 to 18 carbon atoms in the alkyl radical. More specifically, the alkali metal salts of sulfuric acid esters of normal primary aliphatic alcohols having 10 to 18 carbon atoms, particularly those whose principal active ingredient is a water-soluble salt of lauryl sulfuric acid or oleyl sulfuric acid, have proved of value in compounding products of the present invention. Thus the sodium salt of alkyl sulfuric acids obtained from the mixed higher alcohols derived by the reduction of coconut oil, palm kernel oil, babassu oil, or other oils of the coconut oil group or the sodium alkyl sulfate derived from sperm oil alcohols may be employed. In addition, water-soluble alkyl sulfates having pronounced detergent power and derived from high molecular branched chain primary alcohols or from high molecular secondary alcohols may be used.

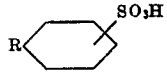
Other aliphatic sulfuric acid esters which may be employed in the preparation of detergent compositions of the present invention include water-soluble salts of sulfuric acid esters of polyhydric alcohols incompletely esterified with high molecular weight soap forming carboxylic acids. Such synthetic detergents include the water-soluble salts of sulfuric acid esters of higher molecular weight fatty acid monoglycerides such as sodium salt of the coconut oil fatty acid mono-ester of

1,2-dihydroxy-propane-3-sulfuric acid ester, triethanolamine salt of monooleoyl diethylene glycol sulfate, sodium mono-myristoyl ethylene glycol sulfate, and sodium mono-lauroyl diglycerol sulfate.

Similarly water-soluble salts of ethers of high molecular weight normal primary alcohols and lower molecular weight hydroxy alkyl sulfuric acid esters may be employed. Specific examples of such synthetic detergents are sodium salt of mono fatty-alcohol-of-coconut-oil ether of glycerol monosulfuric acid and sodium salt of lauryl ether of ethylene glycol monosulfuric acid.

In addition, sulfuric acid ester synthetic detergents such as water-soluble salts of sulfated higher fatty acid alkanolamides, for example the sodium salt of sulfated coconut oil fatty acid ethanolamide and of sulfated babassu oil fatty acid glycerol amide, may be employed in the practice of the invention.

The partially esterified polyhydric alcohols hereinabove referred to are active also in inhibiting curd formation in the case of those detergent compositions which contain in combination with soap an organic synthetic detergent having a true sulfonate group. These synthetic detergents include salts of higher molecular weight mono-fatty acid esters of lower molecular weight hydroxy alkyl sulfonic acids such as the sodium salt of the coconut oil fatty acid mono-ester of 1,2-dihydroxy-propane-3-sulfonic acid, and the oleic acid ester of the sodium salt of isethionic acid. Included also are the higher molecular weight fatty acid amides of lower molecular weight amino alkyl sulfonic acids (for example, sodium and potassium salts of oleic acid amide of N-methyl taurine), the water-soluble salts of the higher molecular weight alcohol esters of sulfocarboxylic acids (for example, sodium salt of the lauryl alcohol ester of sulfoacetic acid), lower molecular weight sulfocarboxylic acid amides of alkylolamine esters of higher molecular weight fatty acids (for example, sodium salt of the sulfoacetamide of amino ethyl laurate), higher alkylated aryl sulfonic acids (for example, sodium and potassium salt of the sulfonic acid derived from the condensation product of benzene and a chlorinated kerosene fraction containing predominantly 10 to 14 carbon atoms per molecule such as represented by the formula



in which R is the alkyl group), and ethers of higher molecular weight alcohols and lower molecular weight hydroxy alkyl sulfonic acids (for example, monolauryl ether of 1,2-dihydroxy-propane-3-sodium sulfonate and monolauryl ether of the sodium salt of isethionic acid).

Although the essential ingredients of the compositions of the present invention comprise essentially a ternary mixture of polyhydric alcohol partially esterified with higher fatty acid, soap and synthetic detergent, it will be appreciated that the incorporation in the mixture of additional ingredients commonly used with cleansing compositions, such as perfumes, starch, urea, triethanolamine, inorganic salts (sulfates, silicates, carbonates, ortho-, meta-, pyro-, and triphosphates and the like), albuminous substances, glycerin, insecticides and germicides and the like, is contemplated as part of the instant invention.

The following examples will illustrate the manner in which the invention may be practiced, but it is to be understood that such details are given merely for exemplification purposes and are not to be construed as limiting the scope of the appended claims. In all instances the proportions are expressed in parts by weight.

Example 1.—Detergent flakes which suds and cleanse efficiently and which do not give objectionable curd in 20 grain water are prepared by milling on soap milling rolls a mixture consisting of 76 parts of sodium soap from 80% tallow and 20% coconut oil and containing about 3% water, 21 parts of the sodium salt of the coconut fatty acid mono-ester of 1,2-dihydroxy-propane-3-sulfonic acid (sometimes called sulfonated coconut oil monoglyceride), and 5 parts of the monoglyceride of coconut fatty acids, together with a little water in order to give good consistency during milling. The resulting milled ribbons are converted into flakes in known manner. The ratio of soap to synthetic in these flakes is about 3.5:1, and the ratio of synthetic to monoglyceride is about 4.2:1.

In the above example, instead of using the sulfonated coconut oil monoglyceride, sulfonated monoglyceride of palm kernel oil fatty acids can be used. Furthermore, instead of using the monoglyceride of coconut oil fatty acids, the corresponding diglycerol mono-ester or the ethylene glycol mono-ester can be used.

Example 2.—Detergent flakes which suds and cleanse efficiently and which do not give objectionable curd in 20 grain water are made by the process of Example 1, using 67 parts of the same soap therein used, 25 parts of the sodium salt of the coconut fatty acid mono-ester of 1,2-dihydroxy-propane-3- sulfuric acid, and 10 parts of the coconut fatty acid mono-ester of propylene glycol. The ratio of soap to synthetic in these flakes is about 2.6:1, and the ratio of synthetic to monoglyceride is about 2.5:1.

In the above example, instead of the mono-ester of propylene glycol, the mono-ester of glycerol can be used.

Example 3.—Detergent flakes which suds and cleanse efficiently and which do not give objectionable curd in 20 grain water are made by the process of Example 1, using 47.4 parts of the same soap therein used, 42.5 parts of a commercial detergent containing about 80% of an alkyl benzene sodium sulfonate in which the alkyl group has about 12 carbon atoms (the remaining 20% being essentially Na_2SO_4), and 20 parts of the monoglyceride of fatty acids having an acid value of 240, and obtained by the oxidation of paraffin hydrocarbons. The ratio of soap to synthetic in these flakes is about 1.35:1, and the ratio of synthetic to monoglyceride is about 1.7:1.

In the above example, palmitic and stearic acids mixed in a 1:1 ratio can be used instead of the oxidized paraffin fatty acids as a source of the monoglyceride.

Example 4.—Detergent bars which suds and cleanse efficiently and which do not give objectionable curd in 20 grain water are prepared by milling on soap milling rolls a mixture consisting of 71 parts of a sodium soap from 80% tallow and 20% coconut oil and containing about 15% water, 27 parts of a commercial synthetic detergent containing about 88% sodium salt of the sulfuric acid esters of the mixed alcohols derived from coconut oil and about 12% Na_2SO_4, and 16 parts of mono-laurin, together with a little water in order to give good consistency during milling and subsequent plodding. The milled ribbons are then plodded in customary soap-making equipment, and the plodded product is cut and

stamped in bar form. The ratio of soap to synthetic in these bars is about 2.5:1, and the ratio of synthetic to monoglyceride is about 1.5:1.

In the above example, instead of using the sulfuric acid esters of the mixed alcohols derived from coconut oil, the sulfuric acid ester of dodecyl alcohol or of oleyl alcohol can be used. Furthermore, instead of mono-laurin, monoolein or the monoglycerides of the mixed fatty acids derived from coconut oil can be used.

Example 5.—Detergent bars which suds and cleanse efficiently and which do not give objectionable curd when used in 20 grain water are prepared by the procedure of Example 4, using 47 parts of the same soap therein described, 50 parts of the sodium salt of lauric acid mono-ester of 1,2-dihydroxy-propane-3-sulfonic acid, and 10 parts of the lauric acid mono-ester of diethylene glycol. The ratio of soap to synthetic in these bars is about 0.8:1, and the ratio of synthetic to mono-ester is about 5:1.

Example 6.—Detergent bars which suds and cleanse efficiently and which do not give objectionable curd when used in 20 grain water are prepared by the procedure of Example 4, using 82 parts of the soap therein described, 23 parts of the commercial synthetic detergent therein described, and 10 parts of a commercial surface-active agent which consists essentially of the palmitic acid mono-ester of the mixed hexitans and hexides obtained by anhydrizing sorbitol. The ratio of soap to synthetic in these bars is about 2.3:1, and the ratio of synthetic to mono-ester is about 2:1.

In the above examples, reference has been made to use in water of 20 grains of hardness per gallon. It is to be understood, however, that 20 grain water is referred to only as being representative of hard waters in general. According to my experience and investigations, my ternary detergent composition is effective in hard water of any municipal water system or any domestically used water source of which I am aware.

Besides possessing resistance to curd formation in hard water, products of the present invention dissolve at a desirable rate in the water, suds profusely, and cleanse efficiently. Addition of the partially esterified polyhydric alcohol to the soap-synthetic detergent mixtures, as specified in the application, tends in general to increase sudsing power of the composition. However, excessive additions of the esters are to be avoided, as they may decrease sudsing power, harm the desired physical properties of the soap bar, flake, or other product, and interfere with handling in some of the common soap manufacturing processes.

It is especially noteworthy that the bar products of my invention have a definite advantage over bars consisting predominantly of synthetic detergent in that they do not dissolve too rapidly, do not become soft, are more soap-like in appearance and feel, behave more like soap in processing operations, and produce a lather which is generally similar in structure and feel to that of soap, being unlike that produced from synthetic alone.

The amount of mono-ester that can advantageously be used is to a degree dependent on the nature and amount of synthetic detergent present in the composition, but it has been found that the most useful products result when the amount of such mono-ester exceeds one sixth of, but is not greater than, the amount of synthetic detergent present and constitutes at least 2 per cent of the combined weight of soap, synthetic detergent and mono-ester.

Most of the above examples cover compositions in which the ratios of essential ingredients come within the preferred ranges, that is, a ratio of soap: synthetic from about ⅔:1 to about 4:1 and a ratio of synthetic:mono-ester from about 1½:1 to about 6:1. The advantages of my discovery, however, are to be realized in compositions falling outside the preferred ranges of proportions, and accordingly compositions coming within the ratios of soap:synthetic of about ½:1 to about 8:1 and of synthetic:mono-ester of about 1:1 to about 10:1 are contemplated as part of the broad invention, the mono-ester constituting at least 2 per cent of the combined weights of soap, synthetic and mono-ester. Optimum results in the case of each composition may be realized by adjustment of the ratios used depending on the types of soap, synthetic detergent and ester employed.

As indicated above, the physical form of the compositions is not a limitation of the invention and may be varied in well known manner. In some instances, however, it may be necessary to adjust temperature conditions or moisture content of the mixture to give a product of the desired consistency for handling in the various processing operations required in the development of the desired physical form. Such adjustments of course are well within the scope of those skilled in the art.

The manner of mixing the ingredients is not a limitation of the invention. Any suitable mixing device such as a series of milling rolls ordinarily used in mixing plastic soap with added ingredients or crutching mechanism of high mixing efficiency as employed in mixing more fluid constituents may be employed to effect homogeneity in the mixture of ester, soap, and synthetic detergent.

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

1. A detergent composition characterized by reduced tendency to form lime soap curd when used in hard water at rinsing dilutions, comprising essentially a ternary mixture of a water-soluble soap, a water-soluble salt of an organic sulfuric reaction product having pronounced detergent properties and having in its molecular structure a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals, and the mono-ester of a polyhydric alcohol having not more than 6 carbon atoms with an aliphatic carboxylic acid having from 10 to 25 carbon atoms, the ratio of soap:sulfuric reaction product salt being from ½:1 to 8:1 and the ratio of sulfuric reaction product salt:mono-ester being from 1:1 to 10:1, and the amount of mono-ester constituting at least 2 per cent of the combined weights of soap, sulfuric reaction product salt, and mono-ester.

2. A detergent composition characterized by reduced tendency to form lime soap curd when used in hard water at rinsing dilutions, comprising essentially a ternary mixture of a water-soluble soap, a water soluble salt of an organic sulfuric reaction product having pronounced detergent properties and having in its molecular structure a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals, and the mono-ester of a polyhydric alcohol having not more than 6 carbon atoms with an aliphatic carboxylic acid having from 10 to 25 carbon atoms, the ratio of soap:sulfuric re-

action product salt being from ⅔:1 to 4:1 and the ratio of sulfuric reaction product salt:mono-ester being from 1½:1 to 6:1.

3. The composition of claim 1 in which the mono-ester of the polyhydric alcohol is derived from a mixture of higher molecular fatty acids of naturally occurring fatty matter.

4. The composition of claim 1 in which the mono-ester of the polyhydric alcohol is derived from the mixed fatty acids of an oil of the group consisting of coconut, palm kernel and babassu oils.

5. The composition of claim 1 in which the mono-ester of the polyhydric alcohol is derived from the mixed fatty acids of coconut oil.

6. The composition of claim 1 in which the organic sulfuric reaction product salt is a water-soluble salt of an alkyl sulfuric acid having from 10 to 18 carbon atoms in the alkyl radical.

7. The composition of claim 1 in which the sulfuric reaction product salt is a water-soluble salt of alkyl sulfuric acids of higher alcohols derived from an oil of the group consisting of coconut, palm kernel and babassu oils.

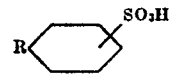
8. The composition of claim 1 in which the sulfuric reaction product salt is a water-soluble salt of alkyl sulfuric acid having 10 to 14 carbon atoms in the alkyl radical and in which the ester is the monoglyceride of fatty acids having 10 to 14 carbon atoms.

9. The composition of claim 1 in which the sulfuric reaction product salt consists of a water-soluble salt of the coconut oil fatty acid mono-ester of 1,2-dihydroxy-propane-3-sulfonic acid.

10. The composition of claim 1 in which the sulfuric reaction product salt consists of a water-soluble salt of the coconut oil fatty acid mono-ester of 1,2-dihydroxy-propane-3-sulfonic acid and in which the ester is the monoglyceride of an oil of the coconut oil group.

11. The composition of claim 1 in which the sulfuric reaction product salt is a water-soluble salt of a higher alkylated aryl sulfonic acid.

12. The composition of claim 1 in which the sulfuric reaction product salt is a water-soluble salt of an alkylated benzene sulfonic acid of the composition:



in which R is an alkyl group having predominantly 10 to 14 carbon atoms.

13. The composition of claim 1 in which the sulfuric reaction product salt is a water-soluble salt of a higher alkylated aryl sulfonic acid and in which the mono-ester is the monoglyceride of an oil of the group consisting of coconut, palm kernel and babassu oils.

14. The composition of claim 1 in which the sulfuric reaction product salt is a water-soluble salt of alkyl sulfuric acids of higher alcohols derived from an oil of the group consisting of coconut, palm kernel and babassu oils, and in which the mono-ester is derived from ethylene glycol and fatty acids of an oil of the group consisting of coconut, palm kernel and babassu oils.

15. The composition of claim 1 in which the mono-ester is derived from mixed hexitans and hexides obtained by partial anhydrization of sorbitol.

16. The composition of claim 1 in which the sulfuric reaction product salt is a water soluble salt of dodecyl sulfuric acid and in which the mono-ester is the monoglyceride of an oil of the group consisting of coconut, palm kernel and babassu oils.

WALTER C. PRESTON.

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

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