(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 147 745**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **84115433.9**

(22) Date of filing: **14.12.84**

(51) Int. Cl.^{4}: **C 11 D 3/37**
C 11 D 9/26

(30) Priority: **21.12.83 US 563852**

(43) Date of publication of application:
10.07.85 Bulletin 85/28

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

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(54) Lime soap dispersing compositions and their use.

(57) Compositions and method of using such compositions in washing applications which comprise at least one water-soluble organic surfactant selected from anionic and nonionic surfactants and a lime soap dispersant having molecular weight of 2,000 to 200,000 that is a homopolymer of a polyalkylene glycol monoacrylate, a copolymer of an acrylamido alkane sulfonic acid and a polyalkylene glycol monoacrylate, or a water-soluble salt thereof, the copolymer being composed of 5 to 80% by weight of polymerized units derived from the sulfonic acid and relative amount of the surfactant to the copolymer is in the range of 125/1 to 1/10.

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LIME SOAP DISPERSING COMPOSITIONS AND THEIR USE

BACKGROUND OF THE INVENTION

The use of soap as a cleaning agent goes back to the dawn of civilization and has had a long record of safety and efficacy. When used as a detergent, soap has two important drawbacks: its poor solubility in cold water and insolubility in water of the calcium and magnesium salts. In an effort to remove these drawbacks, the detergent industry has shifted away from soap and has adopted various synthetic surfactants as the active ingredients in its detergent compositions.

It is well known that in hard water, insoluble soaps are formed which tend to flocculate to form what is called lime scum or lime soap. This tends to be deposited on either the fabrics which have been washed or on vessels in which washing and rinsing is carried out.

In fabrics, the common laundry soils generally consist of about 40% by weight particulate soil and about 60% by weight of oily soil from human sebum or perspiration. The particulate soil component of the laundry soils is mainly composed of about 75% clay and silica, and about 20% lime soaps. Since lime soaps are generally not efficiently removed by the surfactant in the detergent composition nor are they sequestered by sodium tripolyphosphate or other similar material, which can also be present in the detergent composition, the net result is the cumulative build-up of lime soap deposits on washed fabrics. This condition leads to gradual "graying-up" of washed fabrics and to rancid odors of the fabrics which comes from enzymatic decay of the unsaturated fatty acid portion of lime soaps.

Lime scum can deposit on vessels in which washing and rinsing is carried out to form what is known as "bath tub ring".

More than thirty years ago, it was discovered that precipitation of lime soap could be prevented through the addition of lime soap dispersing agents to the soap. These formulations, however, contained sodium pyrophosphate, which was found to be deleterious to the environment due to the phenomenon called eutrophication, or simply, excessive algae growth in bodies of water into which the used wash liquor containing phosphate is discharged.

Lime soap or lime scum is essentially insoluble calcium salts of fatty acids which are in the form of large aggregates of about 0.01 to 0.03 cm or 100 to 300 microns in size. Such aggregates are not effectively dispersed by the surfactants commonly used in detergent formulations. When a lime soap dispersant is present in a detergent composition, it breaks down or disperses the large-sized lime soap aggregates to micron or even sub-micron particles resulting in a milky dispersion. Thus, the presence of a lime soap dispersant in a detergent composition permits flushing or rinsing away of the lime soap with the result that deposition of lime scum on fabrics is reduced or eliminated and formation of bath-tub rings can be prevented.

The lime soap dispersants, therefore, function to prevent formation of insoluble lime soaps or prevent such soaps from flocculating so that they can be flushed away with the washing or rinsing water and do not adhere to fabrics or to surfaces of the washing vessels.

U.S. patent 3,692,704 discloses detergent compositions comprising about 50% detergent and about 50% detergent builder wherein the builder component consists of 60% by weight sodium polyacrylate of Mw 100,000 and 40% by weight of poly (N,N-dicarboxymethyl acrylamide) of Mw 50,000.

U.S. patent 3,719,647 discloses copolymers of (meth)acrylic acid and polyalkylene glycol mono (meth)acrylate as whiteness agents in detergent compositions. They are said to be effective lime soap dispersants.

SUMMARY OF THE INVENTION

In a preferred embodiment, this invention relates to water-soluble homopolymers of polyalkylene glycol monoacrylates and to random copolymers of an acrylamido alkane sulfonic acid and a polyalkylene glycol monoacrylate as novel polymers, as polymers that can be used as lime soap dispersants in detergent and soap compositions, and to the method of using such compositions for cleaning fabrics and hard surfaces, and for personal washing. Such compositions can be phosphate-free or can contain phosphates.

DETAILED DESCRIPTION OF THE INVENTION

The anionic surfactants and soaps do not perform efficiently in medium to hard waters, however, the use of the herein-disclosed lime soap dispersants in conjunction therewith leads to improved cleaning and lathering performance under such conditions. Even with the other generic types of surfactants, cleaning performance thereof in water is adversely affected by the presence of water hardness ions, such as calcium and magnesium. Hardness of natural waters varies widely from about 10 ppm to about 500 ppm of hardness salts expressed as calcium carbonate. The salts that impart hardness to water are generally water-soluble salts of calcium and magnesium such as chlorides, sulfates, nitrates, and bicarbonates. In general, 10 to 120 ppm is considered soft water, 120 to 180 is medium-hard water, and 180 to 500 ppm and above is very hard water. In normal use of soaps and detergents, the undesirable lime-soap scum begins to form even in the 80 ppm, i.e., soft water, and becomes a noticeable problem in medium-hard water and a major problem in very hard water.

Lime soap dispersants are used in soap and detergent products but they serve entirely different purposes in each. In soap products, such as solid bars and liquids, lime soap dispersants enhance lathering and prevent formation of unwelcome rings of calcium or lime soaps in bath tubs and wash basins, when such soap products are used in relatively hard water. In detergent products, such as powders and liquids, lime soap dispersants are used to deterge away the built-up lime soap deposits on washed clothes which are not otherwise removed by other detergent ingredients. Removal of such lime soap deposits on washed clothes results in white clothes staying white longer and avoidance of rancid fatty odors.

The detergent compositions of the present invention can be in the form of liquid solutions, powders, granules, flakes, tablets, and bars. Regardless of form, however, only a small amount of a detergent composition is needed in an aqueous medium to obtain excellent cleaning power. Generally, less than 1% by weight, preferably 0.01 to 0.5%, based on the combined weight of the detergent composition and water, will provide sufficient detergent value for fabric and dish cleaning. For more rigorous applications in washing fabrics and dishes, up to

30%, preferably 5 to 15% of the detergent composition in an aqueous medium can be used. For personal washing, amount of the detergent composition, based on the combined weight of the composition and water, can vary from about 1% to about 10%. Aqueous solutions of the detergent compositions disclosed herein should have pH of 5 to 12.5, preferably 9 to 11. Furthermore, the aqueous solutions of these compositions are effective in a wide range of wash water temperatures. Preferably, wash water temperatures should be in the range of about 45 to 200°F, and especially in the temperature range of about 80 to 160°F.

The compositions disclosed herein can contain phosphates or they can be devoid of phosphates. Suitable phosphates which can be used in such compositions include sodium tripolyphosphate, tetrapotassium pyrophosphate, and others.

The detergent compositions disclosed herein include an organic water-soluble surfactant and a polymeric lime soap dispersant selected from random copolymers of an acrylamido alkane sulfonic acid and polyalkylene glycol monoacrylate or a polyalkylene glycol alkyl or aryl ether monoacrylate, and water-soluble salts of such copolymers. The water-soluble salts of the copolymers are selected from alkali metal salts, ammonium salts, and substituted ammonium salts. The organic water-soluble surfactants that can be used to prepare the lime soap dispersing compositions include anionic and nonionic surfactants. Soaps are considered to be anionic surfactants, and many of the preferred compositions disclosed herein contain soap varying in amount of 1 to 80 parts by weight, based on 100 parts of composition, depending on the particular application.

Other materials which may be present in the detergent compositions of the invention herein in minor or major amounts are those components conventionally present in detergent compositions. These include such components as builders, soil suspending agents, anti-redeposition agents such as sodium carboxymethyl cellulose, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers such as sodium sulfate, alkaline buffers such as sodium silicates and carbonates, optical brighteners, bleaches such as perborates, percarbonates, organic and inorganic chlorine releasing agents, bleach activators, enzymes, detergent boosters and solvents, suds boosters, suds depressants, lime soap dispersants other than those disclosed herein, germicides, fungicides, anti-tarnishing agents, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, fabric softening agents and in the case of liquid compositions, opacifiers and organic solvents. In addition, although any of the conventional well-known detergent builders (phosphate and non-phosphate type) may be employed in the compositions of the present invention at a level of 1 to 80%, the absence thereof does not adversely affect detergent efficiency.

The water-soluble soaps which can be used in the detergent compositions of the invention are the higher fatty acid soaps normally used for washing, for instance the alkali metal, especially sodium or potassium, salts of saturated and unsaturated fatty acids having from 8 to 24, especially 10 to 18 carbon atoms. The soaps can be made by direct saponification of natural oils and fats, such as tallow, palm oil, lard, greases, coconut or palm kernel oils and many others, or they can be made by neutralization of fatty acids derived from such oils and fats or from those made synthetically or derived from petroleum and like sources. Soaps from natural oils and fats, or from fatty acids derived from them, will be predominantly straight-chained with an even number of carbon atoms. The synthetic fatty acids or those from petroleum sources can be straight- or branch-chained containing even and odd number of carbon atoms. Preferred soaps are those made from mixtures of tallow, grease, or palm oils to provide the longer chain, e.g., C_{16-18} fatty acid residues and coconut or palm kernel oil to provide shorter chain, e.g., C_{10-14} fatty acid residues.

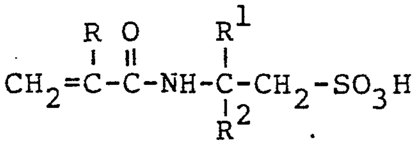
Examples of anionic organic surfactants are the water soluble salts and alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical containing about 8 to 22 carbon atoms and a radical selected from sulfonic acid and sulfuric acid ester radicals. Included in the term alkyl is the alkyl portion of higher acyl radicals. Important examples of anionic surfactants are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols of C_8 to C_{18} carbon atoms produced by splitting the glycerides of tallow or coconut oil, and sodium or potassium alkyl benzenesulfonates in which the alkyl group contains about 9 to 15 carbon atoms. Other examples of alkali metal alkylbenzene sulfonates are those in which the alkyl radical is a straight or branched chain aliphatic radical containing about 10 to 20 carbon atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkylphenol ethylene oxide ether sulfate with about 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyl tauride in which the fatty acids, for example, are derived from coconut oil; sulfonated polycarboxylic acids derived from pyrolyzed calcium citrate; and others known in the art.

Nonionic surfactants can be broadly described as compounds which do not ionize but usually acquire hydrophilic characteristics from an oxygenated side chain, such as polyoxyethylene, while the hydrophobic part of the molecule may come from fatty acids, alkyl phenols, fatty alcohols, fatty amides or fatty amines. Examples of nonionic surfactants include products formed by condensing one or more alkylene oxides of two to four atoms, such as ethylene oxide or propylene oxide, preferably ethylene oxide alone or with other alkylene oxides, with a relatively hydrophobic compound, such as a fatty alcohol, fatty acid, sterol, a fatty glyceride, a fatty amine, an aryl amine, a fatty mercaptan, tall oil, etc. Nonionic surfactants also include those products produced by condensing one or more relatively lower alkyl alcohol amines such as methanolamine, ethanolamine, propanolamine, etc., with a fatty acid such as lauric acid, palmitic acid, tall oil fatty acid, abietic acid, etc., to produce the corresponding amide.

Still other nonionic surfactants include the amine oxides and phosphine oxides and preferably the unsymmetrical trialkylamine oxides and phosphine oxides wherein two of the alkyl groups are lower alkyl groups of 1 to 4 carbon atoms and the third alkyl group is a higher alkyl group of 8 to 18 carbon atoms. Examples of these include dimethyldodecylamine oxide, dimethyldodecylphosphine oxide, dimethyltetradecyl amine oxide, dimethyltetradecyl phosphine oxide, diethylhexadecylamine oxide, diethylhexadecylphosphine oxide, and the like.

Particularly advantageous nonionic surfactants are condensation products of a hydrophobic compound having at least one active hydrogen atom and a lower alkylene oxide for example, the condensation product of an aliphatic alcohol containing from about eight to about 18 carbon atoms and from about three to about 30 mols of ethylene oxide per mol of the alcohol, or the condensation product of an alkyl phenol containing from about eight to about 18 carbon atoms in the alkyl group and from three to about 30 mols of ethylene oxide per mol of alkyl phenol. Other advantageous nonionic surfactants include condensation products of ethylene oxide with a hydrophobic compound formed by condensing propylene oxide with propylene glycol.

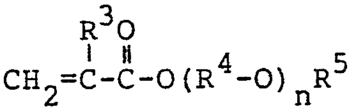
The copolymers contemplated by this invention are copolymers of an acrylamido alkane sulfonic acid monomer and a polyalkylene glycol monoacrylate. Acrylamido alkane sulfonic acid monomers include the acrylamido alkane sulfonic acids and water-soluble salts thereof especially salts selected from alkali metal salts, ammonium salts, and substitute ammonium sats. The term "copolymers", as used herein, shall mean a polymer of two or more different monomers. Acrylamido alkane sulfonic acids suitable herein are defined as follows:



$$CH_2{=}\overset{\overset{\displaystyle R}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^1}{|}}{C}}-CH_2-SO_3H$$

where R is hydrogen or methyl, preferably hydrogen; R^1 and R^2 are alkyl groups each individually containing 1 to 4 carbon atoms, preferably 1 to 2 carbon atoms. Suitable acrylamido alkane sulfonic acids include reaction products of acrylonitrile, fuming sulfuric acid, and C_4 to C_{10} olefins. The preferred monomers being 2-acrylamido-2-methyl propane sulfonic acid and its water-soluble salts, which are commercial chemicals.

Suitable polyalkylene glycol monoacrylates are defined as follows:



$$CH_2{=}\overset{\overset{\displaystyle R^3}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-O(R^4-O)_nR^5$$

where R^3 is hydrogen or methyl, preferably methyl; R^4 is an alkylene group of 1 to 4, preferably 2 to 3 carbon atoms; R^5 is selected from hydrogen, alkyl, and alkenyl groups of 1 to 30, preferably 1 to 18 carbon atoms, aryl groups of 6 to 14 but preferably 6 to 10 carbon atoms, and aralkyl groups of 7 to 30 but preferably 7 to 20 carbon atoms; and n is a number in the range of 2 to 50, preferably about 5 to 15. In the most preferred embodiment, R^5 is hydrogen. Suitable polyalkylene glycol monoacrylates, referred to above, include polyethylene glycol monomethacrylate with molecular weight of 306 and 526, which are commercial products.

Preparation of a copolymer having molecular weight (Mw) of about 20,000 is now presented for illustrative purposes. Pursuant to the procedure outlined herein, 2-acrylamido-2-methyl propane sulfonic acid (AMPS) was polymerized by free radical polymerization with polyethylene glycol monomethacrylate (PEGMM). The PEGMM had an average molecular weight of about 526 and contained about 10 mols of ethyleneoxy units per mol of monomer. Following the procedure, 3.84g of fifty percent sodium hydroxide and 0.03g of hydroxylamine sulfate were dissolved in 20g of water. The mixture was cooled and 10g of AMPS was slowly added to mixture. Then, 40g PEGMM and 0.03g of mercaptopropionic acid were added. The solution was charged to a reservoir connected to a metering pump and the pump set to deliver the monomers in one hour. A syringe was charged with 0.3g of sodium persulfate and 9 ml of water. The syringe was placed in a syringe pump set to deliver the solution over a period of one hour.

A 250 ml 3-neck round bottom flask was equipped with a mechanical stirrer, a condenser with a nitrogen inlet, a thermometer and thermowatch, and monomer and initiator inlets. The flask was charged with 91g water and was then flushed with nitrogen and held under nitrogen during the polymerization. The water was stirred and heated to 80°C and metering was begun. When all monomer and sodium persulfate was in, the mixture was heated at 80°C for one hour to complete polymerization. Degree of polymerization was essentially 100%. The product was a clear solution with a slightly yellow tint. The yield was 164.6g and the solution contained 27.9% copolymer containing 40/60 polymerized units of AMPS to PEGMM.

Copolymers suitable as lime soap dispersants have molecular weight (Mw) in the range of about 2,000 to 200,000 but preferably 5,000 to 100,000. Although the higher molecular weight copolymers can be too viscous and thus make it more difficult to work with, this problem can be minimized, as by diluting the copolymers in a suitable solvent. Suitable lime soap dispersants include copolymers containing 5 to 95% by weight, preferably 10 to 60%, and especially 20 to 50%, of polymerized monomer units derived from acrylamido alkane sulfonic acids or their water-soluble salts, the remaining portion, i.e., 95 to 5, preferably 90 to 40% and especially 80 to 50% by weight, of the copolymers being polymerized monomer units of the polyalkylene glycol monoacrylates.

Suitable homopolymers of polyalkylene glycol monoacrylates have molecular weight (Mw) in the range of about 2,000 to 50,000.

In addition to one or more of the acrylamido alkane sulfonic acid monomers and one or more of the polyalkylene glycol monoacrylate monomers, which are the principal monomers, one or more of other additive monomers can also be used herein to prepare the copolymers useful as lime soap dispersants. The additive monomers are selected from α,ß-unsaturated carboxylic acid monomers which include mono-unsaturated monocarboxylic and dicarboxylic acids containing 3 to 8 carbon atoms, esters thereof, and anhydrides thereof, preferably mono-unsaturated monocarboxylic acids containing 3 to 5 carbon atoms, their lower alkyl esters, and their anhydrides. Suitable examples of such acid monomers include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and esters thereof especially methyl acrylate and methacrylate and ethyl acrylate and methacrylate. On the basis of 100 weight parts of all monomers, amount of such acid monomers can be up to 60 weight parts, preferably 5 to 40 weight parts.

Amount of the homopolymers and copolymers that can be used in the various detergent compositions will depend on the particular composition desired. Set forth below are some examples of a number of different detergent compositions used for various applications wherein the components are given in weight parts and the term "polymer" includes homopolymers and copolymers disclosed and claimed herein.

Bar Soap Composition For Personal Use

Component	Wt. Parts
Alkali Metal Salt of Tallow/Coconut Soap	60-80
LSD Polymer	2-20
Water and Minor Additives	to make 100 parts

Liquid hand soap can be prepared by diluting with water the bar soap detergent composition to about 5 to 30% solids.

Bar Soap Composition For Laundry Use

Component	Wt. Parts
Alkali Metal Salt of Tallow Soap	40-60
Sodium Silicate	10-20
LSD Polymer	2-20
Water and Minor Additives	to make 100 parts

Dry Soap Laundry Powder Composition

Component	Wt. Parts
Alkali Metal Salt of Tallow Soap	60-80
LSD Polymer	2-20
Sodium Silicate	10-15
Sodium Carboxymethyl Cellulose	1-3
Water and Minor Additives	to make 100 parts

Anionic Laundry Powder Detergent Composition

Component	Wt. Parts
Linear Alkylbenzene Sulfonate (LAS)	10-25
Sodium Carboxymethyl Cellulose	1-3
LSD Polymer	0.2-5
Alkaline Builders	35-85
Water and Minor Additives	to make 100 parts

Nonionic Laundry Powder Detergent Composition

Component	Wt. Parts
Nonionic Surfactant	5-15
Alkaline Builders	40-80
Sodium Carboxymethyl Cellulose	1-3
LSD Polymer	0.2-5
Water and Minor Additives	to make 100 parts

Liquid Dishwashing Detergent Composition

Component	Wt. Parts
Anionic and/or Nonionic Surfactant	20-45
Hydrotrope	1-10
Mono or Polyhydric Water-Miscible Alcohol	1-10
LSD Polymer	1-5
Water and Minor Additives	to make 100 parts

Mixed Surfactant Laundry Powder Detergent Composition

Component	Wt. Parts
Anionic and Nonionic Surfactants	1-10
Soap	1-20
LSD Polymer	0.2-10
Alkaline Builders	10-20
Water and Other Additives	to make 100 parts

Generally speaking, the relative ratio of the water-soluble organic surfactant to the polymer can vary from 125/1 to 1/10, preferably 50/1 to 1/1. In bar soap compositions for personal use, the ratio of surfactant to polymer can vary from 40/1 to 3/1; in bar soap compositions for laundry use, the ratio is from 30/1 to 2/1; in dry powder laundry soap compositions, this ratio can vary from 40/1 to 3/1; in anionic laundry detergent compositions, the ratio can vary from 125/1 to 2/1; in nonionic laundry powder detergent compositions, the ratio can vary from 75/1 to 1/1; in liquid dishwashing compositions, the ratio can vary from 45/1 to 1/1; and in mixed surfactant laundry powder compositions, the ratio can vary from 50/1 to 1/10.

It has been discovered that the use of the lime soap dispersing polymers described herein in detergent compositions can impart certain important attributes in addition to their redispersing function. Such attributes include the following: direct replacement of the fatty isethionate soap additives, and partial replacement of the nonionic surfactants in liquid dishwashing products.

The polymers disclosed herein provide synergistic results in terms of lime soap dispersancy property. This is based on the fact that homopolymers of acrylamido alkane sulfonic acid monomers and their salts impart only a moderately effective lime soap dispersing property whereas homopolymers of the polyalkylene glycol monoacrylates and their salts impart only about one-half the lime soap dispersing property. Efficacy of the lime soap dispersing polymers is critically dependent not only on the relative proportion of the monomers but also on the molecular weight (Mw) thereof.

A number of homopolymers and copolymers were prepared varying in composition and molecular weight which were then subjected to a lime dispersion test in order to determine their effectiveness to disperse lime scum. This test follows the general procedure described in published literature. The objective of the test is to measure, by visual titration procedure, the minimum amount of a lime soap dispersant needed to completely disperse a given amount of calcium oleate, a lime soap. The result is expressed as lime soap dispersion index (LSDI) which is calculated as follows:

$$\text{LSDI} = \frac{\text{grams of calcium oleate}}{\text{(min. grams of LSD needed to completely disperse calcium oleate)}}$$

The higher the LSDI, the better is the efficiency of the lime soap dispersant. Generally, LSDI is a measure of the weight of lime soap dispersed by a unit weight of lime soap dispersant.

The lime soap dispersion test used herein utilizes the following reagents:

(a) sodium oleate solution that is made by dissolving 0.50g of USP sodium oleate in 100 ml demineralized water with pH adjusted to 10.5 with sodium hydroxide or hydrochloric acid;

(b) hardness solution that is prepared by dissolving 1.9600g of $CaCl_2 \cdot 2H_2O$ crystals and 1.3553g of $MgCl_2 \cdot 6H_2O$ crystals in 2000 ml of demineralized water and adjusted to a pH of 10.5. Total hardness is 1000 ppm expressed as calcium carbonate;

(c) LSD polymer solution that is prepared by dissolving 0.25g of dry polymer in 100 ml of demineralized water and adjusted to pH of 10.5.

The test procedure is carried out at room temperature of 25°C by pipeting 5 ml of the sodium oleate solution into a 100-ml stoppered graduated cylinder followed by 0.5 ml of the LSD polymer solution. Contents of the cylinder are swirled, 10 ml of the hardness solution is added to the cylinder and enough demineralized water is added to make up the total volume to 30 ml. The cylinder is stoppered and then gently agitated by inverting it and returning it to its original upright position, which is repeated 20 times. At least one minute is allowed to elapse and then the contents are observed critically. If coarse agglomerates of calcium oleate coagulate and float on top, it is apparent that not enough of the lime soap dispersant has been used.

The test is continued by repeating above procedure using a fresh cylinder and increasing volume of the LSD polymer solution by 0.5 ml. The procedure is repeated in increments of 0.5 ml of the LSD polymer. As amount of the LSD polymer is increased, the coarse calcium oleate agglomerates will break down into smaller and smaller particles which will continue to float on the surface. The end point is reached when there are no longer any calcium oleate particles seen floating on the solution surface and the entire test solution appears milky white, which is an indication of total dispersion. The lime soap dispersion index (LSDI) can be calculated as follows:

$$\text{LSDI} = \frac{\text{0.025 (which is the wt. of sodium oleate in each cylinder)}}{\text{vol. of LSD soln at the end point x 0.25/100}}$$

Samples of homopolymers of polyalkylene glycol monoacrylates and copolymers of acrylamido alkane sulfonic acids and the polyalkylene glycol monoacrylates of varying composition and molecular weight (Mw) were prepared and then tested in the form of their sodium salt, as described above, to determine the lime soap dispersion index, which is an indication of its effectiveness as a lime soap dispersant. The higher the LSDI the more effective is the material. The results are set forth in Table I below for the various homopolymers and copolymers wherein AMPS is a contraction for 2-acrylamido-2-methyl propane sulfonic acid that was used in the form of a sodium salt, PEGMM is a contraction for polyethylene glycol monomethacrylate, DEEA represents di-ethoxy ethyl acrylate, AA is a contraction for acrylic acid, MeA represents methylacrylate, and LSDI represents lime soap dispersion index.

TABLE I

Comp. No.	Composition AMPS	PEGMM(10EO)	PEGMM(5EO)	AA	MeA	DEEA	Mol.Wt.(Mw)	LSDI
1	100	0	-	-	-	-	5,000	2.9
2	60	40	-	-	-	-	5,000	13.3
3	40	60	-	-	-	-	5,000	13.3
4	0	100	-	-	-	-	5,000	15.4
5	60	-	40	-	-	-	5,000	13.3
6	40	-	60	-	-	-	5,000	15.4
7	60	20	20	-	-	-	5,000	13.3
8	30	40	-	30	-	-	5,000	5.7
9	20	40	-	40	-	-	5,000	8.0
10	20	60	-	20	-	-	5,000	8.0
11	10	60	-	30	-	-	5,000	8.0
12	60	20	-	-	20	-	5,000	5.7
13	40	30	-	-	30	-	5,000	8.0
14	30	-	-	30	-	40	5,000	7.4
15	100	-	-	-	-	-	10,000	2.7
16	100	-	-	-	-	-	20,000	2.7
17	20	80	-	-	-	-	60,000	16.0
18	40	60	-	-	-	-	60,000	26.7
19	60	40	-	-	-	-	60,000	5.7
20	80	20	-	-	-	-	60,000	1.9

TABLE I continued

Composition							Mol.Wt.(Mw)	LSDI
Comp. No.	AMPS	PEGMM(10EO)	PEGMM(5EO)	AA	MeA	DEEA		
21	40	-	60	-	-	-	20,000	18.2
22	60	20	20	-	-	-	20,000	22.2
23	40	30	30	-	-	-	20,000	22.2
24	30	40	-	30	-	-	20,000	9.1
25	20	40	-	40	-	-	20,000	15.4
26	20	60	-	20	-	-	20,000	13.3
27	10	60	-	30	-	-	20,000	11.1
28	80	20	-	-	20	-	20,000	18.2
29	40	30	-	-	30	-	20,000	28.6
30	-	20	-	80	-	-	20,000	5.7
31	-	80	-	20	-	-	20,000	13.3
32	-	-	10	90	-	-	20,000	3.6

The 40/60 copolymer, which gave LSDI of 26.7, as noted in Table I, above, was again synthesized and determination of the LSDI was repeated. The new sample of the copolymer gave LSDI of 28.6 which confirmed earlier results as to efficacy of the copolymer as to its lime soap dispersing property. During evaluation of the new sample, it was observed that pH of the sodium oleate test solution should be 10.5 and only fresh reagent solution should be used for the test. If old solution is used, the hydrolyzed sodium oleate or the acid-soap complex results in LSDI values that are too low. Also, if pH of the sodium oleate reagent solution is too high, such as about 12, the LSDI values obtained remain on the low side.

The LSDI values of the polymers described herein are far higher than any known commercial lime soap dispersants used in specialty soap bars, that have LSDI values in the range of 2 to 6, and are comparable or better than the upper range of LSDI values of the ethoxylated nonionic surfactants, that have LSDI values in the range of 8 to 25.

PRIOR ART EXAMPLE

Copolymers of acrylic acid (AA) and polyoxyethylene glycol monomethacrylate (PEGMM), disclosed in U.S. patent 3,719,647 as suitable whiteness maintenance or antiredeposition agents, were prepared in the same manner as the copolymers disclosed herein and then tested as lime soap dispersants also in the manner described herein. The polyoxyethylene glycol monomethacrylates, which correspond to the polyalkylene glycol monoacrylates disclosed herein, contained 10 ethyleneoxy units per repeating unit and the copolymers had molecular weight of about 20,000. Results of these tests are given in Table II, below, where weight ratio of ingredients is given followed by lime dispersion index.

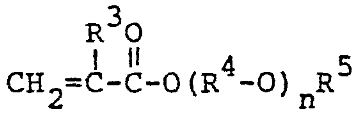
TABLE II

Wt. Ratio AA/PEGMM	Mol.Wt.(Mw)	LSDI
80/20	20,000	5.7
60/40	20,000	8.0
40/60	20,000	4.4
20/80	20,000	13.3

Based on the data in Table I, the optimum copolymer of 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and polyethylene glycol monomethacrylate (PEGMM) at 20,000 molecular weight had LSDI of 26.7 at 40/60 weight ratio whereas at the same weight ratio in this experiment, LSDI was only 4.4. Furthermore, whereas the optimum LSDI with the herein claimed copolymers occurred at 40/60 weight ratio, the optimum LSDI for the AA/PEGMM copolymers occurred at 20/80 weight ratio whereas value of 13.3 LSDI was obtained as compared to 16.0 for the herein claimed copolymers. It should be apparent that the use of AMPS instead of acrylic acid results in different copolymers which provide different results in terms of lime soap dispersing function.

CLAIMS

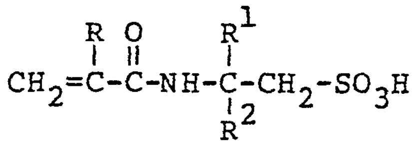
1. Cleaning composition for washing applications comprising an organic water-soluble surfactant selected from anionic surfactants, nonionic surfactants, and mixtures thereof, and a lime soap dispersant selected from homopolymers of polyalkylene glycol monoacrylates, copolymers of at least one acrylamido alkane sulfonic acid and at least one polyalkylene glycol monoacrylate, and water-soluble salts of said homopolymers and copolymers, said polyalkylene glycol monoacrylates are defined as follows:



$$CH_2=\overset{\overset{R^3}{|}}{C}-\overset{\overset{O}{\|}}{C}-O(R^4-O)_nR^5$$

where R^3 is hydrogen or methyl, R^4 is an alkylene group of 1 to 4 carbon atoms, R^5 is hydrogen, an alkyl or alkenyl group of 1 to 30 carbon atoms, an aryl group of 6 to 10 carbon atoms, or an aralkyl group of 7 to 30 carbon atoms, and n is a number in the range of 2 to 50.

2. Composition of claim 1 wherein said acrylamido alkane sulfonic acid is selected from the following:



$$CH_2=\overset{\overset{R}{|}}{C}-\overset{\overset{O}{\|}}{C}-NH-\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{C}}-CH_2-SO_3H$$

where R is either hydrogen or methyl and R^1 and R^2 are individually selected from alkyl groups containing 1 to 4 carbon atoms.

3. Composition of claim 2 wherein the relative weight of said surfactant to said lime soap

dispersant is in the range of 125/1 to 1/10, said copolymers are composed of 5 to 95% by weight of polymerized units derived from said acrylamido alkane sulfonic acids with remainder being polymerized units derived from said polyalkylene glycol monoacrylates, said copolymers including up to 60% by weight, based on the total monomer weight, of polymerized units of one or more additive monomers selected from α,ß-mono-unsaturated monocarboxylic and dicarboxylic acids containing 3 to 8 carbon atoms, esters thereof, and anhydrides thereof.

4. Composition of claim 3 wherein said copolymers are composed of 10 to 60% by weight of polymerized units derived from said acrylamido alkane sulfonic acids, 90 to 40% by weight being polymerized units of said polyalkylene glycol monoacrylates, and up to 40% by weight of polymerized units of one or more of said additive monomers selected from α,ß-mono-unsaturated monocarboxylic acids containing 3 to 5 carbon atoms, lower alkyl esters thereof and anhydrides thereof; said copolymers have molecular weight (Mw) in the range of 2,000 to 200,000 and said homopolymers have molecular weight (Mw) in the range of 2,000 to 50,000.

5. Composition of claim 4 wherein R^1 and R^2 are individually selected from alkyl groups containing 1 to 2 carbon atoms, R^4 is alkylene group of 2 to 3 carbon atoms, R^5 is hydrogen, and n is a number of about 5 to 15, and wherein said water-soluble salts of said lime soap dispersants are selected from alkali metal salts, ammonium salts, and substituted ammonium salts.

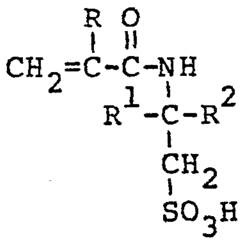
6. Composition of claim 5 wherein said sulfonic acid is 2-acrylamido-2-methyl propane sulfonic acid, said monoacrylate is polyethylene

glycol monomethacrylate containing about 10 ethylene oxide units, and molecular weight (Mw) of said lime soap dispersant is about 60,000.

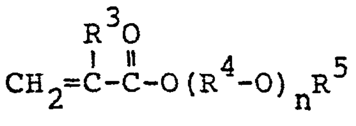
7. Composition of claim 7 selected from (a) bar soap compositions for personal use wherein ratio of said surfactant to said lime soap dispersant is about 40/1 to 3/1, (b) bar soap compositions for laundry use where the ratio is about 30/1 to 2/1, (c) dry soap laundry powder compositions where the ratio is about 40/1 to 3/1, (d) anionic laundry powder detergent compositions where the ratio is about 125/1 to 2/1, (e) nonionic laundry powder detergent compositions where the ratio is about 75/1 to 1/1, and (f) liquid dishwashing detergent compositions where the ratio is about 45/1 to 1/1, and (g) mixed surfactant laundry powder compositions where the ratio is about 50/1 to 1/10.

8. Method for cleaning soiled fabric, soiled hard surface, or soiled human body in an aqueous environment comprising the step of contacting said fabric, hard surface or human body with the composition of claim 7 until substantial removal of the soil is accomplished.

9. A polymer that is a reaction product of an acrylamido alkane sulfonic acid monomer and a polyalkylene glycol monoacrylate monomer, said acid and said monoacrylate are defined respectively as follows:



$CH_2=C(R)-C(=O)-NH-C(R^1)(R^2)-CH_2-SO_3H$



$CH_2=C(R^3)-C(=O)-O(R^4-O)_nR^5$

where R is hydrogen or methyl, R^1 and R^2 are individually selected from alkyl groups of 1 to 4 carbon atoms, R^3 is hydrogen or methyl, R^4 is an alkylene group of 1 to 3 carbon atoms, R^5 is selected from hydrogen, alkyl and alkenyl groups of 1 to 30 carbon atoms, aryl groups of 6 to 14 carbon atoms, and aralkyl groups of 7 to 30 carbon atoms, and n is a number in the range of 2 to 50.

10. Polymer of claim 9 wherein R is methyl, R^1 and R^2 are individually selected from alkyl groups of 1 to 2 carbon atoms, R^3 is methyl, R^4 is an alkylene group of 2 to 3 carbon atoms, R^5 is hydrogen, n is in the range of about 5 to 15, amount of said sulfonic acid monomer is 5 to 95% by weight, based on the total weight of polymerized units of said sulfonic acid monomer and said polyalkylene glycol monoacrylate, said polymer having molecular weight (Mw) in the range of about 2,000 to 200,000.