United States Patent Office 3,275,561 Patented Sept. 27, 1966

3,275,561

LUBRICIOUS DETERGENT COMPOSITIONS

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No Drawing. Filed Oct. 3, 1957, Ser. No. 687,866
2 Claims. (Cl. 252—110)

This invention is concerned with soap and detergent compositions and the manufacture thereof and is particularly directed to improved compositions for use on the skin and to a method for producing such compositions.

This application is a continuation-in-part of our copending application, Serial No. 644,457, filed March 7, 1957, now abandoned.

In the manufacture of soaps, detergent compositions, shaving creams and the like and particularly those which are employed in contact with the skin, it is desirable to produce a product characterized by a quality which may be called lubricity. This quality of lubricity is of considerable importance from the cosmetic standpoint particularly with respect to the "hand," that is, with respect to the feeling experienced by the user of the product. In the case of shaving soaps, the quality of lubricity is more concretely of interest in that a shaving soap, by providing more lubricity, improves the cutting of the hair or beard with less tendency to nicking and cutting of the skin. Further, certain powdered hand soaps currently marketed have failed to achieve wide acceptance for household use on the basis of the housewife's dislike for the unpleasant feeling of such compositions on the skin.

It is an object of the present invention to provide an improved soap composition. It is a further object to provide improved soap compositions characterized by a high degree of lubricity. Another object is to provide an improved method for preparing the new compositions. Yet another object is to provide shaving soap compositions which increase the ease of shaving. Other objects will become apparent from the following specification and claims.

In the present specification and claims, the term "soap," unless specifically designated or modified is employed in the broad generic sense as inclusive of synthetic detergent compositions, shaving soaps, amine salts of long-chain fatty acids, such as triethanolamine oleate or laurate, and the like as well as the true soaps prepared by the saponification of animal or vegetable fats or oils or by the reaction of alkalis with long-chain fatty acids.

In accordance with the present invention, it has been discovered that the incorporation in soaps of certain high molecular weight, water-soluble polymers of acrylamide results in improved lubricity of the soap in use and imparts a more pleasant feeling when the soap composition is applied on the skin. It is among the advantages of the invention that, in addition to the improved lubricity qualities obtained with the new compositions, stiffer and more persistent foams frequently are produced.

In accordance with a further embodiment of the invention, it has been discovered that the incorporation of the high molecular weight polymers of acrylamide in the soap compositions is advantageously accomplished by employing the dry acrylamide polymer in finely divided or pulverulent condition in accomplishing its admixture with the other ingredients of the finished composition.

The term "acrylamide polymer," as herein employed to designate the polymers used in the practice of the invention, is inclusive of homopolymers of acrylamide and copolymers of acrylamide with up to about 15 percent by weight of other suitable monomers such as methacrylamide, acrylic and methacrylic acids and the alkali metal salts and lower alkyl esters thereof, vinyl chloride,

vinyl alkyl ethers and the like, provided each such copolymer is characterized by water-solubility and viscosity properties as set forth below. In the copolymers of acrylamide with acrylic or methacrylic acid or their alkali metal salts, higher proportions of the second ingredient to the acrylamide ingredient may be employed and the expression "acrylamide polymer" includes copolymers of acrylamide with up to about 50 mole percent of acrylic or methacrylic acid or an alkali metal salt thereof.

Water-soluble acrylamide polymers are usually characterized by a greater or less degree of hydrolysis, i.e., contain some free carboxyl groups. This condition is dependent upon the method of manufacture of the polymer, the presence or absence of acrylic or methacrylic acid in the starting monomer mixture, and conditions of storage of the polymer. The polymer products appear to be equivalent whether the carboxyls result from copolymerization of acrylamide with acrylic or methacrylic acid or from hydrolysis of amide or ester groups subsequent to polymerization. In the practice of the present invention, the operable polymers, as above defined, are those having not more than about 50 percent of carboxyl moieties based on the total of carboxyl and carboxamide moieties in the polymer.

The term "percent hydrolysis" as hereinafter employed refers to the percent of carboxamide groups in the homopolymer of acrylamide replaced by carboxyl groups, whether derived by actual hydrolysis of the homopolymer or by copolymerization as set forth above.

The acrylamide polymers employed in the present invention are water soluble and have a low degree of crosslinking. In order to obtain the desired lubricity characteristics, it is critical to employ high molecular weight acrylamide polymers, that is, polymers characterized by a viscosity of at least 4 centipoises for a 0.5 percent by weight solution of the polymer in an aqueous 4 percent by weight sodium chloride solution adjusted to a pH of 5 to 6 at a temperature of 25° C., such viscosity being measured with an Ostwald viscosimeter. When the acrylamide polymer contains carboxyl groups corresponding to over about 10 percent hydrolysis, it is essential to determine the viscosity in aqueous sodium chloride solution at a pH of 5 to 6 and the term "viscosity" as employed in the following claims refers to the viscosity of a 0.5 percent by weight solution of polymers determined under the above conditions. With acrylamide polymers containing carboxyl groups corresponding to less than about 10 percent hydrolysis, the viscosity characteristics may be determined on an aqueous 0.5 percent by weight solution of the polymer in distilled water adjusted to a pH of 3 to 3.5 at a temperature of 25° C. In either case, the minimum limitation of 4 centipoises applies.

In the preparation of the compositions of the invention, it is essential that the acrylamide polymer be thoroughly and intimately admixed with the soap and other ingredients, if any, to produce a uniform finished composition. In preparing certain of the compositions, particularly those in which the finished composition contains sufficient water or in which only minimal amounts of acrylamide polymer are to be introduced, it is convenient to employ the acrylamide polymer in the form of a dilute aqueous solution. In such operations, the aqueous solution of acrylamide polymer may be mixed with the liquefied soap in a crutcher or other mixing device. Alternatively, in soap and detergent compositions containing considerably more water than bar soap and powdered soap products, the acrylamide polymer may be dissolved in all or part of the water employed in the formulation and thereafter blended with the other ingredients. The addition of the acrylamide polymers in the form of aqueous solutions, however, is limited by the fact that such solutions rapidly become more viscous with increasing concentration of

acrylamde polymer. Thus, for example, aqueous compositions containing 5 to 10 percent by weight of the acrylamide polymers of the invention form highly viscous solutions or rubbery gels which are extremely difficult to admix uniformly with other ingredients.

In an alternative and preferred mode of operation, the acrylamide polymer in dry, finely divided form is intimately blended with the other ingredients to form the compositions of the invention. In one such method of operation, bar soap is ground or flaked and mechanically mixed with the dry, finely divided acrylamide polymer prior to milling and molding into cakes. Alternatively, the dry, finely divided acrylamide polymer may be mixed with the liquid soap or detergent in a crutcher or like mixing device. In the latter mode of operation, it is essential that the polymer be added portionwise with vigorous mixing in order to produce a uniform composition. In a further mode of operation, the acrylamide polymer may be milled or otherwise thoroughly mixed with any dry builder or filler ingredients and the resulting finely divided solid composition be added to the soap or detergent in one of the above-described methods of operation. Similarly, in the preparation of powdered soaps and detergents, the acrylamide polymer in finely divided or powdered form is mechanically mixed with the other ingredients of the powdered soap and sieved or ground as required to produce the desired particle size. The incorporation in the soap composition of the acrylamde polymer in dry, finely divided form, particularly when said polymer has been ground to pass a 100 mesh screen, constitutes a preferred embodiment of the invention. As herein employed, the mesh screen sizes refer to the Tyler Standard Screen Scale Sieves wherein a screen of 100 meshes to the inch provide a sieve opening of about 0.147 millimeter.

The amount of acrylamide polymer to be employed will vary depending upon the type of soap or detergent ingredient used, the particular effect desired in the finished soap product and upon the end use of such product. In general, good results have been obtained when employing from about 0.1 to 4 percent by weight of acrylamide polymer based on the total weight of the soap composition. Amounts of from about 0.1 to 1 percent by weight of acrylamide polymer are generally sufficient in compositions based on true soaps whereas somewhat higher amounts of from about 0.5 to 4 percent by weight of acrylamide polymer are usually employed in compositions based on synthetic detergents. The lubricity imparted to a soap composition is dependent upon the viscosity of the polymer employed therein and generally increases with increasing viscosity. Thus, with high viscosity polymers, the desired "hand" of the soap composition is achieved with smaller amounts of polymer than will be required when employing a polymer characterized by a lower viscosity.

The acrylamide polymers employed in the present invention may be prepared by known methods as, for example, by heating suitable solutions of acrylamide monomer or of acrylamide monomer together with other suitable comonomers, as set forth above, in the presence of a free radical initiator such as an alkyl hydroperoxide or an alkali metal persulfate. The resulting acrylamide polymers may be subsequently modified by hydrolysis, if desired. Typical polymers adapted to be employed in the invention are prepared as follows:

(1) *Polyacrylamide.*—100 grams of commercial acrylamide, containing about 1 percent by weight of acrylic acid, and 0.5 gram of potassium persulfate are dissolved in 900 milliliters of water and heated at gradually increasing temperature of from about 50° C. to about 90° C. during a period of 6 hours. The resulting highly viscous gel-like solution of acrylamide polymer may be diluted with water for subsequent use or dried on a drum drier to obtain the polymer product in dry flake form. Typical polymers produced in this manner are characterized by viscosities of 4 to 10 centipoises for aqueous 0.5 percent by weight solutions thereof at pH 3 and at 25° C. Because of some hydrolysis during the polymerization, the product is found to be characterized by hydrolysis of from about 2 to 5 percent.

(2) *Polyacrylamide.*—One-half gallon of an aqueous solution, containing 10 percent by weight of purified acrylamide monomer at a pH of 5.2 is purged of dissolved oxygen by bubbling purified nitrogen therethrough. 0.5 milliliters of 2,2-bis-tertiarytbuylperoxybutane is then admixed with the purged solution and the resulting mixture heated at a temperature of 90° to 95° C. under an atomsphere of nitrogen for eight hours. The resulting acrylamide polymer is characterized by hydrolysis of 1.6 percent and by a viscosity of 7.2 centipoises for an aqueous 0.5 percent by weight solution thereof adjusted to a pH of 3 and a temperature of 25° C.

(3) *Acrylamide-methacrylamide copolymer.*—95 grams of acrylamide, 5 grams of methacrylamide, 0.2 gram of potassium persulfate and 0.1 gram of sodium bisulfite are dissolved in one liter of distilled water and the resulting solution heated to 70° C. for 24 hours. The copolymer product is recovered by precipitation from the solution by the addition of methyl alcohol or by drying on a drum drier. In a similar fashion a copolymer of 92 percent acrylamide with 8 percent methacrylic acid is prepared.

(4) *Acrylamide-acrylic acid copolymer.*—An acrylamide polymer prepared as in (1) above has a degree of hydrolysis of about 5 percent and is characterized by a viscosity of 11.2 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent sodium chloride solution adjusted to a pH of 5 and a temperature of 25° C. 10 grams of this polymer is dissolved in 480 milliliters of water, 0.7 gram of sodium hydroxide dissolved in 10 milliliters of water is added thereto with stirring and the resulting mixture heated at 60° C. for 4 hours. There is obtained an acrylamide-acrylic acid copolymer, that is, an acrylamide polymer characterized by about 18 percent hydrolysis. This polymer is found to have a viscosity of 11.3 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent by weight sodium chloride solution adjusted to a pH of 5 and a temperature of 25° C.

The following examples illustrate the invention but are not to be construed as limiting the same.

Example 1

A shaving cream is prepared from the following ingredients:

	Pounds
Stearic acid, triple pressed	260
Potassium hydroxide U.S.P. (20° Baumé solution)	215
Sodium hydroxide U.S.P. (20° Baumé solution)	58
Witch hazel	20
Borax	3
Water	500
Coconut oil shampoo base (60 percent potassium soap)	120
Glycerine C.P.	160
White mineral oil	5
Perfume	2
Acrylamide polymer	12
	1355

In formulating the above composition, one-half the stearic acid is melted in a corrosion-resistant kettle and the mineral oil is mixed therewith. In another kettle, the potassium and sodium hydroxide are mixed and the borax and glycerine dissolved therein with stirring and heating. Into the resulting solution, the melted stearic acid is poured with vigorous agitation. Stirring is continued, with heating as required, for one-half hour to form a well blended saponified stearic acid mixture. During the above operation, the acrylamide polymer is dissolved in the water in a separate vessel with vigorous

stirring and the resulting solution combined with the coconut oil shampoo base. The acrylamide polymer and coconut oil shampoo base mixture is heated and blended with the hot saponified stearic acid mixture and thereafter the remainder of the stearic acid is melted and mixed portionwise with vigorous stirring with the total mass. When the composition has been thoroughly blended, a sample is withdrawn and analyzed for free fatty acid. If necessary, additional stearic acid or potassium hydroxide is added as required by the analysis to adjust the free fatty acid content to about 3 percent. Thereafter the mass is cooled to about 125° F. with constant stirring and the witch hazel and perfume are added with continued stirring until the composition is smooth. The acrylamide polymer employed is characterized by hydrolysis of 3 percent and a viscosity of 5 centipoises for a 0.5 percent by weight solution thereof in distilled water adjusted to a pH of 3 and a temperature of 25° C. In use, this composition is found to give a stable, small bubble lather having much better lubricity characteristics than an exactly similar composition without the acrylamide polymer ingredient.

Example 2

A dry powdered hand soap was prepared having the following composition:

Ingredient:	Percent by weight
Soap	24.5
Tetrasodium borate-decahydrate	73.5
Acrylamide polymer	2

The soap consisted of about 20 percent coconut oil base sodium soaps and about 75 percent tallow base sodium soaps. The acrylamide polymer employed was characterized by hydrolysis of about 3 percent and by a viscosity of about 9 centipoises for a 0.5 percent by weight solution thereof in distilled water adjusted to a pH of 3 and at 25° C. The acrylamide polymer in flaked form was ground in a hammermill to finely divided condition and mechanically mixed with the other ingredients. This formulation was found to have excellent cleansing and mild abrasive properties combined with a more pleasant soapy feeling on the skin than a similar composition without the acrylamide polymer ingredient.

Example 3

Commercial toilet soap (a blend of sodium soaps from natural fats and oils) was ground and blended with varying amounts of an acrylamide polymer similar to that employed in Example 2. After thorough mixing, each blend of soap and acrylamide polymer was reformed into cakes by pressing in a mold. A portion of the soap was milled in the same fashion and repressed, without any addition of acrylamide polymer, to serve as a check. Evaluation indicated that the soap containing 1, 2 and 4 percent by weight of acrylamide polymer had a soapier feel in use and produced a lather with smaller and stiffer bubbles. In home use by a test panel, a substantial majority of users preferred the soap containing 2 percent of acrylamide polymer as compared to the same soap with no acrylamide polymer. As a result of the increased lubricity and stiffer lather, the hand soap containing 2 percent of acrylamide polymer was found to be excellent as a lather shaving soap. Any of the common bar hand soaps of commerce can be substituted in the above formulations with similar improved results.

Example 4

The following composition was prepared as a bubble-blowing solution:

Ingredient:	Parts by weight
Acrylamide polymer	5
Water	200
Household detergent	1
Potassium soap from coconut oil fatty acids	2

The acrylamide polymer employed was characterized by hydrolysis of about 1.5 percent and a viscosity of 4 centipoises for an aqueous 0.5 percent by weight solution thereof at pH 3 and at 25° C. The household detergent contained 2 percent by weight of sodium lauryl sulfate, 7 percent of sodium tallow alcohol sulfate, 9 percent of sodium dodecylbenzenesulfonate, 50 percent of sodium tripolyphosphate, 0.5 percent of carboxymethylcellulose with the balance perfume, dyes and inerts.

The acrylamide polymer was dissolved with vigorous stirring in the water and the detergent and coconut oil soap thereafter added thereto with stirring. The resulting viscous composition was adapted to be employed with children's bubble-blowing devices to produce high-strength bubbles having remarkable persistence.

Example 5

Following the procedure of Example 2, compositions are prepared as follows:

Ingredient:	Parts by weight
Synthetic detergent	5–10
Ground soap	15–30
Borax	50–80
Acrylamide polymer	1–4

The compositions are used as medium to heavy duty hand cleansers. Any of the acrylamide polymers, as above set forth, may be employed. The ground soap consists of sodium soaps derived from tallow or palm oil and coconut oil. Synthetic detergents such as sodium lauryl sulfate, sodium dodecylbenzenesulfonate, the sodium salt of sulfated coconut oil monoglyceride, nonyl phenyl ether of a long-chain polyglycol or the like may be employed.

Example 6

An abrasive hand cleanser is prepared by blending the following:

Ingredient:	Parts by weight
Sodium dodecylbenzenesulfonate	5.0
Tallow sodium soap	32.0
Coconut oil sodium soap	30.0
Lanolin	2.0
Diatomaceous earth	14.0
Pumice	8.0
Bentonite	4.0
Sodium metasilicate	3.5
Acrylamide polymer (dry, finely ground)	1.5

The acrylamide polymer employed is characterized by hydrolysis of 50 percent and by a viscosity of 15 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent sodium chloride solution adjusted to a pH of 5 and a temperature of 25° C. The lanolin is melted and mechanically mixed with the dry, ground soap. The other ingredients are then blended into the final composition and the latter is milled to provide a dry, free-flowing powder.

Example 7

The base stock for a synthetic detergent bar soap contains 10 percent of sodium tallow base soap, 5 percent of sodium coconut-oil base soap, 74 percent of the sodium salt of sulfated coconut oil monoglyceride, 1 percent of perfume and 10 percent of inerts. This base stock is heated in a blender and 1 percent by weight of dry, finely divided acrylamide polymer, characterized by hydrolysis of 3.5 percent and a viscosity of 9 centipoises for a 0.5 percent by weight solution thereof in distilled water adjusted to a pH of 3 and a temperature of 25° C. is added thereto portion wise. After thorough blending of the above ingredients, the mixture is milled, plodded and extruded in bar form to produce a synthetic detergent bar which, in use, imparts a feeling of improved lubricity to the skin as compared to detergent bars prepared from the

same base stock without the inclusion of the acrylamide polymer.

Example 8

A sodium soap prepared by saponification of coconut oil is run into a crutcher at a temperature of about 160° F. To each 80 parts by weight of this soap is added a mixture of 18.5 parts of finely ground pumice and 0.5 part of acrylamide polymer ground to pass a 100-mesh screen of the Tyler Standard Sieve Series. Thereafter 1 part by weight of perfume is added and the resulting mixture is run into frames for cooling to prepare an abrasive bar soap having desirable lubricity properties when used on the skin. The acrylamide polymer employed is a polyacrylamide characterized by hydrolysis of 6.2 percent and a viscosity of 8.5 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent sodium chloride solution adjusted to a pH of 5 and a temperature of 25° C. In use, this soap is found to give a more pleasant feeling of blandness and lubricity on the skin than an exactly similar abrasive bar soap without the acrylamide polymer ingredient.

Example 9

20 grams of triethanolamine is dissolved in 474.7 grams of water and to the resulting solution 5.3 grams of acrylamide polymer is added with vigorous stirring. Stirring is continued for a period of time to complete solution of the acrylamide polymer and 26.4 grams of stearic acid and 8 grams of hydroxypropyl-sucrose monomyristate added thereto with stirring. The resulting solution is placed in aerosol pressure cans and to each 90 parts by weight of said solution is added 10 parts by weight of a mixture of 4 parts dichlorodifluoromethane and 6 parts 1,2-dichloro-1,1,2,2-tetrafluoroethane. The resulting aerosol shave composition produces a persistent lather having excellent lubricating properties on the skin. The acrylamide polymer employed was a polyacrylamide characterized by hydrolysis of about 6 percent and a viscosity of 5.8 centipoises for a 0.5 percent by weight solution thereof in distilled water adjusted to a pH of 3 and a temperature of 25° C.

A similar composition having desirable persistence and lubricity is prepared in exactly the same manner except that for the 5.3 grams of acrylamide polymer in the above composition there is substituted 0.6 gram of a polyacrylamide characterized by hydrolysis of about 4 percent and a viscosity of about 15 centipoises for a 0.5 percent by weight solution thereof in distilled water adjusted to a pH of 3 and a temperature of 25° C.

Example 10

A shampoo is prepared as follows:

Ingredient:	Pounds
Coconut oil	112
Potash lye, 38° Baumé	83
Water	600
Acrylamide polymer	5
Perfume	9

The coconut oil is saponified with the potash lye to form the coconut oil potassium soap and glycerine and the resulting mixture is filtered while hot. The acrylamide polymer is dissolved in the water by slowly sifting the finely divided polymer into the water while the latter is vigorously agitated. The resulting polymer solution is thoroughly blended with the filtered potassium soap and glycerine at a temperature of about 160° F., the resulting mixture cooled to about 125° F. and the perfume added with continued stirring until the composition is homogeneous. The acrylamide polymer employed is characterized by hydrolysis of 28 percent and by a viscosity of 13 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent sodium chloride solution adjusted to a pH of 5 at a temperature of 25° C.

We claim:

1. A lubricious powered hand soap composition which consists essentially of from 50 to 80 parts by weight of borax, from 15 to 30 parts by weight of a ground soap consisting of the sodium salts of long-chain fatty acids and from about 0.5 to 4 parts by weight of acrylamide polymer, said polymer being water-soluble and selected from the group consisting of the homopolymer of acrylamide, copolymers of acrylamide with up to about 15 percent by weight of a member of the group consisting of methacrylamide, the lower alkyl esters of acrylic and methacrylic acids, vinyl chloride and vinyl alkyl ethers and copolymers of acrylamide with up to about 50 mole percent of a member of the group consisting of acrylic and methacrylic acids and the alkali metal salts thereof and said polymer being characterized by a viscosity of at least about 4 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent by weight sodium chloride solution adjusted to a pH of 5 to 6 and a temperature of 25° C.

2. A lubricious composition for the skin which consists essentially of a major proportion of ingredients selected from the group consisting of non-soap anionic and nonionic synthetic organic detergents in intimate mixture with from about 0.1 to 4 percent by weight, based on the weight of the total composition, of an acrylamide polymer, said polymer being water-soluble and selected from the group consisting of the homopolymer of acrylamide, copolymers of acrylamide with up to about 15 percent by weight of a member of the group consisting of methacrylamide, the lower alkyl esters of acrylic and methacrylic acids, vinyl chloride and vinyl alkyl ethers and copolymers of acrylamide with up to about 50 mole percent of a member of the group consisting of acrylic and methacrylic acids and the alkali metal salts thereof and said polymer being characterized by a viscosity of at least about 4 centipoises for a 0.5 percent by weight solution thereof in aqueous 4 percent by weight sodium chloride solution adjusted to a pH of 5 to 6 and a temperature of 25° C.

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