

1

3,549,546

PROCESS FOR PREPARING LIQUID DETERGENT
Robert S. Moore, Wyoming, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

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2 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing a homogeneous liquid detergent composition containing an anionic organic detergent and a cationic polymer, consisting of dissolving an aqueous solution of the polymer in triethanolamine; dispersing the polymer-triethanolamine solution in an aqueous solution of anionic organic detergent using low shear mixing means; and milling the resultant mixture in a closed system colloid mill.

Liquid detergent compositions, especially shampoo compositions, generally contain an anionic organic synthetic detergent as the principal ingredient. Cationic polymeric substances are desirably incorporated in such compositions for various purposes. For example, anionic organic detergent compositions containing various cationic polymeric substances are disclosed by Lang and McCune in U.S. Letters Patent 3,313,734, granted Apr. 11, 1967. The cationic polymers are employed in that patent to improve hair condition, i.e., wave set retention and hair manageability. Lang, U.S. patent application Ser. No. 586,013, filed Oct. 12, 1966 now Pat. No. 3,400,198, discloses anionic organic detergent compositions containing still other cationic polymers as hair conditioning additives.

Yet another invention which involves the use of cationic polymers in an anionic organic detergent product is disclosed by Parran, U.S. patent application Ser. No. 476,175, filed July 30, 1965 now abandoned. The detergent compositions of the Parran invention contain cationic polymers to promote deposition and retention of particulate substances, e.g., antidandruff agents, on surfaces washed with the composition.

Because of the well known incompatibility of anionic organic detergents and cationic polymeric substances, special measures must be taken to prepare stable homogeneous products containing these materials.

As taught in the aforementioned disclosures, certain ampholytic and polar nonionic detergents serve to "compatibilize" cationic polymers and anionic detergents. However, such ancillary detergents are relatively expensive and manufacturing efficiency and quality control are unfavorably affected by complicating the formulation with these materials.

Apparently stable homogeneous liquid products containing both cationic polymers and anionic detergents can be prepared without such ancillary detergents by using high shear mixing techniques followed by milling in a colloid mill; however, such mixing can result in aeration of the product which ultimately causes visible separation of the ingredients.

It is an object of this invention to provide an improved method for preparing a liquid detergent composition

2

containing an anionic organic detergent and a cationic polymer.

It is a further object of this invention to provide a method for preparing a stable homogeneous liquid detergent composition containing a cationic polymer and an anionic detergent, which is essentially free of entrapped air.

It is a still further object of this invention to provide a method for preparing a stable homogeneous liquid detergent composition containing a cationic polymer and an anionic detergent without using ancillary ampholytic or polar anionic detergents to compatibilize same.

These and other objects are accomplished by the invention hereinafter described and claimed.

In general terms, this invention comprises a process for preparing stable homogeneous liquid detergent compositions containing an anionic organic detergent and a cationic polymer comprising the steps of (1) dissolving an aqueous solution of said polymer in triethanolamine; (2) dispersing the resulting solution in an aqueous solution of said detergent using low shear mixing means to prevent aeration; and (3) milling the resulting dispersion in a sealed colloid mill equipped with enclosed feed and discharge means.

It has been discovered that by dissolving the cationic polymer in triethanolamine prior to adding same to the anionic organic detergent component, a surprisingly uniform dispersion of the polymer is obtained with only mild agitation (low shear mixing). It is, of course, essential that the mixture be uniformly dispersed prior to milling in a colloid mill and this could heretofore be accomplished only by high shear mixing with attendant aeration.

Compositions prepared in accordance with the process of this invention contain, as hereinbefore stated, an anionic organic detergent such as water-soluble soaps and nonsoap synthetic detergents. Operable nonsoap anionic organic detergents include, for example, water-soluble salts of organic sulfuric reaction products having in their molecular structure an alkyl containing from about 8 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. Important examples of this type of nonsoap anionic synthetic detergent, include the sodium or potassium alkyl sulfates, including those derived by sulfation of higher alcohols produced by reduction of tallow or coconut oil glycerides; sodium or potassium alkylbenzene sulfonates, especially those of the types described by Guenther et al. in U.S. Pat. 2,220,099, granted Nov. 5, 1940, and by Lewis in U.S. Pat. 2,477,383, granted July 26, 1949, in which the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkylglyceryl ether sulfonates, especially those ethers of higher alcohols obtained from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium and triethanolammonium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (i.e., tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and others well known in the art, a number being specifically set forth in Byerly, U.S. Pat. Nos. 2,486,921 and 2,486,922.

Additional nonsoap anionic organic synthetic detergents which can be used in this invention include the salts of the condensation products of fatty acids with sarcosinate, i.e., acyl sarcosinate, wherein the acyl radical has a chain length range from about 10 to 18 carbon

atoms. An especially preferred acyl sarcosinate for the purpose of this invention is sodium lauroyl sarcosinate.

Preferably, the nonsoap anionic organic detergent will be of the high sudsing type as for example, the alkylglycerylether sulfonates, the sulfated fatty alcohols or the alkyl ether ethylene oxide sulfates wherein the ethylene oxide chain averages 3 units, and acyl sarcosinates, all as more fully set forth above. These and the foregoing detergents can be used in the form of their sodium potassium or lower alkanolamine (such as triethanolammonium) salts.

Conventional soaps may also be used as the anionic detergent component of this invention. Suitable soaps include the sodium, potassium, and lower alkanolamine salts of higher fatty acids of naturally occurring vegetable or animal fats and oils. For example, sodium, potassium and triethanolamine salts of fatty acids occurring in coconut oil, soybean oils, castor oil, tallow or synthetically produced fatty acids may be used.

If soap is to be used, it would desirably be used in small quantities, less than about 10% and would be admixed with nonsoap anionic detergents to form the final detergent component of the compositions of this invention. Preferably, the triethanolammonium salt of coconut fatty acid would be used, since it is more readily soluble than the salts of higher alkyl chain length fatty acids. Other preferred soaps include the sodium and potassium salts of coconut fatty acid.

Mixtures of any of the foregoing anionic detergents may also be used in the composition of this invention.

The anionic organic detergent can be employed in concentrations ranging from about 4% to about 30% by weight of the total composition with the preferred range being from about 7% to about 20%. Because of the excellent solubility and lathering properties of anionic nonsoap detergents containing predominantly C₁₂ and C₁₄ alkyl chain lengths and their ready availability, these are preferred for the purpose of this invention.

The cationic polymers which can be incorporated in detergent compositions through the practice of this invention include water-soluble polymers at least 30 mole percent of the molecular structures of which are composed of monomeric units containing one or more quaternary ammonium groups and any balances of which are comprised of nonquaternized polymeric units derived from monoethylenically unsaturated groups. Such polymers include, for example, quaternized polyvinylimidazole, quaternized poly(dimethylaminoethylmethacrylate), quaternized poly(diethylaminoethylmethacrylate), quaternized poly(p-dimethylaminomethylstyrene) and others disclosed in U.S. Pat. 3,313,734 having molecular weights of from about 1,000 to about 5,000,000.

Yet other cationic polymers are those disclosed by Parran in U.S. application Ser. No. 476,175, filed July 30, 1965, i.e., polyethylenimine or alkoxylated polyethylenimine having a molecular weight greater than about 100 but less than about 5,000,000.

Still other cationic polymers which can be added to anionic detergents by the process of this invention are (1) the water-soluble quaternary nitrogen-substituted cellulose derivatives available under the code designation JR-1L; (2) the water-soluble linear polyamines available under the trade name Primafloc, and related polymers disclosed in U.S. Letters Pat. 3,300,406, granted Jan. 24, 1967; and (3) the water-soluble polymers of epichlorohydrin and tetraethylene-pentamine available under its trade name Nalco 600. All of these latter polymers are water-soluble cationic tertiary amine or quaternary ammonium-containing polymers having molecular weights within the range from about 2,000 to 3,000,000, and having a cationic charge density

$$\left(\text{i.e., } \frac{\text{Number of positive charges}}{\text{Unit molecular weight}} \right)$$

greater than about 0.001

It can be seen that the present invention finds application in connection with the addition of any cationic polymer to any anionic organic detergent in a liquid form. Thus, the specific nature of the involved cationic polymer is not critical. Rather, it is the inherent incompatibility of cationic materials generally with anionic detergents that renders the present invention useful in its broadest aspect.

The cationic polymer can be incorporated in detergent compositions of the type herein contemplated at concentrations ranging from about 0.1% to about 7.0% by weight. The optimum concentrations will vary depending on the type of polymer employed and its intended purpose in the composition. Detergent compositions containing more than about 7.0% of cationic polymer are difficult to formulate without high shear mixing and concomitant aeration of the product. Concentrations of cationic polymer less than about 0.1% do not generally provide the desired effect in the composition.

Aside from the purposes of the present invention, triethanolamine has been included in detergent compositions for a variety of purposes. For example, it is a base which can be used to adjust the pH of such compositions and is especially suited for this use in compositions wherein the organic anionic detergent is a triethanolammonium salt. In the process of the present invention this material additionally provides a vehicle for introduction of a cationic polymer into an anionic organic detergent to permit uniform dispersion of the polymer.

In the practice of this invention, an aqueous solution of the cationic polymer is dissolved in triethanolamine in quantities sufficient to provide the desired ultimate concentration of each of these materials in the finished detergent composition. Preferably, the aqueous solution of polymer is in a concentration range of from about 1.0% to about 50.0%, more preferably about 40.0%, when mixed with the triethanolamine. The triethanolamine concentration in the aqueous solution of polymer and triethanolamine is desirably within the range from about 15% to about 80%, and best results are obtained when this component is employed at a concentration of about 40% in the polymer/triethanolamine aqueous solution.

The polymer/triethanolamine solution is maintained at a temperature within the range from about 50° to 200° F. and is thoroughly mixed. This solution is then added to an aqueous solution of the anionic detergent, preferably at a concentration of from about 4% to about 60%, together with other desired components in a main mix tank equipped with low shear mixing means. Although temperatures are not critical, the anionic detergent solution is preferably heated to a temperature in the range from about 150° F. to about 175° F. prior to the addition of the cationic polymer/triethanolamine solution. After sufficiently mixing to effect uniform dispersion of all ingredients, the mixture is milled in a closed system colloid mill.

The terms "low shear mixing" and "low shear agitation" are used interchangeably herein and refer to means and/or methods for dissolving or dispersing the ingredients of the involved compositions which do not aerate the compositions to any substantial degree. Any of the well known commercial propeller or turbine type agitators can be used, if operated at speeds or adjustments which will not lead to the entrapment of air bubbles.

The closed system colloid mill specified for use in the present process is available in a variety of designs from a number of manufacturers. The term "closed system" used herein to characterize such mills refers to the air-tight inlet and discharge means which precludes the introduction of atmospheric air during the milling procedures. A general discussion of colloid mills and other mixing means is found in Sagarin, *Cosmetics Science & Technology*, pages 1020-1022 (Interscience Publishers, Inc., 1957).

The process of this invention is fully illustrated by ref-

erence to the following examples which are not to be construed as limiting the invention in any way.

EXAMPLE I

A liquid detergent formulation of the following composition was prepared using the process of this invention.

Component:	Percent by weight
Triethanolamine coconut ¹ sulfate	20.00
Triethanolamine	1.60
Zinc 2-pyridinethiol-1-oxide	1.00
Polyethylenimine/propylene oxide reaction product ²	1.00
Hydroxypropoxyl-substituted methyl cellulose ³	0.24
Coconut ¹ monoethanolamine	4.00
Veegum ⁴	0.95
Coloring	0.10
Perfume	0.25
Distilled water	Balance

¹ The term "coconut" as used herein refers to alkyl groups which are derived from the middle-cut of coconut alcohol having the following approximate chain length distribution: 2%—C₁₀; 66%—C₁₂; 23%—C₁₄; and 9%—C₁₆.

² Polyethylenimine having a molecular weight of 40,000 to 60,000; mole ratio of polyethylenimine to propylene oxide equals 1:1.

³ Methocel 60 HG comprised of from 28% to 30% by weight of methoxyl and from 7% to 12% by weight of hydroxypropoxyl substituents. Degree of substitution with methoxyl and hydroxypropoxyl substituents is 1.68 to 1.82 and from 0.17 to 0.3, respectively.

⁴ Complex colloidal magnesium aluminum silicate.

The above composition was prepared as follows: 40.0 grams of a 50% aqueous solution of the propylene oxide/polyethylenimine was added to 32 grams of triethanolamine and mixed at room temperature in a 100 ml. beaker with an air operated stirrer with a ¾" two-bladed propeller-type agitator operated at low speed until a single phase solution was formed.

The polymer/triethanolamine solution was then added to 1111.2 grams of a 36% aqueous solution of triethanolammonium coconut sulfate heated to 160° F. to 190° F. in a steam-jacketed, stainless steel main mix tank equipped with a "Lightnin" mixer having a 2" diameter turbine operated at approximately 50 r.p.m. 40.0 grams of a 50% aqueous dispersion of zinc 2-pyridinethiol-1-oxide, 88.8 grams of a 4.5% aqueous solution of hydroxypropoxyl-substituted methylcellulose, and 80.0 grams of coconut monoethanolamide were also added to the main mix tank.

361 grams of distilled water were heated to 180° F. to 210° F. and 19.0 grams of Veegum were slowly added thereto in a Waring blender operated to provide a vortex to the bottom of the mixing chamber. The Veegum was allowed to hydrate for one hour with agitation and was then added to the main mix tank.

The remaining ingredients were added to the main mix tank and the total composition was mixed with low shear for 15 minutes. The mixture was then milled at .002 inch gap in a Gaulin colloid mill having sealed feed and discharge ports to prevent introduction of atmospheric air during the milling operation.

The milled product was cooled to 80° F. This liquid detergent composition was found to be stable and homogeneous and essentially free of entrapped air bubbles.

EXAMPLE II

A composition was prepared identical in formulation to the composition of Example I, except that the polyethylenimine/propylene oxide was replaced with an ethoxylated polyethylenimine (polyethylenimine having a molecular weight of 40,000 to 60,000; weight ratio of polyethylenimine to ethylene oxide equals 1:1; and total molecular weight 80,000 to 120,000) and the anionic detergent constituted 21% by weight of the composition rather than 20% as in Example I. The procedure employed in the preparation of this composition was the same as Example I except the aqueous polymer/trietha-

anolamine solution was added to the main mix tank. The product was again a stable homogeneous liquid detergent, essentially free of entrapped air.

EXAMPLE III

Formulations identical to those prepared in Examples I and II but containing triethanolamine dodecylbenzene sulfonate; potassium coconut glyceryl ether sulfonate; the sodium and triethanolammonium salts of the sulfated condensation product of 1 mole of coconut fatty alcohol and 3 moles of ethylene oxide, and sodium lauroyl sarcosinate, respectively, in place of triethanolamine coconut sulfate, are formulated in accordance with the process of Example I. The resulting products are stable homogeneous liquids essentially free of entrapped air.

EXAMPLE IV

Additional compositions are prepared in accordance with the procedure of Example I but using a substantially completely quaternized polyvinylimidazole, having a molecular range of about 100,000; dimethyl sulfate quaternized poly (diethylaminoethyl methacrylate) having a molecular weight of about 500,000 and prepared in accordance with Example I of U.S. 2,723,256 granted Nov. 8, 1955; substantially completely quaternized poly (p-dimethylaminomethylstyrene) having a molecular weight of approximately 250,000; substantially completely methyl phosphate quaternized poly(dimethylaminoethyl methacrylate) having a molecular weight within the range a molecular weight of about 500,000 and prepared as hereinbefore described; and a water-soluble polyethylenimine having an average molecular weight of about 100,000 and a viscosity of 2.5 centipoises in a 1% by weight aqueous solution; respectively, in place of the alkoxylated polyethylenimine. The resulting products are stable homogeneous liquids which are relatively non-aerated.

Unless otherwise specified, the percentage values employed herein refer to percent by weight.

Although the formulations set forth herein in the examples include a number of ancillary ingredients, it is to be understood that the process described and claimed herein is useful in the preparation of stable homogeneous liquid detergents containing any desired organic anionic detergent and cationic polymer without regard to other ingredients.

What is claimed is:

1. A method for preparing a stable, homogeneous liquid detergent composition consisting essentially of (a) a cationic polymer selected from the group consisting of polyethylenimine, alkoxylated polyethylenimine prepared by reacting polyethylenimine with alkylene oxide compounds which contain from about 2 to about 3 carbon atoms, quaternized polyvinylimidazole, quaternized poly (diethylaminoethylmethacrylate), quaternized poly (dimethylaminoethylmethacrylate), and quaternized poly (p-dimethylaminomethylstyrene), said polyethylenimine and alkoxylated polyethylenimine having a molecular weight greater than 100, but less than 500,000, and said quaternized compounds having a molecular weight of from about 1,000 to 5,000,000 and (b) an anionic organic detergent, comprising the steps of (1) admixing an aqueous solution of said cationic polymer at a concentration within the range from about 1% to about 50% with triethanolamine in a quantity sufficient to provide a concentration of triethanolamine in the mixture within the range of from about 15% to about 80%; (2) dispersing the resulting mixture in an aqueous solution of said anionic organic detergent at a concentration within the range of from about 4% to about 50% by weight and at a temperature within the range of from about 150° F. to about 175° F., using low shear mixing means to prevent aera-

7

tion; and (3) milling the resulting dispersion in a sealed colloid mill having enclosed feed and discharge means.

2. A method in accordance with claim 1 wherein the organic anionic detergent is a water soluble detergent salt of a member selected from the group consisting of higher fatty acids, anionic organic sulfuric reaction products having in their molecular structure an alkyl containing from about 8 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group, and acyl sarcosinates wherein the acyl group contains from about 10 to about 18 carbon atoms.

5

10

2,914,482	11/1959	Kopp	-----	252—152
3,150,098	9/1964	Wilson	-----	252—152

LEON D. ROSDOL, Primary Examiner
M. L. HALPERN, Assistant Examiner

U.S. Cl. X.R.
252—137

8

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UNITED STATES PATENTS

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,549,546 Dated December 22, 1970

Inventor(s) Robert S. Moore

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 49, "produces" should read --products--.

Column 3, lines 9 and 10, after "sodium" and before "potassium" should read --,--.

Column 3, line 56, "5,000,000" should read --500,000--.

Column 3, line 75, after "0.001" should read --.---.

Column 5, line 68, "polyethylenimne" should read --polyethyleni

Column 6, line 22, "quar-" should read --qua- --.

Column 6, line 26, "quarternized" should read --quaternized--.

Column 6, lines 31 and 32, "a molecular weight of about 500,000 and prepared scribed" should be deleted, and --from about 1,000 to 5,000,000; JR-1L as hereinbefore described-- inserted theref

Column 6, line 56, "quanternized" should read --quaternized--.

Signed and sealed this 4th day of May 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER,
Commissioner of Paten

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