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[54] **DETERGENT COMPOSITION WITH AN AMIDO-AMINE FABRIC SOFTENING AGENT**

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[51] **Int. Cl.** **D06m 9/00**

[58] **Field of Search** 252/8.75, 89, 102, 8.8, 252/525

[56] **References Cited**

UNITED STATES PATENTS

3,451,844	6/1969	Kirschnek et al.	252/8.8 X
3,452,066	6/1969	Mannheimer	252/8.75 X

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[57] **ABSTRACT**

Detergent compositions consisting essentially of an anionic surface-active agent and an amido-amine fabric softening agent. The compositions provide in laundering operations combined cleansing and fabric softening effects.

7 Claims, No Drawings

DETERGENT COMPOSITION WITH AN AMIDO-AMINE FABRIC SOFTENING AGENT

BACKGROUND OF THE INVENTION

This invention pertains to detergent compositions for textiles consisting essentially of an anionic surface-active agent in admixture with a cation-active textile softening agent. Cationic textile softening agents, such as those exemplified by the substituted tertiary amines, in general, lose their softening activity in the presence of anionic surface-active agents due to precipitation or other chemical interferences. Hence, these textile softeners are added, in laundering operations to the last rinsing liquor, if desired in admixture with nonionic surface-active compounds. This rinse-cycle use of cationic softeners constitutes a conventional use of the substituted tertiary amines which is also confirmed by the teachings of U.S. Pat. No. 3,451,844, issued June 24, 1969.

It is well known that textiles which have been washed in laundering operations whereby current detergent compositions, especially synthetic detergent compositions, have been used will acquire a harsh feel. This constitutes a significant disadvantage, particularly for those textiles which are worn and likely to get in direct contact with the human skin. Until now, this disagreeable feel of the laundered textiles has been eliminated through the addition of textile softening compositions, such as the cationic quaternary ammonium salts, to the rinsing cycle of the washing operation, particularly to the last rinse. However, even this combination of a successive laundering and softening operation leads to a denaturation of the textile, particularly color fading, resulting from the precipitation of remaining traces of anionic surface-active agents from the washing operation with the cationic softening ingredient and which precipitants adhere to the fibers. These problems have been recognized for some time and much effort has been spent in the formulation of detergent compositions exhibiting simultaneous detergency and softening characteristics.

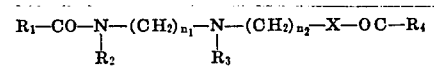
THE PRIOR ART

The teachings of German patent specification (DAS) 1,419,362 recommend the circumvention of the deactivation effects of anionic detergent compositions containing cationic softeners by the addition of a condensation product of a tertiary fatty amine having from eight to 18 carbon atoms and ethylene oxide and/or quaternary- or di-quaternary ammonium salt of the condensation product of tertiary fatty amines with from eight to 18 carbon atoms and ethylene oxide whereby the weight ratio of the softener actives to the stabilizing additives should be within a certain range. These teachings pertain to the stabilization of softening actives during a "classic" softening operation, i.e. during the last rinse cycle of the washing operation. The stabilizing additives suggested may take care of trace amounts of the deactivating anionic ingredients; they are not suitable, however, for being applied together with (the solutions of) synthetic detergent compositions containing a major amount of anionic ingredients. The disclosure of U.S. Pat. No. 3,560,390 confirms the incompatibility of anionic and cationic surface-active agents dissolved in an aqueous laundry solution containing major amounts of anionic ingredients. U.S. Pat. No. 3,325,404 discloses compositions for simultaneously laundering and softening fabrics whereby di-long-alkyl di-short-alkyl ammonium salts are combined with a selected quaternary ammonium compound containing only one alkyl radical having from eight to 20 carbon atoms in the alkyl chain. This combination can be dissolved in aqueous solutions of anionic detergents to yield dispersions having reduced precipitation tendency. The weight ratios of the di-alkyl- to monoalkyl quaternary ammonium compounds are within a well-defined range. These compositions, having directionally less tendency to precipitate, in addition involve additional expenditures flowing from the use of major amounts of stabilizing agents. Another approach to the incompatibility problem is described in U.S. Pat. No. 3,351,483 which discloses the stabilization of the softening ingredient with major amounts of urea whereby the fabric softeners are bound to the additives in form of inclusion-compounds.

However, as is well known, the state of the art listed hereinbefore, does not represent a satisfactory solution to the problems inherent to the formulation of detergent compositions capable of exerting joint cleaning and softening activity. The reasons for these shortcomings are either of a commercial nature, the addition of stabilizing agents being too expensive, and/or of a technical nature, i.e. the stabilization of cationic and anionic surface-active agents in the same aquous detergent milieu is only directionally improved and does not constitute the technically and commercially acceptable solutions to the problem.

SUMMARY OF THE INVENTION

We have now been able to formulate detergent compositions which exert simultaneous washing and softening activity during a single laundering operation. This goal is achieved through the incorporation of cationic-type softeners, being substituted tertiary amines, into current detergent compositions containing anionic surface actives. In more detail, the compositions which form the object of this invention and which exert cleaning and softening characteristics in a single laundering operation contain anionic surface-active agents and the usual detergent additives and a compound of the formula



wherein R_1 and R_4 are each alkyl of from 11 to 21 carbon atoms; R_2 and R_3 are each hydrogen or alkyl of from one to four carbon atoms; X is oxygen or $-NR_5-$, where R_5 is hydrogen or alkyl of from one to four carbon atoms; and n_1 and n_2 are each integers of from 2 to 6.

DETAILED DESCRIPTION OF THE INVENTION

The preferred tertiary amine softeners for use within the compositions of this invention are those described in U.S. Pat. No. 3,451,844 wherein R_1 and R_4 stand for alkyl radicals having from 15 to 17 carbon atoms, R_2 is hydrogen or methyl, X stands for oxygen, the group —NH— or the group $-NCH_3-$, n_1 is 3 and n_2 is an integer from 2 thru 4. Specific examples of the preferred softeners are ethyl-di(ethylene tallowamide)-amine and methyl-(trimethylene tallowamide)-(ethylene N-methyl tallow-amide)-amine, particularly methyl-

(trimethylene -tallowamide)-(ethylene tallowacid)-amine. The disclosure of U.S. Pat. No. 3,451,844 describes softener compounds useful herein and their method of preparation and is hereby incorporated by reference. The tertiary amine softening ingredients shall preferably be used in an amount from about 2 to about 40 percent by weight, especially from about 5 to about 18 percent by weight calculated on the finished detergent composition. The weight ratio of anionic detergent surfactant actives to tertiary amine softening ingredients shall preferably be within the range from 8:1 to 1:4.

All anionic detergents which are known as being suitable for being used in detergent compositions can be used within the compositions as set forth herein. Preferred for use are the anionic synthetic water-soluble salts or organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about eight to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Examples of these preferred anionics are the sodium and potassium salts of the reaction products obtained by sulfating C_8–C_{18} fatty alcohols derived from tallow and coconut oil. Other preferred anionic surfactants include the water-soluble alkyl benzenesulfonates wherein the alkyl group contains from about nine to about 15 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; water-soluble salts of sulfation products of 1 mole of a higher fatty alcohol, such as tallow or coconut oil alcohols, with about 1 to 6 moles of ethylene oxide; water-soluble salts of alkylphenol and ethylene oxide ether sulfates containing up to about 10 ethylene oxide molecules and wherein the alkyl radical contains from 8 to 12 carbon atoms. Other preferred anionic detergents for use in these compositions include the sulfonated olefins as described in e.g. U.S. Pat. No. 3,322,880.

The compositions of this invention can also contain additional surface-active agents such as nonionic, semi-polar, ampholytic and zwitterionic detergents.

The nonionic synthetic detergents which can be used are characterized by the presence of an organic hydrophilic and an organic hydrophobic group. The hydrophilic character of these compounds is mostly based on the presence of alkylene oxide chains, amine oxide, sulfoxide and phosphine oxide radicals. The preferred hydrophobic groups include aliphatic alcohols having from eight to 22 carbon atoms and fatty acid amides.

Examples of semi-polar detergents include the amine oxides, phosphine oxides and sulfoxides. Long chain tertiary amine oxides such as dimethyldodecylamine oxide and bis-(2-hydroxyethyl) dodecylamine are representatives of these classes. Suitable phosphine oxides are disclosed in U.S. Pat. No. 3,304,263 and include: dimethyldodecylphosphine oxide and dimethyl-(2-hydroxydodecyl) phosphine oxide. Suitable long chain sulfoxides correspond to the formula

$$R_1\text{—}\overset{\overset{O}{\|}}{S}\text{—}R_2$$

wherein R_1 and R_2 are substituted or unsubstituted alkyl radicals, the former containing from about 10 to about 28 carbon atoms, whereas R_2 contains from one to three carbon atoms. Specific examples of these sulfoxides are: dodecyl methyl sulfoxide and 3-hydroxy tridecyl methyl sulfoxide.

Ampholytic and zwitterionic synthetic detergents can as well be used. Examples of ampholytic synthetic detergents are: sodium 3-dodecylaminopropionate and sodium 3-dodecylaminopropane sulfonate.

Useful zwitterionic synthetic detergents are 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy propane-1-sulfonate.

The washing and softening compositions of this invention can contain, in addition to the essential ingredients, also other usual additional constituents and additives for such compositions and which are well known to those skilled in the art in this field of technology. Besides the ingredients already listed hereinbefore, there can be added organic and inorganic builders, peroxy-bleach compounds, activators for these peroxy-bleach ingredients, suds-controlling agents including suds-boosters, suds-stabilizing agents and suds-depressing agents, optical brighteners, dyes and perfumes, enzymes, particularly proteases, amylases, lipases, soil-suspending agents, silicate solids, solubilizing agents, non-toxic non-volatile organic solvents and other usual detergent additives.

The detergent builders can be inorganic or organic in nature and can be selected from a wide variety of known builder materials. Useful alkaline inorganic builders are alkali metal carbonates, phosphates, polyphosphates, and silicates. Specific examples of such salts are sodium and potassium tripolyphosphates, carbonates, phosphates and hexametaphosphates. Useful alkaline organic builders are alkali metal, ammonium and substituted ammonium polyphosphonates, polyacetates and polycarboxylates.

The polycarboxylate builder salts useful herein consist of water-soluble salts of polymeric aliphatic polycarboxylic acids of the type described in U.S. Pat. No. 3,308,067. Examples include the polymers of itaconic acid, maleic acid, fumaric acid and mesaconic acid.

Peroxy bleach compounds can be incorporated in an amount of up to 30 percent by weight of the total detergent composition. All bleaching ingredients which are currently used in detergent compositions may fit within the compositions of this invention. Sodium perborate and sodium percarbonate are preferred because of their commercial availability. Also up to 20 percent by weight of the detergent composition of activators for peroxy bleach compounds can be added. They serve to take better profit of the oxy-bleach ingredient at lower temperature. As a rule, they form peracids with the active oxygen of the bleaching compounds; these peracids exert more efficiently and at lower temperature their bleaching activity. Well-known activators are maleic anhydride, phthalic anhydride, tetra-acetylmethylenediamine, tetra-acetylethylenediamine, tri-acetylisocyanurate and benzoylimidazole.

Suds-controlling agents in an amount of up to 10 percent of the finished detergent compositions can be added as well. Their amount and nature depend frequently upon the intended usage of the particular detergent composition. As an example, detergent compositions which are to be used for automatic (machine) laundry operations shall contain suds-depressors such

as, for example, saturated fatty acids having 16 to 22 carbon atoms or siloxanes.

Relatively minor quantities of other detergent additives such as optical brighteners, dyes, perfumes, and so on are incorporated in levels which normally do not exceed 5 percent by weight of the total detergent composition.

The compositions of this invention can also contain enzymes which contribute to the cleaning and soil removal performance of the compositions through their capability of hydrolyzing, and thus rendering more soluble, the soil. Due to the specific activity of an enzyme preparation it is indicated to add mixtures of different enzymes containing, however, at least proteases and/or amylases whereby the ratio of these should be varied according to the expected soil compositions. Lipases and other soil hydrolyzing enzymes can be added as well. Usually, from 0.01 to 5, preferably from 0.2 to 2 percent by weight of enzymes are incorporated into these detergent compositions. It may also be useful to add some stabilizing agents for the enzymatic activity during prolonged storage. Specific enzymes species call for specific stabilizing agents. As an example partially hydrolyzed collagen having a molecular weight of about 10,000 constitutes a satisfactory stabilizing agent for proteases. The usual activators for the enzymatic activity can be added as well. Up to 10 percent of soil-suspending agents can also be used. Wellknown examples of this class of ingredients are carboxymethylcellulose and polymeric ingredients such as those based on the polymerization product of vinyl derivatives and maleic anhydride. Silicate solids can be used up to the same level, i.e., about 10 percent by weight. Additional well-known detergent additives can be incorporated into detergent compositions according to the physical presentations of the compositions and also taking into consideration their intended use. Examples of this class of additives include lower alcohol solubilizers, xylene-toluene- and benzene sulfonic acids, low-volatile non-toxic solvents, particularly aromatic solvents, humidity and so on.

A series of examples is given hereinafter to illustrate the invention and to facilitate its understanding.

EXAMPLE I

A granular detergent composition of the following formula was prepared using conventional spray-drying techniques of all but the tertiary amine softening ingredient which were added concurrently with the base granule to the laundry solutions prior to starting the comparative testing.

Ingredients	Parts by weight
Lineardodecyl alkylbenzene sulfonate - sodium salt	24
Fatty alkyl (tallow 30/coconut 70) sulfate - sodium salt	4
Sodium pyrophosphate	20
Sodium tripolyphosphate	2
Monoethanolamide	2
Sodium sulfate	40
Softening ingredient	see below
Humidity, brighteners, proteases and other minor ingredients	balance to 100

The composition is used for a series of comparative washing tests under the following conditions.

Product concentration	: 0.4% by weight
Wash volume	: 2500 cc
Ratio cloth/washing liquor	: 1/25
Water hardness	: 3.4 milliequivalents (Ca + Mg)/liter
Washing program	: soaking during 20 minutes starting at 30°C without heating followed by simulated handwashing during three minutes whereafter the cloths are rinsed twice in about 5 liter of cold water. Thereafter the test cloths are dried at ambient temperature.
Softening ingredient	: 5% by weight (calculated on the finished detergent composition without softener) of methyl-(trimethylene-tallow amide)-(ethylene-tallow acid)-amines

The softening of the test fabrics is graded by six independent judges who are experts in such evaluations by grading the test swatches by pairs. The gradings are done on 2 replicates (complete round robin comparison between treatments). The standard scale of −3, −2, −1, 0, 1, 2, and 3 is used wherein 0 means that the fabrics are equal, 1 means there is a slight difference, 2 means there is a moderate difference, and 3 means there is a large difference. Woolen, acrylic and terry cotton swatches are used for the softening evaluation. Reference swatches are carried along through the soaking tests whereby the sole difference in treatment between test and reference swatches resides in the absence of softening ingredients in the reference soaking solution.

Fabric	Softening	
	Test Swatch	Reference Swatch
terry cotton	0.3	−0.7
wool	0.5	−0.7
acrylic	0.5	−0.85

EXAMPLE II

A granular detergent composition having the formulation given hereinafter is prepared by conventional spray-drying technique whereby all ingredients are incorporated except the softening ingredient which is added separately to the laundry solution prior to starting a comparative testing.

Ingredient	Parts by weight
Lineardodecyl benzene sulfonate - sodium salt	13.5
Sodium toluene sulfonate	1.5
Monoethanolamide	0.5
C_{16} - C_{22} saturated fatty acid	1.0
Condensation product of tallow alcohols with 11 moles of ethylene oxide	4.0
Sodium salt of maleic anhydride/vinyl methyl ether copolymer	1.0
Sodiumtripolyphosphate	34.0
Silicate solids:ratio SiO_2/Na_2O = 2.0	2.0
Carboxymethylcellulose	1.0
Sodiumsulfate	33.0
Softening ingredient	see below
Humidity, brighteners, dyes, proteases	balance to 100

Washing solutions prepared with that composition and whereto a softening ingredient is added as indicated hereinafter, have been used for comparative testing evaluations thereby considering the following additional parameters;

Machine used: mini-drum maching (wash volume 5 liters) equipped with heating-up cycle to 40°C

Product concentration: water hardness and cloth-/washing liquor ratio: same as in Example I

Test swatches: terry cotton, acrylic.

The test and reference swatches are washed during four cycles and then graded for softening thereby using the evaluation technique described in Example I. The softening ingredient is qualitatively and quantitatively identical to what is indicated for Example I.

The test results are as follows:

Fabrics	Softening	
	Test Swatch	Reference Swatch
terry cotton	0.8	−1.2
acrylic	0.8	−1.6

EXAMPLE III

A granular detergent composition prepared as described in Example I having the following formula is used for comparative softening evaluations.

Ingredient	Parts by weight
Lineardodecyl benzene sulfonate - sodium salt	25
Sodiumtripolyphosphate	25
Carboxymethylcellulose	1
Sodiumsulfate	35
Sodiumchloride	4
Softening ingredient	see below
Humidity, dyes, brighteners, proteases minor ingredients	balance to 100

The softening of test swatches is evaluated after soaking tests carried out as described in Example I. The softening ingredient is identical to the one employed in Example I.

Softening ingredient in % by weight of granular detergent	Fabric	Softening of swatches	
		Reference	Test
7	terry cotton	−0.2	0.6
7	wool	−0.65	0.4
7	acrylic	−0.45	0.4
9	acrylic	−1.5	−0.3
11	acrylic	−1.5	0.4
13	acrylic	−1.5	1.1

Softening ingredient in % by weight of granular detergent	Wash cycles	Fabric	Softening of swatches	
			Reference	Test
7	2	wool	−0.65	0.35
	3	wool	−0.90	0.55
	4	wool	−0.95	0.80
7	2	terry cotton	−0.65	0.95
	3	terry cotton	−1.10	1.15
	4	terry cotton	−1.15	0.90
7	2	acrylic	−0.55	0.40
	3	acrylic	−0.60	0.40
	4	acrylic	−0.85	0.45

EXAMPLE IV

The granular detergent composition of Example II has been used for carrying out the soaking tests as described in Example I. The softening ingredient is identical to the one used in that Example II. 13.5 percent by weight calculated on the finished detergent composition are used for preparing the soaking bath.

The softening results

Wash cycles	Fabric	Softening	
		Test Swatch	Reference Swatch
1	terry cotton	−0.1	−1.0
1	acrylic	0.70	−1.35
2	terry cotton	−0.40	−1.35
2	acrylics	0.85	−1.30
3	terry cotton	0.80	−1.50
3	acrylics	0.95	−1.10

What is claimed is:

1. A detergent composition with softening characteristics consisting essentially of an anionic surface-active agent; and from about 2 percent to about 40 percent by weight of a fabric softening compound of the formula

$$R_1-CO-N(R_2)-(CH_2)_{n_1}-N(R_3)-(CH_2)_{n_2}-X-OC-R_4$$

wherein R_1 and R_4 are each alkyl from 11 to 21 carbon atoms; R_2 and R_3 are each hydrogen or alkyl of from one to four carbon atoms; X is oxygen or $-NR_5-$, where R_5 is hydrogen or alkyl of from one to four carbon atoms; and n_1 and n_2 are each integers of from 2 to 6; wherein the weight ratio of said anionic surface-active agent to said fabric softening compound is in the range of from 8:1 to 1:4.

2. The detergent composition of claim **1** wherein radicals R_1 and R_4 are each alkyl of from 15 to 17 carbon atoms and X is oxygen or —NH—.

3. The detergent composition of claim **1** wherein the fabric softening compound is present in an amount of from 5 percent to about 18 percent by weight of the composition.

4. The detergent composition of claim **1** wherein the anionic surface-active agent is an anionic sulfonate or sulfate.

5. The detergent composition of claim **1** wherein the fabric softening compound is selected from the group consisting of: methyl-(trimethylene-tallowamide)-(ethylene tallowacid)-amine, ethyl-di(ethylene tallowamide)-amine, and methyl-(trimethylene tallowamide)-(ethylene N-methyl tallowamide)-amine.

6. The detergent composition of claim **1** which, in addition, contains up to 30 percent by weight of a peroxy bleach component.

7. The detergent composition of claim **5** wherein the fabric softening compound is methyl-(trimethylene-tallow-amide)-(ethylene tallowacid)-amine.

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