United States Patent Office 3,003,954 Patented Oct. 10, 1961

3,003,954

METHODS AND COMPOSITIONS OF MATTER FOR SOFTENING TEXTILE FIBERS, YARNS, AND FABRICS

Herman Brown, Decatur, Ill., assignor to A. E. Staley Manufacturing Company, Decatur, Ill., a corporation of Delaware

No Drawing. Filed July 19, 1957, Ser. No. 672,863
6 Claims. (Cl. 252—8.8)

This invention relates to methods and compositions of matter for softening textile fibers, yarns, and fabrics. More particularly, it relates to the preparation and use of such compositions of matter containing a cationic surface active agent as the essential softening component.

Chemical softening agents are widely used in the textile industry to improve the hand, drape, and cutting and sewing properties of a fabric. Although the application of a softening agent is usually a finishing operation on the fabric, the softening agent will also exert its effect on the textile material in either the fiber or yarn stages. These agents are essentially lubricants of high spreading and penetrating power and are generally divided into two classes: (1) the nonsubstantive, the members of which for the most part are either anionic or non-ionic, and (2) the substantive class, consisting of cationic surfactants.

The history, use, chemical classification, and limitations of the cationic textile softeners are reviewed at pages P41 to P44, inclusive, in the January 28, 1957, issue of "Proceedings of the American Association of Textile Chemists and Colorists," and at pages 43 to 45, inclusive, and page 178 of the February 21, 1957, issue of "America's Textile Reporter." The latter article calls attention to a general limitation of the cationic textile softeners, namely, their lack of solution compatibility with many anionic materials, particularly those commonly used in textile processing and in laundry operations. These materials, such as soaps, anionic detergents and polyphosphates, all react with and precipitate the cationic softener as a greasy, insoluble, unionized combination of the two large long-chain ions.

This behavior effectively bars the use of the cationic softeners in textile processing solutions containing the incompatible anionic substances. It also eliminates their use on poorly rinsed fabrics previously treated with the anionics. Obviously, the cationic softeners would be more conveniently and cheaply used as after-rinses in commercial and home laundries if the objectionable precipitation with anionics could be suppressed.

I have discovered that the objectionable precipitation of the cationic textile softeners with anionic substances can be prevented by incorporating with the softener a polyether acetic acid or salt selected from the group represented by the general formula $ROACH_2COOM$. In this structural formulation, R denotes a hydrocarbon radical containing from 12 to 16 carbon atoms, which radical may be alkyl, cycloalkyl, aralkyl, aryl, or heterocyclic, and which may be interrupted by hetero atoms or hetero atom groups, and which may be substituted in any way, but in particular with hydroxyl groups. A denotes a chain of one to five ethenoxy groups, and M denotes a cation, such as hydrogen, sodium, potassium, and ammonium.

In addition to preventing the objectionable precipitation of cationic textile softeners with incompatible anionic substances, the polyether acetic acids decrease the slight fabric yellowing property of some of the softeners. Furthermore, the presence of the acetic acid compounds in the softener solution reduces the tendency of the latter to diminish the water absorbency of the fabric. Some cationic textile softeners, if applied too heavily, gradually decrease the water absorbency of the treated fabric.

A primary object of my invention is to provide cationic textile softening compositions of matter which produce no objectionable precipitate when mixed with solutions of anionic substances encountered in textile processing and laundry operations.

It is also an object of my invention to provide a method for suppressing the formation of objectionable precipitates when solutions of cationic textile softeners are mixed with anionic substances encountered in textile processing and laundry operations.

Another object of my invention is to provide modified cationic textile softening compositions of matter with less tendency to yellow fabrics than the base or unmodified composition.

Other objects will become apparent in the following description of my invention.

The foregoing objects are attained in accordance with my invention by mixing one or more selected acetic acid derivatives with the cationic softener or the incompatible anionic substance prior to mixing of the latter two. The essential feature of the method of my invention is that the cationic softener and incompatible anionic substance be allowed to mix or contact one another in solution only in the presence of the polyether acetic acid.

The preferred method of my invention is to mix the polyether acetic acid compound with the softener beforehand. Equally effective, but less convenient, is to add the acetic acid compound to the rinse or textile processing solution prior to adding the softener. Obviously, a part of the polyacetic acid compound can be premixed with the softener or rinse. With respect to the preferred method, my invention also contemplates the preparation of stable mixtures of the softener and acetic acid derivative useful in commercial and home laundries and in commercial processing operations. Unless otherwise specified, all references to percentages herein are by weight.

The polyether acetic acid required in my invention may be prepared according to the general method disclosed in United States Patent 2,623,900. Commercial preparations are marketed by Sandoz Chemical Works, Incorporated, under the trade name Sandopan DTC. The material is available in two concentrations, 27% and 68% active ingredient. The products are clear, light-colored, pourable aqueous gels, which have been adjusted to 7 to 8 pH with alkali or acid.

I have found that the ratio of polyether acetic acid to cationic softener, for effective suppression of undesirable precipitate, depends upon several factors, chief among them being the kind of softener, the kind of anionic substance, and the kind of acetic acid derivative. As little as 10% of the sodium salt of the polyether acetic acid based on the dry substance softener may be enough in some instances, whereas as much as 70% may be required in others. More than 70% of the acetic acid derivative may be used, if desired, but with little increased effect. Less than 10% can be used, also, but in some instances with less than the maximum practical benefit. Useful results are obtained within the range of about 5% to 100% of acetic acid derivative based on softener. Mixtures of the acetic acid derivatives may be used, and in that event the foregoing range of proportions applies to the mixtures.

My invention applies to cationic textile softeners in general, which are members of a larger group of substances known as cationic surface active agents. The cationic surface active agents dissolve or disperse in water, concentrate and orient at interfaces from their aqueous dispersions, and ionize so that the cation includes a hydrophobic hydrocarbon chain containing from 8 to 25 carbon atoms.

The textile softening property is variable among the cationic surface active agents. Commercially useful sof-

teners are found among the following classes of compounds: tertiary amines, quaternary ammonium compounds, amidoamines, imidazolines or glyoxalidines, amino esters, carbamates, biguanidines, phosphonium compounds, pyridinium compounds, and benzimidazoles. My invention applies to all compounds of these types useful as textile softeners.

My invention overcomes a difficulty heretofore encountered in the addition of a cationic softener to the final rinse in an automatic home washing machine equipped with a dispensing device for introducing a rinse additive into the final deep rinse. Since the dispenser frequently contains small residual amounts of "Calgon" (sodium hexametaphosphate) used previously, the addition of cationic softener produces a greasy precipitate. Eventually some of this precipitate lodges on the rinsed clothing, resulting in unsightly spots difficult to remove.

By using the polyether acetic acid derivative in accordance with my invention the formation of an objectionable precipitate in the dispenser wheel is prevented.

The mechanism of the beneficial action of the polyether acetic acid derivative is unknown, but the compound appears to function as a protective colloid. This seems to be borne out in those instances where the compound, though failing to maintain a clear solution of the cationic softener in the presence of the anionic compound, limits the precipitate to a very finely divided or gelatinous one. Precipitates of this nature are not objectionable since they do not cause spots on clothes being rinsed in a washing machine. If the polyether acetic acid derivative were not present, however, the precipitate would be coarse and flocculent and it would produce unsightly spots on any clothing it touched.

In my invention, the presence of by-product salts in the commercial preparations of the polyether acetic acid does not impair the precipitate-inhibiting function of the compound. Nor is this function critically influenced by the pH of the commercial preparation or the kind of cation associated with the substituted acetic acid. Useful precipitate-inhibiting action can be obtained over the wide pH range of about 3 to 10. It is convenient and preferable, however, to use a neutral or slightly alkaline product consisting essentially of the sodium salt of the polyether acetic acid. As mentioned earlier, these products are marketed as pourable gels adjusted to 7 to 8 pH and containing either 27% or 68% active material calculated as the sodium salt of the acid.

Although the polyether acetic acid is weakly anionic, it is compatible with the cationic textile softener. This, plus the fact that it suppresses precipitation of the cationic softener by numerous anionic substances, is quite unexpected.

My invention is further illustrated by the following examples, the specific details of which are not limitative.

Example 1

Six grams of a 75% solution of dimethyl distearyl ammonium chloride in isopropanol and 4.5 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate were mixed thoroughly with 89.5 grams of water at 100° F. The stable solution thus obtained is an improved fabric softener useful in the home laundry. It has the advantage over unmodified cationic softeners in that it yields no precipitate when mixed with aqueous solutions of soaps, anionic detergents and sodium hexametaphosphate. Thus it can safely be used in combination with water softeners such as sodium hexametaphosphate, and any soap or anionic detergent remaining in the rinsed clothes yields no precipitate. A 4.5% solution of dimethyl distearyl ammonium chloride alone in water immediately yields a greasy flocculent precipitate with dilute aqueous solutions of sodium hexametaphosphate, soaps, or anionic detergents.

Example 2

Six grams of a 75% solution of dimethyl distearyl ammonium chloride in isopropanol and 0.7 gram of a 68% aqueous gel of sodium cetyloxyethoxyacetate were mixed with 93.3 grams of water at 100° F. The stable solution thus obtained is an improved fabric softener useful in the final rinse of the home laundry. Although this preparation, due to its lower ratio of acetate to softener, yields a cloudy, finely-divided precipitate with dilute aqueous solutions of soaps, anionic detergents, and sodium hexametaphosphate, the precipitates do not adhere to and spot clothing being rinsed in a home laundry.

Example 3

One hundred grams of a 75% solution of dimethyl distearyl ammonium chloride in isopropanol was blended with 80 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate. The stable thin paste thus obtained is a concentrated modified textile softener particularly useful in commercial laundries. Like the product of Example 1, it yields no precipitate when added to dilute aqueous solutions of soaps, anionic detergents, and polyphosphates such as sodium hexametaphosphate. Thus it can be added to rinse water containing the polyphosphate water softeners, and it can be used without danger of precipitation and fabric spotting on incompletely rinsed fabrics.

Example 4

In a home washing machine was placed 8 pounds of clean white goods and 16 gallons of clean rinse water at 80° F., containing 60 grams of sodium hexametaphosphate and 6 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate. After the mixture had been agitated for five minutes, there was added to it, with continued agitation, 100 grams of a 5% aqueous solution of dimethyl distearyl ammonium chloride. There was no visible clouding or precipitation and after 5 minutes more agitation the white goods were run through a clothes wringer, dried, and examined for spots or discoloration. None was found. In a control test, omitting the sodium cetyloxyethoxyacetate the white goods were plainly marked with numerous small grease spots from the coarse flocculent precipitate of quaternary ammonium compound and hexametaphosphate.

Example 5

Fourteen grams of a 50% aqueous solution of diisobutylphenoxyethyl dimethyl benzyl ammonium chloride and 5 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate were mixed with 125 grams of water at 100° F. The resulting stable solution thus obtained is an improved fabric softener for the home laundry.

Example 6

Fourteen grams of a 50% aqueous solution of N-cetyl N-ethyl morpholinium ethosulfate and 5 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate were mixed with 125 grams of water at 100° F. The resulting stable solution is an improved fabric softener useful in the home laundry.

Example 7

Seven grams of the condensation product of two mols of stearic acid and one mol of hydroxyethyl ethylene diamine was mixed with 5 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate and 125 grams of water at 100° F. The resulting stable solution is an improved fabric softener useful in the home laundry.

Example 8

Seven grams of the substituted urea

$$(R_1R_2)NCON(R_1R_2)$$

where R_1 is $(-CH_2CH_2OH)$ and R_2 is

$$(-CH_2CH_2NHCOC_{17}H_{35})$$

according to Example 8 of United States Patent 2,304,369 was mixed with 5 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate, 125 grams of water and enough acetic acid to adjust the pH of the resulting solution to 8. The stable solution thus obtained in an improved fabric softener useful in the home laundry.

Example 9

The sodium cetyloxyethoxyacetate in Example 1 was replaced with 4.5 grams of a 68% aqueous gel of sodium lauryloxyethoxyethoxyacetate. The stable solution thus obtained is an improved fabric softener useful in the home laundry.

Example 10

The sodium cetyloxyethoxyacetate in Example 1 was replaced with 4.5 grams of 68% aqueous gel of sodium 1,3-di-(butyoxyethoxy)-propyl-2-oxy-acetate. The stable solution thus obtained is an improved fabric softener useful in the home laundry.

Example 11

The sodium cetyloxyethoxyacetate in Example 1 was replaced with 4.5 grams of a 68% aqueous gel of the sodium polyether acetate prepared according to Example 7 in United States Patent No. 2,623,900. The stable solution thus obtained is an improved fabric softener useful in the home laundry.

Example 12

Fifty-four grains of a 75% solution of dimethyl distearyl ammonium chloride in isopropanol and 34 grams of the condensation product of two mols of stearic acid and one mol of hydroxyethyl ethylene diamine were mixed with 70 grams of a 68% aqueous gel of sodium cetyloxyethoxyacetate, 1837 grams of water at 100° F., and 6 grams of glacial acetic acid. The resulting stable solution is an improved fabric softener useful in the home laundry.

Example 13

The amount of 68% sodium cetyloxyethoxyacetate in Example 1 was increased to 7.0 grams. The stable solution thus obtained is an improved textile softening composition.

Example 14

The amount of 68% sodium lauryloxyethoxyethoxyacetate in Example 9 was reduced to 0.33 gram. The stable solution thus obtained, although somewhat more sensitive to precipitation by high concentrations of sodium hexametaphosphate than the composition of Example 9, was much less sensitive than a control softener solution without any added polyacetic acid salt.

In the foregoing examples, the sodium salts of the polyether acetic acids may be replaced with equivalent weights of other water soluble salts or the free acids.

There are numerous embodiments of my invention other than those set forth in the foregoing description and examples. Many modifications of my invention may be made without departing from its scope. For example, water is a convenient rather than a necessary liquid solvent for the compositions in the examples. The lower alcohols and alcohol-water mixtures are equally useful as solvents. Also, the concentrations of cationic textile softener and polyether acetate, and the ratio of one to the other within the range of 5 to 100% are not critical. Furthermore, as illustrated in Example 12, my invention is applicable to mixtures of cationic textile softeners.

As mentioned earlier, there are several broad classes of cationic surface active agents. One includes the amines and quaternary ammonium compounds. Among the amines, only the tertiary amines are useful as textile softeners because the primary and secondary amines intensify the yellowing of fabrics. Another large group consists of basic fatty acid amides or the amido amines. They are made by reaction of a fatty acid or glyceride with substituted or unsubstituted short-chain polyamines such as diethylene triamine. A third group is made up of the imidazolines, or glyoxalidines, derived from certain amidoamines by heating to split out water and form a ring structure. A fourth group consists of amino esters, made by esterifying a fatty acid with an amino alcohol. There is a large miscellaneous class of cationic surface active agents useful as textile softeners comprising the carbamates, biguanidines, phosphonium compounds, pyridinium compounds, and the benzimidazoles.

I claim:

1. A textile softening composition comprising an aqueous solution of at least one cationic surface active agent selected from the class consisting of quaternary ammonium compounds and amido amines and from about 5% to about 100%, based on the weight of said surface active agent of a substance represented by the formula $ROACH_2COOM$, wherein R denotes a hydrocarbon radical containing not less than 12 and not more than 16 carbon atoms, A denotes a chain of 1 to 5 ethenoxy groups, and M is a cation selected from the class consisting of hydrogen, sodium, potassium, and ammonium, said textile softening composition, due to its content of said latter substance, being characterized by its lack of forming an objectionable co-precipitate of anionic laundry compounds and component cationic surface active agent when mixed with laundry rinse waters containing anionic laundry compounds.

2. A textile softening composition according to claim 1 wherein R denotes lauryl and A denotes a chain of two ethenoxy groups.

3. A textile softening composition according to claim 1 wherein R denotes cetyl and A denotes one ethenoxy group.

4. In the method of treating textile materials containing a residual amount of anionic laundry compound comprising contacting said materials with a water rinse solution to which has been added a small proportion of at least one cationic surface active agent selected from the class consisting of quaternary ammonium compounds and amido amines, the improvement comprising mixing said cationic surface active agent with a substance prior to adding the surface active agent to the water rinse solution, said substance being represented by the formula $ROACH_2COOM$, wherein R is a hydrocarbon radical containing not less than 12 and not more than 16 carbon atoms, A is a chain of 1 to 5 ethenoxy groups, and M is a cation selected from the class consisting of hydrogen, sodium, potassium and ammonium, said substance being present to the extent of about 5% to 100% of the weight of the cationic surface active agent.

5. A method according to claim 4 wherein R denotes lauryl and A denotes a chain of two ethenoxy groups.

6. A method according to claim 4 wherein R denotes cetyl and A denotes one ethenoxy group.

References Cited in the file of this patent

UNITED STATES PATENTS

2,183,853	Haussmann et al.	Dec. 19, 1939
2,409,275	Harris	Oct. 15, 1946
2,734,830	Hagge et al.	Feb. 14, 1956

OTHER REFERENCES

Schwartz et al.: Surface Active Agents, Interscience Publishers Inc., N.Y. (1949), pp. 154 and 155.