ABSTRACT OF THE DISCLOSURE

Novel detergent and cleansing agents are disclosed characterized by their ability to inhibit the graying of textile articles which takes place in laundering. In particular, the novel detergent and cleaning agents are effective to prevent the graying of textile articles prepared at least in part with synthetic fibers.

The detergent and cleaning agents of the invention are characterized by a content of 0.1 to 20 wt. percent referred to the total composition of at least one water soluble salt of a polyester containing sulfonic acid groups, the acid component of which is derived from maleic acid and whose alcohol component is derived from a glycol having 2 to 4 carbon atoms or from a polyether thereof, the ratio of the number of maleic acid radicals to the number of sulfonic acid groups amounting to from 2.1 to 1:1. In addition to the aforesaid polyester salts the detergent and cleaning agents contain the conventional surface active materials and the usual additives such as optical brighteners, bleaching agents, dyes, anti-foamers, etc.

This invention relates to detergent and cleaning agents characterized by their ability to inhibit the graying of textile articles in laundering.

More particularly this invention relates to detergent and cleaning agents containing water-soluble salts of sulfonic acid polyesters.

It is known in the prior art to add to detergents and cleansers containing surface active compounds, substances which improve the dirt carrying and retaining ability of the washing solutions. Such substances, which are referred to hereinafter as graying inhibitors, prevent a resorption of the dissolved dirt onto the cleaned surfaces. These substances are usually polyionic polymers which are manufactured from natural substances such as cellulose, gelatins or glue, or are prepared by the polymerization of vinyl compounds, such as acryllic acid, methacrylic acid, maleic acid and mixtures thereof with copolymerizable olefins. Further, the polysulfonates of vinyl polymers have already been proposed as useful gray-inhibiting additives for detergent and cleanser preparations. Of all of the proposed compounds, however, only carboxymethylcellulose has achieved any great technical importance, inasmuch as its gray-inhibiting action excels that of any synthetic polymers that have been known. However, carboxymethylcellulose as well as the above-named synthetic polymers have the disadvantage that their gray-inhibiting action is limited to cellulose fibers, whereas they are practically ineffectual in the washing of synthetic fiber material, particularly materials prepared from polyamides, polyesters and polyolefins. This disadvantage is particularly noticeable in connection with white textiles made of synthetic fibers or mixed fabrics made of synthetic and cellulose fibers, i.e., polyester-cotton mixture, which turn irreversibly gray in use despite repeated washing and thus become unattractive and must be discarded.

In United States Pat. No. 2,454,546, there are disclosed surface-active polyesters of maleic acid and diols containing 3 to 18 carbon atoms, which are converted to the corresponding sulfonates by reaction thereof with alkali bi-sulfites. The aforesaid polyesters can be used as detergents and cleaning agents, but they have practically no gray-inhibiting activity in relation to textiles prepared from synthetic fibers. In the cited U.S. patent the view is advanced that sulfonate-group-containing polyesters prepared from diols containing less than the stated number of carbon atoms are, on the basis of their constitution, excessively hydrophilic, and that they might have wetting properties but unsatisfactory cleaning properties.

It is therefore a primary object of this invention to provide new and improved detergent compositions having increased gray-inhibiting efficiency over previously known detergent compositions.

Another object is to provide improved detergent compositions containing as the gray inhibiting agent, a water soluble salt of a sulfonic acid group containing polymer.

A yet further object is to provide improved gray inhibiting detergent compositions which are surprisingly effective in laundering textile articles prepared at least in part with synthetic fibers. Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter.

It has now surprisingly been found that water soluble salts of sulfonic acid group containing polyesters, the acid radicals of which are derived from maleic acid and whose alcohol component is derived from a glycol having 2 to 4 carbon atoms or from a polyether thereof, the ratio of the number of maleic acid radicals to the number of sulfonic acid groups amounting to from 2.1 to 1:1, possess gray inhibiting properties to an exceptional degree.

As mentioned above, it has already been proposed to combine synthetic detergent compounds with various graying inhibitors to produce anti-graying detergent compositions. As far as is known, however, no one prior to this invention has discovered the particular combination of compounds and proportions described herein that offer extraordinary results in the important area of whiteness maintenance and whiteness retention.

These and other advantages are obtained according to this invention by providing detergent compositions comprising a detergent surfactant compound and as a graying inhibitor 0.1 to 20 wt. percent referred to the total detergent composition of a sulfonic acid group containing polyester, the acid radicals of which are derived from maleic acid and whose alcohol component is derived from a glycol having 2 to 4 carbon atoms or from a polyether thereof, the ratio of the number of maleic acid radicals to the number of sulfonic acid groups amounting to from 2.1 to 1:1.

The polyesters present in salt form in the new detergents and containing sulfonic acid groups are prepared by the known methods. Instances of glycols suitable as starting materials for use in the preparation of the polyesters are ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, and the various isomers of butylene glycol. Also suitable are di-, tri- and polyglycols in which the glycols contain 2 to 4 carbon atoms and the number of glycol ether groups amounts to from 2 to 10. Mixtures of the aforesaid glycols or glycol ethers can also be used. Preferably the starting materials are ethylene glycol and propylene glycol or their polyethers.

The esterification of the glycols or polyglycols with maleic acid or maleic anhydride is carried out, for example, by heating the mixture of acid and glycol for a number of hours, in the presence, if desired, of common esterification catalysts, the water of reaction being removed by the use of vacuum or by means of a solvent that forms an azeotrope with the water.
The polyglycol polyesters can also be manufactured by first reacting 50 mole-percent of the maleic acid in the usual manner with an alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide, and thereafter esterifying the polyglycol esters that are produced with an additional 50 mole-percent of maleic acid or maleic anhydride.

The molar ratio of glycol to acid or anhydride amounts to from 1:1.0 to 0.9:1.1. The degree of polymerization can be varied within certain limits by selecting the molar ratio within this range. In the interest of good gray-prevailing action, however, a high degree of polymerization is desirable. Therefore a molar ratio that is as close as possible to 1:1 will be preferred, in order to prevent premature chain interruptions.

The introduction of the sulfonic acid groups into the polyester is best carried out by adding alkali hydrogen sulfite at the double bond, or by the use of common sulfonylating agents, such as chlorosulfonic acid or sulfur trioxide, in the presence of an inert solvent, particularly dichloromethane, or N,N-dimethylacetamide. If free sulfonic acids develop in the sulfonylation, they are neutralized afterwards.

The polyesters or their alkali and ammonium salts prepared by the above described procedures and containing sulfonic acid groups are insoluble in organic solvents, but easily soluble in water. They can be prepared in secondary amounts of esters of low molecular weight or of unreacted starting substances, which can be removed from the polyesters by extraction with organic solvents and reused in the reaction. Since these compounds, however, do not impair the cleaning properties of the agents, separation is generally unnecessary.

As a result of the insolubility of the high molecular compounds in organic solvents, and because of their content of low-molecular constituents, the usual methods utilized for molecular weight determination are inapplicable. Therefore, it is not possible to state the degree of polymerization and molecular weight of the polyesters with complete accuracy.

The detergents may contain the polyesters according to the invention in the form of any of their water-soluble salts and preferably in the form of their alkali metal and ammonium salts. The ternary ammonium salts is intended also to include the salts of the polyesters with organic ammonium bases. The polyesters can be added to the detergents in the form of their free acids, providing alkanolyne reacting substances are present in a sufficiently great excess for the formation of salts.

In addition to the salts of the polyesters, the new detergents and cleansing agents contain the surface-active substances customarily used in such agents, such as those of the sulfate or sulfonate type, for example, the primary and secondary alkyl sulfates and the sulfates of ethoxylated or propoxyliated fatty alcohols, and alkylbenzenesulfonates, primary and secondary olefin sulfonates, alkylsulfonates and α-sulfafatty esters. Additional compounds of this class which may be used are the high molecular weight sulfated partial ethers and partial esters of polycyclic alcohols; the sulfates of ethoxylated or propoxyliated fatty acid amides and alkylphenols; fatty acid taurides and fatty acid isothiocyanates and homologues thereof. Also suitable are the alkali soaps of fatty acids as well as the fatty acid condensation products of amino acids or degradated proteins; and amphiboles such as alkylbetaines and alkylsulfobetaines. The agents can furthermore contain non-ionic wash-active substances, such as alkyl and acyloxyalkylethers, cocondensation products of polyelelyene glycol and polypropylene glycol, fatty acid sugar esters, aminoxides and fatty acid alkanolamides. Any of the foregoing compounds can also be used in the form of mixtures thereof. If the compounds have an aliphatic hydrocarbon radical, the latter is preferably to be straight-chained and have 8 to 22 carbon atoms. In compounds having araliphatic hydrocarbon radicals, the preferably unbranched alkyl chains contain an average of 6 to 16 carbon atoms.

Furthermore, depending on the purpose for which they are intended, the new detergents and cleansing agents can contain other conventional components such as pyrophosphates, polyphosphates and the more highly condensed phosphates, as well as silicates, in the form of their alkali salts; oxygen-yielding bleaches or bleaches containing active chlorine, such as alkali perborates, alkali percarbonates, alkali hypochlorites, chlorinated cyanacids and their alkali salts; as well as neutral salts such as magnesium silicate and sodium sulfate. Furthermore, sequestering agents may be present, particularly alkali salts of amino-poly(carboxylic) acids, e.g., the sodium salts of aminooracetate acid or of ethylenediaminotetraacetic acid and the alkali salts of hydroxyalkylphosphononic acids and amino-polypolyphosphonic acids, such as the disodium salt of 1-hydroxyethylene-1,1-diphosphonic acid or the hexasodium salt of aminooracetoxyethylphosphonic acid)

Substances for the regulation of the pH can also be components of the mixture. These include sodium carbonate, sodium bicarbonate, lactic acid and citric acid and the like.

The detergents can also contain optical brighteners, such as the derivatives of diaminostilbenesulfonic acid or of diarylpiazolinesulfonic acid. To control sudsing action the detergents may contain suids improvers, such as fatty acid amides, or anti-foaming agents, particularly trialkylmelamines.

The new detergents and cleansing agents may be in solid form, and preferably powder form, or in the form of solutions or pastes. Because of the excellent water solubility of the polyester salts they are particularly well suited for the manufacture of liquid detergent concentrates. Such liquid preparations may contain, in addition, to the above-named components, hydrophobic substances such as alkylbenzenesulfonates of low molecular weight, urea, and organic solvents.

In a number of cases, especially in the washing of textile materials made of cellulose or regenerated cellulose, the cleansing action can be further improved by the addition of standard graying inhibitors, particularly carboxymethylcellulose. The amounts of carboxymethylcellulose to be used will be approximately from 0.1 to 5% of the total weight of the detergent agents.

The new detergents of the invention are suitable for the cleaning of articles of all kinds, but particularly for the washing of textiles which are made of synthetic fibers, cellulose fibers, regenerated cellulose, or of mixtures of the aforesaid types of fibers. In comparison with detergents of the prior art, the new detergents make the washing process itself easier and improve the whiteness of the laundry.

The following examples are given for the purpose of illustrating the invention and are in no wise to be construed as a limitation thereof.

The gray-inhibiting action of the compounds described in the following examples was tested by known methods and include the following:

(A) The "redeposition" method (also known as the "rewash method") involving the washing together of dirty and clean textile material.

(B) The "deposition" method, in which clean textiles are washed in an artificially dirtied wash water.

(A) REDEPOSITION METHOD

In each test 4 cloth samples, each made of Baumwollrenforcé or of synthetic fabric and weighing a total of 8.3 g. were washed up to five times for 30 minutes, together with 1.3 g. of an artificially soiled cotton yarn in alkali hypochlorite. After the Launder-Ometer® (Atlas, Chicago, USA), the reflectivity of the thusly washed samples was tested using a light meter (Elrepho®, Carl Zeiss, equipped with a No. 6 filter).

The realistically simulated dust-sebum combination used for soiling the cotton yarn consisted of a mixture of
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kaolin, iron oxide black, carbon black and synthetic sebum (prepared from a mixture of \(\frac{3}{2}\) fatty acids, \(\frac{5}{2}\) fat and \(\frac{1}{2}\) hydrocarbons). The cotton yarn contained approximately 11% pigments and about 2% sebum after milling.

The detergent which was used in the washing of these samples had the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
<th>Jonal</th>
<th>coconut fatty alcohol sulfate (sodium salt)</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sodium pyrophosphate</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>graying inhibitor</td>
<td>0-10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sodium sulfate</td>
<td>35-25</td>
<td></td>
</tr>
</tbody>
</table>

The concentration of detergent in the wash water amounted to 5 grams per liter and the hardness of the tap water to 10° D.H. The cotton samples were washed at 90° C. for 30 minutes at a goods-to-water ratio of 1:12 (wash water 115 ml.), and the synthetic fabric samples were washed at 60° C. for 30 minutes and at a goods-to-water ratio of 1:30 (wash water 290 ml.). The samples were then rinsed four times with distilled water, dried and ironed, and evaluated photometrically.

(B) DEPOSITION METHOD

The tests in the deposition method were carried out using skin goods in the Terg-O-Tometer® (United States Testing Company, Hoboken, U.S.A.). 10-gram skins of the substrate to be evaluated were washed in one liter of wash water (goods-to-water ratio 1:100) with the addition of 0.2, 0.5, 1.0 and 1.5 g. of standardized carbon black (Degussa 100%) plus 5% of the following:

- n-Dodecylbenzenesulfonate (sodium salt) 7.8
- Coconut fatty alcohol sulfate (sodium salt) 1.1
- Tallow fatty alcohol sulfate (sodium salt) 1.1
- Sodium pyrophosphate 16.0
- Sodium carbonate 14.0
- Graying inhibitor 50.0

In each case, 100 ml. of this stock solution was diluted to one liter with tap water of 10° D.H. The samples were washed at 60° C. for 10 minutes with the Terg-O-Tometer operating at 100 r.p.m. The samples were then rinsed with distilled water three times, dried and photometrically evaluated.

INHIBITOR A

196 g. (2 moles) maleic acid anhydride, 125 g. (2 moles of anhydrous ethylene glycol and 100 ml. xylene were heated together with one drop of concentrated sulfuric acid in a distillation apparatus which was provided with a system for separating the water and returning the solvent. The heat was continued until no further water of reaction separated in the receiver. The xylene was distilled off from the polyester and the latter was then refluxed with a solution of 230 g. anhydrous sodium pyrosulfite (approx. 2.4 moles sodium hydrogen sulfite in 400 ml. of water) until solution of the polyester had been completed. During the heating 140 ml. 10% hydrogen peroxide were introduced, and the mixture neutralized with lime whereby the excess sodium hydrogen sulfite was converted into sodium sulfite. The resulting neutral solution was adjusted to a polyester content of 10 g./l. and amounts as hereinafter set out added to the detergents.

INHIBITOR B

According to the procedure of Example 1, 98 g. (1 mole) maleic acid anhydride and 107 g. (1 mole) diethylene glycol were reacted to form a polyester which was treated with 76 g. sodium pyrosulfite (approx. 0.8 mole sodium hydrogen sulfite) to partially sulfonate the same.

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INHIBITOR C

According to the procedure of Example 1, a polyester was prepared from 1 mole propylene glycol-1,2 and 1 mole maleic acid anhydride and thereafter treated with sodium hydrogen sulfite (1.3 moles) to satisfactorily sulfonate the same.

INHIBITOR D

A sulfonated polyester was prepared from 1 mole butanediol-1,4 and 1 mole maleic acid anhydride followed by treatment with 1.3 moles of sodium hydrogen sulfite. A further sulfonated polyester was prepared from maleic acid and hexanediol-1,2. (Inhibitor E.)

The results of the washing tests are summarized in the following tables. The spraying of polyester fabrics was determined according to method A (redeposition method) after 5 washings in each case. The tests with the Perlon fabric were carried out using method B (deposition method). The abbreviation CMC represents carboxymethylcellulose, which was used for comparison purposes.

TABLE

| Percent remission at an inhibitor concentration of g./l.|
|---------------------------------|-------------|
| Substrate Inhibitor No. 0 0.1 0.2 0.5 |
| Polyamide | 44.1 47.1 49.6 50.0 |
| Polyethylene | 44.1 49.0 54.0 55.0 |
| Polyurethane | 44.1 50.0 54.0 55.0 |
| Nylon | 44.1 50.0 55.0 55.0 |
| Perlon | 44.1 47.4 49.2 50.0 |

TABLE

| Percent remission with an addition of carbon black of g./l. |
|---------------------------------|-------------|
| Method B: Polyamide | 68 64 66 69 |
| Polyethylene | 65 64 66 69 |
| Polyurethane | 65 64 66 69 |
| Nylon | 65 64 66 69 |
| Perlon | 65 64 66 69 |

What is claimed is:

1. A detergent composition consisting essentially of a detergent selected from the group consisting of anionic, amphoteric and non-ionic detergents, and mixtures thereof, and a graying inhibitor in an amount of from 0.1 to 20 weight percent based on total weight of the composition, said graying inhibitor being selected from the group consisting of water-soluble alkali metal and ammonium salts of a sulfonated polyester made by:

(a) preparing a polyester insoluble in xylene substantially entirely from:

1. maleic acid or maleic anhydride,
2. a glycol in the range of 2 to 4 carbon atoms, a polyester thereof having in the range of 2 to 10 glycol ether groups or the corresponding alkylene oxide, in the presence of an esterification catalyst and with removal of the water of reaction, the molar ratio of glycol equivalent to maleic acid equivalent in said polyester being in the range of 1:1.00 to 1:1.09 to 0.9 to 1.1 and
(b) sulfonating said polyester from step (a) to a level of 2:1 to 1:1 sulfonic acid groups per maleic acid removal.

2. The composition of claim 1 wherein said glycol is selected from the group consisting of ethylene, propylene, and butylene glycols.
3. The composition of claim 1 wherein step (b) is accomplished with an alkali metal hydrogen sulfite.

References Cited

UNITED STATES PATENTS


FOREIGN PATENTS

107,498 7/1967 Great Britain.

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U.S. Cl. X.R.

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