DETERGENTS AND CLEANSERS

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ABSTRACT OF THE DISCLOSURE

Novel detergent and cleaning agents are disclosed characterized by their ability to inhibit the graying of textile articles which takes place in laundering. In particular the 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, the acid radicals of which are derived from a dicarboxylic acid and the alcohol component of which is derived from a dialkanolamine or an N-substituted derivative thereof and which has been made water soluble by the introduction of sulfonic acid or alkylsulfonic acid groups into the molecule. 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, sudzers, 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 or polyesters the acid component of which is derived from a dicarboxylic acid and the alcohol component of which is derived from a dialkanolamine or an N-substituted derivative thereof and which has been made water soluble by the introduction of sulfonic acid or alkylsulfonic acid groups into the molecule.

It is known in the prior art to add to detergents and cleaners 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 re- sorption of the dissolved dirt onto the cleaned surfaces. These substances are usually polyatomic polymers which are manufactured from natural substances such as cellulose, gelatins or glue, or are prepared by the polymerization of vinyl compounds, such as acrylic acid, methacrylic acid, maleic acid and mixtures thereof with copolymerizable olefins. Further, the polyunsatellites of vinyl polymers have already been proposed as useful graying-inhibiting additives for detergent and cleaner preparations. Of all 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 become known. However, carboxymethylcellulose as well as the above-mentioned 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.

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 polyester the acid component of which is derived from a dicarboxylic acid and the alcohol component of which is derived from a dialkanolamine or an N-substituted derivative thereof and which has been made water soluble by the introduction of sulfonic acid or alkylsulfonic acid groups into the molecule.

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 polyesters the acid component of which is derived from a dicarboxylic acid and the alcohol component of which is derived from a dialkanolamine or an N-substituted derivative thereof and which has been made water soluble by the introduction of sulfonic acid or alkylsulfonic acid groups into the molecule, 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 compositions of at least one water-soluble salt of a polyester the acid component of which is derived from a dicarboxylic acid and the alcohol component of which is derived from a dialkanolamine or an N-substituted derivative thereof and which has been made water soluble by the introduction of sulfonic acid or alkylsulfonic acid groups into the molecule.

The polyester salts incorporated into the new detergent compositions in accordance with the invention are manufactured by methods already known in the art. The starting materials for preparing the polyester salts can be aliphatic, cycloaliphatic or aromatic, saturated or unsaturated dicarboxylic acids which can contain 3 (malonic) and up to 20 carbon atoms. Instances of particularly suitable acids include malonic, succinic, glutaric, adipic, sebacic, maleic and fumaric acids, benzenedicarboxylic acids and their mixtures. The dialkanolamines which are suitable for use in the reaction to form the polyesters are derived from alcohols having 1 to 6 preferably 2 to 3 carbon atoms, and may be straight-chained or branched, saturated or unsaturated and maybe substituted at the nitrogen atom by aliphatic, cycloaliphatic or aromatic hydrocarbon radicals containing 1 to 18 carbon atoms. Examples of suitable substituted dialkanolamines are N-methyl-diethanolamine, N-methyl-dipropylamine, N-ethyl-diethanolamine, N-propyl-dipropylamine, N-propyl-enediethanolamine, N-butyl-diethanolamine, N-dodecyl-
ethanolamine, N-oleyl diethanolamine, N-cyclohexyldipropylamine and N-phenyl diethanolamine.

The esterification of the reaction components, which are used preferably in a 1:1 molar ratio, is carried out in a known manner for example, by heating the dicarboxylic acid and dialkanolamine for several hours under normal pressure in vacuo or in the presence of a solvent with which the water of reaction can be removed azetropically by distillation. By the addition of any of the conventional esterification catalysts and particularly the strong inorganic or organic acids, the reaction can be accelerated. In place of the free dicarboxylic acids, their reactive derivatives such as their anhydrides and halides can be used as starting materials. Similarly, the dicarboxylic acids in the form of their dimethyl or diethyl esters can be re-esterified in the known manner with the alkanolamines in the presence of conventional re-esterification catalysts.

The introduction of the sulfonic acid groups into the polyester molecule is similarly carried out using known methods. Unsaturated polyesters, such as those obtained by reaction of maleic acid and a dialkanolamine, or those in which the hydrocarbon radical on the nitrogen atom is unsaturated, can be converted into the corresponding sulfonates by adding alkanolsulfites onto the double bond. It is also possible to effect the sulfonation of the double bond with complex compounds of sulfur trioxide and an organic compound such as pyridine-, dioxane or N,N-dimethylformamide. The resulting unsaturated polyesters can be sulfonated, in which the acid radical, such as the malonic acid radical, contains a reactive methylene group.

Furthermore, the unsaturated or saturated polyesters can be reacted with quaternizing agents containing 2 to 6 carbon atoms and a sulfonic acid or sulfone group. Examples of such quaternizing agents are halogen alkylsulfonic acids or their salts, such as, 1-bromopropane-3-sulfonic acid and 1-chloroethane-2-sulfonic acid or their alkali salts, and the alkane sulfonates such as propylsulfonate or butanesulfone. Polymeric sulfobetaines or salts of N-alkyl sulfonic acid form in this reaction. The sulfobetaines can be incorporated into the detergent and cleaning compositions as they are or after neutralizing the sulfonic acid group. The ratio of sulfonating or quaternizing agent to polyester is preferably so selected that, after the reaction is ended, there are from 1 to 2 sulfonic acid groups for every two dicarboxylic acid groups or two dialkanolamine groups.

The polyesters containing sulfonic acid groups and manufactured in the above-described manner are of a resin-like nature, substantially insoluble in water and in organic solvents, but easily soluble in dilute alkali lyes. They may also contain secondary amounts of esters of low molecular weight and of unreacted starting substances which can be removed by extraction with organic solvents and thereafter recycled for further reaction. As these compounds, however, do not impair the cleaning properties of the agents, such 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 inoperative. 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 sulfonic acid polyesters according to the invention in the form of their water-soluble salts and preferably in the form of their alkali metal and ammonium salts. The term 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 alkalinely 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 propoxylated fatty alcohols, and alkylbenzenesulfonates, primary and secondary olefin sulfonates, alkyl sulfonates and $\alpha$-sulfonfatty esters. Additional compounds of this class which may be used are the high molecular weight sulfatized partial ethers and partial esters of polyvalent alcohols; the sulfates of ethoxylated or propoxylated 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 degraded proteins; and ampholytes such as alkyl betaines and alkylsulfobetaines. The agents can furthermore contain non-ionic wash-active substances, such as alkyl and acyl glycolethers, co-condensation products of polyethylene 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 alicyclic 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 cleaners 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 cyanuric acids 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 aminopolyoarboxylic acids, e.g., the sodium salts of aminotriacetic acid or of ethylenediaminetetraacetic acid and the alkali salts of hydroxyalkyldiposphonic acids and aminopolyphosphonic acids, such as: the disodium salt of 1-hydroxyethane-1,1-diphosphonic acid or the heksaoxycarboxylic acid of aminotri-(methylene phosphonic 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 dimethylbenedisulfonic acid or of diarylpyrazolinesulfonic acid. To control Sudsing action the detergents may contain suds improvers, such as fatty acid amides, or anti-foaming agents, particularly trialkylmelamines.

The new detergents and cleaners 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, hydrotropic 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 greying inhibitors, particularly carboxymethylcellulose. The amounts of carboxymethylcellulose to be used will be approximately from 0.1 to 3% of the total weight of the detergents.

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,
5 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 re-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 dirted wash water.

(A) REDEPOSITION METHOD

In each test 4 cloth samples, each made of Baumwollfaser 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 the Launder-Ometer® (Atlas, Chicago, USA). Thereafter, the reflectivity of the thusly washed samples was tested using a light meter (Elrepho®, Carl Zeiss, equipped with a No. 6 filter).

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

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

<table>
<thead>
<tr>
<th>Detergent</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Dodecylbenzenesulfonate (sodium salt)</td>
<td>20</td>
</tr>
<tr>
<td>Coconut fatty alcohol sulfate (sodium salt)</td>
<td>2.5</td>
</tr>
<tr>
<td>Tallow fatty alcohol sulfate (sodium salt)</td>
<td>2.5</td>
</tr>
<tr>
<td>Sodium pyrophosphate</td>
<td>40</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>35-25</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° dH. The cotton samples were washed at 90° C. for 30 minutes at a goods-to-wash water ratio of 1:12 (wash water 115 ml.). The synthetic fabric samples were washed at 60° C. for 30 minutes and at a goods-to-wash 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, USA). 10 gram skins of the substrate to be evaluated were washed in one liter of wash water (goods-to-wash-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 graying inhibitor being tested in each case.

The detergent which was used in these tests consisted of a liquid preparation having the following composition:

<table>
<thead>
<tr>
<th>Detergent</th>
<th>G./L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Dodecylbenzenesulfonate (sodium salt)</td>
<td>7.8</td>
</tr>
<tr>
<td>Coconut fatty alcohol sulfate (sodium salt)</td>
<td>11.1</td>
</tr>
<tr>
<td>Tallow fatty alcohol sulfate (sodium salt)</td>
<td>11.1</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>16.0</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>14.0</td>
</tr>
<tr>
<td>Graying inhibitor</td>
<td>5.0</td>
</tr>
</tbody>
</table>

In each case, 100 ml. of this stock solution was diluted to one liter with tap water of 10° dH. 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.

Example 1

146 g. (1 mole) of adipic acid and 273 g. (1 mole) of N-dodecyl-diaminodine were heated with stirring at a temperature of from 150 to 170° C., until the formation of water of reaction had ended. The polyester which was formed thereafter was reacted in the fused state at 150 to 160° C. with 130 g. (1.06 mole) of propylamine. A portion of the reaction product was dissolved in water with the addition of the equivalent amount of soda lye and adjusted to a content of 10 g. of ester salt per liter. The quantities of this solution which are stated in the following tables were added to the wash water solutions in each case.

Example 2

116 g. (1 mole) of maleic acid, 147 g. (1 mole) of N-propyl-diaminodine and 250 g. of xylene were heated together with 1 g. of p-toluene-sulfonic acid in a distillation apparatus that had been provided with an apparatus for separating the water and feeding back the solvent. The heating was continued until no more water separated in the receiver. The xylene was decanted from the insoluble resin that was developed, and the residue was freed in vacuo of any remaining solvent. The residue was then boiled with a 10% aqueous solution of sodium bisulphite (total 190 g. Na₂S₂O₅ corresponding to 2 moles) until it had completely gone into solution. The solution was likewise adjusted to a content of 10 g. of ester salt per liter.

The results of the washing tests were summarized in the following tables. The graying of polyester fabrics was determined by Method A (redeposition method) after 5 washings in each case. The washing tests made with polyamide fabrics were carried out by Method B (deposition method). The abbreviation CMC designates carboxymethylcellulose (sodium salt) which was used for purposes of comparison.

The results show that the agents of the invention are clearly superior as graying inhibitors as compared to carboxymethylcellulose.

TABLES

<table>
<thead>
<tr>
<th>Substrate, method A</th>
<th>Inhibitor example number</th>
<th>Percent removal at inhibitor concentration of ester/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester, Diliton</td>
<td>CMC</td>
<td>44.1 40.7 41.7 43.8 46.0</td>
</tr>
<tr>
<td></td>
<td>44.1 50.0 52.5 56.5 60.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.1 42.5 47.8 50.4 53.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate, method B</th>
<th>Inhibitor example number</th>
<th>Percent removal with the addition of the following amounts of carbon black grams/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide, Perlon</td>
<td>CMU</td>
<td>68 66 66 69 65</td>
</tr>
<tr>
<td></td>
<td>68 66 69 69 65</td>
<td></td>
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<td>69 66 69 69 65</td>
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<tr>
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<td>72 67 69 69 65</td>
<td></td>
</tr>
</tbody>
</table>

We claim:

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 amount in the range of 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 resin-like sulfonated polyester, and the radicals of said polyester being derived from substantially equal molar amounts of a dicarboxylic acid and a substituted dialkanol amine, said dicarboxylic acid being selected from the group consisting of malonic, succinic, glutaric, adipic, sebacic, maleic, and fumaric acids, the alcohol component of said substituted dialkanolamine having in the range of 1 to 6.
carbon atoms, and said substituted dialkanol amine being N-substituted with a hydrocarbon radical containing in the range of 1 to 18 carbon atoms, said sulfonated polyester being made by:

(a) esterifying said dicarboxylic acid, or a reactive ester, anhydride or halide derivative thereof with said dialkanol amine with heating and removal of the water of reaction to obtain a substantially water and xylene insoluble esterification reaction product, and

(b) sulfonating said esterification reaction product thus obtained within the range of 1 to 2 sulfonic acid groups for every two dicarboxylic acid groups.

2. The composition of claim 1 wherein said substituted alkanol amine is selected from the group consisting of N-methyldiethanol, N-methyldipropanol, N-ethyldiethanol, N-propyldipropanol, N-propylenediethanol, N-butyldiethanol, N-dodecyldiethanol, N-oleyldiethanol, N-cyclohexyl-dipropanol and N-phenyldiethanol amines.

3. The composition of claim 1 wherein the sulfonation of step (b) is effected with propane sultone or sodium bisulfite.

References Cited

UNITED STATES PATENTS

2,454,546 11/1944 Bock et al. .......... 260—75T
2,798,047 7/1957 Toney et al. .......... 252—152

FOREIGN PATENTS

1,077,498 7/1967 Great Britain.

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