DETERGENTS AND CLEANSERS

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3 Claims

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 cleansing agents are effective to prevent the graying of textile articles prepared at least in part with synthetic fibers.

The detergent and cleansing 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 free carboxylic group containing polyester, the acid and alcohol radicals of which respectively are derived from tricarboxylic and/or tetracarboxylic acids and bivalent alcohols. In addition to the aforesaid polyester salts the detergent and cleansing agents contain the conventional surface active materials and the usual additives such as optical brighteners, bleaching agents, sudsers, 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 free-carboxylic group containing polyesters.

It is known in the prior art that dyes and synthetic pigments are colorants which may be substituted at the nitrogen atom by aliphatic or aromatic hydrocarbon radicals, and in which the alkylol...
radicals contain 1 to 6, preferably 1 to 3, carbon atoms, and the alkyl, aryl or alkaryl radicals contain up to 18 carbon atoms. Such compounds include, for example, N-1-methyldiethanolamine, N-ethylidethanolamine, N-butylidethanolamine, N-dodecyl- diethanolamine, N-cyclohexyldiethanolamine and N-phenyldiethanolamine.

The preparation of the polyesters is carried out by the conventional methods, as for example, by heating the mixture of starting materials for several hours under normal pressure or in vacuo, in the presence of either case of a solvent with which the water of reaction can be removed azeotropically by distillation. The reaction can be accelerated by the addition of common esterification catalysts, especially strong inorganic or organic acids. Instead of the free di-, tri- or tetracarboxylic acids, the anhydrides and halides of these acids can also be used as starting materials. Particularly suitable in this connection are the dihalides. Similarly, the polyvalent carboxylic acids, in the form of their diesters derived from univalent alcohols of low molecular weight, can be re-esterified with the bivalent alcohols in the presence of known re-esterification catalysts, in the conventional manner. Examples of such diesters are citric acid dimethyl ester and pyromellitic acid diethyl ester. If alkaline re-esterification catalysts are used, care must be taken to see that they are still present in sufficient excess after the neutralization of the acid carboxyl groups.

By selecting the molar ratio of polybasic acid to bivalent alcohol within a preferred range of 1:1 to 0.9:1:1, it is possible to vary the degree of polymerization within certain limits. In the interest of a good anti-graying action, a high degree of polymerization is desirable. To prevent premature interruption of chain formation, therefore, a molar ratio is preferred that is as close as possible to 1:1.

The polyesters containing free carboxyl 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 polyesters according to the invention in the form of any of their water-soluble salts and preferably in the form of their alkaline 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 acid amides and alklyphenols; fatty acid taurides and fatty acid isothionate salts 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 amphoteric substances such as alkylbetaines and alkylsulfobetaines. The agents can furthermore contain non-ionic wash-active substances, such as alkyl and acyl polyglycol ethers, co-condensation products of polyethylene glycol and propylene 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 cyanuric acid 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 aminopolycarboxylic acids, e.g., the sodium salts of amino triacetic acid or of ethylenediaminetetraacetic acid and the alkali salts of hydroxalkyldiphosphonic acids and aminopolylphosphonic acids, such as the disodium salt of 1-hydroxyethane-1,1-diphosphonic acid or the hexa sodium salt 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 diaminostilbenesulfonic 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 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, 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 graying 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, 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 nowise 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:
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 the Launder-Ometer® (Atlas, Chicago, U.S.A.). Thereafter, 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 kaolin, iron oxide black, carbon black and synthetic sebum (prepared from a mixture of ¼ fatty acids, ½ fat and ¼ 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:

- 20% n-dodecylbenzenesulfonate (sodium salt)
- 2.5% coconut fatty alcohol sulfate (sodium salt)
- 2.5% tallow fatty alcohol sulfate (sodium salt)
- 40% sodium pyrophosphate
- 0-10% graying inhibitor
- 35-25% sodium sulfate

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-wash-water ratio of 1:12 (wash water 115 ml.), and the synthetic fabric samples were washed at 60° C. for 30 minutes 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-Ometer® (United States Testing Company, Hoboken, U.S.A.). Ten-gram skeins of the substance 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, and 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 liquid preparation having the following composition:

- 7.8 g./l. n-dodecylbenzenesulfonate (sodium salt)
- 1.1 g./l. coconut fatty alcohol sulfate (sodium salt)
- 1.1 g./l. tallow fatty alcohol sulfate (sodium salt)
- 6.0 g./l. sodium pyrophosphate
- 14.0 g./l. sodium sulfate
- 5.0 g./l. graying inhibitor

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-Ometer operating at 100 r.p.m. The samples were then rinsed with distilled water three times, dried and photometrically evaluated.

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**TABLE I**

<table>
<thead>
<tr>
<th>Substrate (Method A)</th>
<th>Inhibitor Example</th>
<th>Percent remission at an inhibitor concentration of g/l.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester (Dilon R.)</td>
<td>CMC</td>
<td>46.1 46.7 47.1 45.6 50.0 50.2 46.3 45.7 47.7 46.8</td>
</tr>
<tr>
<td>Merakoll ®</td>
<td>CMC</td>
<td>32.6 42.1 53.0 60.7 66.7 50.1 45.7 45.0 44.0 40.0</td>
</tr>
<tr>
<td>Baumwolle</td>
<td>CMC</td>
<td>76.4 77.2 78.8 79.2 80.1 80.8 81.2 79.1 78.7 77.8</td>
</tr>
<tr>
<td>Cotton</td>
<td>CMC</td>
<td>76.4 77.2 78.8 79.2 80.1 80.8 81.2 79.1 78.7 77.8</td>
</tr>
</tbody>
</table>

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The results of the washing tests are shown in the following table. The degree of graying of polyester fabrics, cotton fabrics and cotton-polypropylene mixture fabrics was determined by Method A (redeposition method) after five washings in each case. The experiments with Perlon fabrics and with a mixture fabric made of 67% polyester and 33% cotton were carried out by Method B (deposition method). The abbreviation CMC as used hereafter designates carboxymethylcellulose, which was used in each case as comparison substance.

The results clearly show the superiority of the agents according to the invention as compared to carboxymethylcellulose.

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We claim:

1. A detergent composition consisting essentially of a detergent selected from the group consisting of anionic, 75 ampholytic, and non-ionic synthetic detergents and mix-
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7
tures thereof, and a graying inhibitor in an amount from 0.1 to 20 weight percent based on the total weight of said composition, said graying inhibitor being selected from the group consisting of the alkali metal and ammonium salts of a resin-like, water and xylene insoluble, polyester containing free-carboxylic groups, the acid radical of said polyester being derived from a polyvalent carboxylic acid selected from the group consisting of citric, tricarballylic, nitrilotriacetic, ethylene diaminotetraacetic, cyclohexanetricarboxylic, trimesic, oxytrimesic and pyromelitic acids, and the alcohol radical of said polyester being derived from a bivalent alcohol from the group consisting of bivalent aliphatic alcohols and amino alcohols, said aliphatic alcohols containing 2 to 18 carbon atoms in the molecule and said amino alcohols being substituted at the nitrogen atom thereof by an alkyl radical having 1 to 18 carbon atoms and containing two alkylol radicls having 1 to 3 carbon atoms, the mole ratio of said polyvalent carboxylic acid to said bivalent alcohol derived radicals in said polyester being in the range of 1.1:0.9 to 0.9:1.

8
cohol in the presence of an esterification catalyst and with removal of the water of reaction, and
(b) dissolving the resin thus obtained in a basic solution containing a cation of said alkali metal or ammonia.

2. The composition of claim 1 wherein said bivalent alcohol is selected from the group consisting of ethylene glycol, hexanediol and N-dodecyldiethanolamine.

3. The composition of claim 1 wherein up to 50 mol percent of said polyvalent carboxylic acid reacting with said bivalent alcohol is replaced with a dicarboxylic acid selected from the group consisting of malonic, succinic, glutaric, adipic, sebamic, maleic and fumaric acids.

References Cited
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