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DETERGENTS AND CLEANSERS

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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 free carboxyl group containing polyamide, the acid and amide radicals of which respectively are derived from tricarboxylic and/or tetracarboxylic acids and diamines. In addition to the aforesaid polyamide salts, the detergent and cleaning 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-carboxyl group containing polyamides.

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 polyanionic 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 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 become 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.

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 free carboxyl group containing polyamide.

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 free carboxyl group containing polyamides, the acid radicals of which are derived from a tricarboxylic and/or tetracarboxylic acids and whose amide radicals are derived from diamines 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, 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 a free carboxyl group containing polyamide, the acid radicals of which are derived from tricarboxylic and/or tetracarboxylic acids and the amide radicals of which are derived from compounds having two aliphatic amide groups.

Polyamides can also be used to produce the same effect in which up to 50 mole-percent of the tri- or tetracarboxylic acid radicals have been replaced by dicarboxylic acid radicals.

The polyamide salts utilized in the formulation of the detergent compositions in accordance with the invention are prepared by known methods.

The starting materials for preparation of the free carboxyl group containing polyamide salts are aliphatic, cycloaliphatic and aromatic tri- and/or tetracarboxylic acids. Instances of preferred acids are citric acid, tricarballylic acid, nitrilo-triacetic acid, ethylenediaminotetraacetic acid, cyclohexanetricarboxylic acid, trimesic acid, oxytrimesic acid and pyromellitic acid. The aforesaid acids can be replaced in amounts of up to 50 mole-percent by saturated or unsaturated aliphatic and cycloaliphatic acids or be aromatic dicarboxylic acids, such as for example malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, maleic acid and fumaric acid and by benzenedicarboxylic acids as well. The polyvalent carboxylic acids that are suitable for use herein preferably contain 6 (citric acid) up to 20 carbon atoms.

The diamines which are employed in the preparation of the polyamides contain preferably 2 to 18 carbon atoms, may be straight-chained or branch-chained, saturated or unsaturated, aliphatic, cycloaliphatic or aromatic, and they may be interrupted by hetero atoms such as O, N and S. Examples of suitable diamines include ethylene diamine, propylene diamine, tetramethylene diamine, pentamethylene diamine, hexamethylene diamine, p-phenylene diamine, benzidene, piperazine, 4,4'-diaminodiphenylsulfone, and 4,4'-diaminodiphenylether.

The preparation of the polyamides is carried out by the conventional method, as for example, by heating the mixture of acid and diamine for several hours in vacuo or in the presence of a solvent with which the water of reaction can be removed azeotropically by distillation. In place of the free di-, tri- or tetracarboxylic acids, their reactive derivatives such as for example, their anhydrides, can be also used as starting materials.

By selecting the molar ratio of the polycarboxylic acid to diamine within a preferred range of 0.9 to 1:1 to 1.1, it is possible to vary the degree of polymerization within certain limits. In the interest of a good anti-graying action, however, a high degree of polymerization is desirable. In order to prevent a premature interruption of chain formation, therefore, a molar ratio is preferred that is as close as possible to 1:1.

The polyamides containing free carboxyl groups which have been 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 amides of low molecular weight and of unreacted starting materials 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 polyamides with complete accuracy.

The detergents may contain the polyamides 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 term ammonium salts is intended also to include the salts of the polyesters with organic ammonium bases. The polyamides 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 polyamides, 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 α-sulfofatty 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 isoethionates 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 alkylbetaines and alkylsulfobetaines. The detergent compositions can furthermore contain non-ionic wash-active substances, such as alkyl and acyl polyglycolethers, 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 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 cleansers 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 aminopolycarboxylic acids, e.g., the sodium salts of aminotriacetic acid or of ethylenediaminotetraacetic acid and the alkali salts of hydroxyalkyldiphosphonic acids and aminopolyphosphonic acids, such as the disodium salt of 1-hydroxyethane-1,1-diphosphonic acid or the hexasodium salt of aminotri-(methylenephosphonic 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 detergent can also contain optical brighteners, such as the derivatives of diaminostilbenedisulfonic 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 cleansers 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 polyamide 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:

(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 fabrics 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 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 ⅓ fatty acids, ⅓ fat and ⅓ hydrocarbons). The cotton yarn contained approximately 11% pigments and 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 harness 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.), and the synthetic fabric samples were washed at 60° C. for thirty (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 carried out using skein goods in the Terg-O-Tometer ® (United States Testing Company, Hoboken, USA). 10-gram skeins 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:

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)
16.0 g./l. sodium pyrophosphate
14.0 g./l. sodium sulfate
5.0 g./1. graying inhibitor

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

192 g. (1 mole) of anhydrous citric acid, 108 g. (1 mole) of hexamethylene diamine and 500 ml. of xylene were heated in a distillation apparatus which was provided with a system for separating the water and feeding back the solvent. The heating was continued until no further water of reaction separated in the receiver. The xylene was decanted from the insoluble resin that had been formed and the residue was dried in vacuo. The recovered polyamide dissolved when stirred in 2 N NaOH solution. The excess lye (about 5%) was neutralized with dilute sulfuric acid and the neutral solution was adjusted to a polyamide content of 10 g./l. Appropriate amounts of this solution were added to the wash water.

In like manner the following were reacted:

	Acid	Diamine
Example:		
2	1 mole of citric acid	1 mole of ethylenediamine.
3	1 mole of pyromellitic acid	Do.
4	do	1 mole hexamethylenediamine.
5	1 mole of nitrilotriacetic acid	Do.
6	Mixture of: 0.5 mole nitrilotriacetic acid + 0.5 mole maleic acid	1 mole ethylenediamine.

The results of the washing tests are summarized in the following tables. The graying of polyester fabrics was determined by Method A (redeposition method) following washings in each case. The washing tests with samples of polyamide fabrics were carried out by Method B (deposition method).

The results show a clear superiority on the part of the agents of the invention over carboxymethylcellulose.

TABLES

Substrate, Method A	Inhibitor according to Example No.	Percent remission at inhibitor concentration of, gram/liter 0	0.1	0.2	0.5
Polyester, Diolen ®	[1] CMC	44.1	40.7	41.7	43.5
	3	44.1	46.0	47.0	47.5
	4	44.1	46.0	46.5	46.5
	5	44.1	45.4	45.6	47.2
	6	44.1	45.8	46.0	47.0

Substrate Method B	Inhibitor according to Example No.	Percent remission at carbon black concentration of, grams/liter 0.2	0.5	1.0	1.5
Polyamide, Perlon ®	[1] CMC	70	64	55	51
	1	73	67	65	60
	2	72	65	58	54
	3	70	65	58	55
	4	74	71	63	60

[1] The abbreviation CMC designates carboxymethylcellulose (sodium salt) which was used for purposes of comparison.

What is claimed is:

1. A detergent composition consisting essentially of a detergent selected from the group consisting of anionic, ampholytic 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 carboxyl group containing polyamide made by condensing with removal of water to a resin-like state substantially insoluble in xylene a polycarboxylic acid and a diamine in the ratio of 0.9 to 1.1 mole per mole (carboxylic acid group/amine group said polycarboxylic acid being selected from the group consisting of citric, tricarballylic, nitrilotriacetic, ethylenediaminotetracetic, cyclohexanetricarboxylic, trimesic, oxytrimesic and pyromellitic acids, and said diamine having in the range of 2 to 18 carbon atoms.

2. The composition of claim 1 wherein said diamine is selected from the group consisting of ethylene diamine, propylene diamine, tetramethylene diamine, pentamethylene diamine, hexamethylene diamine, p-phenylene diamine, benzidene, piperazine, 4,4'-diaminodiphenylsulfone, and 4,4'-di-aminodiphenylether.

3. The composition of claim 1 wherein up to 50 mole percent of said polycarboxylic acid is replaced in poly-

amide by the addition of a dicarboxylic acid selected from the group consisting of malonic, succinic, glutaric, adipic, sebacic, maleic and fumaric acids.

References Cited

UNITED STATES PATENTS

2,584,123	2/1952	Gruenwald	260—7.5X
2,710,856	6/1955	Carpenter	260—102X

FOREIGN PATENTS

1,077,498	7/1967	Great Britain	252—99

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