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COMPOSITION FOR IMPARTING NON-PERMANENT SOIL-RELEASE CHARACTERISTICS COMPRISING AN AQUEOUS ACIDIC SOLUTION OF POLYCARBOXYLATE POLYMER

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7 Claims 10

ABSTRACT OF THE DISCLOSURE

A composition for applying a non-permanent soil-release finish to fabrics comprising a mixture of a polycarboxylate polymer having an acid equivalent weight from about 110 to 175, and a mineral acid. A preferred carboxylate polymer is a copolymer of $\frac{2}{3}$ methacrylic acid and $\frac{1}{3}$ ethyl methacrylate. The composition is particularly useful for applying a soil-release finish in the rinse cycle of a home laundry process.

BACKGROUND OF THE INVENTION

This invention relates to a composition for treating a textile substrate to impart a soil-release characteristic thereto which can be conveniently used in the rinse cycle of a home laundry procedure.

The genesis of synthetically produced textile fibers has brought about a tremendous effort in the textile industry along numerous avenues. There has been much research effort directed to the improvement of these synthetic fibers per se, and improved blends of synthetically produced fibers with natural fibers, i.e., cellulose fibers or keratinous fibers. Results of this research have been successful, and the direction of research has been directed from the synthetic polymer per se and/or blends of said polymers with other naturally occurring fibers, and, more specifically, to the physical characteristics and/or endurance properties of garments produced from synthetic fabrics and/or fabric produced from blends of synthetic fibers and naturally occurring fibers.

Much research has been directed to the attainment of a garment having improved soil-release properties. Many of the synthetically produced fibers that are presently being incorporated in blends with naturally occurring fibers have a propensity to accept and retain oily grime and dirt. Accordingly, when the garment is being worn the soil and/or oily materials accumulate on the garment and settle in the fabric. Once the garment becomes soiled, it is then subjected to a cleaning process for removal of the dirt and/or oily deposits, and only a dry cleaning process will successfully clean the garment.

The cleaning process normally employed, however, is washing in a conventional home washing machine by the housewife. During a wash cycle, it is virtually impossible to remove the soil and/or oily stains from the garment, and secondly, assuming that the undesirable materials are removed from the garment or a fairly clean garment is being washed, soil remaining in the wash water is redeposited onto the garment prior to the end of the wash cycle. Hence, when the garment is removed from the washing machine and subsequently dried, it has not been properly cleaned. Such a condition, heretofore unavoidable, is quite disadvantageous in that the garment after being worn never again assumes a truly clean appearance, but instead tends to gray and/or yellow due to the soil and/or oily materials deposited and remaining thereon. Further use and washing of the garment increases the in-

tensity of graying to the point that ultimately the garment is unacceptable for further wear due to its discoloration. The process of the present invention solves the soiling problem as hereinafter described.

The problem heretofore confronted with fabrics having synthetic fibers incorporated therein, or made entirely of synthetic fibers, has been that the synthetic fibers, as well as being hydrophobic, are oleophilic. Therefore, while the oleophilic characteristics of the fiber permit oil and grime to be readily embedded therein, the hydrophobic properties of the fiber prevent water from entering the fiber to remove contaminants therefrom.

Attempts have been made to reduce the oleophilic characteristics of these synthetic fibers by coating the fibers with a coating that is oleophobic, i.e., will hinder the attachment of soil or oily materials to the fibers. Many polymer systems have been proposed which are capable of forming a film around the fibers that constitute the textile material, particularly acid emulsion polymers prepared from organic acids having reactive points of unsaturation. These treating polymers are known as soil-release agents.

The term "soil-release" in accordance with the present invention refers to the ability of the fabric to be washed or otherwise treated to remove soil and/or oily materials that have come into contact with the fabric. The present invention does not wholly prevent the attachment of soil or oily materials to the fabric, but hinders such attachment and renders the heretofore uncleanable fabric now susceptible to a successful cleaning operation. While the theory of operation is still somewhat of a mystery, soiled, treated fabric when immersed in detergent-containing wash water experiences an agglomeration of oil at the surface. These globules of oil are then removed from the fabric and rise to the surface of the wash water. This phenomenon takes place in the home washer during continued agitation, but the same effect has been observed even under static conditions. In other words, a strip of polyester/cotton fabric treated with a dilute solution of the composition of the present invention and soiled with crude oil, when simply immersed in a detergent solution will lose the oil even without agitation.

Concentrated solutions of soil-release polymers have been padded onto fabrics by textile manufacturers to impart a permanent soil-release finish to the fabric. As the amount of soil-release polymer on the fabric is increased, the ability of the fabric to release soil is increased. However, fabrics with this permanent soil-release finish possess many disadvantages. As the amount of soil-release polymer on the fabric is increased, the fabric has a tendency to become stiffer and lose the desirable hand characteristic of the fabric. Thus, the upper limit on the amount of soil-release polymer to be used is determined by economics and the resulting adverse effect on the fabric. Fabrics with a heavy application of soil-release polymer do not have the same desirable appearance and hand as the same fabrics without the soil-release coating. Furthermore, practically speaking, there is a set range of soil-release agent that can be applied, dictated by commercial success.

Some soil-release polymers are effective fabric treating agents even at very low levels on the fabric, at which levels the appearance and hand of the fabric are not adversely affected. Thus, an ideal method of treating a synthetic fiber containing fabric would be to reapply a very small amount of soil release polymer to the fabric each time the fabric is washed.

Certain polycarboxylate polymers, such as partially hydrolyzed acrylamide polymers and certain copolymers of methacrylic acid with ethyl acrylate, are very effective

soil-release agents at low levels on the fabric. However, these polymers cannot be deposited onto fabrics from dilute solution, as the polymers are so soluble in water that they will not deposit onto the fabric from dilute solution.

SUMMARY OF THE INVENTION

It has now been discovered that a very effective non-permanent soil-release finish can be applied to fabrics using a dilute aqueous solution of a polycarboxylate polymer if the pH of the solution is lowered to 3, most conveniently with sulfuric acid. Lowering the pH of the solution to this level decreases the solubility of the polymer sufficiently to cause the soil-release polymer to deposit onto the fabric. A dilute solution of the soil-release polymer and sufficient acid to lower the pH of the treating water to 3 could easily be made up in the rinse cycle of a typical home laundry process.

Polycarboxylate polymers found to be effective soil-release agents when applied from dilute solution at a pH of about 3 are those polycarboxylate polymers having an acid equivalent weight (i.e., gram per mole of carboxylate) in the range of from about 100 to 175. The preferred acid equivalent weight for these polymers for use in the present invention is about 125.

The preferred soil-release polymers for use in the present invention are about 30% hydrolyzed polyacrylamide or a copolymer of a methacrylic acid with ethyl acrylate made from about $\frac{2}{3}$ methacrylic acid and about $\frac{1}{3}$ ethyl acrylate. Polymers of molecular weights ranging from about two thousand to about five million have been found to be effective; although polymers having a molecular weight of about one million are preferred.

The pH of the treating composition is preferably lowered with sulfuric acid, although other mineral acids such as hydrochloric acid phosphoric and nitric acid could also be used to adjust the pH. As the compositions of the present invention are designed primarily to be used in the rinse cycle of a home laundry procedure, sufficient acid must be used to lower the pH of a dilute solution of the treating composition, i.e., a solution of about 0.05% of the treating composition. The pH of the laundry rinse water is about 7-8, so sufficient acid must be used to lower the pH to about 3. The ratio of said mineral acid to polymer will generally be in the range of about 1.5:1 to about 2.0:1. Where sulfuric acid is employed, it is preferably 4 molar.

The polymers of the composition of the present invention form a hydrophilic film on the fibers upon drying, and afford soil releasability at that point. Each subsequent treatment serves to enhance the soil-release characteristics of the fabric substrate. Since the soil-release finish can be applied with each laundering, the soil-release effect is not lost with repeated washings.

The soil-release properties of pure cellulosic fiber fabrics are much better than those of synthetic fiber containing fabrics, e.g., polyester fibers, in that the synthetic polyester fibers are hydrophobic and thus prevent the ingress of water that is necessary for cleaning the fabric, and also possess an electrical charge that attracts soil particles.

The compositions of the present invention may be used to treat a wide variety of textile materials made exclusively from synthetic polymer materials as well as blends of natural and synthetic fibers. Examples of synthetic fibers which may be successfully employed in the practice of the present invention include those made with polyamide, acrylic, and polyester fibers. Blends of natural and synthetic fibers which may be successfully treated with the compositions of the present invention include fabrics containing 50% polyester/50% cotton, 65% polyester/35% cotton, etc. Cellulose fibers such as viscose, regenerated cellulose, etc., also may be combined with cellulosic fibers. The compositions of the present invention are most effective on fabrics of pure polyester and blends of polyester and cotton with a permanent press finish.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example I

A 0.05% solution of a copolymer of $\frac{2}{3}$ methacrylic acid and $\frac{1}{3}$ ethyl acrylate, having a molecular weight of about one million, is made up and the pH of the solution adjusted to 3 with 4 molar sulfuric acid. Prewashed swatches of 65% polyester/35% cotton with a permanent press finish were soaked for ten minutes in the treating solution and allowed to dry. A control swatch received no polymer treatment.

Three drops of 1:1 used motor oil/mineral oil were dropped into the center of each of the swatches, and the oil mixture was allowed to spread and set for three hours. The swatches were then washed in a solution of 1.5 g./liter of a 10-2-2 (anionic-nonionic-soap) commercially available household laundry detergent for ten minutes at 80-90° F., and rinsed for five minutes.

The final reflectance of the treated swatches was 70 Rd units. The final reflectance of the control swatch was 50 Rd units.

Example II

Prewashed swatches of 65% polyester/35% cotton were soaked for ten minutes in an aqueous treating solution comprising 0.02% of a copolymer of $\frac{2}{3}$ methacrylic acid and $\frac{1}{3}$ ethyl acrylate, the copolymer having a molecular weight of about one million, and enough 4M sulfuric acid to adjust the pH of the solution to 3. This was the equivalent, in a home washing machine, of 0.9 cups per washer of an emulsion made from 161 gms. of 20% copolymer and 55 grams of 4 molar sulfuric acid. The treated swatches were allowed to dry. A control swatch received no polymer treatment.

Three drops of 1:1 used motor oil/mineral oil were dropped into the center of the swatches, and the oil mixture was allowed to spread and set for three hours. The swatches were then washed in a solution of 1.5 g./liter of a 10-2-2 (anionic-nonionic-soap) commercially available household laundry detergent for ten minutes at 80-90° F., and rinsed for five minutes.

The final reflectance of the treated swatches was 68 Rd units. The final reflectance of the untreated swatch was 50 Rd units.

Example III

A prewashed swatch of 65% polyester/35% cotton was soaked for ten minutes in an aqueous treating solution comprising 0.015% of a copolymer of $\frac{2}{3}$ methacrylic acid and $\frac{1}{3}$ methylacrylate, the copolymer having a molecular weight of about one million, and sufficient 4M sulfuric acid to adjust the pH of the solution to 3.0, and about 0.01% of very fine carbon black suspended in the solution. This swatch was labeled A. A similar prewashed swatch, labeled B, was soaked in an aqueous treating solution comprising 0.015% of a copolymer of $\frac{2}{3}$ methacrylic acid and $\frac{1}{3}$ methylacrylate, the copolymer having a molecular weight of about one million, and about 0.01% of very fine carbon black suspended in the solution. This solution had a pH of 7.5. A third swatch, labeled C, was soaked for 10 minutes in water containing about 0.01% of very fine carbon black suspended therein. The swatches were allowed to dry in the air.

The swatches were soiled by rubbing them on a plexiglass plate coated with Spangler's soil (skin soil) and allowed to age for three hours. The reflectance of the swatches in Rd units was then measured.

The swatches were then washed separately in a solution of 1.5 g./liter of a 10-2-2 commercially available household laundry detergent for 10 minutes at 80-90° F., and rinsed for five minutes. The reflectance of the

swatches in Rd units was then measured. The changes in reflectance are shown in Table I.

TABLE I

Swatch	Reflectance before wash, Rd	Reflectance after wash, Rd	Changes in reflectance, Rd
A.....	30.1	69.1	39.0
B.....	63.4	72.3	8.9
C.....	32.5	47.7	15.2

The reflectance before wash shows the ability of the polymer to prevent deposition of soil when in an alkaline solution. This shows the ability of the polymer to prevent deposition of soil when in an alkaline solution. Although in use the soil-release polymer is applied in the rinse cycle from an acidic solution, the pH in the subsequent wash step is alkaline and the polymer, soluble in water at the higher pH, would then function as a soil antiredeposition agent.

The large difference in reflectance between A and C for reflectance after washing and for change in reflectance shows the ability of the polymer to act as a soil-release agent.

Example IV

Identical Dacron polyester swatches were treated by soaking in a tergotometer for 25 minutes in a 0.02% aqueous solution of a copolymer of $\frac{2}{3}$ methacrylic acid, $\frac{1}{3}$ ethylacrylate having a pH of 3 from the addition of 4 molar H_2SO_4 . These swatches were labeled A. Dacron polyester swatches, labeled B, were similarly soaked in a tergotometer in a 0.05% solution of the copolymer at a pH of 3. Dacron polyester swatches labeled C received no treatment.

The swatches were soiled with natural skin soil obtained by the Trowbridge Skin Soil Method, which involved having panelists rub their arms and foreheads with the swatches. The soiled swatches were then pressed with a warm iron to aid in working the soil into the fabric.

The swatches were then washed separately in a solution of 1.5 g./liter of a 10-2-2 commercially available household laundry detergent for 10 minutes at 80-90° F., and rinsed for five minutes. The swatches were dried in the air and the reflectance measured in Rd units. The results are shown in Table II.

Table II

Swatch:	Reflectance after washing, Rd unit
A.....	81.99
B.....	81.83
C.....	79.77

Example V

The cleaned swatches of A and C of Example IV were washed four more times under the washing conditions of Example IV. The changes in reflectance values of the swatches with successive washings is shown in Table III.

TABLE III

Swatch	One extra wash	Two extra washes	Three extra washes	Four extra washes
A.....	81.78	80.42	79.94	81.35
C.....	79.77	79.10	79.34	81.05

Although the soil-release effects of the copolymer are not permanent, this example shows that the effects of the soil-release polymer have some effect even after several washings. In addition, the soil-release polymer did not cause graying of the Dacron.

Example VI

Identical Dacron polyester swatches were soaked in the following aqueous soil-release polymer solutions for the indicated time periods in a tergotometer. The solutions were made pH of 3 with 4 molar H_2SO_4 .

Swatch	Solution	Time, minutes
A.....	0.01% $\frac{2}{3}$ methacrylic acid, $\frac{1}{3}$ ethylacrylate.....	10
B.....	0.02% $\frac{2}{3}$ methacrylic acid, $\frac{1}{3}$ ethylacrylate.....	10
C.....	0.01% $\frac{2}{3}$ methacrylic acid, $\frac{1}{3}$ ethylacrylate.....	25
D.....	0.02% $\frac{2}{3}$ methacrylic acid, $\frac{1}{3}$ ethylacrylate.....	25
E.....	0.01% copolymer of vinyl alcohol and acrylic acid.....	10
F.....	0.02% copolymer of vinyl alcohol and acrylic acid.....	10
G.....	0.01% copolymer of vinyl alcohol and acrylic acid.....	25
H.....	0.02% copolymer of vinyl alcohol and acrylic acid.....	25
I.....	0.01% hydrolyzed polyacrylamide.....	10
J.....	0.02% hydrolyzed polyacrylamide.....	10
K.....	0.01% hydrolyzed polyacrylamide.....	25
L.....	0.02% hydrolyzed polyacrylamide.....	25
M.....	Control, no soak.....

The swatches were soiled with natural skin soil obtained by the Trowbridge Skin Soil Method until all swatches had reflectances within two Rd units of each other. The soiled swatches were then pressed with a warm iron to aid in working the soil into the fabric.

The swatches were washed separately in a solution of 1.5 g./liter of a 10-2-2 commercially available household laundry detergent for 10 minutes at 80-90° F. and rinsed for five minutes. The swatches were air dried, and the reflectance measured in Rd units. The results are shown in Table III.

Table III

Swatch:	Reflectance, Rd units
A.....	84.57
B.....	83.91
C.....	84.25
D.....	84.37
E.....	83.88
F.....	84.20
G.....	83.16
H.....	83.99
I.....	83.64
J.....	83.94
K.....	82.57
L.....	84.41
M.....	79.77

It can thus be observed that the length of time of the soak period in the soil-release polymer solutions had little effect on the soil-release properties of the treated fabric. The 10 minute soak period, which is just as effective as a 25 minute soak period, is ideally suited to a home laundry procedure, as the rinse cycle of a home laundry procedure is generally of about 10 minutes duration.

Example VII

A number of copolymers were evaluated for their effectiveness in imparting soil-release characteristics to Dacron polyester swatches. Identical Dacron polyester swatches were treated with 0.05% aqueous solutions of the copolymers for 10 minutes in a tergotometer made pH of 3 with 4 molar sulfuric acid, and soil repellancy of the treated fabric was determined from the spreading time of a colored oil drop. The copolymers are rated as to their soil-release characteristics on Dacron polyester swatches in Table IV. A rating of 3 indicates clean release in 30 seconds; a 2 rating means release in 100 seconds; a 1 rating means release in 500 seconds; a 0 rating means no release in 500 seconds.

TABLE IV

Copolymer	Acid equivalent weight	Rating
Partially hydrolyzed polyacrylamide	110	2
Hydrolyzed maleic anhydride/methyl vinyl ether	87	0
Partially hydrolyzed polyacrylamide	250	0
2/3 methacrylic acid, 1/3 ethylacrylate	125	3
10:1 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate	75	0
21:1 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate	80	0
20:1 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate	75	0
Do	110	1
10:1 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate	111	1
5:1 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate (soluble fraction)	89	0
10:4 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate (soluble fraction)	107	0
5:1 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate (insoluble fraction)	120	2
10:4 acrylic acid: 1,1 dihydroperfluoroacetyl methacrylate (insoluble fraction)	127	2

This example illustrates that carboxylate copolymers having acid equivalent rates between about 110 and 175 are effective soil-release agents for Dacron polyester when deposited onto the fabric from dilute aqueous solution at pH of 3. The preferred acid equivalent rate for the carboxylate polymers is 125.

What is claimed is:

1. A composition for imparting nonpermanent soil-release characteristics to a textile fabric comprising an aqueous solution of a polycarboxylate polymer having an acid equivalent weight of about 110 to about 175 employed in an amount up to about .05% and a mineral acid in an amount such that the pH of said solution is about 3.

2. The composition of claim 1 wherein the ratio of mineral acid to polymer is from about 1.5:1 to 2.0:1.

3. A composition for imparting nonpermanent soil-release characteristics to textile fabrics comprising an

aqueous solution of a copolymer of methacrylic acid and ethylacrylate employed in an amount up to about .05%, said copolymer consisting of about two-thirds methacrylic acid and about one-third ethylacrylate and having an acid equivalent weight of about 125 and a molecular weight of about 2,000 to about 5,000,000, and sulfuric acid in an amount such that the pH of said solution is about 3.

4. The composition of claim 3 wherein the molecular weight of the copolymer is about one million.

5. The composition of claim 3 wherein the ratio of said sulfuric acid to copolymer is from about 1.5:1 to about 2.0:1.

6. A composition as defined in claim 1 wherein said mineral acid is selected from the group consisting of sulfuric, hydrochloric, phosphoric and nitric acids.

7. A composition as defined in claim 1 wherein said polycarboxylate polymer is selected from the group consisting of about a 30% hydrolyzed polyacrylamide homopolymer, a copolymer derived from acrylic acid and 1,1-dihydroperfluoroacetyl methacrylate and a copolymer of vinyl alcohol and acrylic acid.

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U.S. Cl. X.R.

8-115.6, 137; 117-139.5 A; 252-DIG. 2

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,836,496
DATED : September 17, 1974
INVENTOR(S) : Robert E. Dickson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 7, lines 6, 8, 10, 13, 15, 17, 19 and 21 under "copolymer" in TABLE IV, for "dihydroperfluoroactyl", read --dihydroperfluorooctyl--

In column 8, line 20, for "dihydroperfluoroacetyl" read --dihydroperfluorooctyl--

Signed and Sealed this

Eighth Day of March 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks