United States Patent [19]

Schultz et al.

[11] **3,816,167**

[45] **June 11, 1974**

[54] **STAIN-RELEASING TEXTILES OF SYNTHETIC FIBERS AND PROCESS FOR TREATING TEXTILES OF SYNTHETIC FIBERS**

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[22] Filed: **Oct. 20, 1971**

[21] Appl. No.: **190,921**

[52] **U.S. Cl.**.. **117/138.8 F,** 8/115.6, 117/139.5 CQ, 260/29.6 F

[51] **Int. Cl.**..... **D06m 13/12**

[58] **Field of Search**..... 117/138.8 F, 139.5 CQ; 260/29.6 F; 8/115.6

[56] **References Cited**

UNITED STATES PATENTS

3,459,716	8/1969	Schaefer et al.	117/138.8 X
3,503,915	3/1970	Peterson	117/139.5 X
3,574,791	4/1971	Sherman et al.	117/139.4
3,592,686	7/1971	Barber et al.	117/138.8
3,597,145	8/1971	Marco	117/139.5
3,598,514	8/1971	Sello et al.	117/139.4
3,598,515	8/1971	Moore et al.	260/29.6

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[57] **ABSTRACT**

Stain releasing from synthetic fibers is assured during laundering by applying a treatment of fluoroaliphatic comonomer and polyalkylene glycol cross-linked in situ by an aldehyde-containing prepolymer.

8 Claims, No Drawings

STAIN-RELEASING TEXTILES OF SYNTHETIC FIBERS AND PROCESS FOR TREATING TEXTILES OF SYNTHETIC FIBERS

This invention relates to a process for treating fabrics composed substantially entirely of synthetic fibers to make them stain repellent and durably launderable.

A commercially important and increasingly popular class of fabrics comprises the polyester knits. Other light-weight, wholly synthetic, essentially non-cellulosic materials, such as nylons and polyesters, are also employed as flat or woven fabrics. By the nature of their uses, and for practical purposes, these non-cellulosic fabrics must be washable and it would be desirable that stains could be released and removed by laundering. In actual practice, as is the case with most of the wholly synthetic materials, oily stains tend to be removed from these materials only with difficulty and are seldom removed completely.

In the past, many fabrics have been made stain repellent by treatments with various fluorochemicals. Unfortunately, such treatments have not always promoted the release of ground-in stains, and treatments of non-cellulosic fabrics have heretofore frequently had insufficient durability to repeated launderings. More recently, treatment with segmented copolymers containing hydrophilic components, e.g., the hybrid copolymers of Sherman and Smith, U.S. Pat. No. 3,574,791, has provided improved stain-release, but without providing durability to laundering to substantially totally synthetic fabrics comparable to that conferred on such cellulosic fabrics as 65 to 35 percent polyester cotton blends or fabrics containing natural fibers such as wool, silk or linen.

It is an object of this invention to provide a process for imparting stain release, which is durable to repeated launderings, to fabrics composed essentially of synthetic fibers. Other objects will become apparent hereinafter. It will be understood that fabrics containing only a few percent of cellulosic fibers are composed essentially of synthetic fibers.

It is found that if a copolymer containing fluoroaliphatic groups and hydrophilic groups is combined with and preferably reacted on the surface of fibers with a polyalkylene oxide segment-containing material containing aldehyde sites reactive by condensation with a small amount of aldehyde-containing prepolymer, e.g., aminoplast resin, a durable treatment is provided to the fibers and the fabric comprising them is stain resistant, stain releasing on laundering, durable to extended laundering cycles and at the same time provides a good hand. The term good hand is understood in the art as referring to a quality of desirable texture which is neither limp and "raggy" nor harsh and rough. Similarly, durability to dry cleaning is also attained.

The invention is illustrated with particular reference to specific materials but is generally applicable when there is:

A. a fluoroaliphatic group-containing stain-release copolymer moiety preferably possessing groups reactive with aldehyde groups

B. a polyalkylene oxide segment containing moiety possessing aldehyde-reactive groups or sites and,

C. a limited amount of a reactive aldehyde-containing aminoplast prepolymer moiety, i.e., a water-soluble precondensate of an aldehyde with an amino compound. Reaction of these moieties is commonly brought about by heating in the presence of a very small amount of catalyst of the order of up to about 25 percent the amount of the aminoplast prepolymer.

For convenience, but without limitation, the fluoroaliphatic group-containing stain-releasing moiety (A) may contain OH groups as in U.S. Pat. Nos. 3,356,628 and 3,574,791. Such moieties are characterized by possessing low-energy fluoroaliphatic surfaces in air and polar hydrophilic and oleophobic surfaces under laundering conditions. Laundering is usually effected in aqueous solutions at about 35° to 100° C. The reactive groups may be not only —OH but also under suitable conditions, other aldehyde-reactive groups as

—SH and other aldehyde-reactive sites as the positions in a phenol ring.

Furthermore, for convenience, the polyalkyleneoxide segment-containing moieties possessing aldehyde reactive groups or sites (B) may include, but is not limited to, polyethylene glycol, or part esters or derivatives such as the ureide obtained by capping with a diisocyanate and then reacting with ammonia. Other polyalkylene glycols are also operable. The critical feature is the presence of a polyalkylene oxide segment with molecular weight between about 400 and 20,000 and one reactive site for at least about each 80,000 of molecular weight. Higher concentrations are generally preferred down to about one in 200 of molecular weight. In general, useful polyalkylene oxide segments must have glass temperatures below room temperature and preferably below 0° C in order to avoid a relatively harsh hand.

The reactive aldehyde-containing prepolymer (C) is most conveniently an aminoplast e.g., urea-formaldehyde, melamine-formaldehyde. An extensive list is provided by Marco in U.S. Pat. No. 3,597,145, Col. 4, line 1 to Column 5, line 56, incorporated herein by reference. The most convenient are the prepolymers used in conjunction with a conventional acidic catalyst, such as zinc nitrate, to produce crease-resistance in various cellulosic fabrics. Because the purpose and manner of use is entirely different, the present invention should not be thought of as a crease-resistant treatment. In particular, the amounts of resin used are considerably less than are normally required for crease-resistant treatments.

The so-called crease-resistant resins have been used heretofore only in conjunction with cellulosic fibers alone or in blends. Moore and Sello, U.S. Pat. No. 3,598,515 indicate that no crease-resistant resin is needed for totally synthetic fabrics. Sello et al., U.S. Pat. No. 3,598,514 concur in that statement but they employed conventional quantities of crease-resistant resins with cellulosic blends.

Peterson, U.S. Pat. No. 3,503,915, uses a crease-resistant resin at a relatively high concentration with a polar, water-insoluble, thermoplastic resin and a stain repellent fluoroaliphatic polymer. The last were not soil-releasing polymers.

Sherman and Smith, U.S. Pat. No. 3,574,791, used soil-release polymers in conjunction with conventional quantities of crease-resistant resins on fabrics containing cellulosic fibers. The definitions of fluoroaliphatic employed by them are adopted herein by reference.

Bolstad et al., U.S. Pat. No. 3,068,187, neither exemplify soil-release polymers nor the use of a crease-resistant resin with a polyalkylene oxide component.

Marco, U.S. Pat. No. 3,597,145 exemplifies only cellulosic materials although he mentions others and employs no soil-releasing fluorochemicals.

Barber and Moses, U.S. Pat. No. 3,592,686, use a soil release composition containing as the essential soil release agent a mixture of a fluoroacrylic polymer and an acrylic hydrophilic or water absorbing polymer and employ conventional amounts of crease-resistant resins.

By the present invention in which polyalkylene oxide segment containing materials having aldehyde reactive sites are copolymerized in situ with the aldehyde-containing prepolymer and preferably also the stain-releasing fluoroaliphatic group containing moiety, the disadvantages of lack of durability to laundering and harsh hand are overcome.

The proportions in which these components are used are especially significant in that the aldehyde-containing prepolymer is used at much lower levels than is the case when one is used to promote crease resistance. Thus, a prepolymer which may be used at a level of 4 to 9 percent of the weight of fabric for crease-resistance is here used at a level of only 0.01 to 0.5 percent. It will be understood that in either case, a catalyst such as the commonly employed zinc nitrate is used. The above-described aldehyde-containing prepolymer, at about one tenth the usual level, together with enough fluoroaliphatic group containing reactant to give a level of about 0.05 to 0.5 percent of fluorine on the fabric. Approximately a range of about 0.1 to 1.0 percent by weight of the fluoroaliphatic containing component is used and from about 0.1 to 5.0 percent of polyalkylene oxide-group containing moiety with molecular weight of segment 400 to 20,000.

EXAMPLE 1

This example illustrates the process of the invention using a mixture of an aminoplast precondensate, a water dispersible diol and a functional fluorinated soil fluoroaliphatic group containing stain-release copolymer.

Two 100 percent polyester double knit fabrics, designated as brown and blue respectively were treated, stained, washed, and evaluated by AATCC Test Method 130-1969. The treating procedure is as follows:

Swatches of 100 percent polyester double knit cloth 20 × 20 cm (8″ × 8″) are thoroughly wet by a treating solution prepared by diluting the materials to be tested with distilled water. The ingredients were added so as to result in a concentration of each in the bath of 100 percent of the desired per cent by weight of the fabric. The fabrics were thoroughly wetted in the treating solution, put through a squeeze roll with the pressure adjusted so as to result in 90 percent wet pick-up. The fabrics were then dried for 5 minutes at 70° C and cured at 150° C for 3 minutes in a circulating air oven.

Sample A is an untreated control.

Sample B is treated with a fluorinated soil release polymer prepared as follows:

One mole of polyethylene glycol of an average molecular weight of about 3,000 (Carbowax 4000) is reacted with one mole of methacrylyl chloride. The resulting product is 25 percent dimethacrylate, 25 percent unreacted diol, and 50 percent monomethacrylate. This mixture is copolymerized with N-methylperfluorooctanesulfonamidoethyl acrylate in a 50/50 weight ratio by a procedure disclosed in U.S. Pat. No. 3,574,791, example 19. The resulting ethyl acetate solution of fluorinated polymer is then dispersed in water, the ethyl acetate distilled off and the resulting fluorinated polymer, dispersed in water, and applied to the fabric at a concentration of 0.4 percent solids on the fabric.

Sample C was a treatment according to the present invention. Fabric was treated with a bath of polymer as used for Sample B additionally containing 1.1 percent of polyethylene oxide (MW 600), 0.45 percent formaldehyde melamine precondensate (Aerotex Resin MW) and 0.033 percent zinc nitrate.

The results are tabulated in Table I. In the Tables oil repellency ratings according to AATCC Test Method 118-1966T and stain release ratings according to AATCC Test Method 130-1969 are given for several staining materials. Laundering was done at 120° F (50° C) using 46 g. of Tide detergent. The following abbreviations are employed throughout:

Fabric: Blue=B, Brown=Br, Yellow=Y.

Cleaning: Initial=Init., one laundering=1L, 10 launderings=10 L, 20 launderings=20 L.

Oil repellency rating by AATCC 118-1966T=oil

Stain release ratings: Nujol=N, Dirty motor oil=DM, Castor oil=C.

Table I

Sample	Init. oil	10L oil	20L oil	N	1L DM	C	N	10L DM	C	N	20L DM	C	Fabric
A	0	0	0	3	1.5	2.5	3	1.5	3				B
	0	0	0	3	2	2.5	3.5	2	3				Br
B	5.5	0	0	3.5	2	3	3	2	2.5	3	2	2.5	B
	5.0	0	0	4	2	2.5	3	2	2.5	3	2	2.5	Br
C	6.0	4.0	1.0	5	3.5	5	5	3.5	5	5	3.5	5	B
	6.0	5.0	2.0	5	5	5	5	4	5	5	3	5	BR

EXAMPLE 2

This example illustrates the use of various aminoplast resins. Treating baths were prepared as in Example 1, Sample C, except that amounts and kind of aminoplast were varied as indicated below. Blue and brown 100 percent polyester double knit fabrics were employed.

Sample D, as in Sample C, using 0.45 percent Aerotex Resin MW.

Sample E used 0.28 percent Aerotex Resin 23 (a different modified melamine formaldehyde precondensate).

Sample F used 0.55 percent American Cynamide Resin P-225 (a different melamine-formaldehyde resin).

Sample G used 0.28 percent Permafresh 113B (a modified glyoxal-urea-formaldehyde).

The test results are tabulated in Table 2.

Table 2

Sample	Init. oil	10L oil	20L oil	N	1L DM	C	N	10L DM	C	N	20L DM	C	Fabric
D	6.0	4.0	1.0	5	3.5	5	5	3.5	5	5	3.5	5	Br
	6.0	5.0	2.0	5	5	5	5	4	5	5	3	5	B
E	6.0	4.0	1.0	5	5	5	5	3	5	4.5	3	4	Br
	6.0	5.0	2.0	5	5	5	5	3	5	5	3	4	B
F	4.0	1.0	1.0	5	5	5	5	3.5	4.5	5	3	4.5	Br
	6.0	3.0	1.0	5	5	5	5	3.5	5	4.5	3.5	4.5	B
G	6.0	3.5	0	5	5	4	3.5	2.5	4	4.5	2	3	Br
	7.0	3.5	1.0	5	5	5	5	2.5	5	4	2	3	B

EXAMPLE 3

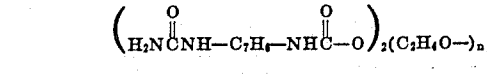
Example 3 is designed to illustrate a range of polyalkylene oxide segment-containing moieties. Treating solutions were prepared using 0.45 percent of the fluoroaliphatic coreactant of Sample C with 0.18 percent Aerotex Resin MW, 0.026 percent zinc nitrate and the polyalkylene oxide moieties indicated were used on blue and yellow 100 percent polyester double knit fabrics.

Sample H: 1.1 percent polyethylene glycol MW 1000

Sample I: 1.1 percent polyethylene glycol MW 400

Sample J: 1.1 percent Adduct of 70 percent ethylene oxide, propylene oxide and ethylene diamine (Tetronic 707).

Sample K: 1.1%



which is the reaction product of toluene diisocyanate capped polyethylene glycol (MW 1000) and ammonia.

Sample L: 1.1 percent polypropylene oxide triol MW 440.

The results are tabulated in Table 3.

Table 3

Sample	Init. oil	10L oil	20L oil	N	1L DM	C	N	10L DM	C	N	20L DM	C	Fabric
H	6.0	5.0	2.0	5	4.5	4.5	4.5	3.5	4.5	5	3.5	4.5	B
	6.0	2.5	1.0	5	4.5	4.5	5	3.5	4.5	5	3	5	Y
I	7.0	4	2	5	5	5	4.5	3.5	4.5	4.5	3	4.5	B
	6.0	4	2	5	5	5	5	3.5	5	5	3	4.5	Y
J	4.0	2.0	1.0	4	3.5	5	3.5	3	4.5	4	2.5	3.0	B
	6.0	5.0	2.0	5	4.5	5	5	4	5	4.5	3	4.5	Y
K	6.0	4.0	1	4.5	4.0	4.5	4.5	3.5	4.5	5	3.5	4	B
	5.0	2.0	0	4.5	3.5	4.5	4.5	3.5	4.5	5	3	4.5	Y
L	6.0	2.0	0	5	4.5	5	5	3	4	4.5	3.5	3.0	B
	5.0	1.0	0	5	4.5	5	5	3	4	5.0	3.0	3.5	Y

EXAMPLE 4

This example illustrates variations in the concentration of polyalkylene oxide-containing moieties. Samples of 100 percent polyester double knit fabric were treated with solutions as above to deposit the following amounts in percent by weight on the fabric.

Sample M: 0.4 percent polymer of Sample C, 2.0 percent polyethylene oxide MW 600, 0.32 percent Aerotex Resin MW and 0.03 percent zinc nitrate.

Sample N: 0.4 percent polymer of Sample C, 0.5 percent polyethylene oxide MW 600, 0.08 percent Aerotex Resin MW and 0.012 percent zinc nitrate.

The results of tests are tabulated in Table 4.

TABLE 4

Sample	Init. Oil	10L Oil	20 L Oil	N	1 L DM	C	N	10 L DM	C	N	20 L DM	C	Fabric
M	6.0	5.0	3.5	5	5	5	5	3.5	5	4.5	3.5	4.0	B
	6.0	5.0	2.0	5	5	5	5	3.5	4.5	4.5	3.5	4.0	Y
N	6.0	4.0	2.0	5	5	5	4.5	4	4.5	4.5	3.5	4.5	B
	5.0	2.0	1.0	5	5	5	5	3.5	4.5	4.5	3.5	4.0	Y

EXAMPLE 5

This example illustrates the preferability of formaldehyde reactive groups in the fluorinated stain-release copolymer. Soil release treatments were prepared containing varying amounts of free hydroxyl groups on the fluoroaliphatic copolymer.

Sample O was essentially the same treatment as Sample C above.

One mole of polyethylene gylcol (MW 3000) was reacted with 1.4 moles of methacrylyl chloride by the procedure of Example 1 and then copolymerized with an equal weight of 50 wt. percent of N-methylperfluorooctane sulfonamidoethyl acrylate, as in Example 1. This copolymer contained about one OH group per 40,000 of molecular weight, and is designated polymer B. It was employed as Sample P in place of the fluorinated polymer used for Sample O in treating blue and yellow polyester.

A copolymer was prepared having about one OH group for 80,000 molecular weight by reacting 1 mole of the above glycol with 2 moles of methacrylyl chloride followed by copolymerization as above. This was used for Sample Q and is designated polymer C.

EXAMPLE 6

This example demonstrates the ineffectiveness of a

TABLE 5

Sample	Polymer	Init. Oil	10 L Oil	20 L Oil	N	1 L DM	C	N	10 L DM	C	N	20 L DM	C	Fabric
0	A	6.0	3.5	3.0	5	4.5	5	4.5	3.5	4.5	4.5	3.5	4.0	B
	6.0		3.0	3.0	5	5	5	5	3.5	4.5	5	3.5	4.0	Y
P	B	7.0	5.0	2.0	5	4.5	5	5	3.5	4.5	4.5	3.5	4.0	B
	6.0		4.0	1.0	5	5	5	5	3.5	4.5	4.5	3.5	4.0	Y
Q	C	7.0	2.0	0	5	4.5	5	4.5	3.0	4.5	4.0	3.0	3.5	B
		7.0	2.0	0	5	5	5	5	3.5	4.5	4.5	3.0	4.0	Y

conventional fluoroaliphatic copolymer as compared to previous examples having fluoroaliphatic group-containing stain-release copolymers. A fluorinated copolymer of 92.5/7.5 weight percent N-ethyl perfluorooctane sulfonamidoethyl methacrylate and isoprene was prepared as described for lot 6 of U.S. Pat. No. 3,503,915. This polymer is referred to as polymer D.

Sample R is a treatment using polymer D alone to give 0.4% solids in the fabric.

Sample S is a treatment using, in percents solid on the fabric, polymer D 0.4% polyethylene glycol MW 600 1.0% Aerotex Resin MW 0.18%, zinc nitrate 0.024%.

These are applied to blue and yellow polyester fabric as above and tested with the results shown in Table 6.

TABLE 6

Sample	Initial Oil	N	1 L DM	C	Fabric
R	5.0	2	2	1.5	B
5.0		1	1.5	1.5	Y
S	5.0	2	2	2	B
	5.0	1.5	2	1.5	Y

What is claimed is:

1. A process for making a textile consisting essentially of non-cellulosic synthetic fibers both stain resistant and durably stain releasing on laundering, comprising treating said textile in the presence of acid catalyst with a stain release finishing composition consisting essentially of

A. a fluoroaliphatic group containing stain-release polymer,

B. a polyalkylene oxide segment-containing moiety having a molecular weight between about 400 and 20,000 and possessing one aldehyde-reactive group or site for at least about each 80,000 of molecular weight and

C. a reactive aldehyde-containing prepolymer in proportions in percent by weight of said textile of about 0.1 to 1.0 of (A), 0.1 to 5.0 of (B) and 0.01 to 0.5 of (C) respectively followed by heating and curing.

2. A process according to claim **1** wherein the fluoroaliphatic group containing stain-release moiety further possesses groups reactive with aldehyde groups.

3. A process according to claim **2** wherein the reactive aldehyde-containing prepolymer is water-soluble aminoplast precondensate.

4. A process according to claim **3** wherein the aminoplast precondensate includes formaldehyde.

5. A fabric consisting essentially of noncellulosic synthetic fibers having improved stain release properties finished with a stain release finish consisting essentially of a cured mixture in percents by weight of said fabric of

A. 0.1 to 1.0 percent of a fluoroaliphatic group containing stain-release polymer,

B. 0.1 to 5.0 percent of a polyalkylene oxide segment containing moiety having a molecular weight between about 400 and 20,000 and possessing one aldehyde-reactive group or site and, (C) 0.01 to 0.5 percent of a reactive aldehyde-containing prepolymer.

6. A fabric according to claim **5** wherein the fluoroaliphatic group containing polymer possesses aldehyde-reactive groups.

7. A fabric according to claim **6** wherein the aldehyde containing prepolymer is a water-soluble aminoplast precondensate.

8. A fabric according to claim **7** wherein the aminoplast precondensate includes formaldehyde.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,167 Dated June 11, 1974

Inventor(s) William J. Schultz and Patsy O. Sherman

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

Column 4, Table 1, line 52, under the column Fabric, "BR" should read — Br —.
Column 7, Table 5, lines 4 and 6, under the column Polymer, "6.0"$_{A}$ and "6.0"$_{B}$ should be under the column Init. Oil.
Column 7, Table 6, line 33, under the column Sample, "5.0" should be under the column Initial Oil.

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—356-334.