

1

3,597,268

METHOD OF IMPARTING SOIL RESISTANCE TO SYNTHETIC TEXTILE MATERIALS AND THE RESULTING MATERIALS

Thomas L. Smith, Cary, N.C., assignor to Hercules Incorporated, Wilmington, Del.

No Drawing. Filed Aug. 13, 1969, Ser. No. 849,922

Int. Cl. B32b 27/02; D06m 15/66

U.S. Cl. 117—138.8

8 Claims

ABSTRACT OF THE DISCLOSURE

Fibers and fabrics based on polypropylene are given improved resistance to deposition of oily soil during laundering by addition to the surface thereof a partially crosslinked reaction product of a specified poly(aminosiloxane) and a polyfunctional carboxylic acid.

This invention relates to improvements in the preparation of synthetic fibers or filaments having soil resistant properties. In a specific embodiment, it relates to the preparation of fibers of improved soil resistance, containing polypropylene.

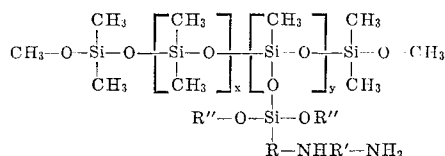
The development of some of the synthetic fiber-forming materials has been seriously hindered by the fact that these materials are highly susceptible to oily soils. This is particularly true of the hydrophobic, non-polar polymers such as polypropylene and the polyesters. These materials, being non-polar or of very low polarity, have a substantial affinity for other non-polar materials as exemplified by oil, grease and the like soils. Not only are these fibers subject to severe soiling with such materials during use, but they also can pick up such soils during laundering if they are laundered in the presence of other garments which are contaminated therewith.

It has been proposed to improve on the soil resistance of such materials by coating them with polar films which have less affinity for oily soils. This approach has experienced some difficulty due to the relative scarcity of candidate materials which exhibit sufficient affinity to adhere to the fiber with any degree of durability.

Now, in accordance with this invention, a method has been found for treating a non-polar synthetic fiber to impart improved soil resistance thereto. Specifically, this method comprises applying to the surface of a fiber comprised of polypropylene a crosslinked polar film comprised of the reaction product of a poly(aminosiloxane) and a polyfunctional carboxylic acid. The polar film is prepared in situ on the fiber by applying thereto a reactive mixture of a poly(aminosiloxane) and a polyfunctional carboxylic acid and curing the same to effect partial crosslinking of the poly(aminosiloxane) and to incorporate free carboxyl groups therein. The poly(aminosiloxane) is applied to the fiber in the amount of about 1 to 10% by weight, based on the weight of the fiber. The application to the fiber can be made either before or after the fiber is incorporated into a fabric.

The method of the invention is useful with 100% polypropylene fibers and with yarns wherein polypropylene fiber is blended with other fibers such as cotton.

The poly(aminosiloxanes) which can be employed in the process of this invention have the general formula



where x is between about 2 and 25, y is 0.5 to $3x$, R and R' are the same or different alkylene radicals hav-

2

ing 1 to 3 carbon atoms and R'' is a methyl or ethyl group. These compounds are reactive with carboxylic acids at either the primary or secondary amine groups or at the methoxy groups to form amides or esters, respectively.

Any polyfunctional carboxylic acid can be employed to crosslink the poly(aminosiloxane) and provide free carboxyl groups. Exemplary of such acids are dicarboxylic acids such as oxalic, malonic, maleic, glutaric, adipic, sebacic, terephthalic, cyclopentanedicarboxylic, itaconic, and tartaric acid, inter alia, and polycarboxylic acids such as citric acid, tricarballic acid, 1,2,4 - hexanetricarboxylic acid, trimelic acid, mellophanic acid, and melitic acid, inter alia. Also useful are water-soluble addition polymers of unsaturated acids such as poly(acrylic acid), and hydrolyzed maleic anhydride copolymers such as copolymers of styrene and maleic anhydride or vinyl ether copolymers of maleic anhydride. The latter class, the polymeric acids, are preferred due to their high carboxyl group content.

The polyfunctional carboxylic acid and the poly(aminosiloxane) are reacted in a ratio such that there is present in the reaction mass at least about 3 carboxyl groups per reactive group (i.e., methoxyl or amino) on the poly(aminosiloxane). When this functionality ratio is below about 3 to 1, the system approaches the stoichiometric ratio so that statistical probabilities favor all of the carboxyl reacting with methoxyl or amino groups and causing a high degree of crosslinking. Under such circumstances, gelling of the reaction mass can occur, or if the product can be applied to the yarn, i.e., if gelling does not occur, there are not sufficient free carboxyl groups present to provide the polarity required for soil resistance. Such highly crosslinked products also have an undesirable stiffening effect on the "hand" of the fabric.

The upper limit of the functionality ratio is less rigid, depending upon the precise make-up of the fiber or fabric being treated. Thus, in the case of an unblended, 100% polypropylene, if the ratio exceeds about 25 to 1, statistical probabilities favor the formation of free carboxyl groups at the expense of crosslinks. Such a finish, while highly polar and, accordingly, highly soil resistant, is not sufficiently durable to be commercially attractive. However, in the case of blended fibers or fabrics, where the polypropylene is blended with a cellulosic material, this ratio can be substantially higher since some of the carboxyl groups will react with the cellulosic material. Bonding of the poly(aminosiloxane) to the fabric thus can take place, while leaving a sufficient number of free carboxyls to impart the desired soil resistance.

The poly(aminosiloxane) and the polyfunctional carboxylic acid are dissolved in a common inert (i.e. non-reactive) volatile solvent for application to the yarn. Suitable solvents are lower molecular weight alkanols and water. The solvent must be relatively volatile in order that it can readily be driven off at low temperatures during curing. Specifically, the solvent should vaporize readily at a temperature below the cure temperature. If the solvent vaporizes much above this temperature, the cure time is increased by an undesirable amount.

Curing of the finish on the fabric is effected by the application of heat thereto. Generally, curing of the finish and solvent removal are accomplished simultaneously at a temperature between about 100° C. and 120° C. Curing is complete in about 5 to 20 minutes at these temperatures. Incomplete cure is indicated by lack of soil resistance, because of a large number of the polycarboxylic acid molecules not having had at least one of their carboxyl groups react with the poly(aminosiloxane). In such cases, the unreacted acid is washed off and lost during laundering. Incomplete cure can be improved by

increasing the temperature or time of cure. However, the thermoplastic nature of the synthetic yarn involved will impose specific temperature limitations.

Evaluation of the soil resistance of fabrics treated according to this invention is accomplished by means of a standard laundering test designed for this purpose. This test comprises laundering the treated yarn in high tallow soap in the presence of a cotton swatch which has been soiled with 0.1% by weight of a standard soil consisting of 6.2% of a 10% dispersion of graphite in mineral oil, 43.8% mineral oil and 50% vegetable oil. The laundered specimen is then rinsed and allowed to dry and color compared to a standard scale to indicate the amount of soil picked up from the soiled swatch during laundering. The standard color scale is the International Grey Scale described in The Technical Manual of the American Association of Textile Chemists and Colorists, Volume 44, B-60, 1968.

In the following examples, the invention is illustrated in several of its embodiments. Parts and percentages, where used, are by weight unless otherwise indicated.

EXAMPLE 1

A light weight 100% polypropylene knit fabric was padded to approximately 100% wet pick-up with an isopropanol solution containing about 1% of a poly(aminosiloxane) and 1.4% of a poly(acrylic acid). The poly(aminosiloxane) had the general formula shown hereinabove where R is $-\text{CH}_2\text{CH}_2-$, and R' is $-\text{CH}_2\text{CH}_2\text{CH}_2-$, R'' is CH_3 , and $y=3x$ with a functionality of 3.6×10^{-3} equivalents of amine and methoxyl per gram. The poly(acrylic acid) had a molecular weight less than about 50,000 and a carboxyl functionality of about 13.5×10^{-3} equivalents/gram. Accordingly, the treating solution had a carboxyl to amine ratio of about 5:1.

The padded fabric was cured for 15 minutes at 120° C. in a tumble dryer. On removal from the dryer, the fabric had a very soft, pleasing hand.

Resistance to soil redeposition was tested by laundering a 3" x 3" swatch of the fabric in the presence of a 3" x 3" cotton swatch soiled with 0.1% by weight of the standard soil described above. Laundering was carried out for 10 minutes at about 80° C. in 200 ml. of an aqueous soap solution (0.4% sodium metasilicate and 0.2% high tallow soap). The laundering step was repeated once with 200 ml. of fresh soap solution, then the fabric was rinsed with clear water for 10 minutes at 80° C.

The samples were air dried and rated on the International Grey Scale. On this scale, a rating of 1 corresponds to heavy soiling and a rating of 5 corresponds to no soiling. The specimens of this example had a rating of 4. A control specimen of the same polymer which had not been treated according to the invention had a rating of 1.

EXAMPLES 2 TO 7

A 70/30 cotton/polypropylene blend fabric was padded with 1% aqueous solutions of the poly(aminosiloxane) containing varying concentrations of citric or malonic acid, and cured for thirty minutes at 120° C. by tumble drying. Specimens of each were submitted to the standard soil redeposition test described in Example 1. Other specimens were laundered 5 times in "All" detergent using conventional home-laundering techniques and then submitted to the soil redeposition test to determine the durability of the finish.

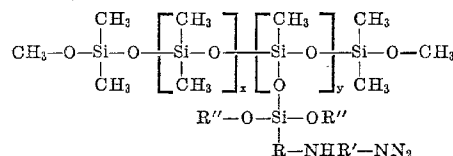
Example Number	Acid	Conc., percent	Functionality ratio ¹	Grey rating	
				Initial	After "All"
Control	None			3	3
2	Citric	1	19	4	4
3	do	2	38	4.5	4
4	do	5	95	5	4
5	Malonic	1	24	3.5	3
6	do	2	48	4.5	4
7	do	5	120	4.5	4

¹ Ratio of COOH to amine plus methoxyl groups.

One additional advantage of the yarns treated according to this invention is realized during conventional home, laundering. When untreated polypropylene fabrics are laundered with soap such as, e.g., "Ivory Snow," it is found that a film of the soap builds up on the fabric, leading to color formation and aggravating the soiling problem. The surface finish of this invention prevents such build-up from taking place.

What I claim and desire to protect by Letters Patent is:

1. A fiber comprised of polypropylene having, applied to its surface, 1 to 10% by weight of a poly(aminosiloxane) comprising the reaction product of a polycarboxylic acid and a poly(aminosiloxane) having the general formula



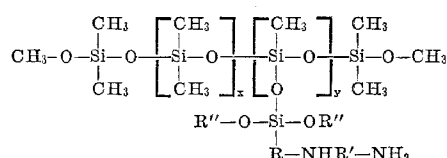
where x is from about 2 to 25, y is 0.5 to 3x, and R and R' are alkylene radicals containing 1 to 3 carbon atoms, and R'' is an alkyl radical having 1 to 2 carbon atoms, said reaction product being partially crosslinked by said polycarboxylic acid and containing free carboxyl groups, the ratio of polycarboxylic acid to poly(aminosiloxane) being such that the ratio of free carboxyl groups to the sum of the methoxyl and amino groups is at least about 3 to 1.

2. The fiber of claim 1 where the poly(aminosiloxane) is partially crosslinked with poly(acrylic acid).

3. The fiber of claim 1 where the poly(aminosiloxane) is partially crosslinked with citric acid.

4. The fiber of claim 1 wherein polypropylene is blended with cotton.

5. A method of improving the resistance to oily soil of fibers comprised of polypropylene which comprises wetting said fibers with a solution containing a poly(aminosiloxane) having the general formula



where x is from about 2 to 25, y is 0.5 to 3x, and R and R' are alkylene radicals containing 1 to 3 carbon atoms, and R'' is an alkyl radical having 1 to 2 carbon atoms, and a polycarboxylic acid in concentrations such that the ratio of COOH to amine and methoxyl groups is at least about 3 to 1, and heating the fiber to remove the solvent and effect a reaction between the poly(aminosiloxane) and the polycarboxylic acid.

6. The process of claim 5 where the polycarboxylic acid is poly(acrylic acid).

7. The process of claim 5 where the fibers are treated in fabric form.

8. The process of claim 7 where the fabric is a cotton-polypropylene blend.

References Cited

UNITED STATES PATENTS

2,972,598	2/1961	Morehouse	260—46.5
3,236,685	2/1966	Caldwell et al.	117—138.8
3,303,048	2/1967	Cooper et al.	117—161X
3,379,564	4/1968	Schwarz	117—138.8
3,494,788	2/1970	Bey	117—139.5
3,383,162	5/1968	Whitfield et al.	8—115.5

WILLIAM D. MARTIN, Primary Examiner

T. G. DAVIS, Assistant Examiner

U.S. Cl. X.R.