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TEXTILE MATERIALS COATED WITH HYDROLYTICALLY STABLE SILOXANE-OXYALKYLENE BLOCK COPOLYMERS CONTAINING SiH

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ABSTRACT OF THE DISCLOSURE

This invention relates to organic textile materials coated with certain hydrolytically stable siloxane-oxyalkylene block copolymers. The copolymers contain at least one siloxane unit containing ≡SiH for every 14 siloxane units present in the copolymers and at least one oxyalkylene block containing at least two oxyalkylene groups. The coatings are durable and impart water repellency and antistatic properties to the textile materials.

This application is a continuation-in-part of United States Ser. No. 168,525 now abandoned, filed on Jan. 24, 1962.

This invention relates to textile materials. More particularly, the invention is directed to organic textile materials which have been treated so as to provide a coating thereon of a hydrolytically stable siloxane-oxyalkylene block copolymer.

It has now been discovered that a class of hydrolytically stable siloxane-oxyalkylene block copolymers containing ≡SiH units can be employed to provide a coating on organic textile materials which improves their physical properties. The hydrolytic stability of these block copolymers is particularly important in that the coating is not hydrolyzed to any appreciable extent when the treated textile is exposed to moisture or is washed in acid or alkaline media.

It is an object of this invention to provide natural, semi-synthetic, and synthetic organic textile materials coated with hydrolytically stable siloxane-oxyalkylene block copolymers.

Another object of this invention is to provide treated organic textile materials which have improved water repellency and which resist the accumulation of charges of static electricity.

A still further object of the invention is to provide compositions and processes for treating organic textile materials with hydrolytically stable siloxane-oxyalkylene block copolymers.

Other objects and advantages of this invention will be apparent upon reference to the following description and the appended claims.

Any natural, semi-synthetic, or synthetic organic textile material can be coated in accordance with this invention. Suitable common natural and semi-synthetic organic textile materials include cotton, linen, ramie, hemp, jute, wood pulp, paper, leather, furs, feathers, cellulose ethers, cellulose esters (e.g., cellulose acetate and cellulose), regenerated cellulose rayons produced by any process (e.g. viscose, cuprammonium, etc.), natural silks, tussore silk, wool, and the like.

Suitable synthetic organic textile materials include those prepared from monofilaments and continuous yarns from fibers such as the polyamides (nylon), the acrylics, and vinyl-, vinylidene-type fibers (Orlon, Acrilan, Creslan, Dynel, Darlon, Verel, Zefran, Velon, Vinyon and Teflon), the polyester fibers (Dacron, Terylene, etc.), and polyethylene fibers. Also included are textiles prepared from mixed or blended yarns produced by spinning combinations of selected natural, semi-synthetic and synthetic fibers from among the above-enumerated textile and fibrous materials.

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The hydrolytically stable copolymers useful in this invention are of the class that are known as "block" copolymers. Block copolymers are composed of at least two sections or blocks, at least one section or block being composed of one type of recurring units or groups (e.g., siloxane units as in the copolymers useful in this invention) and at least one other section or block composed of a different type of recurring units or groups (e.g., oxyalkylene groups as in the copolymers useful in this invention). The copolymers useful in this invention contain one or more siloxane blocks and one or more oxyalkylene blocks.

The siloxane blocks in the block copolymers useful in this invention contain at least two siloxane units that are represented by the formula

$$R_bSiO_{\frac{4-b}{2}} \qquad (1)$$

wherein R is a monovalent hydrocarbon group, a halogen-substituted monovalent hydrocarbon group, or a divalent hydrocarbon group and *b* has a value from 1 to 3. Preferably, each hydrocarbyl radical represented R contains from one to about twenty carbon atoms. The groups represented by R can be the same or different in any given siloxane unit or throughout the siloxane block, and the value of *b* in the various siloxane units in the siloxane block can be the same or different. The divalent groups represented by R link the siloxane block to the oxyalkylene block. Each siloxane block contains at least one group represented by Formula 1 wherein at least one group represented by R is a divalent hydrocarbon group. The siloxane block has a ratio of hydrocarbon groups to silicon atoms from 1:1 to 3:1.

Illustrative of the monovalent hydrocarbon groups that are represented by R in Formula 1 are the alkenyl groups (for example, the vinyl group and the allyl group); the cycloalkenyl groups (for example, the cyclohexenyl group); the alkyl groups (for example, the methyl, ethyl, isopropyl, octyl, dodecyl, octadecyl and eicosyl groups); the aryl groups (for example, the phenyl, naphthyl and terphenyl groups); the aralkyl groups (for example, the benzyl and the phenylethyl groups); the alkaryl groups (for example, the styryl, tolyl and n-hexylphenyl groups); and the cycloalkyl groups (for example, the cyclohexyl group).

Illustrative of the halogen-substituted monovalent hydrocarbon groups that are represented by R in formula (1) are the chloromethyl, trichloroethyl, perfluorovinyl, parabromobenzyl, iodophenyl, alpha-chloro-beta-phenylethyl, parachlorotolyl and bromocyclohexyl groups and the like.

Illustrative of the divalent hydrocarbons groups represented by R in formula (1) are the alkylene groups (such as the methylene, ethylene, propylene, butylene, 2,2-dimethyl-1,3-propylene, decylene and eicosylene groups), the arylene groups (such as the phenylethylene group). Preferably, the divalent hydrocarbon group is an alklene group containing from two to four successive carbon atoms. Siloxane groups containing divalent hydrocarbon groups as substituents are illustrated by groups having the formulas:

$$-CH_2CH_2SiO_{1.5},\quad -CH_2\overset{\displaystyle CH_3}{\overset{|}{C}H}CH_2\overset{\displaystyle CH_3}{\overset{|}{Si}}O_{1.0}\quad \text{and}\quad -CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}O_{0.5}$$

These divalent hydrocarbon groups are linked to a silicon atom of the siloxane block by a silicon-to-carbon bond and to an oxygen atom of the oxyalkylene block by a carbon-to-oxygen bond.

The siloxane block can contain siloxane units that are represented by Formula 1 wherein either the same hydrocarbon groups are attached to a silicon atom (e.g., the dimethylsiloxy, diphenylsiloxy and diethylsiloxy groups) or different hydrocarbon groups are attached to a silicon atom (e.g., the methylphenylsiloxy, phenylethylmethylsiloxy and ethylvinylsiloxy groups).

The siloxane block in the block copolymers useful in this invention can contain one or more types of siloxane units that are represented by Formula 1 provided that at least one group has at least one divalent hydrocarbon substituent. By way of illustration, only ethylenemethylsiloxy groups

$$-(C_2H_4)\overset{\displaystyle CH_3}{\overset{|}{Si}}O-$$

can be present in the siloxane block, or the siloxane block can contain more than one type of siloxane group, e.g., the block can contain both ethyleen methylsiloxy groups and diphenylsiloxy group, or the block can contain ethylenemethylsiloxy groups diphenylsiloxy groups and diethylsiloxy groups.

The siloxane block contained in the block copolymers useful in this invention can contain trifunctional siloxane units (e.g., monomethylsiloxane groups, $CH_3SiO_{1.5}$), difunctional siloxane groups [e.g. dimethylsiloxane groups, $(CH_3)_2SiO-$], monofunctionoal siloxane units [e.g., trimethylsiloxane units, $(CH_3)_3SiO_{0.5}$], or combinations of these types of siloxane units having the same or different substituents. Due to the functionality of the siloxane groups, the siloxane block can be predominately linear, or cyclic, or crosslinked, or it can have combinations of these structures.

The siloxane block contained in the block copolymers useful in this invention can contain organic end-blocking or chain terminating organic groups as well as the monofunctional siloxane chain terminating group encompassed by Formula 1. By way of illustration, the siloxane block can contain such organic end-blocking groups as the hydroxy group, the aryloxy groups (such as the phenoxy group), the alkoxy groups (such as the methoxy, ethoxy, propoxy and butoxy groups), the acyloxy groups such as the acetoxy group, and the like.

The siloxane blocks in the block copolymers useful in this invention each contain at least two siloxane units that are represented by Formula 1 and at least one siloxane unit represented by Formula 2, below. Preferably, the siloxane blocks contain a total of at least five siloxane units that are represented by Formula 1 and by Formula 2, below. That part of the average molecular weight of the copolymer that is attributable to the siloxane blocks can be as high as 50,000 or greater.

A siloxane block must also contain, in addition to the groups represented by Formula 1, one or more siloxane units represented by the formula:

$$(2)\qquad R_e\overset{\displaystyle H_f}{\overset{|}{Si}}O_{\frac{4-e-f}{2}}$$

wherein R has the meaning defined in Formula 1, e has a value from 0 to 2, f has a value from 1 to 2 and e plus f has a value from 1 to 3.

The important feature of the foregoing unit is the presence of a $\equiv$SiH group which serves as a cross-linking or insolubilizing site, necessary for the bonding of the copolymer to the substrate. The presence of this group also imparts lasting water-repellency of the resulting coated substrate, even through the surprisingly good water repellency and durability to laundering would not normally be expected from a non-hydrolyzable polymer structure containing such hydrophilic groups which remain as an integral part of the resulting coating after cure.

The relative amount of the $\equiv$SiH groups in the polymer is also important. While at least one siloxane block of the copolymer must contain at least two siloxane units represented by Formula 1 and at least one unit represented by Formula 2, in addition the ratio of the total number of units represented by Formula 1 to the total number of units represented by Formula 2 in the polymer must not exceed 13:1, respectively, i.e., there must be at least one unit represented by Formula 2 in every fourteen siloxane units present in the polymer.

The oxyalkylene blocks in the block copolymers useful in this invention each contain at least two oxyalkylene groups that are represented by the formula:

$$(3)\qquad -R'-O-$$

wherein R′ is an alkylene group. Preferably, the alkylene group represented by R′ in Formula 3 contains from two to about ten carbon atoms, and most preferably from two to three carbon atoms. Illustrative of the oxyalkylene groups that are represented by Formula 3 and the oxyethylene, oxy-1,2-propylene, oxy-1,3-propylene, oxy-2,2-dimethyl-1,3-propylene, oxy-1,10-decylene groups, and the like.

The oxyalkylene blocks in the block copolymer useful in this invention can contain one or more of the various types of oxyalkylene groups represented by Formula 3. By way of illustration, the oxyalkylene blocks can contain only oxyethylene groups or only oxypropylene groups or both oxypropylene groups and oxyethylene groups, or other combinations of the various types of oxyalkylene groups represented by Formula 3.

The oxyalkylene blocks in the block copolymers useful in this invention can contain organic end-blocking or chain terminating groups. By way of illustration, the oxyalkylene blocks can contain such end-blocking groups as the hydroxy group, the aryloxy group (such as the phenoxy group), the alkoxy groups (such as the methoxy, ethoxy, propoxy and butoxy groups), alkenyloxy groups (such as the vinyloxy and the allyloxy groups). Also a single group can serve as an end-blocking group for more than one oxyalkylene block. For example, the glyceroxy group

$$\begin{array}{ccc} CH_2 & CH & CH_2 \\ | & | & | \\ O & O & O \\ | & | & | \end{array}$$

can serve as an end-blocking group for three oxyalkylene chains.

The oxyalkylene blocks in the block copolymers useful in this invention each contain at least two oxyalkylene groups that are represented by Formula 3. Preferably, each block contains at least five such groups. That part of the average molecular weight of the copolymer that is attributable to the oxyalkylene blocks can be 50,000 or greater.

The bock copolymers useful in this invention can contain siloxane blocks and oxyalkylene blocks in any relative amount. The copolymer can contain, for example, from 5 parts by weight up to 95 parts by weight of siloxane blocks and from 5 parts by weight to 95 parts by weight of oxyalkylene blocks per 100 parts by weight of the copolymer. Preferably, the copolymer contains 5 parts by weight to 50 parts by weight of the siloxane blocks and from 50 parts by weight to 95 parts by weight of the oxyalkylene blocks per 100 parts by weight of the copolymer.

The block copolymers useful in this invention can contain more than one of each of the blocks and the blocks can be arranged in various configurations such as linear, cyclic or branched configurations.

The following are representative of the hydrolytically stabe siloxane-oxyalkylene block copolymers useful in this invention. In the formulas, Me represents a methyl group

(CH_3—), Et represents an ethyl group (CH_3CH_2—), and ϕ represents a phenyl group (C_6H_5—).

(a)
$$\begin{array}{l}\mathrm{Me_3SiO(Et\underset{|}{Si}O)_5(EtSiHO)_6SiMe}\\ \qquad\qquad\quad \mathrm{CH_2CH_2O(C_3H_6O)_{14}(C_2H_4O)_{18}C_4H_9}\end{array}$$

(b)
$$\mathrm{Me_3SiO}\left(\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{H}\end{array}\right)_6\left(\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{CH_2CH_2CH_2O(C_2H_4O)_7Me}\end{array}\right)_7\mathrm{SiMe_3}$$

(c)
$$\mathrm{Me_3SiO}\left(\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{CH_2CH_2CH_2O(C_2H_4O)_7Me}\end{array}\right)\left(\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{H}\end{array}\right)_{37}\mathrm{SiMe_3}$$

(d)
$$\begin{array}{l}\qquad\qquad\qquad\qquad\quad\ \mathrm{H}\\ \qquad\qquad\qquad\qquad\quad\ |\\ \mathrm{Me_3SiO(\phi_2SiO)_9(Et\underset{|}{Si}O)_3SiMe_2}\\ \qquad\qquad\qquad\quad \mathrm{CH_2CH_2O(C_3H_6O)_{11}C_4H_9}\end{array}$$

The polysiloxane-oxyalkylene block copolymers that are useful in this invention can in general be prepared by two convenient methods. The first method, known as the metathesis process, involves forming a mixture of a siloxane polymer containing a silicon-bonded, halogen-substituted monovalent hydrocarbon group and an alkali metal salt of an oxyalkylene polymer and heating the mixture to a temperature sufficiently elevated to cause the siloxane polymer and the salt to react to produce the copolymer. This process can be illustrated by the following equation:

(7)
$$\text{siloxane-}(\mathrm{O\overset{|}{\underset{|}{Si}}R^2X})_r + (\mathrm{MO})\text{-oxyalkylene} \longrightarrow \text{siloxane-}(\mathrm{OSiR^2O})_r\text{-oxyalkylene} + r\mathrm{MK}$$

wherein R^2 is a divalent hydrocarbon group, r is an integer that has a value of at least 1 and preferably 1 to about 4, X is a halogen atom, M is an alkali metal, siloxane denotes a siloxane block and oxyalkylene denotes an oxyalkylene block.

The second method, known as the addition process, involves forming a mixture of an organo-siloxane polymer containing a hydrogen-siloxy group

$$(\text{i.e., a } \mathrm{H\overset{|}{\underset{|}{Si}}O} \text{ group})$$

an oxyalkylene polymer containing an alkenyloxy end-blocking or chain terminating group and a platinum catalyst and heating the mixture to a temperature sufficiently elevated to cause the siloxane polymer and the oxyalkylene polymer to react to produce the copolymer. This process can be illustrated by the following equation:

(8)
$$\text{oxyalkylene-}(\mathrm{OR^3})_r + [\mathrm{H\overset{|}{\underset{|}{Si}}O}—]_r\ \text{siloxane} \longrightarrow \text{oxyalkylene-}[\mathrm{OR^4SiO}—]_r\ \text{siloxane}$$

wherein oxyalkylene, siloxane and r have the meaning defined for formula (7), OR^3 is an alkylenyloxy group (such as the vinyloxy and the allyloxy groups) and R^4 is an alkylene group containing at least two successive carbon atoms.

When the polysiloxane-oxyalkylene block copolymer contains silicon-bonded hydrogen atoms, i.e., contains two units represented by Formula 2 hereinabove, the addition process is preferable. If the metathesis process is used, many of the silicon-bonded hydrogen atoms will react with the alkali metal ions present in the reaction mixture.

When the copolymer useful in this invention contains olefinically unsaturated groups attached to silicon (for example, when R in Formulas 1 or 2 above, is alkenyl or cycloalkenyl such as vinyl or cyclohexenyl) it is preferable to prepare these copolymers by addition of the alkenyloxy-end-blocked oxyalkylene polymer to a monomeric, hydrolyzable silane containing silicon-bonded hydrogen, followed by co-hydrolysis or co-condensation with other hydrolyzable silanes containing silicon-bonded hydrogen and

silicon-bonded olefinically unsaturated hydrocarbon groups using conventional techniques known to those versed in the art. For example, the reaction of

$$CH_2{=}CHCH_2(OC_2H_4)_6OCH_3$$

with CH_3SiHCl_2 in the presence of a platinum catalyst followed by cohydrolysis of the product with

$$CH_2{=}CHSi(CH_3)Cl_2,$$

CH_3SiHCl_2, and $(CH_3)_3SiCl$ gives a copolymer of this invention containing units having the formulas

$$[CH_3O(C_2H_4O)_6CH_2CH_2CH_2Si(CH_3)O]$$

$[CH_2{=}CHSi(CH_3)O]$, and $[CH_3SiHO]$, end blocked with $[(CH_3)_3SiO]$ groups.

The textile materials useful for treatment and resulting in the coated articles of manufacture of this invention can be in the form of single filaments, rovings, yarns, mats, cloth, and the like.

The coated textile materials of this invention can be prepared by conventional procedures for treating textile fibers, yarns and cloth. The coated textile materials can most conveniently be prepared by immersing the textile in a siloxane-oxyalkylene block copolymer, removing the excess liquid by a standard padding procedure and allowing the coating to dry at room temperature. The block copolymer can also be applied to the textile material by brushing, spraying, painting or other convenient methods.

In preparing the coated textile material of this invention, whether by immersion, brushing, spraying or other method, it is preferably to employ a siloxane-oxyalkylene block copolymer in the form of a solution in a volatile liquid organic solvent, or in the form of an aqueous emulsion of the block copolymer.

After applying the solution or emulsion of the block copolymer to the textile material, the excess solvent and/or water is removed by known expedients such as air drying or heating in a vented oven. In some instances, it is also desirable to heat the coated fiber at temperatures up to about 200° C. in order to cure the water repellent coating; however, curing at about room temperature is adequate.

Operable liquid organic solvents include any volatile liquid organic compounds in which the siloxane-oxyalkylene block copolymer is soluble or can be dispersed and which is not injurious to the textile. Illustrative of liquid organic solvents useful in preparing the coated organic textile materials of this invention are the ethers such as diethyl ether, dibutyl ether, ethyl isopropyl ether, dioxane, tetrahydrofuran and ethylene glycol dimethyl ether; a aliphatic hydrocarbons such as petroleum ether, cyclohexane, isoctane and decane; aromatic hydrocarbons such as benzene, toluene, and cumene; halogenated hydrocarbons such as chlorobenzene, chloroform and trichloroethylene; and other solvents such as carbon tetrachloride and disulfide, and the like.

The compositions containing siloxane-oxyalkylene block copolymers useful in this invention, can in addition to a liquid organic compounds and/or water, contain other ingredients conventionally employed in the treatment of organic textiles. For example, the treated compositions can contain emulsifying agents to improve the compatibility of the block copolymer or other ingredients with the liquid organic compound, or can contain a curing catalyst to improve water repellent properties.

Any conventional emulsifying agent used in textile treating compositions, that is, non-ionic, anionic, or cationic emulsifying agents, can be employed. However, for purposes of compatibility, the non-ionic emulsifying agents are normally preferred. Illustrative of these are alkyl ethers of polyalkylene glycols such as polypropylene glycol monobutyl ether, polyethylene glycol 2-ethylhexyl ether and polyethylene glycol monobutyl ether, and esters of polyhydric alcohols such as glycerol monosterate, polyoxyethylenedistearate and propylene glycol monolaurate, or substances such as polyvinyl alcohol. Other operable emulsifying agents include, for example, triethanolamine, propanolamine, morpholine, oleic acid, stearic acid, and the like.

The treating compositions can also contain curing catalysts which function to improve the bond between the coating composition and the textile substrate. Curing catalysts are particularly advantageous with the block copolymers containing silicon-bonded hydrogen atoms used to improve the water repellency of the textile. Suitable curing catalyst include organic salts of lead, tin, zinc, copper, zirconium, titanium, and the like. Preferred organic moieties of such organic salts are the acid radicals derived from fatty acids such as lauric acid, palmitic acid, oleic acid, stearic acid, coconut fatty acid, and 2-ethylhexanoic acid.

The block copolymers of this invention which have the combined properties of forming water repellent coating on textiles and forming stable self-emulsions in water include, for example, those compounds in which the siloxane blocks have a total molecular weight between about 1000 and 3500 and contain primarily methylhydrogen siloxy units and in which the oxyalkylene blocks have a total molecular weight of between about 300 and 3000 and contain primarily ethylenoxy units. Examples of block copolymers which are self-emulsifying and capable of providing water repellent coatings on organic textiles are those prepared by reacting an average of from one to about five of the silicon bonded hydrogen atoms in a polysiloxane having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\Si\\|\\H\end{array}\right)_x SiMe_3$$

wherein x has a value from about 25 to about 40, with the olefinically unsaurtated group of an alkenyloxy endblocked oxyalkylene polymer having the general formula:

$$CH_2{=}CHCH_2O(C_2H_4O)_yMe$$

wherein y has a value from about 5 to about 15.

The present invention is further illustrated by the following examples.

Example 1

The following compositons were prepared employing a block copolymer useful in this invention having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_6\left(\begin{array}{c}Me\\|\\Si{-}O\\|\\CH_2CH_2CH_2O(C_2H_4O)_7Me\end{array}\right)_7 SiMe_3$$

(a) Two grams copolymer, about 96.7 grams water, about 1.3 grams zinc octasol emulsion (curing catalyst) containing about 3 weight percent zinc.

(b) One gram copolymer, about 98.4 grams water, about 0.6 grams zinc octasol emulsion containing about 3 weight percent zinc.

(c) One-half gram copolymer, about 99.2 grams water, about 0.3 grams zinc octasol emulsion containing about 3 weight percent zinc.

(d) Two-tenths of a gram copolymer, about 99.7 grams water, about 0.1 gram zinc octasol emulsion containing about 3 weight percent zinc.

A piece of nylon cloth was immersed in each of the compositions (a) through (d) and then heated for fifteen minutes at 100° C. The anti-static properties of the treated nylon samples were then tested by rubbing the cloth samples on wool and then holding them above cigarette ashes contained in a Petri dish. There was no significant ash pick-up. In contrast to the excellent anti-static properties of the treated cloth, nylon cloth (1) as received and nylon cloth (2) which was heated at 100° C. for fifteen minutes when rubbed on wool and placed over the cigarette ashes picked up layers of ash over the entire surfaces of the samples.

EXAMPLE 2

A block copolymer useful in this invention was prepared which had the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\CH_2CH_2CH_2O(C_2H_4O)_7Me\end{array}\right)\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_{37} SiMe_3$$

This hydrolytically stable block copolymer is referred to hereinafter as Copolymer–I. Two grams of Copolymer–I, about 97 grams water, and about 1 gram zinc octasol emulsion (curing catalyst) containing about 3 weight percent zinc were placed in an eight-ounce jar and shaken. An 8-inch by 8-inch cotton print cloth was placed in the emulsion and shaken for thirty seconds. The cloth was then padded on a padder roll, stretched on a rack and dried at 160° C. for six minutes. The water repellency of the so treated cotton cloth was measured by a standard AATCC spray test and given a spray rating of 90.

The treated cotton cloth was then allowed to stand at room temperature over a week-end, and was again subjected to a standard AATCC spray test. The cloth which had cured at room temperature over the week-end gave a spray rating of 100.

EXAMPLE 3

A mixture was prepared comprising about 50 weight percent of Copolymer–I and about 50 weight percent of a polymer having the formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_{33} SiMe_3$$

This mixture is referred to hereinafter as Mixture–II. Two treating solutions were prepared, one containing two grams of Copolymer–I, about 96.6 grams of water and about 1.4 grams zinc octasol emulsion (curing catalyst) containing about 3 weight percent zinc. A second solution was prepared containing two grams of Mixture–II, about 96.6 grams of water and about 1.4 grams zinc octasol emulsion (curing catalyst) containing about 3 weight percent zinc. Two 8-inch by 8-inch samples of cotton cloth were immersed in each treating solution and shaken for thirty seconds. The treated cloth samples were then padded on padder rolls and dried for five minutes at 100° C. and then five minutes at 160° C. The water repellency of the treated cotton cloth samples was then tested by standard AATCC spray tests before washing, after one washing in a standard automative wash cycle using a commercial detergent, and again after three and five such washings. The results of these tests are summarized in the table below.

SPRAY TEST RESULTS

Treating solution containing—	Cloth sample	After initial treatment	Spray ratings After 1 washing	After 3 washings	After 5 washings
Copolymer-I	1	100	80+	80+	80+
Do	2	100	80+	80+	80+
Mixture-II	1	90	80−	0+	
Do	2	80+	80−	0+	

The foregoing specification and the examples are illustrative. Still other variations within the spirit and scope of this invention will readily present themselves to the skilled artisan.

What is claimed is:

1. An organic textile material coated with a siloxane-oxyalkylene block copolymer comprising (a) at least one siloxane block containing at least two siloxane units represented by the formula:

$$R_bSiO_{\frac{4-b}{2}} \qquad (1)$$

wherein R is a hydrocarbyl radical containing from one to about twenty carbon atoms and selected from the class consisting of monovalent hydrocarbon groups, halogen-substituted monovalent hydrocarbon groups, and divalent hydrocarbon groups and b has a value from 1 to 3 inclusive, and at least one siloxane unit represented by the formula

$$R_e\overset{H_f}{\overset{|}{Si}}O_{\frac{4-e-f}{2}} \qquad (2)$$

wherein R has the meaning defined hereinabove, e has a value from 0 to 2, f has a value from 1 to 2, and e plus f has a value from 1 to 3, said siloxane block containing at least one of said siloxane units wherein at least one R group is a divalent hydrocarbon group and the ratio of the total number of units represented by Formula 1 to the total number of units represented by Formula 2 in the polymer not exceeding 13:1, respectively, and (b) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R'O—, wherein R' is an alkylene group containing from two to about ten carbon atoms, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon group and said copolymer containing from 5 to 95 parts by weight of the polysiloxane block and from 5 to 95 parts by weight of the oxyalkylene block per 100 parts by weight of the copolymer.

2. Nylon cloth coated with a siloxane-oxyalkylene block copolymer having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_6\left(\begin{array}{c}Me\\|\\SiO-\\|\\CH_2CH_2CH_2O(C_2H_4O)_7Me\end{array}\right)_7SiMe_3$$

wherein Me represents the methyl group.

3. Cotton cloth coated with a siloxane-oxyalkylene block copolymer having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\CH_2CH_2CH_2O(C_2H_4O)_7Me\end{array}\right)\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_{37}SiMe_3$$

wherein Me represents the methyl group.

4. A method for improving the water repellency of an organic textile material which comprises applying thereto a liquid siloxane-oxyalkylene block copolymer having (a) at least one siloxane block containing at least two siloxane units represented by the formula:

$$R_bSiO_{\frac{4-b}{2}}$$

wherein R is a hydrocarbyl radical containing from one to about twenty carbon atoms and selected from the class consisting of monovalent hydrocarbon groups, halogen-substituted monovalent hydrocarbon groups, and divalent hydrocarbon groups and b has a value from 1 to 3 inclusive, and at least one siloxane unit represented by the formula

$$R_e\overset{H_f}{\overset{|}{Si}}O_{\frac{4-e-f}{2}} \qquad (2)$$

wherein R has the meaning defined hereinabove, e has a value from 0 to 2, f has a value from 1 to 2, and e plus f has a value from 1 to 3, said siloxane block containing at least one of said siloxane units wherein at least one R group is a divalent hydrocarbon group and the ratio of the total number of units represented by Formula 1 to the total number of units represented by Formula 2 in the polymer not exceeding 13:1, respectively, and (b) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R'O—, wherein R' is an alkylene group containing from two to about ten carbon atoms, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon group and said copolymer containing from 5 to 95 parts by weight of the polysiloxane block and from 5 to 95 parts by weight of the oxyalkylene block per 100 parts by weight of the copolymer; thereafter removing the excess liquid from the textile material; and curing the textile material at least at room temperature.

5. The method of claim 4 wherein at least some of the oxyalkylene groups represented by the formula —R'O— are oxyethylene groups.

6. The method of claim 4 wherein the oxyalkylene groups represented by the formula —R'O— are oxyethylene groups.

7. A method for improving the water repellency of nylon cloth which comprises applying thereto a siloxane-oxyalkylene block copolymer having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_6\left(\begin{array}{c}Me\\|\\SiO\\|\\CH_2CH_2CH_2O(C_2H_4O)_7Me\end{array}\right)_7SiMe_3$$

wherein Me represents a methyl group; thereafter removing the excess polymer from the cloth; and curing the cloth at least at room temperature.

8. A method for improving the water repellency of cotton cloth which comprises applying thereto a siloxane-oxyalkylene block copolymer having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\CH_2CH_2CH_2O(C_2H_4O)_7Me\end{array}\right)\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_{37}SiMe_3$$

wherein Me represents a methyl group; thereafter removing the excess polymer from the cloth; and curing the cloth at least at room temperature.

9. A method for improving the water repellancy of an organic textile material which comprises applying thereto an emulsion of a reaction product of a polysiloxane having the average formula:

$$Me_3SiO\left(\begin{array}{c}Me\\|\\SiO\\|\\H\end{array}\right)_xSiMe_3$$

wherein x has a value of from about 25 to about 40, with the olefinically unsaturated group of an alkenyloxy endblock oxyalkylene polymer having the general formula:

$$CH_2{=}CHCH_2O(C_2H_4O)_yMe$$

wherein Me represents a methyl group and y has a value from about 5 to about 15, the oxyalkylene polymer having reacted with from one to about 5 of the silicon-bonded hydrogen atom in the polysiloxane; thereafter removing the excess emulsion from the textile material; and curing the textile material at least at room temperature.

10. A method for imparting anti-static properties to an organic textile material which comprises applying thereto a liquid siloxane-oxyalkylene block copolymer having (a) at least one siloxane block containing at least two siloxane units represented by the formula

$$R_bSiO_{\frac{4-b}{2}}$$

wherein R is a hydrocarbyl radical containing from one to about twenty carbon atoms and selected from the class consisting of monovalent hydrocarbon groups, halogen-substituted monovalent hydrocarbon groups, and divalent hydrocarbon groups and b has a value from 1 to 3 inclusive, and at least one siloxane unit represented by the formula

$$\mathrm{R}_e\overset{\mathrm{H}_f}{\overset{|}{\mathrm{Si}}}\mathrm{O}_{\frac{4-e-f}{2}}$$

wherein R has the meaning defined hereinabove, e has a value from 0 to 2, f has avalue from 1 to 2, and e plus f has a value from 1 to 3, said siloxane block containing at least one of said siloxane units wherein at least one R group is a divalent hydrocarbon group and the ratio of the total number of units represented by Formula 1 to the total number of units represented by Formula 2 in the polymer not exceeding 13:1, respectively, and (b) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R′O—, wherein R′ is an alkylene group containing from two to about ten carbon atoms, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon group and said copolymer containing from 5 to 95 parts by weight of the polysiloxane block and from 5 to 95 parts by weight of the oxyalkylene block per 100 parts by weight of the copolymer; thereafter removing the excess liquid from the textile material; and curing the textile material at least at room tempertaure.

11. A method for imparting anti-static properties to nylon cloth which comprises applying thereto a siloxane-oxyalkylene block copolymer having the average formula:

$$\mathrm{Me_3SiO}\left(\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{H}\end{array}\right)_6\left(\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{CH_2CH_2CH_2O(C_2H_4O)_7Me}\end{array}\right)_7\mathrm{SiMe_3}$$

wherein Me represents a methyl group; thereafter removing the excess polymer from the cloth; and curing the cloth at least at room temperature.

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