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PROCESS FOR RENDERING KERATINOUS FIBERS RESISTANT TO SHRINKAGE

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U.S. Cl. 117—141 7 Claims

ABSTRACT OF THE DISCLOSURE

Process for treating keratinous fibers with one or more organoposysiloxanes having in the molecule organic substituents containing both imino and amino radicals. The process finds application in rendering wool and other keratinous fibers resistant to shrinkage on laundering.

This invention relates to a shrink resistant treatment for keratinous fibers.

Wool fibers are known to have a scaly, ratchet-like surface which, by reason of interlocking of scales and fiber travel, gives rise to such properties as fulling, felting and shrinking. Unless wool is given a shrinkproofing treatment garments will shrink or felt in use or during washing. Several methods for shrinkproofing are available, these being generally either chemical treatments which modify the structure of the wool by removing the scales or treatments which depend for their effect on the woollen fibers being coated with a resin. Neither type of treatment has been completely successful. The chemical treatments tend to degrade the fibers and the resin treatments tend to be difficult to apply uniformly over the fiber surface and are also liable to give the treated fabric an unsatisfactory hand.

It has been proposed to reduce the shrinkage of wool during laundering by treatment with various organosilicon compounds. For example, in U.K. Pat. Nos. 594,901, 613,267 and 629,329 it is proposed to reduce the normal tendency of wool to shrinkage by treating the wool with certain alkyl or aryl silanes. In U.K. Pat. No. 746,307, there is disclosed a process for preventing the shrinkage of wool in which the wool is treated with a composition consisting of a diorganopolysiloxane, in which the organic substituents are alkyl, phenyl or alkenyl, and a siloxane containing silicon-bonded hydrogen atoms. While the known processes using organosilicon compounds confer a degree of shrink resistance on woollen fabrics, this effect has not been durable to laundering.

There has consequently existed a need for a shrink resistant treatment for wool having improved durability to laundering while retaining as far as possible the softness of the fibers (i.e. a satisfactory hand).

It is the object of this invention to avoid the inadequate properties realized with prior art wool treatments and achieve both softness and durability of shrink resistance by treatment of keratinous fibers with certain aminosiloxane compositions.

Accordingly, this invention provides a process for rendering keratinous fibers resistant to shrinkage which comprises applying thereto from 0.5 to 10% by weight based on the weight of the fibers of one or more organopolysiloxanes of the unit general formula

$$R_nSiO_{\frac{4-n}{2}}$$

wherein n has an average value of from 1.9 to 2.1 and R represents an organic radical attached to silicon through a silicon to carbon bond, from 0.25 to 50 percent of the total R substituents being monovalent radicals having less than 30 carbon atoms and containing at least 3 carbon

atoms and at least one primary or secondary amino radical —NX_2, wherein X represents hydrogen, an alkyl radical or an aryl radical, the remaining R groups (i.e. from 99.75 to 50 percent of the total R substituents) being selected from the group consisting of hydrogen atoms, monovalent hydrocarbon radicals, halohydrocarbon radicals, carboxyalkyl radicals and cyanoalkyl radicals containing 1 to 30 carbon atoms, and at least 70 percent of said remaining R substituents being monovalent hydrocarbon radicals having less than 19 carbon atoms.

The invention also includes a shrink resistant keratinous fibers whenever treated according to said process.

In the polyorganosiloxanes employed in the process of this invention, at least 0.25 percent and up to 50 percent of the total R substituents should consist of the specified amino and imino-containing monovalent radicals. The preferred organopolysiloxanes are, however, those in which the amino and imino-containing substituents comprise from 1 to 5 percent of the total R substituents.

The amino radicals present in the R substituents are those of the formula —NX_2 wherein X represents a hydrogen atom, an alkyl radical or an aryl radical, at least one X being hydrogen. Preferably, the alkyl and aryl radicals represented by X are those having less than 19 carbon atoms and are, e.g. methyl, ethyl, propyl, butyl, octadecyl or phenyl.

The amino and imino-containing substituents may contain up to 30, preferably from 3 to 11, carbon atoms. The nitrogen atom of any imino or amino radical in R should be linked to the silicon atom through a chain of at least 3 carbon atoms. Examples of the operative imino and amino-containing substituents are the —

$$—(CH_2)_3NHCH_2CH_2NH_2$$
$$—(CH_2)_4NHCH_2CH_2NH_2$$
$$—CH_2CH\cdot CH_3CH_2NHCH_2CH_2NH_2 \text{ and}$$
$$—(CH_2)_3NH(CH_2)_6NH\cdot CH_3$$

radicals, the first and third of these being preferred on the basis of commercial availability. Also operative are polyalkyleneimine radicals, e.g. those of the general formula

$$R''_2NCH_2CH_2(NHCH_2CH_2)_xNH_yR'—$$

wherein each R'' is a hydrogen atoms, an alkyl radical or an aryl radical of 1 to 18 carbon atoms, x has a value from 1 to 10 inclusive, y is 1 or 2 and R' is a saturated divalent or trivalent hydrocarbon radical having at least 3 carbon atoms. The remaining R groups bonded to silicon (i.e. 50 to 99.75 percent of the total R groups) can be hydrogen atoms, hydrocarbon radicals, halohydrocarbon radicals, cyanoalkyl radicals or carboxyalkyl radicals. The organic substituents contain 1 to 30 (preferably 1 to 18) carbon atoms. At least 70 percent of the remaining R substituents in the polyorganosiloxane are monovalent hydrocarbon radicals having less than 19 carbon atoms. Such radicals include alkyl radicals, e.g. methyl, ethyl, propyl, nonyl, tetradecyl and octadecyl, aryl radicals, e.g. phenyl and naphthyl, aralkyl radicals, e.g. benzyl and beta-phenylethyl, alkaryl radicals, e.g. ethylphenyl, and alkenyl radicals, e.g. vinyl and allyl. A proportion of the remaining R substituents may be other than hydrocarbon radicals, for example, hydrogen atoms, halogenated hydrocarbon radicals, e.g. chlorophenyl and other substituted hydrocarbon radicals, e.g. carboxyalkyl and cyanoalkyl. Preferably, substantially all of the remaining R substituents are methyl radicals.

The preferred polyorganosiloxanes, therefore, include copolymers of dimethylsiloxane units with delta-aminobutyl(methyl)siloxane units or gamma-aminopropyl (methyl)siloxane units, copolymers of dimethylsiloxane units with methyl(N - beta - aminoethyl-gamma-aminopropyl)siloxane units and copolymers of dimethylsiloxane

units with methyl(N-beta-aminoethyl-gamma-aminoisobutyl)siloxane units. If desired, the copolymers can be end-stopped with suitable chain terminating units, for example, trimethylsiloxane units, dimethylphenylsiloxane units and dimethylvinylsiloxane units. Also, if desired, at least some of the imino and amino-containing substituents can be present in the chain terminating units.

Methods of preparing the polyorganosiloxanes employed in the process of this invention are well known in the art.

The polyorganosiloxanes can vary in consistency from low molecular weight freely flowing liquids having a viscosity of 100 cs. or less at 25° C. to viscous gummy materials having viscosities in excess of 100,000 cs. at 25° C. The molecular weight of the polysiloxane used will depend primarily on the desired nature of the shrink-proofing coating. Lower molecular weights make for a harder, more durable coating but require a higher pick up of siloxane by the fiber for a given shrink-proofing effect than do the higher molecular weights. Organopolysiloxanes having an average degree of polymerization in the range from 50 to 400 are generally preferred.

Any suitable coating of impregnating technique may be employed in carrying out the application of the polyorganosiloxane to the fiber according to the process of this invention. The organosiloxane may be applied as such or, more preferably, as a dispersion or solution in a liquid carrier. Suitable carriers include organic solvents, for example, hydrocarbons and halogenated hydrocarbons, e.g. benzene, hexane or perchloroethylene. Conveniently, the polyorganosiloxane is applied by spraying or by immersion of the fiber in an organic solvent solution of the polyorganosiloxane. The term keratinous fibers as employed herein includes fibers of any animal hair, for example, sheep wool, mohair, cashmere, alpaca wool and vicuna wool. The fibers may be treated in any desired form, for example, as yarn, as fabric or as made up or partially made up goods. In general, the best results are obtained with keratinous fibers which have been chlorinated.

The application conditions should be chosen such that the pick up of polyorganosiloxane by the fiber is from 0.5 to 10% by weight of polyorganosiloxane based on the weight of the fiber. In most cases, the desired property is attained with less than 10% by weight and it is preferred to use from 0.5 to 5%.

After application of the organopolysiloxane, the fibers are dried and aged to fix the siloxane on the fiber. Although some fixation may occur on aging at room temperature, inconveniently long aging periods are required to obtain optimum results. Drying of the fiber and fixing of the siloxane is, therefore, preferably achieved by heating the treated fibers to temperatures in the range from 40 to 160° C. for from one minute to one hour.

If desired, the polyorganosiloxane may be applied in conjunction with organosiloxanes of the type normally employed as water repellent treatments for fibers, for example, polydimethylsiloxanes, methylhydrogenpolysiloxanes and mixtures of the two.

The following examples illustrate the invention.

Example 1

An organopolysiloxane having a viscosity of 20,000 cs. at 25° C. and composed of 3 mole percent of methyl(N-beta,aminoethyl-gamma-aminoisobutyl)siloxy units, 97 mole percent of dimethylsiloxy units and end-stopped with trimethylsiloxy units was dissolved in toluene in a proportion of 5 parts by weight of polysiloxane to 95 parts by weight of toluene.

This solution was used to treat 3 samples of 1:1 cover factor knitted botany wool fabric by padding at 100% mangle expression. After treatment, the samples were allowed to air dry at 22° C. for 1 hour and then placed in an air circulating oven for 5 minutes at 110° C.

A square of 20 cm. side was marked out on each of the treated samples employing a template and the samples were then washed in a 1.25% by weight pH 7 phosphate buffer solution containing 1 g./liter of sodium dioctyl sulphosuccinate. The temperature of the wash water was 40° C. and washing was carried out in an International Cubex machine according to the method of IWS Specification W.S.S. 128, Test Method No. 101.

After 5 minutes, the wash was interrupted and the dimensions of the marked square measured with the fabric in the wet state. The wash was then continued for 3 hours after which time the marked square was measured again.

The area felting shrinkage of the samples was then calculated according to the formula

$$\text{Percent area felting shrinkage (FS)} = [\text{percent width shrinkage (WS)} + \text{percent length shrinkage (LS)}] - \frac{[WS \times LS]}{100}$$

The width shrinkage and length shrinkage were determined according to the formula

Width or length shrinkage=dimension after 5 minutes—dimension after 3 hours.

The average value of percentage area felting shrinkage for the 3 samples was 13.1%. The value for untreated wool fabric when subjected to the same test procedure was 71%.

Example 2

The procedure of Example 1 was repeated except that the organopolysiloxane was replaced with one having the same molecular composition but having a viscosity of 5000 cs. at 25° C.

The value of percentage area felting shrinkage was 20.5%.

That which is claimed is:

1. A process for rendering keratinous fibers resistant to shrinkage which comprises applying thereto from 0.5 to 10 percent by weight, based on the weight of the fibers of at least one organopolysiloxane liquid having a viscosity in the range from 100 cs. to 100,000 cs. at 25° C. of the unit formula

$$R_nSiO_{\frac{4-n}{2}}$$

wherein n has an average value of from 1.9 to 2.1 and R represents an organic radical attached to silicon through a silicon to carbon bond, from 0.25 to 50 percent of the total R substituents being monovalent radicals composed of carbon, hydrogen and nitrogen, said radicals having less than 30 carbon atoms and containing at least 3 carbon atoms distant from the silicon atom at least one imino and at least one primary or secondary amino radical —NX_2 wherein X represents a hydrogen atom, an alkyl radical or an aryl radical, the remaining R substituent being selected from the group consisting of hydrogen atoms, monovalent hydrocarbon radicals, monovalent halogenated hydrocarbon radicals, carboxyalkyl radicals and cyanoalkyl radicals, said radicals containing 1 to 30 carbon atoms, at least 70 percent of the remaining R substituents being monovalent hydrocarbon radicals having less than 19 carbon atoms and thereafter drying the fiber and fixing the siloxane by heating the treated fibers to a temperature in the range from 40° to 160° C. for from one minute to one hour.

2. A process as claimed in claim 1 wherein the imino and amino-containing substituents have from 3 to 11 carbon atoms.

3. A process as claimed in claim 1 wherein the imino and amino-containing radicals comprise from 1 to 5 percent of the total silicon-bonded substituents in the organopolysiloxane.

4. A process as claimed in claim 2 wherein the imino and amino-containing radicals are the

$$-(CH_2)_3NHCH_2CH_2NH_2$$

or $-CH_2 \cdot CH \cdot CH_3CH_2NHCH_2CH_2NH_2$ radicals.

5. A process as claimed in claim 2 wherein the substituents present in addition to those containing imino and amino radicals are substantially all methyl radicals.

6. A process as claimed in claim 1 wherein the organopolysiloxane is applied in a proportion of from 0.5 to 5% by weight based on the weight of the fibers.

7. A process as claimed in claim 1 wherein the keratinous fibers have been chlorinated prior to application of the organopolysiloxane.

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8—128 A; 117—139.5 A, 161 ZA