United States Patent

Tichenor

[15] 3,655,420

[45] Apr. 11, 1972

[54] SYNTHETIC ORGANIC TEXTILE FIBER WITH IMPROVED, DURABLE, SOFT, LUBRICATED FEEL

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[22] Filed: **Mar. 6, 1970**

[21] Appl. No.: **17,205**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 813,280, Apr. 3, 1969, abandoned.

[52] **U.S. Cl.** .....**117/138.8 A,** 8/115.6, 117/138.8 UA, 117/138.8 N, 117/138.8 F, 117/139.5 A, 117/161 ZA, 117/161 ZB, 252/8.6, 260/824 EP

[51] **Int. Cl.** **D06m 15/66,** D06c 19/00

[58] **Field of Search** .....117/138.8 UA, 138.8 F, 138.8 N, 117/139.5 CQ, 139.5 A, 161 ZA, 161 ZB; 8/115.6; 252/8.6; 260/348 SC, 825, 824 EP, 29.2 M

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[57] **ABSTRACT**

Process comprising treating synthetic organic textile fibers with a finishing composition that is (1) a mixture of a polyepoxide and an aminosiloxane, (2) a mixture of an epoxysiloxane and a polyamine, or (3) a mixture of an epoxysiloxane and an aminosiloxane, and thereafter curing said composition by subjection to elevated temperature. The treated fibers possess a durable, soft, lubricated feel.

5 Claims, 3 Drawing Figures

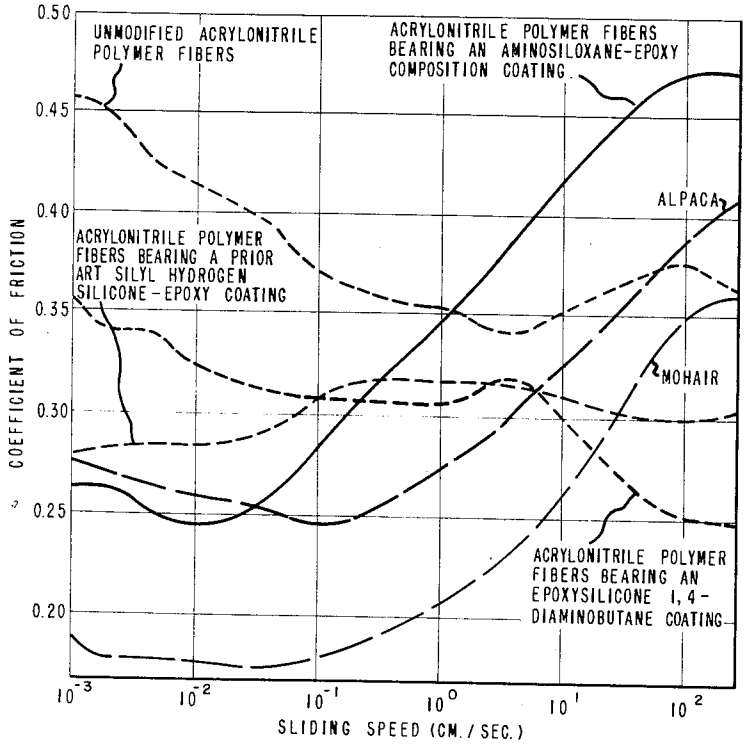
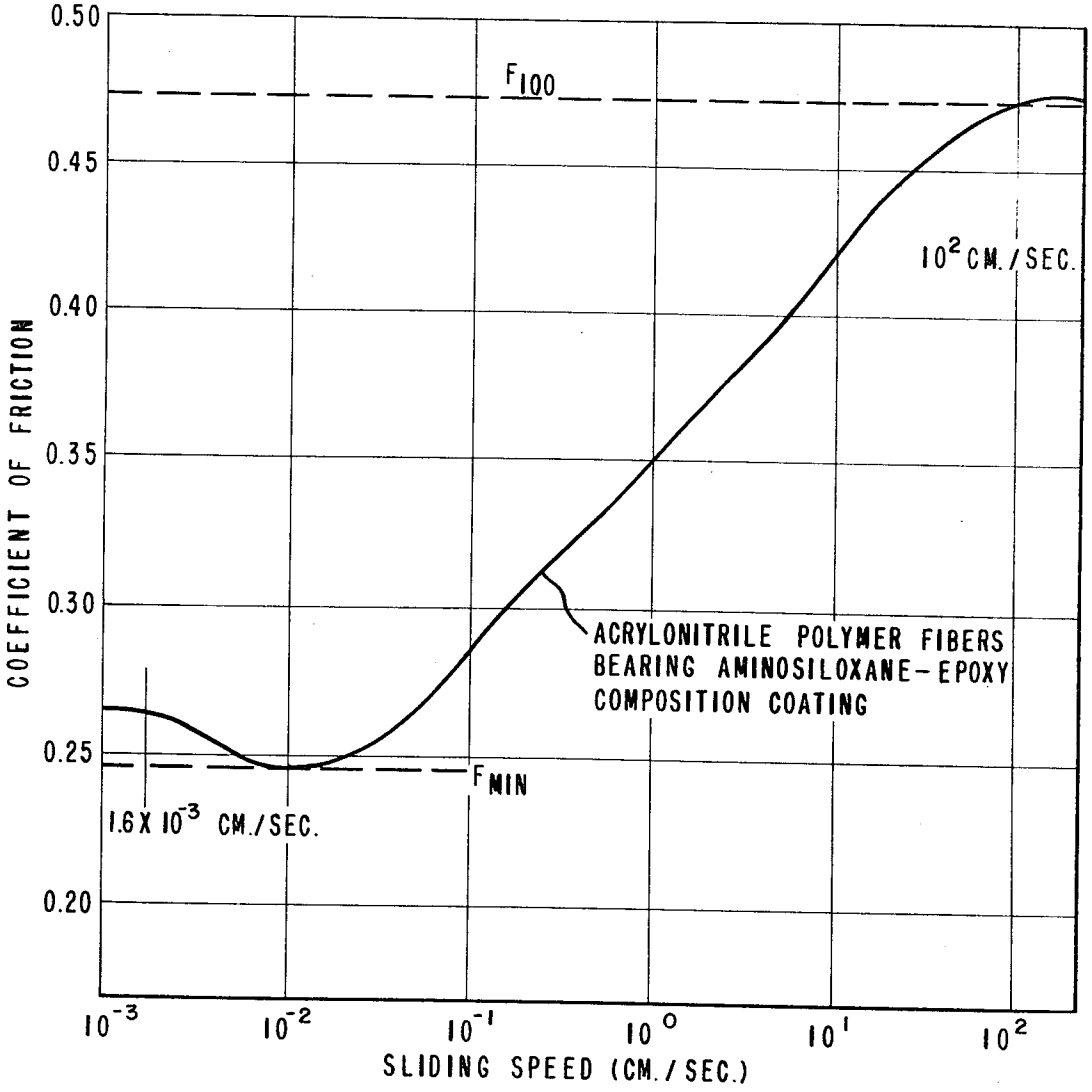


FIG. 1

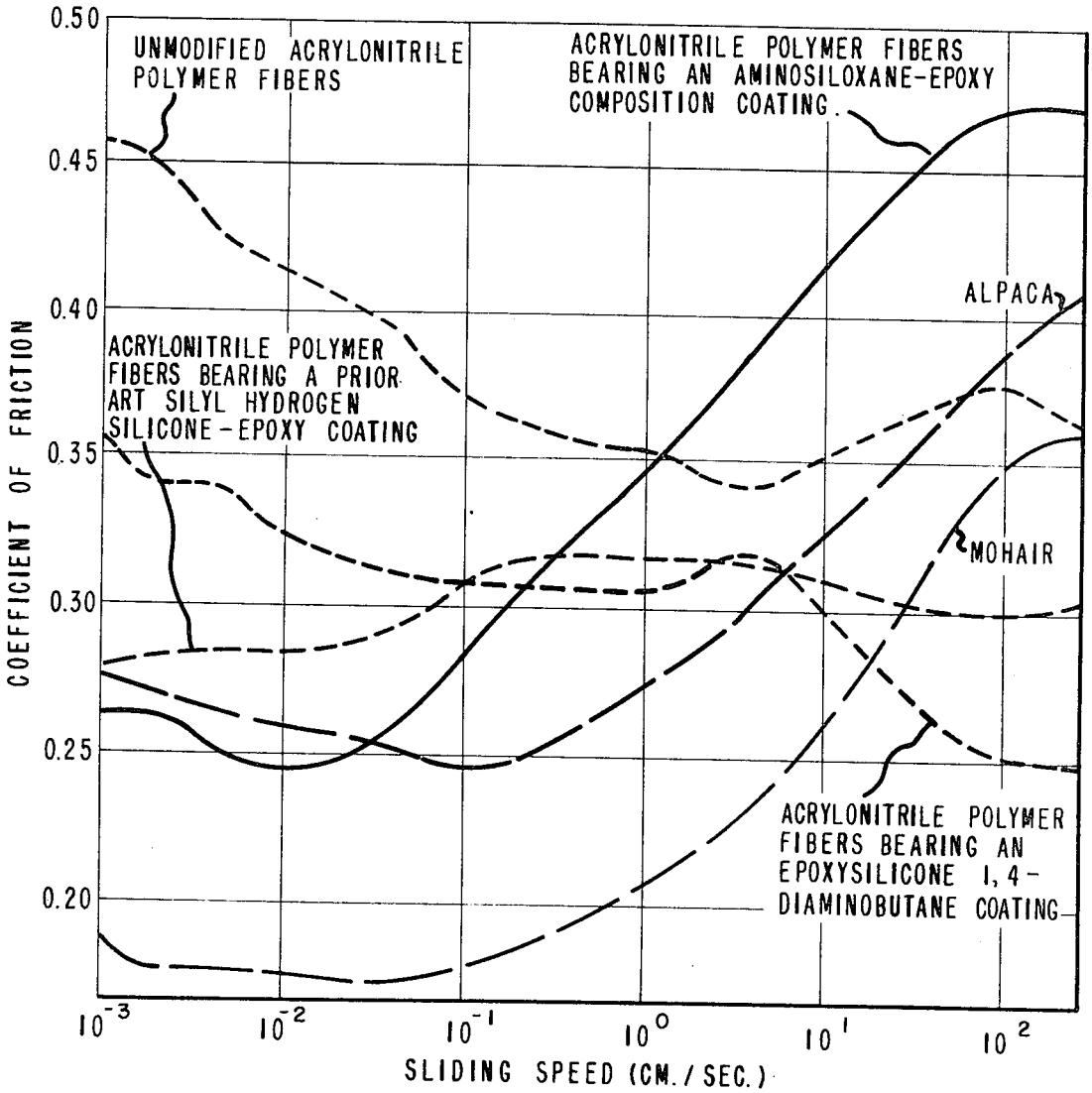


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FIG. 2

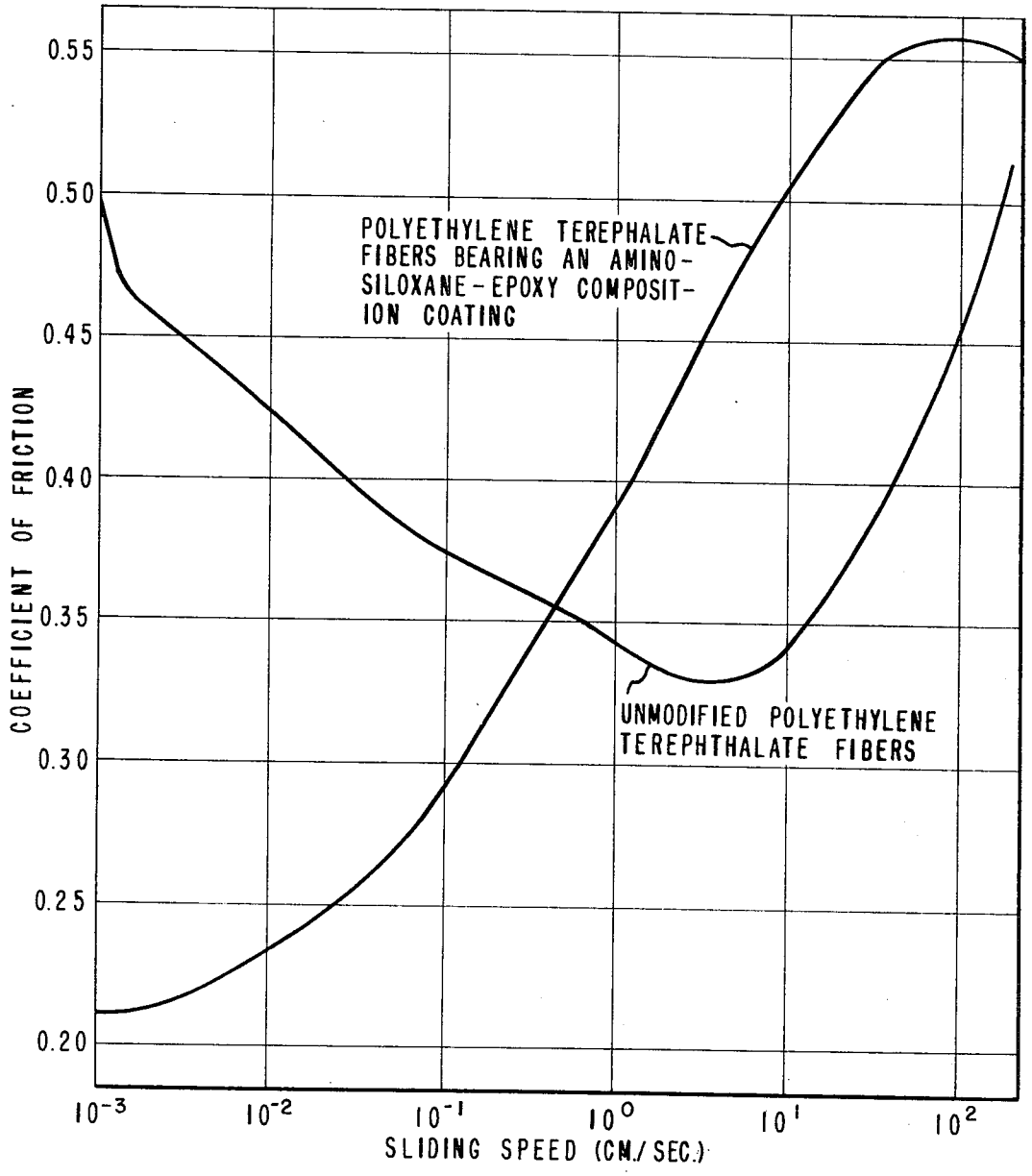


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FIG. 3



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SYNTHETIC ORGANIC TEXTILE FIBER WITH IMPROVED, DURABLE, SOFT, LUBRICATED FEEL

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of application Ser. No. 813,280, filed Apr. 3, 1969, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to synthetic organic textile fibers, and, more particularly, to treating such fibers to provide a durable, soft, lubricated feel.

It is desired to provide a technique for producing textile fibers having a durable, soft, lubricated feel similar to that possessed by cashmere and other luxury animal fibers such as alpaca and mohair. Some temporary finishes have been used to impart the cashmere feel to fibers, but these finishes are removed by washing. Thus, condensation products of long chain fatty acids, acid chlorides, or acid anhydrides with alkanolamines yield finishing compositions which impart a soft, slick hand to fibers, but which are not fast to washing.

Somewhat more durable and otherwise satisfactory finishes are the silicones. These are made by hydroylsis of various mixtures of mono-, di-, and tri-alkyl chlorosilanes followed by condensation in which water is split out from two or more different molecules. The resulting polymers impart a pleasant, lubricated feel to synthetic organic fibers. If the silicone is made from an alkyl hydrogen-chlorosilane so that the polymer will contain some hydrogen groups bonded directly to silicon, (i.e., silyl hydrogen), the finish will be somewhat durable because cross-linking will occur as the silicon hydrogen groups are hydrolyzed to silanol and these condense to form interchain bridges. But even these silicones will not resist repeated scouring.

Greatly improved scouring resistance is provided by finishes applied as aqueous dispersions of polyepoxides and of siloxanes containing silyl hydrogen atoms. However, these dispersions are not storage-stable, and can produce nonuniform results in commercial practice, because cross-linking reactions commence prior to application especially in the presence of acidic, alkaline, or metallic ion impurities, or when the temperature of the dispersion is elevated.

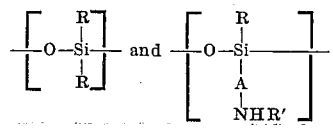
Improved scouring resistance is also provided by finishes known heretofore made from reactive siloxanes containing free amine groups and a serially-applied fixative containing diisocyanate groups or other groups complementary to amines. However, the serial application process is expensive and complex, imposes requirements of immiscibility between the two solutions or dispersions, and is limited to such mixing of siloxane and fixative as can occur after application.

The pleasant, lubricated feel imparted to synthetic organic fibers by silicone finishes has been attributed to the lower coefficient of friction of fibers coated with the finish with respect to the uncoated fibers. While the synthetic organic fibers coated with the silicone finishes available hitherto have been regarded as more similar to the luxury animal fibers than are the uncoated fibers, a need has been felt for such fibers having a highly durable finish still more closely resembling the characteristics of the luxury animal fibers. An additional need is for a simple process for applying durable silicone finishes onto textile fibers.

SUMMARY OF THE INVENTION

The present invention broadly provides a process for treating synthetic organic textile fibers with a finishing composition that is (1) a mixture of a polyepoxide and an aminosiloxane, (2) a mixture of an epoxysiloxane and a polyamine, or (3) a mixture of an epoxysiloxane and an aminosiloxane. Specifically, this invention provides a process for treating synthetic organic textile fibers comprising applying to said fibers a finishing composition and thereafter curing said composition by subjection to elevated temperature said composition being selected from the group consisting of:

1. a mixture of about 0.05 to 3 parts by weight of a soluble epoxy compound having at least two epoxy groups per molecule, together with 1 part by weight of a liquid aminosiloxane wherein there is one oxygen atom bridging each pair of neighboring silicon atoms and all other silicon valences are bonded only to carbon atoms, said aminosiloxane consisting essentially of repeating units of the formulae:



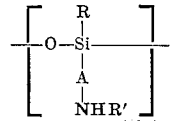
wherein

R is a lower alkyl or aryl group,

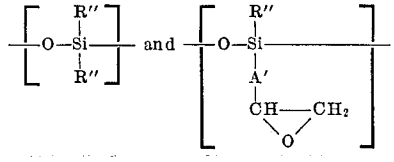
R′ is hydrogen or a lower alkyl or aryl group,

A is an alkylene group having two to five carbon atoms or an arylene or substituted arylene group having six to 10 carbon atoms, provided R′ and A are selected so that not more than one aromatic ring is attached directly to the amino nitrogen atom,

said aminosiloxane containing at least 35 of said repeating units at least two of which have the formula:



2. a mixture of about 0.3 to 20 parts by weight of a liquid epoxysiloxane wherein there is one oxygen atom bridging each pair of neighboring silicon atoms and all other silicon valences are bonded only to carbon atoms, said epoxysiloxane consisting essentially of repeating units of the formulae:

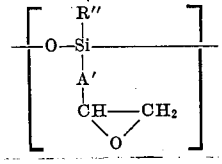


wherein

R″ is a lower alkyl or aryl group,

A′ is an alkylene group having two to five carbon atoms or an arylene or substituted arylene group having six to 10 carbon atoms,

said epoxysiloxane having an epoxy group content of at least 1 percent based on the total weight of said epoxysiloxane, and containing at least 35 of said repeating units at least two of which have the formula:



together with 1 part by weight of an amine compound having at least two amino groups per molecule, wherein each of said amino groups has at least one hydrogen atom and not more than one aromatic ring attached directly to the nitrogen atom; and

3. a mixture of about 0.05 to 20 parts by weight of said epoxysiloxane together with 1 part by weight of said aminosiloxane.

The products of this invention possess a durable, soft, lubricated feel. The preferred products are fibers coated with a cross-linked (i.e., cured) composition of an aminosiloxane and a polyepoxide or epoxysiloxane, i.e., mixture (1) or (3).

above. These preferred fibers possess a remarkable resemblance to the feel of such luxury animal fibers as cashmere, alpaca and mohair. Such a cross-linked mixture of an aminosiloxane and a polyepoxide or epoxy-siloxane is herein referred to as an "aminosiloxane-epoxy composition."

BRIEF DESCRIPTION OF THE DRAWINGS

The drawings are plots of the friction coefficients, measured over a wide range of sliding speeds, of various fibers. The shape of these plots has been found to correlate well with the feel of fibers.

FIG. 1 is a plot of the friction coefficient, measured over a wide range of sliding speeds, of a sample of acrylonitrile polymer fibers coated with a preferred aminosiloxane-epoxy composition of this invention.

FIG. 2 is a plot of the sample shown in FIG. 1, superimposed on corresponding plots of samples of alpaca and mohair, untreated fibers of acrylonitrile polymer, fibers of acrylonitrile polymer coated with an epoxysiloxane-polyamine composition, and fibers of acrylonitrile polymer coated with a certain cured siloxane composition of the prior art.

FIG. 3 is a plot of samples of untreated polyethylene terephthalate fibers and polyethylene terephthalate fibers treated with an aminosiloxane-epoxy composition of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of this invention broadly comprises treating synthetic organic textile fibers with a finishing composition that is (1) a mixture of a polyepoxide and an aminosiloxane, (2) a mixture of an epoxysiloxane and a polyamine, or (3) a mixture of an epoxysiloxane and an aminosiloxane, and then heating the treated fibers to cure the composition. This process produces textile fibers having a durable, soft, lubricated feel. The fiber finishes obtained in accordance with this invention are more durable than the finishes obtained with the aminosiloxane or the epoxysiloxanes when used alone. The aminosiloxane when used alone remains fluid and tacky, but when combined on the fiber with a polyepoxide or with an epoxysiloxane it gives a soft, dry, slick hand to fibers and to fabrics made from the fibers. Similar synergistic results are obtained when the epoxysiloxane is reacted with a polyamine.

All of the fiber finishes provided by the process of this invention are highly durable on the fiber and impart a pleasant, lubricated feel to the fiber, as contrasted with the corresponding untreated fiber. Moreover, it has unexpectedly been found that synthetic organic fibers bearing an aminosiloxane-epoxy composition exhibit frictional characteristics over a range of measuring speeds highly analogous to the frictional characteristics of luxury animal fibers. Garments made of the fibers coated with the aminosiloxane-epoxy composition have a slick, soft feel markedly resembling the feel of garments made of luxury animal fibers. Surprisingly, the luxurious feel of garments of these fibers is long-lasting and persists throughout many laundering or dry cleaning cycles to which the garment is subjected during normal wear.

The character of the desirable frictional behavior of the synthetic organic fibers bearing the aminosiloxane-epoxy composition will be more clearly understood by reference to the accompanying figures, which are plots of the friction coefficients, measured over a wide range of sliding speeds, of various fibers. Referring to FIG. 1, the coefficient of friction vs. sliding speed of an acrylonitrile terpolymer coated with an aminosiloxane-epoxy composition as described in Example XIII is plotted in the manner described hereinafter. It will be observed that the coefficient of friction curve of this fiber of the present invention is characterized by a relatively low initial coefficient of friction; the curve dips slightly lower to a minimum (F_{min}) as the sliding speed is increased, and then rises sharply and progressively as the sliding speed is increased to 100 cm./sec. (F_{100}). This characteristic curve is observed with other fibers of this invention having an aminosiloxane-epoxy composition coating.

It has been discovered that natural luxury animal fibers also have similar characteristic curves. Referring to FIG. 2, it will be seen that with alpaca and mohair, for example, the coefficient of friction is initially relatively low, and dips slightly lower to a minimum as the sliding speed increases, and then rises sharply and progressively as the sliding speed is increased to 100 cm./sec. Thus the coefficient of friction curve for the fiber of this invention (the curve shown in FIG. 2 is the same as shown in FIG. 1) has the same characteristics as the natural luxury fibers. By contrast, the coefficient of friction of an untreated acrylonitrile polymer fiber shows a sharp progressive decrease as the sliding speed is increased, followed by only a modest rise, and at 100 cm./sec., it is substantially lower than the initial value. The acrylonitrile polymer fibers having other silicone-epoxy coatings (also described in Example XIII) also have markedly different coefficient of friction curves as shown in FIG. 2.

Thus, FIG. 2 graphically illustrates the phenomenon that the acrylonitrile polymer fibers of the present invention coated with an aminosiloxane-epoxy composition feel to the human hand remarkable similar to the natural luxury fibers. Other silicone-epoxy compositions, including prior art compositions such as silyl hydrogen silicone-epoxy compositions, while providing considerable improvement in slickness compared to unmodified acrylonitrile polymer fibers, do not realistically simulate the feel of the natural luxury fibers. FIG. 3 illustrates the characteristic coefficient of friction curve of a polyethylene-terephthalate fiber treated in accordance with this invention as described in Example XVII.

Plots of the coefficient of friction of fibers, with respect to the sliding speed at which the measurement is made, are prepared as follows, except where otherwise specified. The test is carried out on staple fibers, and if the sample is submitted as a tow it is first cut to staple fibers, preferably about 3 inches in length. A 2.0 g. sample of the staple fibers is carded by hand until the fibers are roughly parallel and lie as a sheet on one of the sample cards. About 0.8 g. of this card "web" is laid onto the surface of 2-inch wide, two-sided pressure-sensitive tape, wrapped around a 2-inch diameter cardboard tube. Fibers are distributed axially around the tube to provide an even coverage of the tape. Both ends of the fiber-covered tape are then wrapped with narrow masking tape to anchor them more firmly.

An 0.25 g. portion of the carded fibers is then applied evenly to the surface of a 1×9-inch strip of one-sided pressure-sensitive plastic tape. Since the tape is longer than the fibers, it is necessary to apply them in overlapping sheets, similar to application of shingles on a roof. The last half inch of each end of the tape is not covered with fibers and is folded over to provide a reinforced anchorage for attachment to the apparatus to measure friction.

The staple-covered tape is draped over the staple-covered cylinder to provide 180° contact. The fibers at the interface contact each other at approximately right angles. One end of the tape is attached to a force-recording cell and the other is attached to a static load of 30 g. The cylinder is then rotated so that its circumference turns in the direction from the force-recording cell to the static load. Friction force data are recorded at sliding speeds ranging from 1.6×10^{-3} to 100 cm./sec. depending on the rotating speed of the cylinder.

Friction coefficients are calculated using the following equation:

$$T_2/T_1 = e^{F\theta}$$

T_2 = Frictional force from strain gauge.

T_1 = Weight attached to staple-covered tape.

θ = Contact angle of tape with cylinder in radians = 3.14.

F = Friction coefficient.

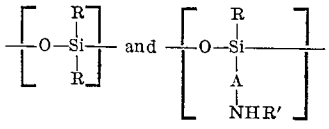
A curve such as that shown in FIG. 1 is plotted and a mathematical ratio is calculated. This ratio, called the "Objective Preference Index" and abbreviated "OPI" is obtained by dividing the difference between the value of the coefficient of friction at 100 cm./sec. (F_{100}) and the value of the coefficient of friction at the minimum point in the curve (F_{min}) by the coefficient of friction at the minimum point (F_{min}) in ac-

cordance with the equation:

$$OPI = (F_{100} - F_{min})/F_{min}$$

The present invention provides not only excellent fiber properties, but also marked process advantages. The components are intimately mixed before application, so that uniformity of the cured finish is promoted and only a single application is made. Only two components are required to be mixed together, which provides a simple mixing procedure. The aqueous dispersions of each component are relatively storage-stable, which promotes uniform results in commercial practice. Finally, the curing step takes place rapidly and smoothly.

Aminosiloxanes suitable for use in this invention are characterized by being liquid and by having one oxygen atom bridging each pair of neighboring silicon atoms, and all other silicon valences being bonded only to carbon atoms. Thus, these aminosiloxanes have no silyl hydrogen atoms. These aminosiloxanes are further characterized by consisting essentially of repeating units of the formulae:



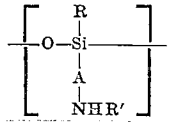
wherein

R is a lower alkyl or aryl group,

R′ is hydrogen or a lower alkyl or aryl group,

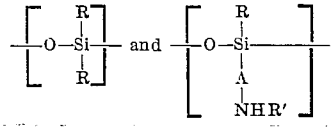
A is an alkylene group having two to five carbons or an arylene group or substituted arylene group having six to 10 carbons, provided R′ and A are selected so that not more than one aromatic ring is attached directly to the amino nitrogen atom.

These aminosiloxanes contain both types of repeating units, and contain a total of at least 35, preferably 100 to 600, of these repeating units, at least two, preferably four to 20, of which are units of the formula:



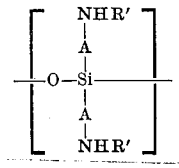
The degree of polymerization, i.e., the average total number of these two repeating units per molecule, may be as high as 1,500 or even higher, provided the aminosiloxane is liquid. The lower alkyl groups in these aminosiloxanes generally have one to four carbon atoms and the lower aryl groups generally have six to nine carbon atoms. Thus, R may be, for example, methyl, ethyl, propyl, isopropyl or phenyl.

The repeating units, i.e., the



groups usually, but not always, occur randomly in these aminosiloxanes. The aminosiloxanes consist essentially of these two repeating units. Minor amounts of other types of units may be present, provided that the basic properties of the aminosiloxane are not significantly altered, and provided all silicon atoms in the compound are bonded only to oxygen and carbon atoms as described above. Branching units may be incorporated in minor amounts to obtain branched compounds, provided the compounds are liquid. The terminal end groups are usually trialkyl silyl groups, although other terminal end groups, such as hydroxyalkyl silyl groups or non-silicon-containing groups may be used or there may be no terminal end groups if the molecule is a ring.

If desired, additional amino groups may be present in the second repeating unit shown immediately above, for example, by substituting the R group to provide a unit of the formula:



Also, the R′ group may be replaced with additional —A—NHR′ radicals. It is essential that the amino group be separated from each other and from the silicon atoms by a connecting chain of at least two carbon atoms.

A range of aminosiloxanes having variable weight percentages of amine groups and variable degrees of polymerization are useful. Since aminosiloxanes with a high degree of polymerization are too viscous for easy application, the preferred aminosiloxanes have a degree of polymerization of 100 to 600. The amine content may range from about 0.1 percent to about 5 percent by weight. However, the amine content is from about 1 percent to about 3 percent by weight in the preferred aminosiloxanes, i.e., those used in preparing the optimum fiber products having the highest values for Objective Preference Index and the greatest similarity to the natural animal fibers.

The soluble epoxy compounds used in this invention, also referred to herein as "polyepoxides," are characterized by having at least two epoxy groups per molecule. These polyepoxides must not be significantly cross-linked, and thus, are further characterized by being soluble in any suitable solvent, such as absolute ethanol. This limitation does not imply that the polyepoxide must be soluble in the liquid medium, if any, in which the finishing compound is prepared. A diepoxide such as resorcinol diglycidyl ether is a suitable polyepoxide for use in this invention. Other suitable polyepoxides may be conveniently made by reacting epichlorhydrin with a polyhydroxy compound. One of the preferred polyhydroxy compounds is glycerol. The preparation of polyepoxides from epichlorhydrin and glycerol is described in U.S. Pat. No. 2,872,428.

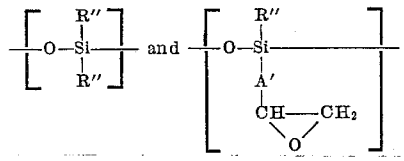
Other suitable polyhydroxy compounds include bisphenol A [i.e., 2,2-bis(4-hydroxy phenyl)propane]; 4,4′-dihydroxy diphenyl ether; 4,4′-dihydroxy benzophenone; ethylene glycol; diethylene glycol; and propylene glycols. Polyethylene oxide derivatives made by reacting ethylene oxide with polyhydroxy compounds are also suitable for reacting with epichlorhydrin. Thus, glycerol, ethylene glycol and the polyhydroxy aromatic derivatives listed above may first be reacted with from 1 to 20 moles of ethylene oxide before reacting with epichlorhydrin. Further details of the preparation of suitable polyepoxides are given in U.S. Pat. No. 2,913,356.

When epichlorhydrin reacts with a hydroxy group, it forms an ether. But the epoxy group can react either with a hydroxy group or with another epoxy group so that the resulting products are polymers, rather than simple epoxy ethers. For the purposes of this invention, it is preferable to use low molecular weight polymers or the simple polyepoxy compounds. Polyepoxides with molecular weights of not over 5,000 are acceptable, but products in the range up to 1,000 are preferred. In most cases, the products used are mixtures of various molecular weights and may contain, and preferably do contain, some monomeric compounds having two or more epoxide groups. Diglycidyl ether itself may be used.

It is preferred that the polyepoxides be water soluble or easily water dispersible for convenience in using, but they can be used in organic solvents, if desired.

Polymers containing epoxide groups and siloxane groups in the same molecule, as disclosed in U.S. Pat. No. 3,055,774 to Gilkey et al., are also useful in this invention. Disiloxanes such as 1,3-bis-(3-glycidoxypropyl)tetramethyl-disiloxane or low molecular weight polysiloxanes containing more than one epoxide group per molecule will yield slick fibers when cross-

linked with aminosiloxanes. Epoxy-modified polysiloxanes are particularly useful in combination with the aminosiloxanes and polyamines of this invention. Epoxy siloxane compounds of this type are characterized by being liquid and by having one oxygen atom bridging each pair of neighboring silicon atoms, and all other silicon valences being bonded only to carbon atoms. Thus, these epoxysiloxanes have no silyl hydrogen atoms. These epoxysiloxanes are further characterized by consisting essentially of repeating units of the formulae:

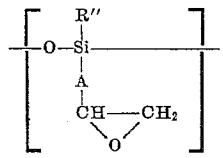


wherein

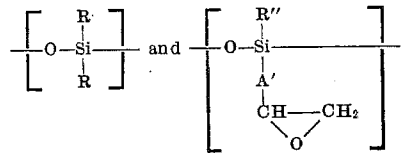
R'' is a lower alkyl or aryl group,

A' is an alkylene group having two to five carbon atoms or an arylene or substituted arylene group having six to 10 carbon atoms.

These epoxysiloxanes contain both types of repeating units, and contain a total of at least 35, preferably 100 to 600, of these repeating units, at least two, preferably four to 20 of which are units of the formula:

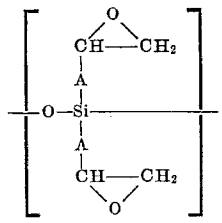


The epoxy group content of these epoxysiloxanes must be at least 1 percent based on the total weight of the compound. The lower alkyl groups present in these epoxysiloxanes generally have one to four carbon atoms, for example, methyl, ethyl, propyl and isopropyl, and the lower aryl groups generally have six to nine carbon atoms, for example, phenyl. The repeating units, i.e., the



groups usually occur randomly in these epoxysiloxanes. The epoxysiloxanes consist essentially of these two repeating units. The limitations concerning the maximum degree of polymerization, possible other repeating units, and terminal end groups previously described with regard to the aminosiloxanes, also apply to these epoxysiloxanes.

If desired, additional epoxy groups may be present in the second repeating unit shown immediately above, for example, by substituting the R'' group to provide a unit of the formula:



Additional epoxy groups may be added, provided the epoxy oxygen atoms are separated from each other and from silicon atoms by a connecting chain of at least two carbon atoms.

It is preferred that the epoxy siloxanes be water soluble or easily water dispersible for convenience in using, but they can be used in organic solvents or without solvents, if desired.

These epoxysiloxanes may be used in conjunction with the aminosiloxanes described above or the amine compounds described below, to provide results similar to that obtained with a combination of the aminosiloxane and the described epoxy compound. In all cases improved and useful slickness is obtained in the treated fiber as compared with the untreated fiber. However, only when an aminosiloxane is employed as one ingredient to the fibers exhibit marked similarity to the natural luxury animal fibers, accompanied by high values for the Objective Preference Index.

The amine compounds that are used in combination with the epoxysiloxanes in accordance with this invention are characterized by containing primary and/or secondary amino groups and having at least two amino groups per molecule. Examples of suitable amines are ethylene diamine, diethylene triamine, and other alkylene and arylene polyamines, N-alkyl alkylene diamines, N-alkyl arylene diamines, diazines such as piperazine (hexahydropyrazine), amino-piperidines such as 2-aminohexahydropyridine. Primary amines are preferred over secondary amines. Tertiary amines are not operable for use in this invention.

In mixtures of epoxysiloxanes and aminosiloxanes alone, the ratio of epoxysiloxane to aminosiloxane may vary from about 0.05:1 to about 20:1 by weight, but in mixtures of aminosiloxanes with epoxy compounds other than epoxy siloxanes and in mixtures of epoxysiloxanes with amino compounds other than aminosiloxanes, the ratio of the nonsiloxane compounds to the siloxane compounds may vary from about 0.05:1 to about 2:1 by weight, with the preferred ratios in all cases varying according to the specific compounds employed. The amino-siloxane-epoxy composition may be prepared as solution in an organic solvent or, preferably, as an aqueous dispersion. The concentration of the composition in such a solution or dispersion may vary over a wide range, but a siloxane concentration of 2 to 20 percent by weight is generally adequate. Similarly, the amount of amino-siloxane-epoxy composition that is applied onto the fibers may vary over a wide range, depending upon the particular effect that is desired to be obtained. Generally about 0.1 to 3 percent of siloxane, based on the dry weight of the fibers, will be adequate, and about 1.0 to 2 percent siloxane is usually preferred.

It is preferred that the amine-containing compound and the epoxide-containing compound be mixed only a short time before using. The aminosiloxane or epoxysiloxane can be dispersed in water by means of cationic or nonionic surface active agents. Suitable cation active agents are stearyldimethylbenzyl ammonium chloride, stearoylcolamino-formylmethyl pyridinium chloride, and cetyltrimethyl ammonium chloride. A suitable nonionic type is an ether of nonylphenol and a polyalkylene glycol. After the components are dispersed and mixed, the resulting composition is applied to the fibers, preferably at room temperature, inasmuch as heating tends to cause premature cross-linking and precipitation of the polymers.

When a solvent solution of finishing composition is desired, the siloxane-containing compound is usually just dissolved in a suitable solvent such as methylene chloride or other chlorinated hydrocarbon or ethanol and then the epoxy compound is added. The organic solvent solution can then be applied to the fibers, or it may be added to water containing an emulsifying agent to form an emulsion of the siloxane and the polyepoxide, and the resulting emulsion can be applied to the fibers. The product can also be made by applying solutions or dispersions of the two ingredients to the fiber in serial manner and then curing them together on the fiber; although for economic reasons and optimum product uniformity the ingredients are generally applied together in solution or dispersion in accordance with the process of the invention.

The product can also be made using salts of the aminosiloxane formed by mixing the aminosiloxane with a sufficient quantity of a relatively volatile acid to neutralize all the amino groups. Neutralization of the aminosiloxane retards reaction between it and the polyepoxide. This retardation is particularly useful if it is desired to expose the coated fibers to elevated temperatures, e.g., during crimping, before evaporating dispersing medium or solvent and curing the composition.

Removal of the volatile acid during evaporation and curing regenerates the aminosiloxane which then reacts readily with the polyepoxide.

All synthetic organic textile fibers, such as fibers of acrylonitrile polymers, polyamides or polyesters, may be treated in accordance with this invention. Fibers of acrylonitrile polymers, including homopolymers and copolymers, are especially benefited by this invention. Suitable polyamide fibers for treatment in accordance with this invention are fibers of poly(hexamethylene (hexamethylene adipamide), polycaprolactam, and polyamides from bis(4-aminocyclohexyl)-methane and dicarboxylic acids containing six to 16 carbon atoms, such as poly(methylene-di-1,4-cyclohexylene dodecane-diamide).

The composition used in this invention may be applied to fibers in the form of a tow or staple fibers, to filaments or spun yarn or even to finished fabric. However, it is the prime object of the present invention to treat the fiber in the form of tow or staple where it would be most economical and where the application can best be controlled to give uniform results. The treated tow or rope may conveniently be cut into staple after impregnation and before curing.

After the finishing composition is applied to the fibers, any dispersing medium or solvent is evaporated and the composition is cured by subjection to elevated temperatures, usually within the range of 110° to 160° C. for about 15 to 40 minutes. Lower temperatures may be used, at a sacrifice of curing time, and in some instances higher temperatures may even be used. In every case the temperature should be low enough to prevent the fiber substrate from being deleteriously affected.

When this invention is used to treat fibers in the form of tow, it has been found that best results are obtained if the tow to be treated is free of oily finishes. The finishing composition made from the free amine is preferably not applied before hot crimping because the heat would cause premature polymerization of the mixture. The fibers may be lubricated with a textile finish before crimping, if desired. After crimping, the finishing composition may be applied without removing the crimp.

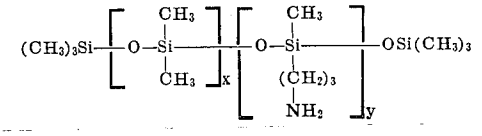
After treatment in accordance with this invention, fibers have a soft, slick finish that is remarkably durable. This finish will not only withstand repeated wearing and washing or dry cleaning of garments made from treated fibers, but will withstand the rigorous scouring and dyeing operations that are employed in the numerous steps involved in converting tow into staple, then into yarn, and finally into fabrics and garments. Moreover, it is surprising that this finish does not interfere with ordinary dyeing operations. These remarkable properties make this invention particularly useful for treating tow.

In addition to providing a durable, soft and lubricated feel to fibers, the process of this invention imparts other remarkable properties to fibers. For example, fibers finished by the process of this invention yield fabrics which have less tendency to form pills on the surface. Also, the fabrics do not glaze as badly as do fabrics from untreated fibers. Glazing is a condition where fibers are flattened and shaped into a plane surface so that the fabrics have a "shine." It is caused by hot pressing which fixes the fibers in place and they become slightly adherent to each other. It is believed that the finishing composition decreases glazing by acting as a release agent, keeping the fibers from sticking together and from being fixed in a plane surface. This freedom of motion is also believed responsible for some improvement in wrinkle resistance imparted by these agents to the fabric. The silicones alone produce similar benefits, but only temporarily. The effects are largely lost after one or two scourings or dry cleanings.

The following examples illustrate some of the preferred embodiments of this invention. In these examples, the siloxane retention percentage is measured by determining the silicon content in the respective fiber or fabric. This is done by fusing the sample of fiber or fabric with potassium carbonate and forming with ammonium molybdate the yellow silicomolybdate. The solution is then reduced with aminonaphthol sulfonic acid to yield molybdenum blue which is measured colorimetrically, for example, by the technique disclosed by Carlson et al., "Spectrophotometric Determination of Silicon," A*Analytical Chemistry*, *24*, 472 (1952). Alternately, one may grind the fiber, press the resulting powder into a pellet and measure the silicon content by X-ray fluorescence, for example, by the technique disclosed by Shiou-Chuan Sun, "-Fluorescent X-Ray Spectrometric Estimation of Aluminum, Silicon, and Iron in the Flotation Products of Clays and Bauxites," *Analytical Chemistry*, *31*, 1322 (1959). Except where otherwise specified, all parts are by weight.

EXAMPLE I

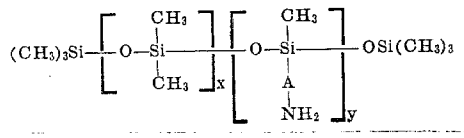
Eight parts of an aminosiloxane having the formula:



and having a degree of polymerization (i.e., the value of $x+y$ which is abbreviated hereinafter as "DP") of 500 and an NH_2 content of 0.2 percent (aminosiloxane supplied by Union Carbide Corp., designated Y 5230) is stirred with 391 parts of methylene chloride, and 1.2 parts of a polyepoxide is added. This polyepoxide is a liquid mixture of linear and moderately branched propylene ether polymers containing hydroxyl groups, chloromethyl groups, and an average of at least two epoxy groups per molecule; it is a condensation product of glycerine and epichlorhydrin; it has a pale yellow color; it has a viscosity of 90 to 150 centipoises at 25° C. (polyepoxide supplied by the Shell Chemical Corp., designated "Eponite" 100). The resulting solution is used to treat 52.2 parts of an acid-dyeable staple fiber made by dry spinning from solution in dimethyl formamide a polymer of 92.2 parts acrylonitrile, 5.4 parts methyl vinyl pyridine, and 2.4 parts methyl acrylate. The treatment consists of dipping the staple into the solution, removing and squeezing to 100 percent pickup of the solution (i.e., the fibers picked up an amount of composition equal to their own dry weight). This staple is then heated for 20 minutes at 70° C. and then 30 minutes at 130° C. to fix the finish on the fiber. The staple is next carded into a sliver. This sliver is combined with 22.8 parts of an untreated, acid-dyeable, high-shrinkage sliver made from a polymer of 89.6 parts acrylonitrile, 4.7 parts methyl vinyl pyridine and 5.7 parts methyl acrylate. The combined slivers are spun into a 6/1cc (886 denier) yarn having 5Z turns per inch twist (1.97 turns per cm.). The yarn is dyed in skein form for 1.75 hours at the boil at a pH of 2.5 with Pontacyl Brilliant Blue RR (Dye Index No. 42735). For each 100 parts of fiber, 2 parts of dyestuff, 3 parts sodium sulfate and 0.5 part of leveling salt are dissolved in 200 parts water and the pH adjusted to 2.5 with sulfuric acid. Dyeing is 1 hour 45 minutes at the boil. After dyeing, the fiber is scoured at 70° C. using a sodium alcohol sulfate detergent. It is rinsed and dried. The boiling causes shrinking of the high shrinkage fiber yielding a bulky yarn and causes the treated fibers to come to the surface. This yarn is next knit into a novelty construction on a Passap Duomatic flat bed knitting machine and tested for slickness before and after scouring and before and after mechanical, dry abrasion. The slickness is retained through all these operations; that is, opening and carding of the staple, twisting and drafting of the sliver, skeining and dyeing of the yarn, knitting, scouring and abrading of the fabric.

EXAMPLE II

Eight parts of a trimethyl silyl-end-capped, random copolymer of dimethyl siloxyl and methylaminopropylsiloxyl which is described by the formula:



having a DP of 200 and an NH_2 content of 1.82 percent (amino siloxane supplied by Union Carbide Corp., designated Y 5455) is added to 391 parts absolute ethanol with stirring and 1.2 parts polyepoxide is added. Fifty parts of a basic-dyeable staple fiber spun from a polymer of 95.8 parts acrylonitrile and 4.2 parts sodium styrenesulfonate are dipped into the siloxane-epoxide solution then pressed to remove excess solution, leaving 100 percent of solution on the fiber. The fiber is dried and heated 35 minutes at 130° C. to cause interaction of the aminosiloxane and the epoxide on the fiber. The treated fiber is next carded and formed into sliver A.

A bicomponent staple fiber with a homopolymer of acrylonitrile on one side and making up 75 percent of the filament, and a copolymer of 95 parts acrylonitrile and 5 parts sodium styrenesulfonate on the other side and making up 25 percent of the filament is slickened in the same manner except from methylene chloride solution and converted into sliver B. Sliver A and sliver B are blended on a pin drafter and spun into a 10/1cc (531 denier) yarn with 7.1Z turns per inch (2.8 turns per cm.) twist. This yarn is knit into a jersey fabric having 16 courses per inch (6.3 courses per cm.) and the fabric is scoured and then dyed at the boil at a pH of 4.5. The resulting fabric is soft and slick, and the slickness is not destroyed by hand abrasion. The bicomponent fiber crimps during the dyeing and results in a bulky yarn.

EXAMPLE III

Ten parts of the aminosiloxane described in Example II are mixed with 489 parts of absolute ethanol and 1.5 parts of the polyepoxide of Example I added to the solution. The resulting solution is used to saturate 50 parts of 10 denier per filament staple fiber identical to that treated in Example I. After squeezing out the excess solution so that the solution pickup on the fiber is 100 percent, the fiber is dried by heating 30 minutes at 70° C. then further heated at 130° C. for an additional 30 minutes. The treated fiber is carded and the resulting sliver blended with untreated acid-dyeable high-shrinkage sliver of Example I. The blended fibers are spun into a 6/1cc (886 denier) yarn with 5Z turns per inch (1.97 turns per cm.) twist. The yarn is skein-dyed at a pH of 2.5. This causes bulking of the yarn due to the shrinkage of the high-shrinkage fraction and the migration of treated fibers to the surface. The yarn is knit into a flat fabric and found to be soft and slick and the finish is durable to hand abrasion.

EXAMPLE IV

This example demonstrates the application of a combination of an aminosiloxane and a polyepoxide from an emulsion.

Part A. 1.9 parts of an emulsifying agent (stearoyl colamino formyl-methyl pyridinium chloride) are dissolved in 184 parts water by stirring. Then 37.5 parts of a polyepoxide is added slowly with stirring.

Part B. 7.5 parts of an emulsifying agent (stearoyl colamino formyl-methyl pyridinium chloride) are dissolved in 1,470 parts of water with stirring and there is then added a solution of 150 parts of the amino siloxane of Example II in 150 parts of isopropyl alcohol.

Parts A and B are then mixed with stirring and the resulting emulsion is used for treating a tow of an acrylic fiber spun from a polymer made by copolymerizing 88.9 parts acrylonitrile, 5.4 parts of methyl vinyl pyridine, and 5.7 parts methyl acrylate by passing the tow over applicator rolls. The rate of application is such that 3 percent of siloxane is applied to the fiber on a dry weight basis. The tow is next cut into staple fiber and dried at 130° C. for 30 minutes. This fiber is carded to yield Sliver A. This is blended with slivers of some of the same fiber compositions which have been stretched and broken on the Turbo Stapler to give high-shrinkage Sliver B which was not treated according to the present invention. A 70/30 blend of Sliver A and Sliver B are spun into a 6/1cc (886 denier) yarn with 5Z turns per inch (2 turns per cm.) twist. The yarn is wound into skeins and dyed 2 hours at the boil at a pH of 2.5 using acid colors. This yarn is knit on a Stoll JBO Flat Bed Machine into a two-color welt construction. Even though the finish is subjected to rigorous process conditions, including scouring and dyeing, during the necessary steps to convert tow into fabrics, the final fabric is soft and slick and it retains these properties through at least five home laundry cycles.

The relative coefficient of friction "*f*" for the treated fiber and for the untreated fiber is determined as follows:

A flat, horizontal plane is covered with carded staple fiber to be tested. A weighted aluminum block covered with emery cloth is placed upon the fiber-covered surface. The block is attached to a strain gauge and the force required to move one with relation to the other is measured. The fiber-to-fiber friction is measured. The values for treated and untreated unblended staple are 0.110 and 0.184, respectively. The significant difference in the measurement is 0.02.

EXAMPLE V

This example demonstrates the application of aminosiloxane/polyepoxide to a polyester fiber.

A solution is prepared by adding 8 parts of the aminosiloxane of Example II and 1.2 parts of polyepoxide to 790 parts ethanol. Seventy-seven parts of semi-dull staple fibers of 3 denier and a cut length of 1.5 inches (3.8 cm.) spun from poly(ethylene terephthalate) are dipped into the solution and the excess solution squeezed out to leave a 100 percent pickup of solution on the dry weight of the fiber to deposit 1 percent of aminosiloxane on the fiber. The staple fiber is dried and cured 30 minutes at 130° C. and spun into a 10/cc (531 denier) 14 turns per inch (5.5 turns per cm.) yarn. The yarn is knit into a 16 stitch per inch (6.3 stitch per cm.) jersey fabric. This fabric is dyed with a disperse dyestuff at the boil at a pH of 5.5. The resulting fabric is much softer and slicker than a similar fabric made from fibers which have not been treated with aminosiloxane-polyepoxide.

EXAMPLE VI

The example demonstrates the use of a combination of an epoxysiloxane and a diamine as a fiber finish.

Eight parts of epoxysiloxane having 5 percent epoxy group and a viscosity of 700 CSTKS and 1.6 parts of 1,6-diaminohexane are dissolved in 390 parts of absolute ethanol. One hundred parts of the basic-dyeable staple fiber of Example II are dipped into this solution and the excess solution squeezed out to leave 100 percent wet pickup. The fiber is then cured 30 minutes at 130° C. and then spun into a 10/cc (531 denier) 7.1Z turns per inch (2.8 turns per cm.) yarn. This yarn is knit into a 16 stitch/inch (6.3 stitch/cm.) jersey fabric and dyed at a pH of 4.5 with basic cationic dyes. After scouring and drying, this fabric has a soft, slick hand which is retained through many launderings and repeated abrasions.

EXAMPLE VII

This example demonstrates the application of a combination of an epoxysiloxane and an aminosiloxane to a fiber from an emulsion.

Part A. 33.3 parts of the epoxysiloxane of Example VI are dissolved in 33.3 parts of isopropyl alcohol and the resulting solution poured slowly into a solution of 1.7 parts of the emulsifying agent of Example IV in 600 parts of water with stirring.

Part B. 16.7 parts of the aminosiloxane of Example II are dissolved in 16.7 parts isopropyl alcohol and the resulting solution poured with stirring into a solution of 0.8 parts of the above-emulsifying agent in 300 parts water.

Parts A and B are thoroughly mixed and immediately applied to a tow of an acrylonitrile polymer fiber comprising a terpolymer of 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinyl pyridine so as to leave 2 percent of the total siloxane on the fiber, based on the dry weight of the fiber. This tow is then cut into staple and heated 30 minutes at 130° C. to bring about the reaction between the amino groups and the epoxy groups. The staple fiber is decidedly softer and slicker than an untreated fiber.

Seventy-seven parts of this staple fiber are blended with 33 parts of a staple fiber of the same chemical composition but having been broken on an apparatus, described in U.S. Pat. No. 2,748,426, for stretch-breaking tow into staple fiber (manufactured and sold under the tradename "Turbo Stapler" by the Turbo Machine Co. of Lansdale, Pa.) to give a high shrinkage of over 30 percent. The blended fibers are next spun into a 6/cc (886 denier) yarn with 5Z turns per inch (1.97 turns per cm.). This yarn is two-plied, wound into skeins and dyed with acid colors at a pH of 2.5. The dyed yarn is knit into a two-color welt construction. The fabric possesses a durable, soft, slick hand.

EXAMPLE VIII

This example demonstrates finishing a fiber with the reaction product of an epoxysiloxane and a polyoxy propylene diamine.

Fifty-four parts of an epoxysiloxane having 5 percent epoxy group are dissolved in 3,920 parts of ethanol containing 27 parts of a polyoxypropylene diamine with a DP of about 400. The resulting solution is used to treat 1,000 parts of an acrylonitrile polymer fiber comprising a terpolymer of 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinyl pyridine. The excess solution is pressed from the fiber leaving a 100 percent wet pickup. The fiber is next heated for 30 minutes at 130° C. The resulting fiber is spun into a 6/cc (886 denier) yarn with 5Z turns per inch (2 turns per cm.). The yarn is two-plied, skeined, and dyed with acid dyes at a pH of 2.5. It is next knit into a two-color welt construction. The fabric has the slick, soft feel of mohair. This feel is durable to hand abrasion and to laundering.

EXAMPLE IX

This example demonstrates the treatment of a fabric by this invention.

An acrylic fiber of 10 denier per filament is spun from a terpolymer of 92.2 parts acrylonitrile, 5.4 parts methyl vinyl pyridine and 2.4 parts methyl acrylate. The fiber in the form of a tow is broken on a Turbo Stapler. Part of the fiber is heat-set with steam and has a low shrinkage. That which is not heat-set has a shrinkage of at least 30 percent. Seventy parts of the low shrinkage fiber in the form of sliver is blended with 30 parts of high shrinkage sliver. Blending is on spinning frame. The final sliver is spun into a 6/cotton count (886 denier), 5 turns per inch (1.97 turns per cm.) "Z" twist yarn. This yarn is knit into a two-color welt construction on a Stoll JBO Bed Knitting Machine.

Twenty-five parts by weight of this fabric are treated with a solution of 2 parts of the aminosiloxane of Example II and 0.3 parts of polyepoxide in 198 parts of absolute ethanol. The fabric is squeezed to remove excess solution and leave 100 percent solution on the fiber. It is next dried and heated 30 minutes at 130° C. The resulting fabric is found to be pleasantly soft and slick. Fabrics from other fibers can be treated likewise.

EXAMPLE X

This example demonstrates the use of an in-line mixing process for preparing the finish for application to the fiber.

The aminosiloxane and the polyepoxide of Example II, a surface active agent (trialkyl polyoxyalkylene quaternary ammonium chloride) and water are fed into a Gifford-Wood 2-inch (5.08 cm.) Pipeline Homomixer in a ratio of 1 part aminosiloxane, 0.25 part polyepoxide, 0.03 part surface active agent and 14 parts water, all by weight. The resulting dispersion is pumped continuously onto a moving tow of 87,500 denier spun from a terpolymer 88.9 parts of acrylonitrile, 5.4 parts methyl vinyl pyridine and 5.7 parts methyl acrylate. The tow is cut into 4.5 inch (11.4 cm.) staple and the staple is heated 30 minutes at 130° C. The staple is next converted into sliver and 77 parts of this sliver are blended on a pin drafter with 33 parts of sliver of composite fiber spun from two polymers in side-by-side relation along the length of the fiber, Polymer A being a mixture of 84 parts of a polymer from 100 percent acrylonitrile and 16 parts of a copolymer of 95.8 percent acrylonitrile and 4.2 percent sodium styrene sulfonate, and Polymer B being a copolymer of 95.8 percent acrylonitrile and 4.2 percent sodium styrene sulfonate.

The final blended sliver is spun into a 6/1cc (886 denier) yarn with 5.0 "Z" turns per inch (2 turns per cm.). This yarn is two-plied with 2.5 "S" turns per inch (1 turn per cm.). The plied yarn is skien dyed and knit into a two-color welt construction. The fabric is pleasantly soft and slick and retains these properties after repeated launderings.

EXAMPLE XI

This example demonstrates the application of the finish of this invention to a composite two-component fiber.

A staple fiber of 3.5 denier per filament and 3 to 3.5 inch (7.6 to 8.9 cm.) length is spun from two different polymers to yield a composite fiber. One polymer component (polymer A) is a terpolymer of 93.6 parts acrylonitrile, 6.0 parts methyl acrylate and 0.4 part sodium styrene sulfonate. The other component (Polymer B) consists of 90 parts of acrylonitrile polymer and 10 parts of Polymer A. The composite fiber contains approximately equal amounts of Polymer A and Polymer B in side-by-side relation along the length of the fiber.

Two hundred twenty-five parts of this staple fiber are treated with a solution of 40 parts of the aminosiloxane of Example II and 6.0 parts of the polyepoxide of Example II in 1,954 parts of isopropyl alcohol. The staple is partially freed of solution by squeezing then dried 20 minutes at 140° C. to fix the finish on the fiber. The treated staple is carded and spun into a 6/1cc (886 denier) yarn with 5.5 "Z" turns per inch (2.2 turns per cm.). This yarn is two-plied with 2.8 "S" turns per inch (1.1 turns per cm.) and knit into a half cardigan construction. After scouring and dyeing 1.5 hours, at the boil, the resulting fabric has a soft, smooth feel.

EXAMPLE XII

Thirty parts of the aminosiloxane having the formula shown in Example I and having a degree of polymerization of about 500 and a NH_2 content of 0.2 percent is mixed with 1.5 parts of a polyethylene oxide surfactant. The mixture is stirred for 5 minutes at 2,300 r.p.m. after which 15 parts of water are added at the rate of 1.5 parts of water every 2 minutes while stirring is continued. The emulsion which is formed inverts, after which 49 parts of water is then added at a slower stirring speed, followed by 4.5 parts of the polyepoxide used in Example I. The resulting mixture, which contains 30 percent aminosiloxane and 4.5 percent polyepoxide, is diluted with water to form an emulsion containing only 2 percent of the aminosiloxane. The 2 percent emulsion is used to treat 120 parts of a staple fiber made by dry-spinning from solution in dimethyl formamide a polymer of 96 parts of acrylonitrile and 4 parts of sodium styrene sulfonate. The squeezing pressure employed during application is such that the pick-up of emulsion on the fiber is 100 percent on the weight of the fiber. The staple fiber is then heated for 30 minutes at 130° C. to evaporate water and cure the finish on the fiber. After the curing step, the fiber is spun in a blend with 30 percent of a staple fiber made of a polymer of 88.9 parts of acrylonitrile, 5.4 parts methyl vinyl pyridine and 5.7 parts of methyl acrylate, but containing no silicone finish, to a 6 cc. yarn having 5Z turns per inch twist. The yarn is plied and dyed at a pH of 2.0. The

dyed yarns are knitted to fabric. The resulting knitted fabrics are rated as very slick.

EXAMPLE XIII

Into a 2-inch (5.08 cm.) pipeline mixer (commercially available as a Gifford-Wood pipeline homomixer) is fed a mixture of 1,870 parts of water, 67.6 parts of the polyepoxide of Example I, 338 parts of the aminosiloxane of Example II, and 7.2 parts of a surface active agent comprising a polyoxyalkylene derivative of a secondary alcohol (commercially available surface active agent identified as Tergitol 13–S–12). The resulting dispersion is pumped continuously onto a moving tow of 450,000 denier of an acrylonitrile polymer fiber comprising a terpolymer of 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine. The tow is dried and cured continuously by passing through an oven at a rate to provide 8.2 minutes residence in an environment at 135° C. The tow is cut into staple fibers 3 inches long and the staple is scoured for 1 hour at the boil in a 0.5 percent aqueous solution of a commercially available surfactant (identified as Igepal CO–880) acidified to a pH of 2.5 with sulfuric acid. The staple fibers are rinsed and dried. A plot is prepared of the coefficient of friction of the fibers, with respect to the sliding speed at which the measurement is made. This coefficient of friction plot is shown in FIG. 1. The Objective Preference Index of this fiber, calculated as hereinbefore described, is 0.94.

Similar plots of the coefficient of friction, with respect to the sliding speed at which the measurement is made, are prepared and the corresponding Objective Preference Indexes are calculated for the following fibers: an untreated sample of the same acrylonitrile polymer staple fiber employed in the above paragraph; a commercially available sample of alpaca fiber; a commercially available sample of mohair fiber; an acrylonitrile polymer staple fiber bearing a cured coating of epoxysilicone and 1,4-diaminobutane, prepared as described below; and an acrylonitrile polymer staple fiber bearing a cured coating of a silicone containing silyl hydrogen atoms mixed in admixture with a soluble polyepoxide, and analyzing 2.06 percent silicone. The Objective Preference Indexes calculated for these fibers are given in Table 1, the fibers being listed in the same order described. The curves for all of these fibers are shown in FIG. 2. It will be noted that the fiber of the invention, bearing the cured aminosiloxane-epoxy coating, is very similar in shape to the curves obtained with the natural alpaca and mohair fibers, in that the initial coefficient of fraction is relatively low and dips slightly lower to a minimum as the sliding speed is increased, then rises very sharply and progressively as the sliding speed is further increased. The untreated acrylonitrile polymer staple fiber has a high initial coefficient of friction which decreases somewhat as the sliding speed is increased. The acrylonitrile polymer staple fibers bearing cured coatings of other silicones have low initial coefficients of friction as contrasted with the untreated acrylonitrile polymer staple fibers; but the curves do not rise as the sliding speed increases, so that the coefficients of friction are low regardless of speed.

TABLE 1

Fiber composition:	Cured coating	OPI
Acrylonitrile polymer:	Aminosiloxane-epoxy	0.94
Acrylonitrile polymer:	None (control)	0.12
Alpaca:	None (control)	0.57
Mohair:	None (control)	1.03
Acrylonitrile polymer:	Epoxysilicone-1,4-diaminobutane	0.0
Acrylonitrile polymer:	Silyl hydrogen silicone polyepoxide	0.07

The next-to-last item in Table 1 is prepared by applying a mixture of 4 cc. of 0.40 g. of a dimethyl polysiloxane having 1 percent pendant epoxide groups and a viscosity of 4,000–8,000 centistokes in 40 cc. of benzene and 4 cc. of a solution of 0.01 g. of 1,4-diaminobutane in 40 cc. of benzene to 2.0 g. of a 9 denier per filament, 3-inch staple fiber of the same acrylonitrile polymer described in the first paragraph of this example. After evaporation of the solvent, the staple is cured 15 minutes at 135° C. and then scoured 1 hour at the boil as in the first paragraph of this example, rinsed, and dried.

EXAMPLE XIV

Solutions of the following materials are made in 40 cc. of benzene:

A. 0.32 g. of the aminosiloxane described in Example II
B. 0.28 g. of the aminosiloxane described in Example II
C. 0.24 g. of the aminosiloxane described in Example II
D. 0.08 g. of the polyepoxide of Example I
E. 0.12 g. 1,3-bis-(3-glycidoxypropyl)tetramethyldisiloxane
F. 0.16 g. resorcinol diglycidyl ether

To 2 g. of unmodified 9 denier per filament staple fibers of a terpolymer comprising 88.8 parts acrylonitrile, 5.8 parts methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine in a beaker is added a mixture of 4 cc. of solution (A) and 4 cc. of solution (D) above, and the mass of fibers is worked to distribute the applied solution as evenly as possible. The benzene is allowed to evaporate at room temperature, and the sample is then cured 15 minutes at 135° C. in a forced draft oven. The procedure is repeated for a mixture of solution (B) and solution (E); and repeated again for a mixture of solution (C) and solution (F). Each of the samples of cured fibers is then scoured at the boil for one hour in a solution of 0.5 percent of a commercially available surfactant (identified as Igepal CO–880) acidified to a pH of 2.5 with sulfuric acid. After thorough rinsing, the samples are dried at room temperature and their frictional characteristics are evaluated by calculation of Objective Preference Indexes. The results are given in Table 2.

TABLE 2

Epoxy Crosslinking Agent	OPI
None (no coating)	0.12
1,3-bis-(3-glycidoxypropyl) tetramethyldisiloxane	0.64
Resorcinol diglycidyl ether	0.78
Polyepoxide of example I	0.89

EXAMPLE XV

An aqueous dispersion of a coating composition is prepared from 163.4 g. of water, 0.6 g. of a commercially available dispersing agent (identified as Tergitol 15–S–12), 6.0 g. of the polyepoxide of Example I, and 30.0 g. of the aminosiloxane described in Example II. These ingredients are added in the order listed into a commercially available blending apparatus (Waring Blendor) and are agitated at high speed until emulsified (approximately 3 minutes). The resulting emulsion is diluted to 0.66 percent silicone with water and applied to untreated 9 denier per filament staple fibers of a terpolymer comprising 88.8 parts acrylonitrile polymer, 5.8 parts methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine to give a 2 percent coating on the fibers. The fibers are mixed thoroughly in a beaker, and the wet, coated staple is then dried and cured in a forced draft oven at 135° C. for 15 minutes. The cured fibers are then scoured at the boil for one hour in a solution of 0.5 percent of a commercially available detergent (identified as Igepal CO–880) acidified to a pH of 2.5 with sulfuric acid.

The procedure described in the preceding paragraph provides a fiber having a cured coating containing 20 percent of the polyepoxide crosslinking agent, based on the weight of the aminosilicone. This procedure is repeated, employing various proportions of the ingredients, and the frictional characteristics of the fibers are evaluated by calculation of Objective Preference Indexes. The results are given in Table 3.

TABLE 3

Weight Aminosilicone	Weight Polyepoxide (g.)	% Polyepoxide	OPI
33.0 g.	3.0 g.	9	0.89
30.0	6.0	20	0.97
27.0	9.0	33	0.79
24.0	12.0	50	0.81

EXAMPLE XVI

Solutions of the polyepoxide of Example I in various amounts, as shown in Table 4, are made up in 40 cc. of benzene each. A solution of 0.32 g. of the aminosiloxane of Example II having an amine content of 1.8 percent of 40 cc. of benzene is also prepared, together with similar 40 cc. benzene solutions of aminosiloxanes having amine contents of 0.4, 1.0 and 6.0 percent (aminosiloxanes supplied by Union Carbide Corp., designated Y–6165, Y–5477, and Y–5078 respectively) as shown in the table and in the amounts indicated therein. Mixtures of 4 cc. of the aminosiloxane solutions with 4 cc. of the corresponding polyepoxide solutions are applied to 2.0 g. portions of untreated 9-denier per filament staple fibers of a terpolymer comprising 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine. The fibers are mixed thoroughly in a beaker, and the wet, coated staple is then dried, cured, and scoured as in Example XV. The frictional characteristics of the fibers are evaluated by calculation of Objective Preference Indexes, and the results are given in Table 4.

TABLE 4

% Amine in Amino-siloxane	Wt. of Amino-siloxane	Wt. of Epoxide	% Poly-Epoxide*	OPI
0.4	0.38 g.	0.02 g.	5	0.32
1.0	0.36	0.04	10	0.38
1.8	0.32	0.08	20	0.92
6.0	0.22	0.18	45	0.16

*Based on total weight of coating

The fiber having the coating containing 6.0 percent amine and 45 percent polyepoxide, although slicker than unmodified fiber, has a low OPI value and resembles the natural luxury animal fibers less than the other fibers do.

EXAMPLE XVII

A mixture of 87.5 g. of the aminosiloxane of Example II and 1.75 g. of a commercially available dispersing agent (identified as Tergitol 15–S–12) is made and 204 ml. of water is added slowly with vigorous stirring to produce a 30 percent emulsion of the aminosiloxane in water. To this is added, in order, 9 ml. of glacial acetic acid, 17.5 g. of the polyepoxide of Example I and 3,189 ml. of water to produce an emulsion containing 2.5 percent of the aminosiloxane. The emulsion is applied to a 30,000 denier rope of polyethylene terephthalate polymer fiber of 8 denier per filament by dipping the rope into the emulsion and wringing off excess until the emulsion pickup is 20 percent based on the rope's dry weight. The rope is then crimped in a stuffer-box crimper and dried and heated for 8 minutes by passage through a forced-draft oven at 135° C. to cross-link the surface modifier and relax and crystallize the fiber. A textile finish to provide acceptable textile processibility is applied to the dried, cured rope, and the rope is then cut to 4.5-inch staple fiber. The staple analyzes 0.68 percent aminosiloxane, based on dry fiber weight. The staple is scoured 1 hour at the boil in a 0.5 percent aqueous solution of a commercially available surfactant (Igepal CO–880) acidified to pH 2.5 with sulfuric acid, rinsed, and dried. A control fiber is prepared in the same way except that 20 percent water is applied in place of 20 percent aminosiloxane emulsion. The surface modified fiber has an OPI of 1.64, as contrasted with an OPI of 0.40 for the control. The tactile softness and slickness of knit fabrics made using the surface modified fiber is very pleasing to the hand, and similar to the handle of mohair, whereas the fabric knit from the control fiber lacks the mohair-like hand. The friction plots of the treated and untreated polyester fibers of this example are shown in FIG. 3.

EXAMPLE XVIII

Yarns unraveled from the fabrics prepared in Examples I–V, VII, XI, and XII are examined for their frictional characteristics in a modification of the test described above for calculation of the Objective Preference Index. In the modified test, the cardboard tubes are covered with several layers of the yarns unraveled from the fabrics and the 1×9-inch strip of one-sided pressure-sensitive plastic tape is covered with close-packed, parallel yarn arrays. Plots of the coefficient of friction of the yarns, with respect to the sliding speed at which the measurement is made, are prepared and the Objective Preference Index is calculated as previously described. It is noted that the values for the Objective Preference Index of the yarns are lower than the corresponding values for the staple fibers, although the shapes of the curves are similar. For example, the shape of the curve for the control sample of 100 percent mohair yarn is similar to the shape of the curve for 100 percent mohair staple fibers, but the OPI for the mohair yarn is only 0.53 as compared with 1.03 for the mohair fibers. Similarly, the yarn unraveled from the fabric of Example II, made of aminosiloxane-epoxy coated polyacrylonitrile fibers prepared in accordance with the invention, has an OPI of only 0.50 as compared with an OPI of 0.94 for the similar aminosiloxane-epoxy coated polyacrylonitrile staple fiber shown in Table 1, although the shape of the curves are similar. The results obtained with the yarns are given in Table 5.

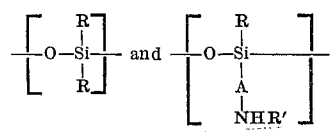
TABLE 5

Example No.	OPI of Yarn Unraveled from Fabric of Example
I	0.13
II	0.50
III	0.32
IV	0.47
V	0.34
VII	0.32
XI	0.21
XII	0.15
Yarn of polyester fibers with no coating	0.20
Yarn of polyacrylonitrile fibers with no coating	0.0
Yarn of 100% mohair	0.50

I claim:

1. A synthetic organic textile fiber having a coating composition selected from the group consisting of:

1. a cured mixture of about 0.05 to 3 parts by weight of a soluble epoxy compound having at least 2 epoxy groups per molecule, together with 1 part by weight of a liquid aminosiloxane wherein there is one oxygen atom bridging each pair of neighboring silicon atoms and all other silicon valences are bonded only to carbon atoms, said aminosiloxane consisting essentially of repeating units of the formulae:



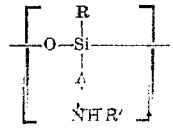
wherein

R is a lower alkyl or aryl group,

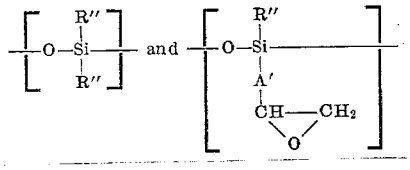
R′ is hydrogen or a lower alkyl or aryl group,

A is an alkylene group having two to five carbon atoms or an arylene or substituted arylene group having six to 10 carbon atoms, provided R′ and A are selected so that not more than one aromatic ring is attached directly to the amino nitrogen atom,

said aminosiloxane containing at least 35 of said repeating units, at least two of which have the formula:



2. a cured mixture of about 0.3 to 20 parts by weight of a liquid epoxysiloxane in each molecule of which there is one oxygen atom bridging each pair of neighboring silicon atoms and all other silicon valences are bonded only to carbon atoms, said epoxysiloxane molecule consisting essentially of repeating units of the formulae:

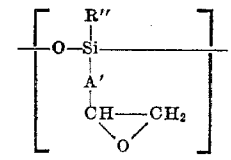


wherein

R″ is a lower alkyl or aryl group,

A′ is an alkylene group having two to five carbon atoms or an arylene or substituted arylene group having six to 10 carbon atoms,

said epoxysiloxane having an epoxy group content of at least 1 percent based on the total weight of said epoxysiloxane, and containing at least 35 of said repeating units at least two of which have the formula:



together with 1 part by weight of an amine compound having at least two amino groups per molecule wherein each of said amino groups has at least one hydrogen atom and not more than one aromatic ring attached directly to the nitrogen; and

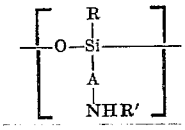
3. a cured mixture of about 0.05 to 20 parts by weight of said epoxysiloxane together with 1 part by weight of said aminosiloxane;

said coating composition being present in an amount sufficient to provide the fiber with an improved, durable, soft, lubricated feel.

2. The fiber of claim 1 wherein said fiber comprises an acrylonitrile polymer.

3. The fiber of claim 2 wherein said composition is selected from the group consisting of (1) a cured mixture of said epoxy compound and said aminosiloxane and (2) a cured mixture of said epoxysiloxane and said aminosiloxane.

4. The fiber of claim 3 wherein said composition is a cured mixture of said epoxy compound and said aminosiloxane wherein said aminosiloxane contains 100 to 600 of said repeating units, four to 20 of which are units of the



5. A textile fiber of claim 1 wherein said composition is selected from the group consisting of (1) a cured mixture of said epoxy compound and said aminosiloxane and (2) a cured mixture of said epoxysiloxane and said amino siloxane.

* * * * *