United States Patent Office 3,668,001 Patented June 6, 1972



3,668,001

# FIBROUS STRUCTURE HAVING DURABLE ELASTICITY AND CREASE-RESISTIVITY AND ITS MANUFACTURE

Kenjiro Hosokawa, Osaka, Masao Matsui, Takatsuki, and Noria Endo, Michio Ishikawa, and Susumu Tokura, Osaka, Japan, assignors to Kanegafuchi Boseki Kabushiki Kaisha, Tokyo, Japan

No Drawing. Filed May 29, 1969, Ser. No. 829,135
Claims priority, application Japan, Mar. 28, 1969, 44/23,608
Int. Cl. D06m 15/00
U.S. Cl. 117—139.4 29 Claims

## ABSTRACT OF THE DISCLOSURE

A fibrous structure such as yarns, fabrics, clothes and the like, having durable elasticity and crease-resistivity, particularly ladies hosiery having excellent smoothness, softness and stretchability, which is manufactured by applying homogeneously to a fibrous structure at most 10% by weight, based on the structure, of polyorganosiloxane prepolymer in the form of its non-aqueous solution together with catalyst for polymerization thereof and then by heating the structure at 50–200° C. to polymerize prepolymer thereon into polyorganosiloxane having an elongation at break of at least 50%, a tensile strength at break of 1–50 kg./cm.$^2$ and a hardness of 5–50°.

This invention relates to fibrous structures, such as yarns, knitted goods, woven fabrics, non-woven fabrics, made-up clothes and the like, which are provided with durable elasticity and crease-resistivity, particularly to ladies hosieries having excellent smoothness, softness and stretchability, and also to a manufacture thereof.

By the term "fibrous structure" used in this specification and claims is meant a structure composed of staple fibers, continuous filaments or a mixture thereof, such as a yarn, strand, rope, net, knitted goods, woven fabric, non-woven fabric, felt, filter-cloth, substrate for synthetic leather, garment and the like. One of the most important fibrous structures in the present invention is a knitted fabric, especially a ladies hosiery.

In order to improve characteristics, particularly elastic properties, of fibrous structures, it has so far been regarded as an appropriate method to incorporate a polyurethane elastomeric yarn in the structure, which, however, needs a complicated process and cannot be said to be the most suitable way for obtaining a fabric with light weight. Methods for improving crease-resistivity which have been generally put in practice are: (1) to increase resiliency of fibers in the structure (by resin-finishing with a condensation resin), (2) to impart a sizing effect to the structure (by finishing with a polymerization resin or latex), (3) to lubricate fibers (by finishing with a silicone resin or an emulsion of polyethylene), etc. And in fact, the above method (1) is not effective for the improvement of elasticity, particularly, an elastic recovery from extension of knitted or woven fabrics, though it contributes to the improvement of crease-resistivity, and the method (2) is aimed to fix the fibers to each others in the structure, so that they may not be slid and shifted when the structure is deformed or folded up, but on the contrary, it has such a drawback that the structure, e.g. fabric is apt to be sharply creased. Such a drawback is somewhat eliminated when a soft resin is applied, but the softening alone is not enough for fully satisfying all effects originally expected from the sizing. Furthermore, the above-mentioned method (3) seems to be a good one at a glance, for silicone type softening agents or water-repellents are coated over the surface of the fiber and act to



decrease the frictional resistance of the fiber. However, the bending and abrasion resistances, the tearing strength and tensile strength at break of the resin itself are so small that it is impossible to expect durability in elasticity and crease-resistivity of the article treated with such agents.

On the other hand, a matter of great concern for imparting a shrink-proofing ability to fibrous structures, specifically woolen structures, is a chemical finish for preventing an irreversible shrinkage of fibers (a felting effect) which is caused by interlacing of fibers in the woollen mass. Upon interpretation by Speakman, Harris and many other chemists through their various studies, that the felting is based on a differential frictional effect (DFE) of scales on the surface of the fiber and in addition, is due to extensibleness and high elastic recovery of wool fibers in water which are inherent thereto, a number of methods, heretofore, have been proposed and tried as the shrink-proof finish. Those methods are, for instance, (4) to modify the scale to decrease the DFE, (5) to cover the scales to eliminate the DFE, (6) to introduce cross-linkages into the molecular structure of the fiber to improve its modulus in a wet state, whereby its resistance to deforming force is enhanced and (7) to bond cross-over contacts of fibers to hinder their relative movement. For the method (4), use has so far been made of oxidizing agents such as an inorganic or organic chlorinated compound and a monopersulphuric acid which have ability for breaking cystine linkages, and in fact, since those agents have been put to practical use in the form of aqueous solution in which the wool fibers swell, it has been impossible to treat fibers, attacking their scales alone without destroying their cortices. For the method (5), cellulose acetate, silicone resins, melamine resins, etc. are supposed to be applicable as the covering agent, but none but a process of interface polymerization of nylon has been employed to add to practical value, though it cannot be said to be satisfactory as yet because of harsh hand of the finished structure, according to the result of the inventors' investigation. The method (6) wherein diisocyanates, acrylic monomers or methacrylic monomers are used as cross-linking agents, and the method (7) such as the so-called Lanaset process in which methylol melamine is employed and the so-called Pontex process in which a rubber latex is applied, are both disadvantageous for practical purposes on account of inferiority in hand and in durability of effect of the resulting product as well as in view of the high cost for the production in either case. As explained above, it has so far been difficult to hinder the felting-contraction without any concern for bringing about harsh hand, degradation of fiber strength, yellowish discolouration, etc. of the treated fibrous structure, anyway.

Furthermore, stretchable ladies' hosieries, for instance, stockings have heretofore been knit with a so-called torque-yarn prepared by a false-twisting or high-twisting process and however, the torque-yarn as such adds to the cost due to its low production efficiency and further it has such a drawback that the knitting operation is difficult owing to its intensive torques. Therefore, recently use has been made of a process for manufacturing stretchable hosieries, which process comprises knitting into hosieries a unitary composite filament having latent crimps, namely, a filament consisting of at least two components of fiber-forming thermoplastic synthetic polymers differing in shrinkability upon heating wherein said components are adherent and disposed in an eccentric relation with each other throughout the entire length of the filament, and thereafter heating the resultant hosieries by means of steam or another heating medium to develop crimps of composite filaments.

However, stretchable hosieries, specifically stockings made from a unitary composite filament, generally have such a disadvantage that they have filament-loops on their

own surface which are formed of the crimped filament when the stockings shrink, whereby another body in contact therewith is readily caught so that a run or laddering is formed on the stockings in consequence. It may be possible to prevent the formation of run to some extent by knitting into what is called non-run stitches, while on the contrary, stockings having non-run stitches are, in general, inferior both in stretchability and in softness. Particularly, stockings main portion of which is knit with a unitary filament, generally exhibit less softness, because a filament of comparatively high denier has to be employed to impart enough strength to the stockings, and the non-run stitches further reduce the softness. The softness of the stockings may be somewhat increased by employing a multi-filament yarn of 15–30 denier of 2–5 composite filaments to form the main portion of the stockings and nevertheless, stockings composed of the multi-filament yarn of composite filament generally have drawbacks such as an enfeeblement in extensibility as well as in recoverability from extension, due to a mutual frictional resistance of the unitary filaments which constitute the multi-filament yarn, and moreover the softness is still not entirely satisfactory.

A method for decreasing fragility of stockings of plain stitches knit with a composite filament and increasing the extensibility and softness of stockings of non-run stitches knit with a composite filament as well, is for instance, to impart smoothness to the stockings by means of softening agents. However, usual softening agents which comprise oils and surface active agents as the principal components thereof provide fibrous structures with an extremely low durability for washing.

We, the inventors, have made various studies and investigations, to overcome the above-mentioned difficulties, on the finishing of fibrous structures to impart the afore-mentioned various favourable characteristics thereto, discovered the facts that a physical treatment is more preferable to a drastic chemical treatment and that from such viewpoint, there needs a polymer for covering fibres which possesses the ability of forming thin and tough film, the ability of adhering to fibers, the durability for mechanical stresses such as compression and extension and which further does not swell in water and at last accomplished the present invention by utilizing a silicone elastomer having an excellent elastic recovery from extension, a high tensile strength at break, etc.

It is an object of the present invention to obtain fibrous structures, such as yarns, knitted goods, woven fabrics, non-woven fabrics, made-up clothes and the like, which are provided with a durable elasticity, crease-resistivity, shrink-proof ability and durability for washing.

Another object of the present invention is to furnish highly stretchable knitted fabrics, particularly ladies' hosieries having a durable smoothness, increased softness and prolonged life of utility.

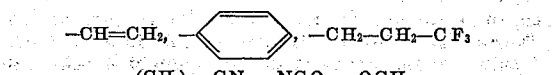
Still another important object of the invention is to provide a process for manufacturing fibrous structures having a durable elasticity, crease-resistivity, shrink-proof ability and durability for washing, more particularly highly stretchable ladies' hosieries possessing a durable smoothness, increased softness and prolonged life of utility, easily and cheaply in a commercial production.

Other objects and attending advantages will become apparent from the following description of the invention.

The above-mentioned objects are attained by applying homogeneously a non-aqueous solution of poly-organosiloxane prepolymer, in such an amount as not exceeding 10% by weight of the polyorganosiloxane component, together with a catalyst onto fibrous structures and then by subjecting the resulting structures to a heat-treatment at 70–200° C. to complete the polymerization of said prepolymer, whereby polysiloxane having an elongation at break of at least 50%, a tensile strength at break of 1–50 kg./cm.$^2$ and a hardness of 5–50° is fixed upon said structure.



The polyorganosiloxane prepolymer to be applied to the present invention is a linear polysiloxane having hydroxy groups directly bonded to its silicone atoms as its end groups, which is represented by the general formula, $HO—(SiRR'O—)_n—H$, wherein R and R' are respectively lower alkyl groups having 1–5 carbon atoms such as methyl, ethyl, propyl, butyl and pentyl groups, or may be




etc. Mention may be made of numerous compounds as such. What is commonly put to use comprises, as its principal constituent, those having lower alkyl groups as side chains thereof, such as poly (dimethyl siloxane) diol and poly (diethyl siloxane) diol or those having aromatic groups as side chains thereof, such as poly (methylphenyl siloxane) diol and poly (diphenyl siloxane) diol. A polyorganosiloxane prepolymer having its principal constituent of poly (lower alkyl siloxane) diol is preferable for the objects of the present invention. When R and R' are, for instance, phenyl groups instead of $CH_3$— groups, the heat resistivity of the prepolymer is increased and when nitrile groups are introduced, the oil-resistivity is improved. However, the present invention is not restricted by the sort of the side chain, and R and R' may be same or different groups. Besides, alkyl hydrogen polysiloxane e.g. methyl hydrogen polysiloxane can be effectively employed in combination with those compounds as mentioned above.

The non-aqueous solution of polyorganosiloxane prepolymer may contain polyetheric compounds, such as polyoxyethylene alkyl ether, polyoxyethylene alkylphenol ether, polyoxyethylene alkyl amine, polyoxyethylene alkylphosphate and polyoxyethylene sorbitan fatty acid ester, which are effective for providing the treated structures with an anti-static property and for eliminating waxy hand of the structure. Number of moles of oxyethylene units contained in the polyoxyethylene group of the above-listed polyetheric compounds is preferably about 5 to 40 and as far as polyoxyethylene fatty acid esters and polyoxyethylene alkylphosphate concern, it should be confined in the range between about 5 and 20. An appropriate number of carbon atoms possessed by the alkyl groups in the compounds is as follows:

| Compound: | Number of carbon atoms in alkyl group |
|---|---|
| Polyoxyethylene fatty acid ester | 12–18 |
| Polyoxyethylene alkyl ether | 10–18 |
| Polyoxyethylene alkylphenol ether | 4–12 |
| Polyoxyethylene alkyl phosphate | 10–18 |
| Polyoxyethylene sorbitan fatty acid ester | 10–18 |

In addition to the above-mentioned compounds, polyethylene glycol having its degree of polymerization of 1–4,000, more preferably 40–2,000, can also be effectively used.

A suitable amount of the polyetheric compounds to be added to the non-aqueous solution is 1–50% by weight based on the polyorganosiloxane prepolymer and preferably 3–20% by weight. These polyetheric compounds may be employed either solely or in combination of more than one.

Generally, the degree of polymerization of the prepolymer can be properly selected according to one's purpose. For instance, a prepolymer having a degree of polymerization of about 50–2,000 is considerably high in viscosity such as of about 30–100,000 cs., so that it is convenient to employ solvent, and on the other hand in case that the degree of polymerization lies between about 20 and 50, since the prepolymer has a low viscosity and high permeability, it can be readily used in the form of an aqueous emulsion in general.

A mixture of more than one of prepolymer differing in chemical structure or in degree of polymerization can, of course, be used. However, in the present invention, since the above-mentioned prepolymer should be polymerized upon a heat treatment into a polymer having the aforementioned physical properties, the degree of polymerization of the prepolymer is limited to an extraordinarily high order such as at least 50, preferably at least 100, whereas that of the prepolymer used for common softening agents and water-repellents is not more than 50, so that it is essential in the present invention to use a non-aqueous solvent as the solvent or thinner for the prepolymer.

A polyorganosiloxane as such can be obtained easily by hydrolyzing, for instance, organohalogen silane, organoalkoxy silane, etc. to polymerize, by polycondensing oligomers of (polyorganosiloxane) diol or by ring-opening polymerization of cyclic polyorganosiloxane having a low molecular weight.

The prepolymer is converted, with a heat-treatment and by the aid of the catalyst, to a tough elastomer having its molecular weight of more than one hundred thousand and more specifically of several hundred thousands to several millions. The thus formed elastomer may contain more or less cross-linkages and/or branches in its molecules, or may consist of linear molecules.

In the process of the present invention, non-aqueous solution containing generally 0.1–10% by weight of polyorganosiloxane component is applied to the fibrous structure by means of dipping, padding, spraying, etc., at a room temperature in such an amount as not exceeding 10% by weight of polyorganosiloxane component. The concentration of polyorganosiloxane, pick-up, etc., are appropriately controlled according to the shape of the fibrous structure, the sort of the fibers, etc., to keep the adsorption amount of polyorganosiloxane component not more than 10% by weight based on the structure.

As the catalyst to be applied in the process of the present invention, use may be made of an inorganic acid, such as hydrochloric acid and sulphuric acid; an alkali, such as caustic potash and caustic soda; an alkali silanolate derived from organosilanol; an inorganic salt, such as iron chloride; a metal oxide, such as lead oxide, zinc oxide and tin oxide; etc.

The most suitable is metal salts of an organic acid, such as dibutyl tin dilaurate, dibutyl tin dioctoate, dibutyl tin succinate, stannous octoate and chelate compounds of tin. The above-mentioned catalysts may be used solely or in combination of more than one.

The addition amount of the above-described catalyst may be suitably determined according to the kind of polyorganosiloxane prepolymer applied, its concentration treating conditions and further according as the kind of catalyst employed, and it is usually 0.01–5.0% by weight and preferably 0.1–1.0% by weight, based on the polyorganosiloxane component in the prepolymer applied.

Moreover, in addition to the above-mentioned catalyst, an organic silane compound, such as an isocyanate of silane compound, an alkoxysilane, an acetate of silane compound, etc., may be further added, as an accelerator of cross-linking reaction, for the purpose of improving the adhesivity of the polyorganosiloxane to the fibrous structure. As another catalyst for effecting cross-linking reaction, a peroxide, such as benzoyl peroxide may be used and a bi- or poly-functional compound, such as triol and a vinyl compound may be incorporated to the polymerization materials to produce a polymer having cross-linkages or branches in its molecules.

When fibrous structures including polyamidic fibers are treated, it is preferable to incorporate the solution of prepolymers with a small amount of compound having an affinity for polyamide, such as that having amino groups, imino groups, carboxyl groups, amide linkages or urea linkages; and compounds having a reactivity with polyamide, for instance, formaldehyde. As a result of the above, the adhesion between the fibrous structure and the polyorganosiloxane is improved and particularly, durability of adhesion is highly improved. The above-mentioned compound is usually added in an amount not more than 15% by weight based on the polyorganosiloxane.

As a non-aqueous solvent to be put to use in the process of the present invention, for instance, mention may be made of toluene, xylene, benzene, perchloroethylene, trichloroethylene, gasoline for an industrial use, chloroform, methyl chloroform, methylene chloride, etc. These solvents can be employed either solely or in combination of more than one.

A usual silicone resin for textile finishing with a non-aqueous solvent which was available in the market was tried, but the formed resinous film showed a low elongation at break, a small bending resistance and little durability for washing.

The fibrous structure to which a polyorgano-siloxane prepolymer and a catalyst have been applied is subjected to a heat-treatment at 50–200° C. to complete their reaction. The optimum temperature in the heat-treatment varies depending upon respective kinds of the treated fibrous structure, of the polyorganosiloxane and of the catalyst applied and upon the adhering amounts of the polyorganosiloxane and of the catalyst, and further it is in an interrelationship with the period of treating time. The temperature lower than 50° C. is not advantageous, because a polymer possessing required physical properties is not obtained or a prolonged period of treating time is required. In case the temperature gets higher than 200° C., there appear such defects that the treated article is discoloured and degraded, and its resiliency is lowered. The preferable range of the treating temperature is 100–180° C.

The period of treating time can be in the broad range of 20 seconds to 60 minutes and however, particularly preferably in the range of 1 minute to 10 minutes.

The prepolymer is converted, with a heat-treatment and by the aid of the catalyst, into a network having its molecular weight of more than several hundred thousands to form a tough elastomer having an elongation at break of at least 50%, a tensile strength at break of 1–50 kg./cm.$^2$ and a hardness of 5–50°.

Heretofore, for the purpose of obtaining cloths for umbrellas, rain-coats, etc. which have water-proofing and water-repellent abilities, finishing processes such as roll-coating, knife-coating and doctor-coating of taffeta, sail-cloth of synthetic fiber, tarpaulin, etc. with an acrylic resin, a urethanic resin, etc. have been well-known, and in fact, those finishing processes are similar to the so-called rubber-coating, so that it is the present situation that the merit and hand of the base cloth are lost. Since the above-mentioned coating methods have their object for providing a water-proofing ability to the coated article and according to these methods, resinous film is superimposed and adhered on the surface of the fibers, then the hand of the article becomes rubber-coated tone, so that the hand of the fiber itself cannot be effectuated. We, the inventors, have found out each of the afore-mentioned requirements, as a result of various investigations on the properties of the resin to be used, various physical properties of the fixed polymer after a polymerization treatment, the amount of the fixed polymer, etc.

Namely, in the present invention, as described hereinbefore the polymer which has been polymerized after adhered onto or impregnated into a fibrous structure satisfies each condition of an elongation at break of at least 50%, a tensile strength at break of 1–50 kg/cm.$^2$ and a hardness of 5–50°.

Furthermore, the preferable polymer, when formed in a shape of string or thin tape, exhibits an elongation at break of at least 80%, more preferably at least 100%, and a modulus of at most 1 g./d.

The elongation at break, tensile strength at break and hardness are to be determined according to JIS–C–2123 as follows:

## ELONGATION AND TENSILE STRENGTH AT BREAK

A test-piece in the shape of dumb-bell is cut out of silicone rubber sheet which is formed on a glass plate or in a porcelain vessel by polymerizing the same solution of polyorganosiloxane prepolymer as is applied to a fibrous structure according to the present invention. The size of the test-piece is 5 mm. width, 20 mm. length and 3 mm. or less thickness, respectively for its straight portion. The test-piece is stretched at 20° C. on Instron universal tension tester (manufactured by Instron Engineering Corp., U.S.A.) at a stretching rate of 500±25 mm./min. until it breaks, and then the maximum load and length of the straight portion are observed. The elongation and tensile strength at break are calculated by the following formulae respectively:

$$E_B=\frac{L_1-L_0}{L_0}\times 100$$

where, $E_B$ is percentage of elongation at break; $L_0$, the original length (mm.) of the straight portion; and $L_1$, the length (mm.) of the straight portion at break.

$$T_B=\frac{F_B}{A}$$

where, to $T_B$ is tensile strength at break (kg./cm.$^2$); $F_B$, the maximum load (kg.); and A, cross-sectional area (cm.$^2$) of the straight portion.

When four obtained values resulted from repeated tests with respect to $E_B$ or $T_B$, on four test pieces are denoted as $S_1$, $S_2$, $S_3$ and $S_4$ which are in a relation of:

$$S_1 \geqq S_2 \geqq S_3 \geqq S_4$$

then $E_B$ or $T_B$ is determined by the following equation:

$$E_B \text{ or } T_B=0.5S_1+0.3S_2+0.1(S_3+S_4)$$

## HARDNESS

A flat-surfaced test-piece having its thickness of at least 12 mm. is prepared. When its thickness is less than 12 mm., a plurality of such test-pieces are superimposed each other until total thickness reaches to 12 mm. or more. Upon the test-piece is placed a spring-type hardness tester which comprises a flat pressing surface provided with a hole having a diameter of at least 10 mm., a vertical pressing needle which is sprung forth out of said hole beyond the pressing surface and is positioned at the center of said hole, and a pointer which exhibits the amount of movement of the needle according as the hardness of the test-piece.

When the elongability is less than 50%, the formed film is so brittle that the fibrous structure having durable elasticity, crease-resistivity, shrink-proof ability and durability for washing cannot be obtained. The preferable value of the degree of elongation at break lies in the range of 150–800%. Tensile strength at break is 1–50 kg./cm.$^2$ and preferably 3–20 kg./cm.$^2$. When it is lower than 1 kg./cm.$^2$, the formed film is so brittle that the resultant fibrous structure is not satisfactory as its mechanical strength decreases, and on the other hand, when it is higher than 50 kg./cm.$^2$, the hand and feel of the treated fibrous structure are considerably impaired, whereas the hardness increases. The hardness should be 5–50° and preferably 8–30°. In case that it is less than 5°, the film-formability is insufficient, and on the other hand the hardness which exceeds 50° is not desirable, because the treated fibrous structure becomes rigid and the hand and feel are markedly deteriorated.

Furthermore, an important requirement for obtaining a fibrous structure having durable elasticity, crease-resistivity, shrink-proof ability and durability for washing together with desirable hand, is the amount of the polyorganosiloxane adhered to the fibrous structure. Namely, in the present invention, at most 10% by weight of the polyorganosiloxane having the aforesaid physical properties must be adhered or impregnated to the fibrous structure. The amount of the adhered or impregnated polyorganosiloxane is usually in the range of 0.05–10% and preferably 0.2–5% by weight based on the fibrous structure. When the amount is less than 0.05% by weight, the effect of the treatment is insufficient and on the other hand, when it exceeds 10% by weight, it is undesirable because defects such as the lowering of compression degree, the decrease of bulkiness and chalk marks are brought about.



Fibrous materials which constitute fibrous structures to be applied to the present invention are natural fibers, synthetic fibers, regenerated cellulose or their blends in the form of staple, filament or their mixture. As the natural fibers, mention may be made of wool, silk, cotton, hemp, etc.; as the synthetic fibers, polyesters, polyamides, polyureas, polyacrylonitrile, polyvinyl alcohol, polyolefins, polyvinyl chloride, polyvinylidene chloride, polyurethanes, etc.; and as the regenerated celluloses, viscose rayon, cupra, cellulose acetate, cellulose triacetate, etc.

Although the fibrous structures may be composed of staples alone, like as a spun staple yarn, needle-locked non-woven fabrics and the like, yet the process of the present invention can be more favourably applied to fibrous structures comprising at least 20% of continuous filaments, such as yarns, knitted goods, woven fabrics, made-up clothes and the like, which are, for instance, yarns on a skein, cloths, piece-goods, shirts, hosieries, tights, gloves and the like. As for the texture of the fibrous structure a coarse structure may be provided with the greatest effects. The present invention is, of course, not confined within knitted goods, woven fabrics and non-woven fabrics. The process of the present invention is particularly effective for fibrous structures, especially for lady's hosieries, consisting of continuous filaments alone and even in case that continuous filaments are used along with staple yarns, for instance, as blended yarns, mixed woven fabrics, etc., durable elasticity and excellent crease-resistivity are imparted to such structures, as long as the content of the continuous filaments is 20% or more.

Now, a treatment of lady's hosieries e.g. stockings which is one of the most important embodiment of the present invention will be described in detail hereunder.

For the manufcture of lady's stockings, both of a multi-filament yarn and a unitary filament yarn can be applied in general and however, the multi-filament yarn most desirably applied to the present invention is that of 10–30 denier of 2–5 filaments which consists of composite filaments having latent crimps that can be developed upon heating. The composite filament as such can be prepared by the process comprising; separately melting at least two fiber-forming thermoplastic synthetic polymers, extruding the molten polymers simultaneously from the same orifice of a spinneret to form a unitary filament consisting of at least two components of said polymers differing in shrinkability upon heating wherein said components are adherent to and disposed in an eccentric relation with each others throughout the entire length of the filament, and drawing the extruded filament.

Stockings composed of a multi-filament yarn mean those having their principal portion e.g. a leg portion knit with a multi-filament yarn either solely or in combination with a unitary filament yarn. Furthermore, a unitary composite filament yarn having latent crimps can be used with advantages. Stockings composed of a unitary filament yarn means those having their principal portion knit with a unitary filament yarn and their toe, heel, sole and welt may be with a multi-filament yarn.

The principal portion of the stockings may be knit into any stitches, for instance plain stitches, non-run stitches (run-proof stitches), meshes, micromeshes, jac-

quards and the like. By the term "stockings" used herein is meant lady's seamless stockings, panty-stockings and the like. Subsidiary portions of stockings, namely, toe, heel, welt, pants, etc., needless to say, may be knit in any fashion with any sort of yarn.

A process for manufacturing stretchable stockings from a composite filament yarn comprises sequential steps of knitting, crimp-developing, dyeing and boarding. In order to obtain highly stretchable stockings, it is necessary to treat the stockings with polyorganosiloxane prepolymer after the crimp-developing step, namely, the treatment according to the present invention may be conducted before the dyeing step, or before or after the boarding step. However, since stockings treated with polyorganosiloxane have somewhat decreased dyeability, it is more desired to conduct the polyorganosiloxane treatment after the dyeing step. Particularly, it is preferable to perform the polyorganosiloxane treatment on stockings which have been boarded and then allowed to relax for a period sufficient for releasing their residual shrinkages, for in this way the stockings are provided with the most uniform and balanced appearance and with an excellent extensibility.

The dyed stockings are steeped in a non-aqueous solution of polyorganosiloxane prepolymer, squeezed to gain a suitable pick-up and dried to polymerize the prepolymer. A baking or curing step may be further added after the drying step, if required, to accelerate the polymerization reaction. It is most preferable to carry out the polymerization reaction, i.e. the hardening treatment, as the stockings are in a sufficiently contracted condition, so that attention should be paid to minimize the tension of the stockings to the possible extent.

The amount of the polyorganosiloxane fixed upon stockings is preferably 0.1–10% by weight based on the weight of the stockings and more preferably 0.3–3% by weight. If it is to small, the stockings exhibit less smoothness, while it is too large, they are not only provided with an excessively increased smoothness, but also in the worst case, the polyorganosiloxane adheres lumpily onto stitches, forming films upon meshes of the stockings, so that the appearance of the stockings is markedly impaired. Since an uneven adhesion of polyorganosiloxane readily leads to the formation of the film, care should be taken so that the solution of prepolymer adhered on the stockings may be kept in a uniform condition during the drying step.

As it is possible in most cases, to break and get rid of the film formed over meshes by applying an intensive tension of the stockings, a step as such may follow the hardening treatment. Namely, it is one of the most suitable processes, for instance, to treat stockings with polyorganosiloxane prepolymer after dyeing and then conducting the hardening treatment which is followed by boarding, because most of the afore-said films is eliminated due to the tension applied thereto when boarding.

Stretchable stockings obtained according to the process of the present invention exhibit extremely excellent softness, smoothness, extensibleness and durability, and fit comfortably on account of the fixed polyorganosiloxane thereupon. Those effects can be more enhanced by knitting the principal portion i.e., leg of the stockings with a multi-filament yarn consisting of composite filaments. Moreover, the softness and smoothness of the resultant stockings are so stable that they are not substantially diminished by washing. The smoothness provided by the process of the present invention is far superior to that furnished by treating with a conventional softening agent comprising silicone oil (an aqueous emulsion of silicone oil, etc.). Furthermore, stockings manufactured according to the process of the present invention possesses such a smoothness that they show less probability of breakage due to scratching or yarn catching incidents. Stockings having their principal portion knit with a multi-filament yarn are more excellent in run-proofing ability, because even if some filaments of the multi-filament yarn be broken owing to a certain incident, yet other filaments of the yarn can sustain the stockings as unbroken.

Stocking prepared by the process of the present invention also display an excellent ability of recovering from extension.

There is seen an appreciable tendency that the appearance of the stockings having their main portion knit with a unitary filament yarn is impaired as the amount of the adhered polyorganosiloxane increases, while in case of the stockings knit from a multi-filament yarn, the above-mentioned tendency is reduced.

As is apparent from the description made hereinabove, of the preferable embodiment of the present invention, the fibrous structure of the present invention exhibits excellent tensile elasticity and compressive elasticity according to the resisting force against an external force which is due to an action of incorporated polyorganosiloxane as a member in the fibrous structure, and therefore, the obtained fibrous structure is provided with durable elasticity and crease-resistivity, and displays shrink-proof ability and durability for washing.

A resin finish of fibrous structure in the past has been accompanied with an action of fixing cross-over contacts in the structure, which has provided the structure, specifically fabrics, with flat hand, and it has been inevitable for the stretchability of the structure such as knitted goods to be impaired on account of the fixation of cross-over contacts of yarn loops. However, in the process of the present invention, as the resin is high in tensile elasticity as well as in toughness, even if it exists on the cross-over contact of fibers, the treated structure not only becomes stabe but also exhibits a satisfactory stretchability.

In addition to the astonishing improvement in elasticity and crease-resistivity of fibrous structures, the process of the present invention has outstanding features including that the crease-proof finish of silk structure can be effected without deteriorating its hand and that the shrink-proof finish of woollen structure has been realized and particularly, woollen structure having a wash-and-wear property which is durable for washing can be readily obtained, and furthermore, it is a prominent merit that since the fibers are treated with non-aqueous solution in which the fibers do not swell, so the fibers are not deformed keeping their contour in entirely natural state.

Another great advantage of the present invention is that the fibers are not degraded and the tearing strength of the structure is markedly increased. Besides, fabrics obtained by the process of the present invention have resiliency and dimensional stability, so that they are easier to cut and make up into garments with than the non-treated fabrics.

Another important merit of the present invention is that when fibrous structures are treated with a solution of polyorganosiloxane prepolymer containing the aforementioned polyetheric compound, the resultant structures possess a surpassing antistatic property, whereas most of resin-finishes provide structures which are readily statically electrified. Thus numerous troubles with which the static electrification is accompanied, such that an electrified body is readily soiled, difficult to process and uncomfortable to wear, can be solved by the present invention. Moreover, the application of the polyetheric compound eliminates the waxy hand of the fibrous structures which may be a trouble sometimes encountered by a polyorganosiloxane finish, particularly when the adhesion amount of the prepolymer becomes in excess of the preferable limit.

Still another advantage which the fibrous structure of the present invention has is that although it is observed the dyeability of the structure of the present invention is slightly decreased as compared with that of non-treated structure, none the less it is able to be post-dyed, by which a great merit is brought about. Hitherto, a dyeing process of fibrous structures, such as fabrics and made-up clothes,

has been carried out by means of a wince or a rotary dyeing machine, during which process creases, particularly rope marks given to the structures have been concerned about. Since the fibrous structure of the present invention is excellent elasticity and crease-resistivity, it is scarcely crease-set in water, so that the above-stated difficulty is overcome. Such a merit has never been obtained by any conventional resin-finishing process, till heat-stabilized and chemical-proofing polyorganosiloxanes are adequately put in use according to the process of the present invention.

A usual silicone resin for textile finishing having a low degree of polymerization with a non-aqueous solvent which was available in the market was tried, but the formed resinous film showed a low elongation at break, a small bending resistance and little durability for washing.

The present invention will be illustrated in detail with reference to examples hereinafter. The word "Part" used in the examples means "part by weight." Methods for determining tensile elasticity (load for elongation, a degree of elasticity) compressive elasticity (a degree of compression, a degree of resiliency), tearing strength, degrees of elongation, crease-resistivity and shrinkage, and conditions for washing and dry cleaning in the examples are as follows:

## TENSILE ELASTICITY

(1) Load for elongation.—A specimen having its effective length of 10 cm. and its width of 2.5 cm. is stretched on Instron universal tension tester at a stretching rate of 10 cm./min. and then the load (g.) corresponding to a certain constant elongation of the specimen is denoted as load for elongation.

(2) A degree of elasticity.—A degree of elasticity is represented by the following equation:

$$\text{Degree of elasticity (percent)} = \frac{l_1 - l_2}{l_1 - l} \times 100$$

where, $l_1$ (cm.) is the length of specimen when a load of 500 g. is applied to in the same manner as the above (1), $l_2$ (cm.) is the length measured after standing for one minute under the load followed by further standing for another one minute under no load and $l$ (cm.) is the original length of the specimen.

## COMPRESSIVE ELASTICITY

Four pieces of cloth are superimposed to each others, the total thickness ($t$ mm.) after a load of 10 g./cm.$^2$ is applied to for one minute is measured, then the thickness ($t_1$ mm.) after another load of 300 g./cm.$^2$ is applied to for one minute is measured and the thickness ($t_2$ mm.) after standing for another one minute under no load is determined. Then, a degree of compression and a degree of resiliency are expressed by the following equations:

$$\text{Degree of compression (percent)} = \frac{t - t_1}{t} \times 100$$

$$\text{Degree of resiliency (percent)} = \frac{t_2 - t_1}{t - t_1} \times 100$$

## A DEGREE OF ELONGATION

When a specimen having its effective length of 20 cm. and its width of 15 cm. is stretched on Instron universal tension tester at a stretching rate of 20 cm./min., the length ($L_1$ cm.) of the specimen corresponding to the load of 4 kg. is measured. L cm. is the original length of the specimen. The degree of elongation is represented by the following equation:

$$\text{Degree of elongation (percent)} = \frac{L_1 - L}{L} \times 100$$

Crease-resistivity is determined according as the method B prescribed in JIS L–1079–5, 22.2 B, which corresponds to a so-called Monsanto's method as prescribed in AATCC 66–1959 T or in ASTM D 1295–60 T.

## A DEGREE OF SHRINKAGE

### Broad-cloth (65% polyester staple/35% cotton)

Measurement is conducted according as the method F–3 in JIS L–1042 as follows:

1.36 kg. of sample-cloth together with a sufficient amount of water are put into a washing machine. Steam is supplied to the washing machine concurrently with its start of operation, to raise rapidly the temperature of water until it reaches to 100° C., when the steam supply is stopped and powderly soap is charged in an amount of 0.05% by weight. After 40 minutes soaping, the hot water is replaced with clean cold water, the temperature of which is rapidly raised to 60° C. and washed for another 10 minutes. The washed sample-cloth is dried on a flat bed press and then the distance between marks which have been previously marked on the sample-cloth is measured. From averaged values obtained from respective three measurements in the directions of warp and of weft, the degree of shrinkage is calculated by the following formula:

$$\text{Degree of shinkage (percent)} = \frac{L - L'}{L} \times 100$$

where, L is distance before washing and L' distance after washing.

### Fabrics of wool or wool/silk

Measurement is conducted according as the IWS-method as follows:

Upon the sample-cloth, respective three sets of marks in the direction of warp and of weft are marked.

One kilogramme of sample-cloth together with 25 liters of water containing 0.45% by weight of sodium dihydrophosphate, 0.80% by weight of sodium monohydrophosphate and 0.05% by weight of a nonionic surface active agent is put into a washing machine, soaked for 15 minutes and washed for another 5 minutes. After drying by steam pressing, the degree of shrinkage is measured and calculated in the same manner as the case of broad-cloth.

## WASHING

Washing is carried out continuously for 2 hours at 25° C. in an aqueous solution of 2 g./l. of Monogen (the trade name of a neutral soap manufactured by Daüchi Kogyo Seiyaku K.K.) with bath ratio of 50:1, by means of a reversibly rotating automatic washing machine.

## DRY CLEANING

Dry cleaning is carried out at 25° C. for 3 hours with 50 time bath of perchloroethylene.

## TEARING STRENGTH

The measurement of the tearing strength is conducted according as the C-method prescribed in JIS L–1079, such as follows:

Respective three test-pieces in the directions of warp and of weft, having 6.5 cm. width and 10 cm. length are mounted on an Elmendorf tearing tester.

The center of the long side of the test-piece is cut by 2 cm. wide. The maximum load (kg.) shown when the remaining width of 4.5 cm. is torn off is observed.

Example 1.—A double jersey fabric (the length extended in the wale direction was 70 mm./50 courses) knitted with a false-twist textured nylon-6 yarn of 70 denier of 18 filaments/2 ply was scoured at 70° C. for 20 minutes in a 30 times bath containing 1 g./l. each of an anionic surface active agent and of soda ash, dried (density, wale: 30/inch; course: 45/inch), padded with the solution having the below-described composition (pick-up: 100%), dried again at 80° C. and then was heat-treated at 150° C. for 2 minutes.

The thus obtained fabrics (density, wale: 37/inch; course: 45/inch) contained 1.5% by weight of polyorganosiloxane, displayed a favourable soft hand as well as desirable draping, and exhibited an excellent elastic

recovery from elongation, desirable crease-resistivity and water-repellency.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol containing 20% by mole of γ-cyanopropyl methyl siloxane unit, having a degree of polymerization ($\overline{P}$) of about 1,200 | 100 |
| Stannous octoate | 2 |
| Methyl triisocyanate silane | 2 |
| Gasoline for an industrial use | 900 |

For the purpose of comparison, a treatment was carried out in the same manner as above, except that use was made of a conventional silicone finishing agents KS 714 (a 30% trichloroethylene solution of methyl hydrogen polysiloxane manufactured by Shin-etsu Kagaku Kogyo K.K., $\overline{P}$: about 30) which had been used as a water-repelling finishing and that the bath having the following composition was used.

COMPOSITION OF TREATING SOLUTION (FOR COMPARISON)

| | Parts |
|---|---|
| KS 714 (manufactured by Shin-etsu Kagaku Kogyo K.K.) | 50 |
| Catalyst D7 (manufactured by Shin-etsu Kagaku Kogyo K.K.) | 20 |
| Gasoline for an industrial use | 950 |

The afore-mentioned polyorganosiloxane solution and KS 714 were respectively polymerized to obtain sheets having the thickness of 0.7 mm. The sheet obtained from the former exhibited the under-mentioned physical properties, while that obtained from KS 714 was so brittle that the elongation at break and tensile strength at break were unable to be measured.

Elongation at break—752 g.
Tensile strength at break—6 kg./cm.$^2$
Hardness—10°

The tensile elasticity and the compressive elasticity of the treated fabrics comparing with those of the untreated fabrics are shown in Table 1. The tensile elasticity appearing in the Table 1 was measured when the specimen was stretched 30% in the course direction.

TABLE 1

| | Tensile elasticity before washing | | Compressive elasticity, percent | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Before washing | | After washing | | After dry cleaning | |
| | Load for elongation (g.) | Degree of elasticity (percent) | Degree of compression | Degree of resiliency | Degree of compression | Degree of resiliency | Degree of compression | Degree of resiliency |
| Untreated article | 152 | 80.3 | 18.9 | 71.2 | | | | |
| Treated article of the invention | 120 | 94.3 | 20.6 | 94.3 | 19.8 | 92.5 | 20.3 | 92.2 |
| Comparison | 130 | 87.8 | 19.2 | 82.3 | 16.2 | 71.5 | 17.5 | 73.2 |

Example 2.—The fabric obtained in Example 1 was steeped in the dye-bath having the under-mentioned composition at 25° C. with a bath ratio of 30:1 and after the temperature was raised to 95° C. at the end of 40 minutes heating, the heating was continued to keep its temperature for another 60 minutes.

The dyed fabric of the present invention showed a good effect of uniform dyeability comparing with the untreated fabric. Moreover, it was little creased, the elesticity of the fabric was kept satisfactory and further the dimensional change of the fabric was negligibly small. The result is shown in Table 2 which follows. The tensile elasticity was measured when the specimen was stretched 30% in the course direction.

TABLE 2

| | Contraction, percentage of fabric | | Tensile elasticity | | Compressive elasticity, percent | |
|---|---|---|---|---|---|---|
| | Wale | Course | Load for elongation (g.) | Degree of elasticity (percent) | Degree of compression | Degree of resiliency |
| Untreated article | 1 | 7 | 148 | 78.8 | 17.8 | 70.8 |
| Treated article of the invention | 0.5 | 0 | 123 | 92.5 | 21.2 | 93.2 |

The contraction percentage of the fabric represents in percentage the ratio of the length lost by contraction after dyeing to the length before dyeing.

Example 3.—A fabric of double half tricot knitted with a raw silk yarn of 21 denier of 7 filaments/2 ply was scoured at 100° C. for 1 hour in a 40 times bath containing 3 g./l. of potash soap, then subjected to a beam-dyeing in a bath containing 10% by weight of Direct Deep Black EAC (a trade name of direct dye manufactured by Ciba Co.) and was dried at 100° C. on a stenter-drier (density, wale: 42/inch; course: 46/inch). The thus dried fabric was steeped in the solution having the under-mentioned composition, squeezed at a pick-up of 60%, dried again at 80° C. and then heat-treated at 120° C. for 2 minutes.

The thus obtained fabric (density, wale: 42/inch; course: 45.5/inch) exhibited excellent crease-resistivity and elasticity, so that it was suitable for lady's clothes and gloves.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol containing 5% by mole of methyl hydrogen siloxane unit ($\overline{P}$: about 900) | 100 |
| Dibutyl tin dilaurate | 3 |
| Tetraethoxy silane | 3 |
| Perchloroethylene | 900 |

For the purpose of comparison, a treatment was carried out in the same manner as above, except that the bath having the following composition containg KS 724 (a 30% trichloroethylene solution of methyl hydrogen polysiloxane manufactured by Shin-etsu Kagaku Kogyo K.K., $\overline{P}$: about 30) was used.

COMPOSITION OF TREATING SOLUTION (FOR COMPARISON)

| | Parts |
|---|---|
| KS 724 (manufactured by Shin-etsu Kagaku Kogyo K.K.) | 50 |
| Catalyst PD (manufactured by Shin-etsu Kagaku Kogyo K.K.) | 10 |
| Perchloroethylene | 950 |

The result of comparison between two fabrics is shown in Table 3 which follows:

TABLE 3

| | Compressive elasticity (percent), before washing | | Crease-resistivity (percent) | | | |
|---|---|---|---|---|---|---|
| | | | Before washing | | After dry-cleaning | |
| | Degree of compression | Degree of resiliency | Wale | Course | Wale | Course |
| Article of the invention | 22.0 | 96.5 | 77.7 | 79.4 | 77.1 | 77.7 |
| Comparison | 19.3 | 93.2 | 57.2 | 58.3 | 58.3 | 66.6 |

The afore-mentioned polyorganosiloxane solution and KS 724 were respectively polymerized and formed into sheets. The sheet obtained from the former exhibited the under-mentioned physical properties, while that obtained from KS 724 was so brittle that it was impossible to measure the elongation at break.

Elongation at break—650%
Tensile strength at break—6 kg./cm.²
Hardness—10°

Example 4.—A skein (500 g.) of a false-twist textured nylon-6 yarn of 70 denier of 18 filaments/2 ply was steeped for one minute in the bath used in Example 1, after which it was put into a centrifugal separator to dry up to a water content of 22% and then air-dried. The dried yarn was heat-treated at 150° C. for 10 minutes.

The amount of the polyorganosiloxane fixed onto the obtained yarn was 0.3% by weight.

The treated yarn exhibited an excellent elastic recovery from extension. The treated yarn and the untreated yarn were knitted into respective socks (with plain stitch, wale: 28/inch; course: 41/inch). The socks knitted with the treated yarn were superior in both stretchability and fit, showed little variation in density of stitches caused by a fluctuation of tension in the knitting process and also the knitting operation was smoothly performed. The result is shown in Table 4 which follows:

TABLE 4

| Physical property | Specimen | |
|---|---|---|
| | Untreated article | Treated article of the invention |
| Compressive elasticity: | | |
| Degree of compression (percent) | 21.6 | 28.8 |
| Degree of resiliency (percent) | 70.8 | 86.5 |
| Degree of elongation: | | |
| Wale (percent) | 140 | 200 |
| Course (percent) | 94 | 150 |

Example 5.—Piqué, both for warp and weft of which a rayon yarn of 150 denier of 32 filaments had been used (density, warp: 65/inch; weft: 84/inch), was padded with the bath used in Example 3 and squeezed with a pick-up of 85% and heat-treated at 160° C. for 3 minutes. The fixed amount of the polyorganosiloxane on the fabric was 1.3% by weight. The result is shown in Table 5 which follows:

TABLE 5

| | Compressive elasticity (percent | | Crease-resistivity (percent | |
|---|---|---|---|---|
| | Degree of compression | Degree of resiliency | Warp | Weft |
| Article of the invention | 14.2 | 94.2 | 145 | 131 |
| Untreated article | 12.8 | 80.2 | 98 | 103 |

Example 6.—A fabric of piled tricot which had been knitted with a nylon-6 filament yarn of 70 denier of 18 filaments was heat-set at 170° C. and after scouring at 70° C. for 20 minutes in a 20 folded bath containing 2 g./l. of a nonionic surface active agent, it was fluorescence-dyed with 1% by weight of Whitex RP (a trade name of an anionic fluorescence dye manufactured by Sumitomo Kagaku Kogyo K.K.) and 1% by weight of acetic acid.

The fabric had its densities of 38/inch for the wale and 72/inch for the course.

The above-mentioned fabric of piled tricot was padded with solution having the under-stated composition and squeezed with a pick-up of 160%. Subsequently it was heat-treated at 170° C. for 45 seconds to obtain a fabric which was provided with durable elasticity and crease-resistivity.

The fixed amount of polyorganosiloxane on the obtained fabric was 4.9% by weight.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol ($\overline{P}$: about 1,000) | 180 |
| Dibutyl tin octyl maleate laurate | 2 |
| Phenyl triisocyanate silane | 2 |
| Trichloroethylene | 820 |

For the purpose of comparison, a treatment was carried out in the same manner as above, except that KS 714 used in Example 1 was used. The result is shown in Table 6. The tensile elasticity was measured when the specimen was stretched 70% in the wale direction.

TABLE 6

| | Tensile elasticity | | | |
|---|---|---|---|---|
| | Before washing | | After washing | |
| | Load for elongation (g.) | Degree of elasticity (percent) | Load for elongation (g.) | Degree of elasticity (percent) |
| Untreated article | 142 | 22.2 | 148 | 20.5 |
| Treated article of the invention | 150 | 95.3 | 153 | 93.2 |
| Comparison | 135 | 85.8 | 143 | 65.2 |

The afore-mentioned polyorganosiloxane was polymerized and formed into a sheet having a thickness of 0.7 mm. which exhibited the following physical properties.

Elongation at break—424%
Tensile strength at break—3 kg./cm.²
Hardness—8°

Example 7.—A satin fabric that had been woven with a cellulose acetate filament yarn of 150 denier of 60 filaments as warps and with a top-dyed woollen yarn of 60 count as wefts, was padded with the treating bath used in Example 3 and squeezed with a pick-up of 80%. It was then heat-treated at 130° C. for 3 minutes to obtain a resilient fabric which was provided with an excellent crease-resistivity. Comparison of it with the untreated fabric is shown in Table 7 which follows:

TABLE 7

| | Crease-resistivity (percent) | |
|---|---|---|
| | Warp | Weft |
| Treated article of the invention | 81.7 | 77.8 |
| Untreated article | 54.5 | 61.6 |

Example 8.—A sports-wear with half sleeves knitted with a false-twist textured polyester yarn of 150 denier of 48 filaments/2 ply (having plain stitches, density, wale: 25/inch; course: 40/inch), was steeped for one minute in the solution having the under-mentioned composition and put into a centrifugal separator to dry up to 40% of water content. After air-drying, it was boarded and heat-treated at 160° C. for 2 minutes. The obtained sports-wear exhibited an excellent resilient hand and had satisfactory tensile elasticity, compressive elasticity and crease-resistivity. The fixed amount of polyorganosiloxane on the sports-wear was 0.6% by weight.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol ($\overline{P}$: 1,300) | 100 |
| Dibutyl tin octyl maleate laurate | 0.8 |
| Phenyl triisocyanate silane | 0.8 |
| Trichloroethylene | 900 |

Example 9.—Socks for gentlemen knitted with textured nylon-6 filament yarn of 70 denier of 32 filaments/2 ply (density( wale: 29/inch; course; 43/inch), were soaked in the solution having the under-mentioned composition, squeezed with a pick-up of 45% and then heat-treated at 150° C. for 1 minute. The fixed amount of polyorganosiloxane on the obtained socks was 1.1% by weight. The socks had favourable fit and excellent elasticity and moreover feet felt none of stuffiness and humidity inherent in nylon socks when they were worn.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol containing 5% by mole methyl hydrogen siloxane unit ($\overline{P}$: 500) | 160 |
| Dibutyl tin dilurate | 3 |
| Tetraethoxy silane | 3 |
| Perchloroethylene | 900 |

Example 10.—A double jersey fabric knitted with a false-twist nylon-6 filament yarn of 70 denier of 18 filaments/2 ply was scoured at 70° C. in a 30 folded bath containing 2 g./l. of a nonionic surface active agent, dyed with 1.2% of Hakkol BS conc. (a trade name of anionic fluorescence dye manufactured by Showa Kagaku K.K.) and dried. In order to study of the optimum amount of the resin to be employed, treating solutions same as that used in Example 6 but the concentration of resin varied from 0.5 to 40% by weight, were prepared. The above-mentioned dried fabrics were padded with those solutions, squeezed with a pick-up of 175%, dried again at 80° C. and then heat-treated at 150° C. for 2.5 minutes. The compressive elasticity and the crease-resistivity of the resulted fabric were measured and shown in Table 8 which follows:

When the fixed amount of resin exceeds 10% by weight, the degree of compression is lowered and the hand and feel approach extremely to those of rubber-coating.

Example 11.—Two hundred grammes of a raw silk yarn of 21 denier of 7 filaments/2 ply in the form of a skein were scoured at 100° C. for 1 hour with a 40 folded bath containing 3 g./l. of potash soap and dried. The dried skein was steeped in the treating solution same as that used in Example 3, put into a centrifugal separator (to dry up to the water content of 42%), air-dried and then was heat-treated at 105° C. for 10 minutes.

The so obtained yarn was put into a jet-type hank dyeing machine, whereby it was steeped in the dyebath with bath ratio of 40:1 containing solution of 1.2% by weight of Kiton Fast Violet R (a trade name of an acidic dye manufactured by Ciba Co.) and of 2% by weight of potash soap, was boiled for 20 minutes, dried gradually, washed with water and then dried again. The resulting yarn exhibited good effect of uniform dyeing and the problem of the lousiness as well as the napping which had previously been arisen in silk dyeing techniques, was eliminated and the handling of the yarn was made easier. A lady's suit was knitted with three of the obtained yarn (plain stitch, wale: 27/inch; course: 40/inch) and the article having excellent crease-resistivity and elasticity was obtained. The result is shown in Table 9 which follows:

TABLE 9

| | Compressive elasticity (percent) | | Crease-resistivity (percent) | |
|---|---|---|---|---|
| | Degree of compression | Degree of resiliency | Wale | Course |
| Untreated article | 18 | 88 | 49.5 | 63.9 |
| Article of the invention | 24 | 95 | 80.6 | 80.6 |

Example 12.—Twill of 2 woollen yarns/2 wool-silk blended yarns (warp: worsted yarn of 2/54 count; weft: worsted yarn of 2/54 count and silk yarn of 2/21 denier; density of warp: 42/inch; density of weft: worsted yarn, 38/inch and silk yarn, 38/inch) was padded with the same solution as used in Example 1 (pick-up: 66%), dried at 80° C. and then was heat-treated at 120° C. for 3 minutes.

The thus obtained fabric contained 0.98% by weight of polyorganosiloxane, displayed a favourable resilient hand and increased crease-resistivity, shrink-proof ability and durability for washing.

For the purpose of comparison, a treatment was carried out in the same manner as above, except that the same bath as used at the comparison test in Example 1 was employed.

The tensile strength, elasticity, crease-resistivity and shrinkage for washing (percentage of shrinkage and W.W., i.e. Wash-and-Wear property) of the treated fabric comparing with those of the untreated fabric as well as of comparison-tested one are shown in Table 10.

TABLE 8

| | Concentration of solution | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 0.075 | 0.15 | 0.45 | 0.75 | 1.5 | 3.0 | 4.5 | 6.0 | 7.5 |
| Amount of silicone fixed | 0 | 0.13 | 0.26 | 0.78 | 1.31 | 2.62 | 5.24 | 7.86 | 10.48 | 15.5 |
| Physical property: | | | | | | | | | | |
| Compressive elasticity: | | | | | | | | | | |
| Degree of compression (percent) | 18.6 | 21.1 | 22.4 | 22.4 | 21.9 | 20.8 | 20.3 | 19.6 | 18.5 | 16.3 |
| Degree of resiliency (percent) | 69.8 | 79.6 | 82.3 | 83.5 | 85.8 | 84.8 | 85.2 | 87.5 | 86.2 | 84.3 |
| Crease resistivity: | | | | | | | | | | |
| Wale | 55.6 | 77.8 | 80.6 | 82.2 | 85.0 | 92.2 | 90.6 | 93.4 | 91.7 | 89.5 |
| Course | 58.9 | 84.4 | 88.4 | 86.6 | 85.6 | 87.8 | 88.9 | 90.6 | 90.0 | 88.4 |
| Hand | Bad | Good | Good | Good | Good | Good | Good | Good | (1) | (1) |

(1) Slightly bad.

TABLE 10

| | Tearing strength (g.) | | Compressive elasticity (percent) | | Crease-resistivity (crease recovery (percent)) | | Durability for washing | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Shrinkage (percent) | | |
| | Warp | Weft | Degree of compression | Degree of resiliency | Warp | Weft | Warp | Weft | W and W |
| Untreated article | 1,472 | 1,280 | 18.6 | 89.1 | 86.1 | 78.8 | 8.2 | 6.5 | 2 grade. |
| Treated article of the invention | 1,888 | 1,600 | 22.2 | 92.5 | 92.5 | 89.8 | 1.0 | 1.3 | 4 grade. |
| Comparison | 1,580 | 1,310 | 20.2 | 90.5 | 87.5 | 81.2 | 2.8 | 4.6 | 2 grade. |

Example 13.—A double jersey fabric knit from worsted yarn of 1/44 count (density, wale: 39/inch; course: 34/inch) was hot-tumbled to relax. The resultant fabric having the density of wale of 38/inch and that of course of 35/inch, was padded with the same bath as used in Example 3 (pick-up: 85%), dried at 70° C. and was heat-treated at 120° C. for 4 minutes. The resultant fabric (density, wale: 38/inch; course: 35.5/inch) contained 1.28% by weight of polyorganosiloxane, displayed a favourable soft hand and draping, and exhibited an excellent recovery from elongation, desirable crease-resistivity, durability for washing and water-repellency.

For the purpose of comparison, a treatment was carried out in the same manner as above, except that the same bath as used at the comparison test in Example 3 was used. The result of comparison of those fabrics is shown in Table 11 which follows:

TABLE 11

| | Compressive elasticity (percent) | | Compressive elasticity (after dry cleaning) (percent) | | Durability for washing | | | Tensile elasticity (50% elongation) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Shrinkage (percent) | | | | |
| | Degree of compression | Degree of resiliency | Degree of compression | Degree of resiliency | Wale | Course | W and W | Load (g.) | Degree of elasticity (percent) |
| Untreated article | 24.4 | 89.5 | 25.2 | 88.2 | 12.8 | 15.4 | 1.5 grade | 165 | 84.8 |
| Treated article of the invention | 27.5 | 95.0 | 27.3 | 94.0 | 2.2 | 1.3 | 4 grade | 152 | 95.6 |
| Comparison | 25.2 | 91.5 | 24.8 | 89.5 | 10.1 | 8.5 | 2 grade | 158 | 88.7 |

Example 14.—Twill which had been woven with Torelon yarn (a trade-name of polyacrylic yarn manufactured by Toyo Rayon K.K.) (warp: 1/50 count; weft: 1/32 count; density of warp: 86/inch; density of weft: 80/inch) was padded with the solution having the understated composition (pick-up: 60%), dried at 80° C. and then heat-treated at 170° C. for 30 seconds. The resultant fabric contained 1.62% by weight of polyorganosiloxane, displayed a favourable resilient hand and exhibited an excellent crease-resistivity.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol ($\overline{P}$: about 200) | 180 |
| Dibutyl tin octyl maleate laurate | 3 |
| Phenyl triisocyanate silane | 3 |
| Trichloroethylene | 820 |

For the purpose of comparison, a treatment was carried out in the same manner as above, except that the same bath as used at the comparison test in Example 1 was employed. The result of comparison of those fabrics is shown in Table 12 which follows:

TABLE 12

| | Compressive elasticity (percent) | | Crease-recovery (percent) | | Crease-recovery (percent) (after washing) | |
|---|---|---|---|---|---|---|
| | Degree of compression | Degree of resiliency | Warp | Weft | Warp | Weft |
| Untreated article | 20.5 | 85.1 | 85.5 | 87.3 | 81.6 | 83.8 |
| Treated article of the invention | 27.0 | 89.5 | 89.8 | 92.3 | 87.9 | 89.9 |
| Comparison | 22.8 | 86.7 | 86.2 | 88.5 | 83.2 | 84.2 |

The afore-mentioned polyorganosiloxane solution was polymerized to obtain a sheet having a thickness of 0.7 mm. which exhibited an elongation at break of 424%, a tensile strength at break of 3 kg./cm.$^2$ and a hardness of 8°.

Example 15.—Skier's socks knit from woolen yarn which had had their toes and heels reinforced by nylon-6 yarn (composition: 85% of wool and 15% of nylon; density, wale: 5/inch; course: 8/inch) were soaked in the solution having the under-described composition, worked in a centrifugal separator to reduce the water content to 100% and then dried at 150° C. for 1.5 minutes. The resultant socks contained 2.5% by weight of polyorganosiloxane, displayed favourable elastic and warm hands, and had a suppressed felting tendency due to washing as well as wearing.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol containing 5% by mole of methyl hydrogen siloxane unit ($\overline{P}$: about 1,200) | 160 |
| Dibutyl tin dilaurate | 3 |
| Tetraethoxy silane | 3 |
| Perchloroethylene | 840 |

Comparison of the socks treated as above, those non-treated and those treated with conventional shrink-proof finish, is shown in Table 13 which follows:

TABLE 13

| | Compressive elasticity [1] (percent) | | Durability for washing | | |
|---|---|---|---|---|---|
| | Degree of compression | Degree of resiliency | Shrinkage of wale (percent) | Shrinkage of course (percent) | Felting tendency |
| Untreated article | 46.8 | 84.6 | 7.8 | 8.5 | Large. |
| Treated article of the invention. | 48.2 | 96.5 | 1.2 | 0.8 | Small. |
| Comparison (shrink-proof finish).[2] | 46.8 | 86.6 | 1.8 | 1.5 | Medium. |

[1] Compressive elasticity was measured with respect to two socks which were superimposed on each other.

[2] Socks for comparison were treated with aqueous solution of 3.0% by weight of Basolan DC (a trade name of a felt-resistant agent for wool manufactured by Badische Anilin & Soda Fabrik, A.G. in Germany).

Example 16.—A skein of pure woollen yarn (500 g./skein) was soaked in the same bath as used in Example 1 for one minute, worked in a centrifugal separator to reduce the water content to 50% and then subjected to air-drying, followed by 15 minute cure at 100° C. The amount of polyorganosiloxane fixed upon the yarn was 0.78% by weight. No appreciable shrinkage of the yarn was observed and the resultant yarn has favourable hand. A sweater knit with the thus treated yarn exhibited favourable hand and durability for washing, and had an excellent dimensional stability. Moreover, knitting operation was far more smoothly performed with the treated yarn than with the untreated yarn.

Comparison between the two sweaters knit respectively with the treated yarn and with the untreated yarn is shown in Table 14 which follows:

TABLE 14

| | Compressive elasticity (percent) | | Tensile elasticity | | Durability for washing | | |
|---|---|---|---|---|---|---|---|
| | Degree of compression | Degree of resiliency | Load (g.) | Degree of elasticity (percent) | Shrinkage (percent) Wale | Course | Felting |
| Untreated article | 38.2 | 87.8 | 150 | 76.2 | 15.2 | 10.8 | Marked. |
| Treated article of the invention | 42.5 | 94.8 | 136 | 88.2 | 3.5 | 2.5 | Slight. |

Example 17.—A Fuji-silk fabric, i.e. a fabric woven with silk spun yarn of 2/140 count as its warps and with silk spun yarn of 1/66 count as its fillings (density, warp: 112/inch; filling: 88/inch) was padded with the solution having the under-mentioned composition, squeezed at a pick-up of 70% and then cured for 2 minutes at 130° C. The resultant fabric contained 0.5% by weight of polyorganosiloxane and exhibited thick hand and an excellent crease-resistant ability.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol ($\overline{P}$: about 80) | 50 |
| Dibutyl tin octyl maleate laurate | 1 |
| Phenyl triisocyanate silane | 1 |
| Perchloroethylene | 950 |

The comparison between the fabric treated according to the process of the present invention and untreated fabric is shown in Table 15 which follows:

TABLE 15

| | Tearing strength (g.) | | Compressive elasticity (percent) Before dry cleaning | | After dry cleainng | | Crease-recovery (percent) Before dry cleaning | | After dry cleaning | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Warp | Weft | Degree of compression | Degree of resiliency | Degree of compression | Degree of resiliency | Warp | Weft | Warp | Weft |
| Untreated article | 1,920 | 2,048 | 27.2 | 78.8 | 26.5 | 79.2 | 76.8 | 77.2 | 75.2 | 76.2 |
| Treated article of the invention | 2,368 | 2,816 | 27.0 | 89.7 | 26.2 | 88.2 | 86.6 | 89.4 | 87.6 | 87.2 |

Example 18.—Broadcloth woven with 40 count blend spun yarn of 65% by weight of polyester staple and 35% by weight of cotton (density, warp: 120/inch; weft: 70/inch) was scoured, bleached, fluorescence-dyed, padded with the same solution as was used in Example 3, squeezed at a pick-up of 70% and then cured for 3 minutes at 160° C. The resultant fabric contained 1.05% by weight of polyorganosiloxane and exhibited thick hand and crease-resistant ability.

The characteristics of the treated fabric are shown as compared with those of untreated fabric in the following Table 16.

TABLE 16

| | Compressive elasticity (percent), before washing | | Degree of crease recovery (percent) Before washing | | After washing | |
|---|---|---|---|---|---|---|
| | Degree of compression | Degree of resiliency | Warp | Weft | Warp | Weft |
| Untreated article | 29.5 | 75 | 80.0 | 78.8 | 78.8 | 74.4 |
| Article of the invention | 30.5 | 83 | 85.6 | 82.7 | 83.5 | 81.8 |

Example 19.—A double jersey fabric (the length extended in the wale direction was 70 mm./50 course) knitted with a false-twist textured nylon-6 yarn of 70 denier of 18 filaments/2 ply, was scoured at 70° C. for 20 minutes in a 30th folded bath containing 1 g./l. each of an anionic surface active agent and of soda ash, dried, padded with the solution having the under-described composition (pick-up: 100%), dried again at 80° C. and then cured for 2 minutes at 150° C.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 30% by weight of dimethyl polysiloxane diol prepolymer ($\overline{P}$: about 400) | 100 |
| Dibutyl tin diluarate | 1 |
| Polyoxyethylene sorbitan monolaurate | [1] $x$ |
| Perchloroethylene | 900 |

[1] Amount of this polyetheric compound was varied to be 0%, 3.3%, 10%, 16.5% and 30% each by weight based on the polysiloxane prepolymer, whereby 5 kinds of solution were prepared.

Fabrics treated with the solution containing the polyoxyethylene sorbitan monolaurate showed markedly decreased waxy hand and anti-static property as compared with the fabric treated with the solution not containing the polyetheric compound, and exhibited an excellent elasticity.

The comparison of those fabrics is shown in Table 17 which follows:

TABLE 17

| Properties | Amount of POESL[1] added (percent) 0 | 3.3 | 10 | 16.5 | 30 | Untreated (Gray) |
|---|---|---|---|---|---|---|
| Waxy hand | [2] | [3] | [3] | [3] | [3] | |
| Compressive elasticity | 88.5 | 88.2 | 87.8 | 86.2 | 84.8 | 72.0 |
| Frictional electrostatic pressure (V) [4] | 2,000 | 700 | 400 | 200 | 150 | 5,400 |

[1] POESL=Polyoxyethylene sorbitan monolaurate.
[2] Distinct.
[3] Markedly reduced.
[4] Determination of the frictional electrostatic pressure was conducted as follows.—Sample cloth was rubbed with a pure cotton cloth at a speed of 1,050 r.p.m. at 20° C. and 65% R.H. and then generated electrostatic pressure was measured.

Example 20.—Men's socks (density, wale: 29; course: 43) knit with a false-twist textured nylon-6 yarn of 70 denier of 32 filaments/2 ply, were soaked in the solution having the under-mentioned composition, worked in a centrifugal separator to reduce the water content to 170%; dried at 70° C. and then cured for 5 minutes at 120° C.

COMPOSITION OF TREATING SOLUTION

| | Parts |
|---|---|
| Trichloroethylene solution of 15% by weight of dimethyl polysiloxane diol containing 5% by mole of methyl hydrogen siloxane unit ($\overline{P}$: about 500) | 160 |
| Dibutyl tin dilaurate | 3 |
| Tetraethoxy silane | 3 |
| Polyoxyethylene laurylphosphate | [1] $x$ |
| Perchloroethylene | 840 |

[1] Amount of this polyethyeric compound was varied to be 0%, 3,3%, 10%, 16.5% and 30% each by weight based on the polysiloxane, whereby 5 kinds of solution were prepared.

The socks treated with the solution containing the polyetheric compound showed an adequately suppressed smoothness and an excellent elasticity, while those treated with solution not containing the polyetheric compound exhibited smoothness so much that their soles were slippery and felt rather dangerous when worn.

The comparison of those socks is shown in Table 18 which follows:



TABLE 18

| Properties | Amount of POELP[1] added (percent) 0 | 3.3 | 10 | 16.5 | 30 | Gray |
|---|---|---|---|---|---|---|
| Waxy hand | [2] | [3] | [4] | [4] | [4] | |
| Compressive elasticity | 92.2 | 92 | 90.8 | 90.2 | 88.5 | 78 |
| Elastic recovery at 5% elongation | 93.8 | 93.5 | 92.8 | 91.8 | 90.8 | 72 |

[1] POELP=Polyoxyethylene lauryl phosphate.
[2] Too slippery.
[3] Reduced.
[4] Markedly reduced.

Example 21.—Nylon-6 having its inherent viscosity of 1.24 in m-cresol solution at 25° C. and a copolymer of 9 parts of nylon-6 with 1 part of polyhexamethylene isophthalamide having its inherent viscosity of 1.24 were separately melted and two melts of equal weight were conjugated in a side by side relation which were extruded concurrently from an orifice having its diameter of 0.25 mm. on a spinneret plate at 280° C. to form a unitary filament wherein two polyamidic components were adhered and disposed in a side by side relation with each other throughout the entire length of the filament. The extruded filament was air-quenched, oiled, wound on a take-up tube at a speed of 700 meters per minute and then drawn to 4.1 times its original length to obtain a unitary filament yarn $Y_1$ of 15 denier. A multi-filament yarn $Y_2$ of 45 denier of 7 filaments was obtained substantially in the same manner as above except that the draw ratio was 3.7.

Each of yarns $Y_1$ and $Y_2$ was passed through a heated metallic tube having its inside diameter of 3 mm. and length 50 cm., at a relaxed condition to develop slight crimps and wound on a bobbin. When the yarn $Y_1$ was processed, the temperature of the heater tube was 140° C., the feed-in speed was 280 m./min. and the delivery speed was 211 m./min., and when the yarn $Y_2$, the temperature of the heater tube was 180° C., the feed-in speed was 200 m./min. and the delivery speed was 150 m./min. Stockings with plain stitches were knit on a circular knitting machine which was provided with 400 needles, using the above processed yarn $Y_1$ for the leg portion and the yarn $Y_2$ for the toe, heel and welt. After looping, the knitted stockings were steamed at 100° C. under a tensionless condition for 30 minutes to develop their crimps, put into a sack and dyed in a rotary drum type dyeing machine. The dyed stockings were boarded and steamed at 116° C. for 45 seconds, taken off the board after drying and allowed to stand in a room of 65% R.H. at 25° C. for 1 day to shrink. The resultant stockings were denoted as "stockings $S_1$." The stockings $S_1$ were soaked in a solution which consisted of 1.5 parts of poly-dimethyl siloxane diol prepolymer having its degree of polymerization of about 150, 98.5 parts of trichloroethylene and 0.01 part of benzoyl peroxide, subjected to a centrifugal squeezing followed by drying, and then cured in hot air at 165° C. for 15 minutes. The thus treated stockings which were denoted as "stockings $S_2$," had 0.6% of polyorganosiloxane adhered thereon.

Other stockings were manufactured substantially in the same manner as above except that after dyeing, they were finished with an aqueous emulsion of softening agent comprising a silicone oil and a cationic surface active agent (adhesion amount of the softening agent was 1.1% by weight) and then subjected to boarding, which were denoted as "stockings $S_3$."

The stockings $S_2$ and $S_3$ were very smooth and soft, whereas the stockings $S_1$ exhibited a little hard hand.

The above-mentioned stockings $S_1$, $S_2$ and $S_3$ were test used by 60 persons. One user wore three pairs, ench one pair of those three kinds of stockings, so as to use one pair every three days until all of them were broken and their lives were recorded. The stockings were washed in hot water with neutral soap after wearing for a day. In this way, the interrelation between the life and the number of breakages with respect to 60 pairs of stockings of a sort was observed and it was made clear that the

number of unbroken stockings decreased in inverse proportion as the time of wear and such relation was approximated by the exponential function shown in the Equation 1.

$$X=Ae^{-kt} \quad (1)$$

where,

X: Number of unbroken stockings
A: Number of stockings tested (120)
$e$: 2.718 (constant)
$k$: Coefficient of decrease
$t$: time

When the Equation 1 is applicable, average life of wear is shown by the reciprocal of the coefficient $k$, i.e. $1/k$. Average life of the stockings $S_1$, $S_2$ and $S_3$ were 75 hours, 82 hours and 77 hours respectively. The stockings $S_3$ had lost their softness after washing, whereas the stockings $S_2$ did not lose their softness as well as smoothness.

Too much adhesion of polyroganosiloxane led to an undesirable result. In the following Table 19 will be shown a result of measurements of elongation and recovery of leg portion with respect to stockings which were manufactured substantially in the same manner as that of the manufacture of the stockings $S_2$ except the amount of polyorganosiloxane adhered.

TABLE 19

| Amount of polyorganosiloxane adhered (percent) | Elongation (percent) | Recovery (percent) |
|---|---|---|
| 0 | 132 | 88.4 |
| 0.3 | 134 | 90.9 |
| 0.5 | 134 | 91.3 |
| 0.7 | 135 | 91.5 |
| 1.0 | 135 | 90.0 |
| 2.3 | 134 | 91.2 |
| 4.3 | 133 | 87.4 |

Method for determining percentages of elongation and recovery was as follows:

Distance ($L_0$) between the welt and the heel of stockings was measured.

Next, the welt of the stocking was fixed, from which the stocking was hung, attaching a load of 2 kg. at the bottom end of its leg portion and one minute later the distance ($L_1$) between the welt and the heel was measured. Then, the load was taken off and one minute later the distance ($L_2$) between the welt and the heal was measured again. The percentage of elongation and that of recovery were calculated by the Formulae II and III respectively.

$$\text{Percentage of elongation (Percent)}=\frac{L_1-L_0}{L_0}\times 100 \quad (II)$$

$$\text{Percentage of recovery (Percent)}=\frac{L_1-L_2}{L_1-L_0}\times 100 \quad (III)$$

As is apparent from Table 19, when the amount of polyorganosiloxane adhered is in excess of 4%, the percentage recovery is small. From the viewpoint of smoothness, even an amount of less than 1% gives good results and more amount seems to be unnecessary.

Next, stockings $S_4$ were manufactured substantially in the same manner as that of the manufacture of the stockings $S_2$ except that the leg portion was knit into non-run stitches. The stockings $S_4$ were extremely soft and stretchable, and further well fitted. On the contrary, non-run stockings which had not been treated with polyorganosiloxane were awfully poor in their stretchability as well as in their softness.

Example 22.—Nylon-6 having its inherent viscosity of 1.21 in m-cresol solution at 25° C. and a copolymer of 88 parts of nylon-6 with 12 parts of polyhexamethylene isophthalamide having its inherent viscosity of 1.23 were separately melted and two melts of equal weight were conjugated in a side by side relation which were extruded concurrently from an orifice having its diameter of 0.25 mm. on a spinneret plate at 280° C. to form a unitary filament wherein two polyamidic components were adhered and disposed in a side by side relation with each other throughout the entire length of the filament. The extruded filament was air-quenched, oiled, wound on a take-up tube at a speed of 700 meters per minute and then drawn to 4.0 times its original length to obtain a unitary filament yarn $Y_3$ of 18 denier. Multi-filament yarns $Y_4$ of 18 denier of 2 filaments and $Y_5$ of 45 denier of 7 filaments were obtained substantially in the same manner as above except that for the latter yarn the draw ratio was 3.7.

Each of yarns $Y_3$, $Y_4$ and $Y_5$ was passed through a heated metallic tube having its inside diameter of 3 mm. and length of 50 cm., at a relaxed condition to develop slight crimps and wound on a bobbin as respective yarn $Y_{13}$, $Y_{14}$ and $Y_{15}$. When yarns $Y_3$ and $Y_4$ were processed, the temperature of the heater tube was 135° C., the feed-in speed was 280 m./min. and the delivery speed was 211 m./min., and when the yarn $Y_5$, the temperature of the heater tube was 180° C., the feed-in speed was 200 m./min. and the delivery speed was 150 m./min. Stockings with plain stitches were knit on a circular knitting machine which was provided with 400 needles, using the above processed yarn $Y_{14}$ for the leg portion and the yarn $Y_{15}$ for the toe, heel and welt. After looping, the knitted stockings were heated with a saturated steam at 100° C. under a tensionless condition for 30 minutes to develop their crimps, put into a sack and dyed in a rotary drum type dyeing machine. The dyed stockings were boarded and steamed at 114° C. for 45 seconds, taken off the board after drying and allowed to stand in a room of 65% R.H. at 25° C. for 1 day to shrink. The resultant stockings were denoted as "stockings $S_5$." The stockings $S_5$ were soaked in a solution which consisted of 1.5 parts of polydimethyl siloxane diol prepolymer having its degree of polymerization of about 150, 98.5 parts of perchloroethylene and 0.01 part of benzoyl peroxide, subjected to a centrifugal squeezing followed by drying, and then cured in a hot air at 160° C. for 5 minutes. The thus treated stockings which were denoted as "stockings $S_6$," had 0.6% of polyorganosiloxane adhered thereon. Another stockings $S_7$ were obtained substantially in the same manner as above except that the yarn $Y_{13}$ was used for leg portion. Still another stockings were manufactured substantially in the same manner as above except that after dyeing, they were finished with an aqueous emulsion of softening agent comprising a silicone oil and a cationic surface active agent (adhesion amount of the softening agent was 1.0% by weight) and then subjected to boarding, which were denoted as "stockings $S_8$."

The stockings $S_6$ and $S_8$ were very smooth and soft, whereas the stockings $S_5$ and $S_7$ exhibited a little hard hand and a less softness.

Those stockings $S_5$, $S_6$, $S_7$ and $S_8$ were test used. They were washed in hot water with neutral soap after wearing for a day. The stockings $S_8$ had lost entirely their softness after five day wearings, whereas the stockings $S_6$ did not lose their softness as well as smoothness.

Too much adhesion of polyorganosiloxane led to an undesirable result. In the following Table 20 will be shown a result of measurements of elongation and recovery of leg portion with respect to stockings which were manufactured substantially in the same manner as that of the manufacture of the stockings $S_6$ except the amount of polyorganosiloxane adhered.

TABLE 20

| Amount of polyorganosiloxane adhered (percent) | Elongation (percent) | Recovery (percent) |
|---|---|---|
| 0 | 145 | 84.0 |
| 0.3 | 151 | 90.5 |
| 0.5 | 150 | 91.9 |
| 0.7 | 163 | 92.1 |
| 1.0 | 162 | 91.5 |
| 2.5 | 163 | 91.1 |
| 4.5 | 169 | 86.5 |

Stockings $S_7$ showed an elongation of 135% and a recovery of 91.5%.

Method for determining percentages of elongation and recovery was same as that in the foregoing Example 21.

As is apparent from Table 20, when the amount of polyorganosiloxane adhered is in excess of 4%, the percentage recovery is small. From the viewpoint of smoothness, even an amount of less than 1% gives good results and more amount seems to be unnecessary.

Example 23.—Stockings $S_5$, $S_6$ and $S_7$ obtained in Example 22 were test used by 80 persons. One user wore three pairs, each one pair of those three kinds of stockings, so as to use one pair every three days until all of them were broken and their lives were recorded. In this way, the interrelation between the life and the number of breakages with respect to 80 pairs of stockings of a sort was observed and it was made clear that the number of unbroken stockings decreased in inverse proportion as the time of wear and such relation was approximated by the exponential function shown in the Equation 1 hereinbefore. Average life of the stockings $S_5$, $S_6$, $S_7$ and $S_8$ were 85 hours, 92 hours, 82 hours and 87 hours respectively. Thus, the stockings manufactured according to the present invention had an average life longer than that of stockings which were finished with a conventional softening agent.

Example 24.—Nylon–66 having its inherent viscosity of 1.15 in *m*-cresol solution at 25° C. and a copolymer of 4 parts of nylon-66 with 6 parts of nylon-610 having its inherent viscosity of 1.16 were separately melted and two melts of equal weight were conjugated in a side by side relation which were extruded concurrently from an orifice having its diameter of 0.25 mm. on a spinneret plate at 290° C. to form a unitary filament wherein two polyamidic components were adhered and disposed in a side by side relation with each other throughout the entire length of the filament. The extruded filament was air-quenched, oiled, wound on a take-up tube at a speed of 600 meters per minutes and then drawn to 3.9 times its original length on a snubbing pin at 80° C. to obtain a filament yarn $Y_6$ of 20 denier of 3 filaments. A multifilament yarn $Y_7$ of 45 denier of 7 filaments was obtained substantially in the same manner as above except that the draw ratio was 3.6. The yarn $Y_6$ was given twists of 120 turns per meter and passed through a heated metallic tube at 160° C. having its inside diameter of 3 mm. and length of 50 cm. with a feed-in speed of 600 meters per minute and a delivery speed of 550 meters per minute. The thus heat-treated yarn $Y_{16}$ was then wound on a pirn. The yarn $Y_7$ was treated to obtain a yarn $Y_{17}$ in substantially the same manner as above except that the feed-in speed was 250 meters per minute, the delivery speed was 222 meters per minute and the temperature of the heater tube was 180° C. Stockings with run-resistant stitches were knit on a seamless knitting machine which was provided with 401 needles, using the above processed yarn $Y_{16}$ for the leg portion and the yarn $Y_{17}$ for the toe, heel and welt. After looping, the knitted stockings were heated with a saturated steam at 100° C. under a tensionless condition for 30 minutes and were further heated with a saturated steam at 120° C. for 10 minutes to develop their crimps. The crimped stockings were put into a sack and dyed, which were then boarded and steamed at 119° C. for 45 seconds, taken off the board after drying and allowed to stand in a room of 65% R.H. at 25° C. for 1 day to shrink.



The resultant stockings were denoted as "stockings $S_9$." The stockings $S_9$ were soaked in a solution which consisted of 2 parts of polydimethyl siloxane diol prepolymer having its degree of polymerization of about 100, 98 parts of trichloroethylene and 0.02 part of benzoyl peroxide, subjected to a centrifugal squeezing to attain various amounts of adhesion followed by drying, and then cured in a hot air at 150° C. for 3 minutes. In the following Table 21 will be shown a result of measurement of elongation and recovery of leg portions with respect to those stockings differing in the adhesion amount of the polyorganosiloxane, which measurement was performed in the same manner as that in the foregoing Example 22.

TABLE 21

| Amount of polyorganosiloxane adhered (percent) | Elongation (percent) | Recovery (percent) |
|---|---|---|
| 0 | 192 | 80.4 |
| 0.3 | 208 | 84.9 |
| 0.5 | 212 | 90.1 |
| 0.7 | 215 | 89.7 |
| 1.0 | 209 | 88.2 |
| 2.5 | 223 | 89.5 |
| 4.5 | 230 | 82.6 |

All of stockings on which polyorganosiloxane had been adhered exhibited more excellent softness as compared with those which had not been treated with polyorganosiloxane.

Another stockings $S_{10}$ which had 0.5% by weight of polyorganosiloxane adhered thereupon were obtained in the same manner as that in the manufacture of the above-mentioned stockings except that a unitary filament of 20 denier was employed for the leg portion. The stockings $S_{10}$ had a degree of elongation of 181% and a recovery of 86.2%, and exhibited a rather hard hand that was undesirable, whereas the stockings $S_9$ which had been manufactured according to the process of the present invention displayed an excellent hand.

Generally, in case that hosieries or stockings knit with a multi-filament yarn are treated with a polyorganosiloxane prepolymer according to the process of the present invention, they can be given larger amount of polyorganosiloxane as compared with those knit with a unitary filament yarn and moreover the more adhesion of the prepolymer not only effects the better appearance of the stockings, but also intensifies, in most cases, their stretchability more than effects.

What is claimed is:

1. A process for manufacturing a fibrous structure composed of at least 20% by weight of continuous filaments and at most 80% by weight of staple fibers having durable elasticity, crease-resistivity and shrink-proof ability, which comprises applying homogeneously to said fibrous structure a non-aqueous solution comprising polyorganosiloxanediol prepolymer having an average degree of polymerization of at least 50 selected from the group consisting of poly(dimethylsiloxane)diol, poly(diethylsiloxane)diol, poly(methylphenylsiloxane)diol, and poly(diphenylsiloxane)diol and a catalyst for polymerization thereof, said solution being applied an amount such that the polyorgananosiloxane component is fixed on said fibrous structure in an amount of not exceeding 10% by weight based on said structure and then subjecting the thus treated fibrous structure to a heat treatment at a temperature of 50–200° C. to complete the polymerization of said prepolymer.

2. A process as claimed in claim 1, wherein the fibrous structure is composed of staple fibers.

3. A process as claimed in claim 1, wherein the fibrous structure is composed of continuous filaments.

4. A process as claimed in claim 1, wherein the fibrous structure is knitted goods composed of crimpable composite filament yarn.

5. A process as claimed in claim 4, wherein the knitted goods are ladies' hosieries.

6. A process as claimed in claim 4, wherein said yarn is a multi-filament yarn.

7. A process as claimed in claim 6, wherein the knitted goods are ladies' hosieries.

8. A process as claimed in claim 1, wherein the polyorganosiloxane prepolymer comprises poly (dimethyl siloxane) diol as its principal component and methyl hydrogen polysiloxane as its subsidiary component.

9. A process as claimed in claim 1, wherein said prepolymer has an average degree of polymerization of at least 100.

10. A process as claimed in claim 1, wherein the non-aqueous solution of polyorganosiloxane prepolymer is a solution in an organic solvent comprising at least one organic compound selected from the group consisting of toluene, xylene, benzene, perchloroethylene, polychloroethylene, gasoline for an industrial use, chloroform, methyl chloroform and methylene chloride.

11. A process as claimed in claim 1, wherein said catalyst is at least one organic tin compound selected from the group consisting of dibutyl tin dilaurate, dibutyl tin dioctoate, dibutyl tin succinate, stannous octoate and chelate compounds of tin.

12. A process as claimed in claim 1, wherein said catalyst is contained in an amount of 0.01–5% by weight based on the polyorganosiloxane component.

13. A process as claimed in claim 1, wherein said catalyst is contained in an amount of 0.1–1.0% by weight based on the polyorganosiloxane component.

14. A process as claimed in claim 1, wherein said catalyst comprises at least one accelerator of cross-linking reaction selected from the group consisting of isocyanates of silane compound, alkoxy silane, acetates of silane compound, and benzoyl peroxide.

15. A process as claimed in claim 14, wherein said accelerator is contained in an amount of not exceeding 15% by weight based on the polyorganosiloxane component.

16. A process as claimed in claim 1, wherein said non-aqueous solution further contains at least one polyetheric compound selected from the group consisting of polyoxyethylene alkyl ether, polyoxyethylene alkylphenol ether, polyoxyethylene alkylamine, polyoxyethylene alkylphosphate, polyoxyethylene sorbitan fatty acid ester and polyethylene glycol.

17. A process as claimed in claim 15, wherein the amount of said polyetheric compound contained is 1–50% by weight based on the polyorganosiloxane prepolymer.

18. A process as claimed in claim 15, wherein the amount of said polyetheric compound contained is 3–20% by weight based on the polyorganosiloxane prepolymer.

19. A process as claimed in claim 1, wherein the heat-treatment temperature is of 100–180° C.

20. A process as claimed in claim 1, wherein the structure is subjected to said heat-treatment for 20 seconds to 60 minutes.

21. A process as claimed in claim 1, wherein the structure is subjected to said heat-treatment for 1 minute to 10 minutes.

22. A process as claimed in claim 1, in which said polyorganosiloxanediol prepolymer is selected from the group consisting of poly(dimethylsiloxane)diol, poly(diethylsiloxane)diol and poly(diphenylsiloxane)diol.

23. A fibrous structure composed of at least 20% by weight of continuous filaments and up to 80% by weight of staple fibers said filaments having impregnated therein not more than 10% by weight of a polyorganosiloxanediol prepolymer having an average degree of polymerization of at least 50, wherein the prepolymer is selected from the group consisting of poly(dimethylsiloxane)diol, poly(diethylsiloxane)diol, poly(methylphenylsiloxane)-diol and poly(diphenylsiloxane)diol.

24. A fibrous structure as claimed in claim 23, wherein the elongation at break is 150–800%.

25. A fibrous structure as claimed in claim 23, wherein the tensile strength at break is 3–20 kg./cm.$^2$.

26. A fibrous structure as claimed in claim 23, wherein the hardness is 8–30°.

27. A fibrous structure as claimed in claim 23, wherein the fixed amount of polyorganosiloxane is 0.2–5% by weight based on the fibrous structure.

28. A fibrous structure as claimed in claim 23, wherein the fixed amount of polyorganosiloxane is 0.3–3% by weight based on the fibrous structure.

29. A durable elastic crease resistant fibrous structure having an elongation at break of at least 50%, a tensile strength at break of 1–50 kg./cm.$^2$ and a hardness of 5–50° which has a heat cured polymer formed by heat treatment of the prepolymer wherein the prepolymer is selected from the group consisting of poly(dimethylsiloxane)diol, poly(diethylsiloxane)diol, poly(methylphenylsiloxane)diol and poly(diphenylsiloxane)diol, bonded thereon.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,684,379 | 7/1954 | Guillissen et al. | 260—448.2 |
| 2,717,258 | 9/1955 | Kantor | 260—46.5 X |
| 2,902,468 | 9/1959 | Fianu | 260—46.5 |
| 2,732,320 | 1/1956 | Guillissen et al. | 117—161 |
| 2,832,518 | 4/1958 | Doyle et al. | 117—138.8 X |
| 2,876,209 | 3/1959 | deBenneville et al. | 117—138.8 X |
| 3,065,111 | 11/1962 | Reeves et al. | 117—161 |
| 3,268,465 | 8/1966 | Gilkey et al. | 117—135.5 X |
| 3,385,812 | 5/1968 | Brachman | 117—161 X |
| 3,445,276 | 5/1969 | Pikula | 117—161 X |
| 3,476,581 | 11/1969 | Weitzel et al. | 117—62 |

WILLIAM D. MARTIN, Primary Examiner

T. G. DAVIS, Assistant Examiner

U.S. Cl. X.R.

117—138.8 N, 139.5 A, 141, 145, 161 ZA