Aug. 14, 1973 YOSHIHISA SHICHIJO ET AL **3,752,648**

PROCESS FOR IMPROVING ACRYLIC FIBER ARTICLES

Original Filed Sept. 6, 1967 3 Sheets-Sheet 1

FIG. 1

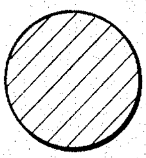


FIG. 2

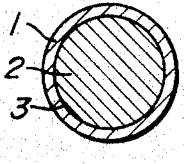


FIG. 3

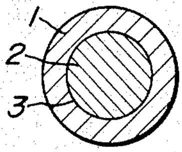


FIG. 4

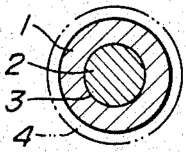


FIG. 5

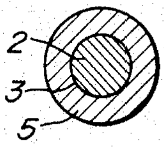


FIG. 6A

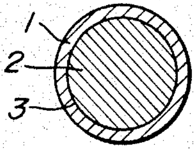


FIG. 6B

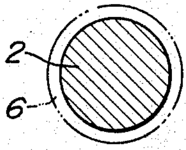


FIG. 7

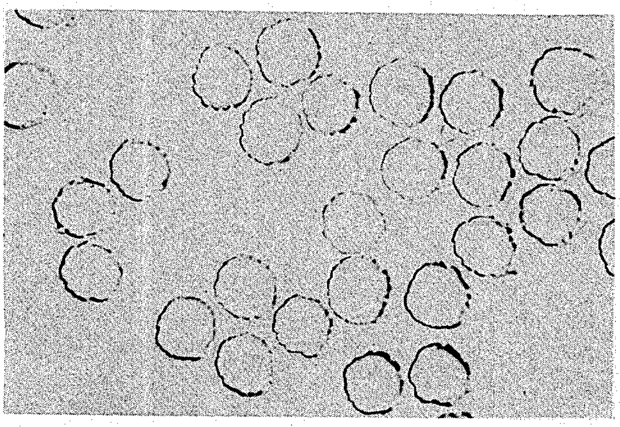
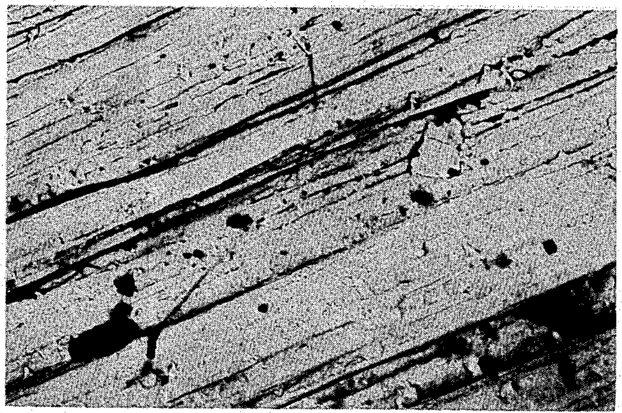


FIG. 8



Aug. 14, 1973 YOSHIHISA SHICHIJO ET AL **3,752,648**

PROCESS FOR IMPROVING ACRYLIC FIBER ARTICLES

Original Filed Sept. 6, 1967 3 Sheets-Sheet 3

FIG. 9

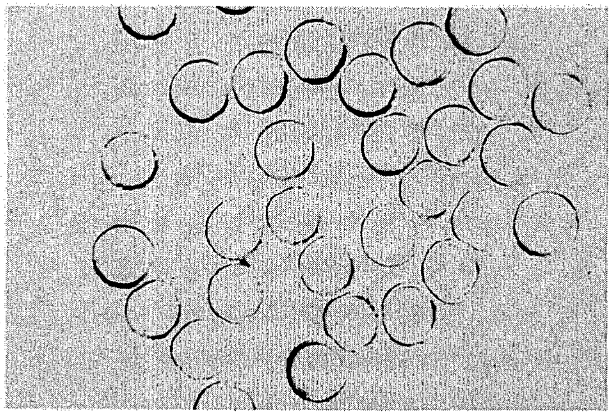


FIG. 10

United States Patent Office

3,752,648
Patented Aug. 14, 1973

3,752,648

PROCESS FOR IMPROVING ACRYLIC FIBER ARTICLES

Yoshihisa Shichijo, Tokyo, Hiroyuki Yamaguchi, Kyoto, Katsuyoshi Tsuji, Osaka, and Kenji Maki, Kyoto, Japan, assignors to Asahi Kasei Kogyo Kabushiki Kaisha, Osaka, Japan

Continuation of abandoned application Ser. No. 665,838, Sept. 6, 1967. This application Nov. 25, 1970, Ser. No. 92,901
Claims priority, application Japan, Sept. 10, 1966, 41/59,462; May 17, 1967, 42/30,884
Int. Cl. D06m 3/26
U.S. Cl. 8—130.1 7 Claims

ABSTRACT OF THE DISCLOSURE

An acrylic fiber article is treated with a solvent for said fiber in a manner such that the swelling and dissolving actions of said solvent act on a portion of the cross section of the individual fibers and then treating the resultant article with a treating agent consisting of said solvent, of which the concentration, temperature and treating time have been adjusted so as to dissolve or disperse only those layers of the fibers on which the solvent has acted to remove said layers therefrom.

This application is a continuation of our earlier application Ser. No. 665,838 filed Sept. 6, 1967 and now abandoned.

The present invention relates to a process for improving an acrylic fiber fabric which is an entirely novel process, according to which an improvement of acrylic synthetic fiber is accomplished by peeling the surface layer portion of said fiber by contacting it with solvents treatment with differential concentrations.

In accordance with the process of the present invention, said article comes to have a very soft touch and elegant luster. Furthermore, in accordance with the treatment of the process of the present invention, levelling dyeability of the fiber article is improved, uneven dyeing is improved, and thereby the fiber article can be dyed clearly. Still further, the thus treated fiber article is characterized in that the antisoiling properties thereof are greatly improved. The process of the present invention is effective for all acrylic fibers, particularly it is an excellent treatment process for the improvement of acrylic filament yarn. That is, an article of acrylic filament yarn has the defects that said article has a stiff touch and is apt to produce uneven dyeing when dyed. These defects in said article can be overcome by applying the present process thereto, whereby silk-like handling and luster, and clear dyeing can be obtained.

The reason why such excellent effect have resulted is not sufficiently clarified yet, but it is believed that this effect is mainly attributable to the peeling of the surface layer portion of the acrylic synthetic fiber. That is, the rough surface of an acrylic fiber can be smoothed by this treatment. This is one of the effects expected by peeling, and for that reason, adequate luster is displayed, antisoiling property is improved and touch of the fiber is improved. Softening of the fiber or fiber article may be attributed to the facts that the stiff surface layer portion of the fiber is removed, and that the composition of the fiber aricle is changed due to the removal of the stiff surface layer portion of the fiber. The improvement in dyeability can be considered to result from the removal of portions of the fiber surface layer having different dyeability.

In the accompanying drawings, FIG. 1 is a schematic view of the cross section of acrylic synthetic fiber. FIGS. 2, 3 and 4 are schematic views of the cross section of fiber wherein the progress of action of the solvent employed

is illustrated in case acrylic synthetic fiber is contacted with said solvent. FIG. 5 is a schematic view of the cross section of fiber showing the presence of coagulated and regenerated polymer on the surface layer of the fiber subjected to the solvent treatment. FIG. 6A is a schematic view showing a state wherein acrylic fiber is subjected to a solvent treatment in accordance with the process of the present invention to produce thereon the layer on which the solvent has acted, and FIG. 6B is a schematic view showing the state of the thus treated fiber from which the acted layer has been removed and peeled.

FIG. 7 is a microscopic photograph of the cross section of acrylic fiber filament yarn (75 denier, 38 filaments), and FIG. 8 is an electro-microscopic photograph of the side view of said filament yarn.

FIG. 9 is a microscopic photograph of the cross section of the same filament yarn as above which has been treated according to the process of the present invention, and FIG. 10 is an electro-microscopic photograph of the side view of the thus treated filament yarn.

Various processes have hitherto been proposed with respect to treatment of acrylic synthetic fiber. None of these processes, however, has not been found yet, in which a significant improvement was accomplished by a process capable of being advantageously put into practice on a commercial scale. It is said that it is extremely difficult to change properties of acrylic fiber once produced to a preferable aspect thereof by after-treatment and yet permanently.

Extensive studies carried out by the present inventors on improving acrylic synthetic fiber have resulted in an accomplishment of a peeling of the surface of acrylic fiber by a solvent treatment of multi-process, which was not successfully carried out heretofore. Further, it has been found that when this peeling treatment is applied to acrylic fiber fabric, properties of the fiber surface, physical properties of the fiber and composition of the fiber article unexpectedly change, thereby the fabric is exhibiting excellent improving effects such as silk-like handling, luster, improved dyeability and antisoiling. The present invention has been completed on the basis of the above finding.

In the case of cellulose fiber or polyamide fiber, peeling of the surface layer of fiber has heretofore been carried out as one of the means for studying the fiber structure, but no example has been found where this peeling was applied to the fiber as a process for improving fiber article. In the case of acrylic fiber, study of the fiber according to this peeling means has not been attempted yet. Accordingly, properties of the acrylic fiber peeled are entirely unknown and the fact that the peeling treatment can be applied to the fiber fabric as a process of improvement thereof surpasses all imagination.

As the known process for treating acrylic synthetic fiber fabric with the solvent thereof, there is a process which comprises treating the fabric with a relatively dilute solution of the solvent substance thereof and subjecting the treated article to drying and heating. In this process, when the solvent solution is concentrated on the individual fibers and said fibers become to possess solubility, a portion of fiber is dissolved, of which solubilized polymer layer acts as adhesive among the fibers, thereby causing adhesion of the fibers among themselves. As a result, the fabric is stiffened in accordance with the same principle as in the case where the fabric is stiffened by sizing. The stiffness thus given by such solvent treatment returns back nearly to the former state as the result of adhesion among the fibers being released by crumpling and fraying during washing. In this manner, the conventionally known solvent finishing takes steps of imparting tackiness to the fiber surface and causing adhesion of the fibers among themselves, which has mainly been applied to stiff finishing of the fabric and has not positively been directed to effect peeling of the fiber.

In general, when fiber is contact with the solvent thereof, swelling and dissolving actions thereof extend first to the fiber surface and gradually to the inside of the fiber, the polymer constituting the fiber is eluted from the fiber surface into the solvent and eventually the whole of fiber is dissolved therein. In order to peel the surface layer portion of fiber, this is accomplished in principle by subjecting the fiber to the solvent treatment under such conditions where only the surface layer portion is dissolved. In the case of acrylic fiber, however, it is impossible to carry out such peeling as above according to a mere solvent treatment. The reason why acrylic fiber cannot be peeled is that when the fiber is in contact with the solvent, the layer affected (hereinafter referred to as acted layer of solvent) by swelling and dissolving actions of said solvent forms a gel-like layer or high viscosity layer which does not readily sever itself therefrom and disperse into the solvent. That is, it is the characteristic of acrylic fiber that the acted layer of solvent proceeds toward the inside of the fiber before dissolving and dispersing of the surface of said acted layer do sufficiently proceed, whereby a thick-acted layer of the solvent is always present thereon.

Thus, the above state is schematically illustrated as shown in each of FIGS. 1–4. That is, FIG. 1 is a schematic view showing the cross section of acrylic fiber before its contact with the solvent. FIG. 2 is a schematic view showing an initial state where the fiber has contacted with dimethyl formamide which is one of the solvents thereof, wherein portion **1** shows the acted layer of dimethyl formamide and portion **2** is a portion which has not been effected by action of the solvent. In FIG. 2, **3** is a boundary between the acted layer and non-acted layer, and in the case of acrylic fiber, this boundry appears relatively clear. FIG. 3 is a schematic view showing a state where the action of the solvent has considerably extended to the inside of the fiber, and in this stage the acted layer merely is thickened and is not ready to initiate dispersion. FIG. 4 is a schematic view showing a state where after the time further has passed the fiber possesses a thick acted layer and a small amount of fiber polymer represented by portion **4** has been eluted into the solvent. Accordingly, the fiber cannot substantially be peeled, because the acted layer polymer of solvent is coagulated and regenerated by the desolvent treatment which has to be performed subsequently to the solvent treatment at the spot of the fiber to form a separate phase from the original fiber. FIG. 5 is a schematic view showing a state where the solvent treated fiber shown in FIG. 4 has already been washed with water and dried, and a portion represented by **5** shows a non-orient coagulated and regenerated polymer layer.

Based on the studies on the subject carried out by the present inventors, it has become possible to peel the fiber surface layer by forming a desired acted layer of solvent on acrylic fiber by a combination of special solvent treatment comprising two stage process or multi process more than two stage process thereof and ingeniously removing this acted layer of solvent therefrom. The conventionally known solvent treatment process of acrylic synthetic fiber has entirely been devoid of consideration into the acted layer of solvent. It has been absolutely unknown that an unexpected excellent improving effect can be obtained by removal of this acted layer of solvent.

This invention presents a process for a fabric made of acrylic fiber. In accordance with the present invention, an acrylic fabric is contacted with a solvent for acrylic fibers in a manner such that swelling and dissolving actions extend to a portion of the cross-section of the constituent fiber of said fabric thereby forming a swollen layer on each of said fibers and then positively removing said swelled layer therefrom by contacting said fabric with a solution of a solvent substance capable of dissolving or dispersing only said swelled layer.

Acrylic fiber, as referred to in the present specification includes poly acrylonitrile fiber, acrylic fiber consisting of copolymer of 85% (wt.) or more of acrylonitrile with up to 15% (wt.) of other monomer copolymerizable therewith and the so-called Moda acrylic fiber consisting of acrylonitrile and other monomer.

The shapes of the cross-section of fiber include not only ordinary ones of the fibers spun through round spinning nozzle but also those of heteromorphic cross-section of the fiber spun through non-circular spinning nozzle, conjugated yarn consisting of components of polymers having different composition, and further yarns spun according to any of wet spinning method and dry spinning method.

Acrylic fiber articles as used herein imply the articles consisting of the acrylic synthetic fibers as defined above such as woven fabric and knitted fabric. These fiber articles are not always necessary to be constituted by only the acrylic fiber, and those as mixed spun, mixed woven, mixed stranded and mixed knitted by natural fiber, semi synthetic fiber or other synthetic fibers than the acrylic fiber which may naturally be included in the scope of the process of the present invention.

In the process of the present invention, a fabric is contacted with solvents with differential capability of solvent action. At least two solvent baths are required and each bath has a greater strength than the next succeeding bath. When the acrylic fiber is in contact with a solvent having property sufficient to dissolve said fiber, swelling and dissolving actions of said solvent extend from the surface of the fiber to the inside thereof, and eventually the whole portion of the fiber becomes to be affected by the actions of said solvent. However, when a contact between the fiber and solvent is limited within a certain time defined, the acted layer of solvent can be sustained to an extent up to a portion of the fiber in the cross-section thereof. Dimensions of the acted layer of solvent have a great influence on the effect of the present invention. Generally, the larger is the acted layer of solvent, the bigger is the degree of improvement. The dimensions of the acted layer of solvent cannot summarily be defined depending on the desired object of improvement, the kind of solvent substance employed, means and conditions of subsequent process steps, the kind of fiber articles desired and the like. It is, however, preferably in general that the acted layer of solvent constitutes a portion corresponding to 1 to 50% of the weight of the original fiber.

Contact time between the fiber and solvent is dominated by the desired dimension of acted layer of solvent, strength of dissolving action of the solvent, temperature, size of the fiber, shape of the fiber article and the like. The contact time may be several seconds in some cases under the conditions where dissolving action of the solvent is strengthened, and may be required to be from several ten minutes to several hours under the conditions where dissolving action of the solvent is weakened, in some cases.

Inorganic compound and as inorganic acids and salts thereof and a number of organic compounds have been known as substances capable of serving as solvents of of acrylic synthetic fiber. As examples of inorganic acids, there may be mentioned nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, chlorosulfonic acid. As examples of salts, there may be mentioned thiocyanates such as sodium thiocyanate, potassium thiocyanate, calcium thiacyanate, ammonium thiocyanate and zinc thiocyanate, halide such as calicum iodide, lithium iodide, zinc iodide, lithium bromide, magnesium bromide, zinc bromide, stannous chloride and zinc chloride, nitrates such as nickel nitrate and manganese nitrate, perchlorates such as calcium perchlorate and aluminum perchlorate. As examples of organic solvent substances, there may be mentioned amide compound such as N,N-dimethyl formamide, N,N-dimethyl acetamide, N-methyl pyrrolidone and 2-

oxazolidone, nitrile compound such as malononitrile, adiponitrile and β-hydroxy propionitrile, sulphone and sulphoxy compounds such as dimethyl sulphoxide and ethyl methyl sulphone, thiocyanate compound such as methylene dithiocyanate, nitro compound such as nitro benzene, nitro phenol and nitro ethanol, amino compound such as phenylene diamine and triamino toluene, phosphorus compound such as tris (dimethylamide) phosphite and dimethyl phosphite, carbonate compound such as γ-butyrolactone, maleic anhydride and ethylene carbonate. Besides the above, there may also be mentioned acetone, dimethyl cyanoacetamide and tetrachloroethane. In practice, these substances may be used singly or aqueous solution thereof, a mixture of inorganic and organic substances capable of being mutually mixed with each other and mixed solution thereof. Furthermore, a mixed solvent can be used as well. Strength of dissolving action of the solvent employed relies on the kind of solvent substance, concentration, and temperature employed. Above all, concentration of the solvent substance employed is important, and in this process step the concentration having sufficient action to dissolve the acrylic synthetic fiber to be treated is required, which has also to be adjusted to an appropriate concentration in line with the conditions of the succeeding process step. Treatment temperature may be varied within the wide temperature range of from a temperature as low as minus scores degrees centigrade to a temperature as high as plus scores degrees centigrade.

The process step in which the acted layer is formed by the solvent is not always limited to a single process step. In some cases, a process comprising two steps or more may be adopted therefor by using the solvent of the same or different kind or the solvent having a different concentration. Furthermore, in some cases, the fiber article may be pretreated with a solution of solvent substance which has scarcely or not all the dissolving action prior to the solvent treatment.

In removing the acted layer formed on the fiber by the solvent, a solution of a solvent substance with weaker concentration in such a manner that only the acted upon layer can be dissolved or dispersed into the bath.

When a solvent used for removing the acted layer is a strong solvent of the fiber to be treated, removal of the acted layer can be carried out, but simultaneously a new acted layer of solvent is formed on said fiber. Therefore, the improvement effect expected in the present invention may not be exhibited, because in the subsequent washing and drying, polymer is coagulated and regenerates on the surface of said fiber. Accordingly, the treatment agent used for removing the acted layer, which has an action of newly dissolving the fiber to be treated as weak as possible, is prefered. In general, a solution of solvent substance having a lower swelling action than that of the solvent used in the preceding step is preferably used.

By way of example, in the first step the acrylic fiber article can be contacted with 71% by weight sulfuric acid and in the second step the resultant fiber article is treated with less than 71% by weight sulfuric acid. Alternatively, in the first step the acrylic fiber article can be contacted with at least 95% by weight of dimethyl sulfoxide and in the second step the resultant fiber article is treated with less than 95% by weight of dimethyl sulfoxide. In another embodiment, the acrylic fiber article is treated in the first step with at least 51% by weight of nitric acid and the resultant fiber article is treated in the second step with less than 51% by weight of nitric acid. This optimum concentration range is not definite depending on the kind of the solvent substance employed and may be varied according to the kind of solvent diluting said solvent substance, temperature or mechanical conditions of the treatment. FIG. 6A is a schematic view showing the cross-section of the fiber on which the acted layer has been formed by the solvent treatment, wherein a portion of **1** shows the acted layer of solvent, **2** is a portion which has not been affected by the action of the solvent, and **3** is a boundary between the acted layer and non-affected portion. FIG. 6B is a schematic view showing a state of the fiber peeled from which the acted layer of solvent has been removed, wherein a portion of **6** shows that the removal of the acted layer has been carried out by peeling. When this removal process step is carried out by using a solution of a solvent substance which is unable to sufficiently dissolve or disperse the acted layer, polymer is coagulated and regenerated on the fiber, whereby the purpose of peeling cannot be accomplished.

Control of dissolving action of this solution for the fiber to be treated and the acted layer may also be carried out by means of temperature. That is, both the solvent treatment process step forming the acted layer and removal process step for removing said acted layer may be carried out at the same concentrations except that only the temperatures are changed. Usually, the temperature range to be applied thereto is from scores of degrees centigrade below zero to scores degrees centigrade.

The treatment time for removing the acted layer is short when dissolving action of the treatment agent is strong to the acted layer, same as in the case of the solvent treatment process step forming the acted layer, for example, the treatment time may be good enough for several seconds in some cases. When the dissolving action is weak, several hours may be required in some cases. This process step is not limited to a single step, and it can be carried out by the steps comprising two steps or more. The fiber article, of which the removal process step of the acted layer has been completed, is transferred to the following step, for example, dyeing or finishing process, through desolvent treatment process step such as washing and drying.

The fiber is peeled by the solvent treatment and the succeeding removal process step of the acted layer. Degree of the peeling can be determined by percentage of loss in weight of the fiber, percentage of diminution of area of the cross-section of the fiber or electro microscopic observation of the fiber surface. Degree of the peeling in accordance with the process of the present invention is dominated by the degree of improvement of the fiber article desired, and therefore this cannot summarily be decided, but this is preferably about 1 to about 50% in terms of percentage of loss in weight. In the peeled fiber obtained in accordance with the process of the present invention, there may be present a small amount of regenerated polymer layer depending on the treatment conditions, in some cases. As long as the amount of this regenerated polymer layer is small, this does not give particularly an adverse influence upon the improvement effect. During the above-mentioned treatment process step, there may be added thereto the substances capable of promoting or relieving dissolving action or stabilizing substance, for example, inorganic compounds such as sodium sulfate, ammonium sulfate, zinc sulfate, ammonium thiocyanate, ammonium nitrate, ammonium chloride and the like, organic compounds such as ammonium succinate, ammonium acetate, urea, ethylene glycol, polyethylene glycol and the like, surfactant, high molecular weight compounds such as polyacrylonitrile, polyacrylic acid, polyvinyl alcohol, cellulose derivatives and the like. These additives can also be used for the purpose of controlling the handling and luster of the improved fiber articles in accordance with the process of the present invention.

By treating acrylic fiber article in accordance with the process of the present invention, said article becomes to give very soft touch and elegant luster. Furthermore, in accordance with the treatment of the process of the present invention, levelling dyeability of the fiber article is improved, uneven dyeing is improved, thereby the fiber article can be dyed clearly. Still further, the thus treated fiber article is characterized in that antisoiling property thereof is greatly improved. The process of the present invention is effective to all the acrylic fibers, particularly it is an excellent treatment process as the improvement process of acrylic filament yarn. That is, article of acrylic filament yarn has the defects that said article has stiff touch and is apt to produce uneven dyeing when dyed. These defects of said article can be overcome by applying the present process thereto, whereby silk-like handling and luster, and clear dyeing can be obtained.

From what such excellent effect has been resulted is not sufficiently clarified yet, it is believed that this effect has mainly been attributable to the peeling of the surface layer portion of acrylic synthetic fiber. That is, rough surface of acrylic fiber can be smoothened by this treatment. This is one of the effects expected by peeling, and for that reason, adequate luster is displayed, antisoiling property is improved and touch of the fiber is improved. Softening of fiber or fiber article may be attributed to the facts that stiff surface layer portion of the fiber is removed, and that composition of the fiber article is changed due to the removal of stiff surface layer portion of the fiber. Improvement of dyeability can be considered to be resulted from the removal of portions of the fiber surface layer having different dyeability. Furthermore, smoothening of the fiber surface is considered to contribute toward a resplendence of the dyed product.

The following examples are given to explain the present invention more fully, but these examples are not to be construed as limiting the invention.

EXAMPLE 1

Tricot knitted from acrylic filament yarn of 75 denier was dipped in a 95% aqueous dimethyl sulfoxide solution at 20° C. for 80 minutes then dipped in a solution consisting of 85% dimethyl sulfoxide and 15% methanol at 20° C. for 30 minutes, then dried and finished. As the result of the treatments, weight of the knitted fabric was reduced by 5.8%. The treated knitted fabric had luster and handling which have a resemblance to those of silk, and had no stripe uneven dyeing when dyed.

EXAMPLE 2

Individual woven fabrics made of acrylic filament yarn of 75 denier were dipped and treated with an aqueous zinc chloride solution under the conditions of the first bath denoted in the following table, then dipped and treated with the second bath conditions, thereafter were washed with water and dried. Percentages of loss in weight and properties of the treated woven fabrics are shown in the following table.

Woven fabric No.	Treatment conditions	
	First bath conditions	Second bath conditions
A	60% aqueous zinc chloride solution, 20° C., 20 sec.	52% aqueous zinc chloride solution, 20° C., 10 min.
B	62% aqueous zinc chloride solution, 20° C., 20 sec.	Do.
C	66% aqueous zinc chloride solution, 30° C., 30 sec.	Do.

	Properties					
	Loss in weight (percent)	Softness		Brightness		Crease resistance, warp plus weft (deg.)
		Warp	Weft	Vertical	Parallel	
A	4.9	9.28	6.93	1.20	2.72	226
B	9.7	12.89	8.14	1.27	2.94	216
C	12.1	24.62	15.56	1.25	3.06	186
Non-treated	0	1.99	3.68	1.05	2.06	198

In the above table, softness of the woven fabric is a value as measured according to cantilever method of ASTM, D1388–64, and the greater is this value, the softer is the woven fabric. Brightness is shown by the following equation according to 60° contrast brightness of Japanese Industrial Standard—Z8741, the incident light being 60°.

$$\text{60° contrast brightness} = \frac{\text{Strength of reflected light at 60° of angle of received light}}{\text{Strength of reflected light at 0° of angle of received light}}$$

The greater is the value, the strong is the brightness. Further, in the above table, "vertical" means the case where warp of the woven fabric is placed vertically to the incident face, and "parallel" means the case where this is placed in parallel. Crease resistance is crease recovering angle as measured based on AATCC66–1959T, and the greater is the value, the better is the crease resistance.

EXAMPLE 3

Woven fabric prepared from 75 denier acrylic filament yarn was dipped in a 75% aqueous sulfuric acid solution at 20° C. for 10 seconds, then dipped in a 70% aqueous sulfuric acid solution at 20° C., for 10 seconds, and further dipped in a 60% aqueous sulfuric acid solution at 20° C. for 5 minutes. Thereafter, it was washed with water and dried. As the result of the treatment, weight of the woven fabric was reduced by 33.7%. The treated woven fabric had handling and luster like silk, and had the following antisoiling property.

	Antisoiling percentage
Non-treated woven fabric	55
Treated woven fabric	72

The term "antisoiling percentage" as herein used implies surface reflection percentage as measured after a sample fabric was dipped in a soiling bath containing a dispersion of 1.5 g. of carbon black and 0.5 g. of olive oil in 100 ml. of water, for 3 minutes, washed with hot water, thoroughly washed with water and dried. Surface reflection percentage is shown by contrasting a reflection percentage of the surface of sample fabric against a light of 575 mμ with standard magnesium plate, and the larger is the value, the more is the whiteness.

EXAMPLE 4

Twilled woven fabric prepared from 40 denier acrylic filament yarn was dipped in a 46% aqueous sodium thiocyanate solution at 80° C. for 3 minutes, then dipped in a 46% aqueous sodium thiocyanate solution at 15° C. for 2 minutes, washed with water and dried. As the result of the treatments, weight of the woven fabric was reduced by 3.2%. The treated woven fabric had luster like silk.

EXAMPLE 5

Plain woven fabric made of acrylic filament yarn was treated with a solution consisting of 40% of zinc chloride, 20% of calcium chloride and 40% of water at 20° C. for 7 seconds, then dipped in a solution consisting of 36% of zinc chloride, 18% of calcium chloride and 46% of water at 20° C. for 10 minutes, then was washed with water and dried. As the result of the treatments, weight of the woven fabric was reduced by 10.0%. The treated woven fabric had luster and handling like silk, and no stripe spot was observed when it was dyed.

EXAMPLE 6

Plain woven fabric made of 30 counts single yarn of acrylic fiber spun yarn in an aqueous solution consisting of 10% of ammonium thiocyanate, 55% of sodium thiocyanate and 35% of water at 30° C. for 20 seconds, then dipped in a 45% aqueous sodium thiocyanate solution at 20° C. for 10 minutes, was then washed with water and dried. As the result of the treatments, weight of the woven fabric was reduced by 24.4%. The treated woven fabric had elegant luster with softness and the following resisting property for soiling.

	Antisoiling percentage
Non-treated woven fabric	47
Treated woven fabric	69

Antisoiling percentage was measured in the same manner as in Example 8.

EXAMPLE 7

Woven fabric made of mixed spun yarns consisting of 55% of acrylic fiber and 45% of cotton was dipped in dimethyl acetamide at 60° C. for 10 seconds, then dipped in a 95% aqueous dimethyl acetamide solution at 20° C. for 3 minutes, was then washed with water and dried. As the result of the treatment, weight of the woven fabric was reduced by 6.5%. The treated woven fabric was soft with good touch.

EXAMPLE 8

Woven fabric made of 75 denier acrylic filament yarn as warp and 40 counts spun cuprammonium rayon fiber spun yarn as weft, was dipped in a 90% aqueous malononitrile solution at 20° C. for 30 seconds, then dipped in a solution consisting of 80% of malononitrile and 20% of acetone at 20° C. for 3 minutes, was then washed with water and dried. As the result of the treatments, weight of the woven fabric was reduced by 4.6%. Luster and handling of the treated woven fabric are like the woven fabric made of silk as warp and silk spun yarn as weft.

EXAMPLE 9

Crepe de Chine was prepared with 40 denier acrylic filament yarn (200 times/m. S twisted) as warp and 40 denier acrylic filament twisted yarn (1200 times/m. S twisted and Z twisted yarn), and scoured and creped. Thereafter, it was heat set at 130° C. for 30 seconds. The woven fabric was dipped in an aqueous solution containing 52% of nitric acid and 0.5% of urea at room temperature for 35 seconds, then dipped in an aqueous solution containing 45% of nitric acid and 0.5% of urea at room temperature for 60 minutes, was then washed, neutralized, dyed and subjected to finishing heat set. As the result of the treatment, weight of the woven fabric was reduced by about 14%. The treated woven fabric had handling and luster like silk with draping property, and no substantial uneven dyeing was observed when dyed.

EXAMPLE 10

Twilled woven fabric was prepared with 40 denier acrylic filament yarn (100–300 times/m. S twisted) as warp and 75 denier acrylic filament yarn as weft (100–200 times/m. S twisted yarn), was then heat set at 140° C. for 20 seconds and was dyed with cationic dyestuff [Astrozon Yellow 7(G)2]. The acrylic filament yarn used in this woven fabric was of a heterogeneous cross section system, having the cross section of pentagonal slope spun through spinning nozzle of asterisk shape. The woven fabric was dipped in a treatment liquid containing 72% of sulfuric acid at about 35° C. for 60 seconds, then dipped in a treatment liquid of 70% sulfuric acid at about 10° C. for 3 minutes. Then, it was washed with water, neutralized, dried and finished with heat set. As the result of the treatments, weight of the woven fabric was reduced by about 1%, and the treated woven fabric had handling, luster and draping property very much like silk.

EXAMPLE 11

Jersey was prepared by knitting crimped yarn prepared from 100 denier acrylic filament composite fiber having different copolymer components. The knitted fabric was treated with an aqueous solution containing 55% of nitric acid and 1.5% of urea at 0° C. for 2 seconds, then treated with a solution containing 50% of nitric acid and 1.5% of urea at room temperature for 10 minutes, was then washed with water, neutralized and finished with dyeing. The treated knitted fabric had elegant handling and luster with draping property like silk.

EXAMPLE 12

Plain woven fabric prepared from 100 denier acrylic filament yarn having the triangular cross-section was dipped in an aqueous solution of 1.5% of polyethylene glycol (average polymerization degree: 1000), then subjected to magle squeeze with a roller at 30° C. and dried at 100° C. for 2 minutes. Then, it was dipped in a 96% aqueous ethylene carbonate solution at 30° C. for 2 minutes, again dipped in 90% by weight ethylene carbonate at 30° C. for 10 minutes, finally was then washed with water and dried. As the result of the treatments, weight of the woven fabric was reduced by 9%. The treated woven fabric was soft with good handling like silk.

EXAMPLE 13

Plain woven fabric 30 counts single yarn of acrylic fiber spun yarn was dipped in an aqueous solution consisting of 76% of sulfuric acid and 1% of ammonium sulfate at 25° C. for 42 seconds, then dipped in a 66% aqueous sulfuric acid solution at 40° C. for 10 minutes, and was then washed with water. As the result of the treatments, weight of the woven fabric was reduced by 15%. The treated woven fabric had elegant luster with softness.

EXAMPLE 14

Sweater made of 80 counts two folded acrylic fiber yarn was dipped in a 62% aqueous potassium thiocyanate solution at 5° C. for 1 minute, then dipped in a 57% aqueous potassium thiocyanate solution at −5° C. for 1 hour, and was then washed with water. As the result of the treatments, weight of the sweater was reduced by 13%. The treated sweater had good touch.

EXAMPLE 15

Plain oven fabric prepared with 100 denier acrylic filament as warp and 75 denier vinylidene chloride filament as weft, was dipped in an 86% aqueous phosphoric acid solution at 30° C. for 10 minutes, then dipped in an 82% aqueous phosphoric acid solution at 30° C. for 2 hours, and was then washed with water. As the result of the treatments, weight of the woven fabric was reduced by 4%. The treated woven fabric provided good luster, handling and antisoiling property.

EXAMPLE 16

Twilled woven fabric prepared from 75 denier acrylic filament was dipped in 100% dimethyl sulfoxide at −15° C. for one minute, then dipped in a 54% aqueous zinc chloride solution at 20° C. for 20 minutes. As the result of the treatments, weight of the woven fabric was reduced by 6%. The thus treated woven fabric was less in stripe spots and was level dyed, compared with a woven fabric made of ordinary yarn.

EXAMPLE 17

Plain woven fabric made of acrylic fiber spun yarn (52 counts single yarn) was dipped in a 61% aqueous sodium thiocyanate solution at 10° C. for 10 seconds, and further dipped in a 50% aqueous thiocyanic acid solution at 10° C. for 10 minutes, and was then dried. As the result of the treatment, weight of the woven fabric was reduced by 42%, and the treated woven fabric showed soft handling.

We claim:

1. A process for improving a fabric made of acrylic fiber consisting of at least 85% of acrylonitrile with a solvent for said acrylic fiber, comprising contacting said fabric with a first solution of a solvent substance for said acrylic fiber in a concentration such that the swelling actions of the solvent extend to a portion of the cross-section of the constituent fibers, thereby forming an acted upon surface layer on each of said fibers, and then positively removing said swollen surface layer by contacting the fabric with a second solution of a solvent substance whose concentration, temperature and treating time is ad-

justed to dissolve or disperse only said acted upon surface layer.

2. A process according to claim **1**, wherein the acrylic fiber fabric is in the form of a woven fabric.

3. A process according to claim **1**, wherein the solvent substance is selected from the group consisting of nitric acid, sulfuric acid, phosphoric acid, sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, zinc chloride, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide, ethylene dicarbonate, and mixtures thereof.

4. A process according to claim **1**, wherein the acrylic fiber article is treated with said solvent substances in a manner such that the swelling and dissolving actions extend from 1 to 50% of the extent of the cross-section of the individual fibers.

5. A process according to claim **1** wherein the first solution of solvent substance contains 71% by weight sulfuric acid, and the second solution contains less than 71% by weight sulfuric acid.

6. A process according to claim **1** wherein the first solution of solvent substance contains at least 95% by weight dimethyl sulfoxide, the second solution contains less than 95% by weight dimethyl sulfoxide.

7. A process according to claim **1** wherein the first solution of solvent substance contains at least 51% by weight nitric acid and the second solution contains less than 51% by weight nitric acid.

References Cited

UNITED STATES PATENTS

3,111,362	11/1963	Fang et al.	8—115.5
2,920,934	1/1960	Schaefer et al.	8—130.1
3,236,587	2/1966	Genereux	8—130.1
3,403,969	10/1968	Kautny et al.	8—130.1

LEON D. ROSDOL, Primary Examiner

H. WOLMAN, Assistant Examiner

U.S. Cl. X.R.

8—115.5, 177 R