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HIROYUKI YAMAGUCHI ET AL

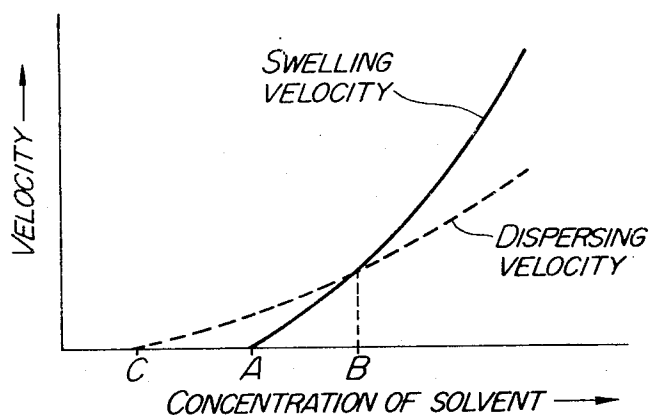
3,679,355

METHOD FOR IMPROVING POLYACRYLONITRILE FIBER BY PEELING
OFF THE FIBER SURFACE WITH SOLVENTS

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2 Sheets-Sheet 1

FIG. 1



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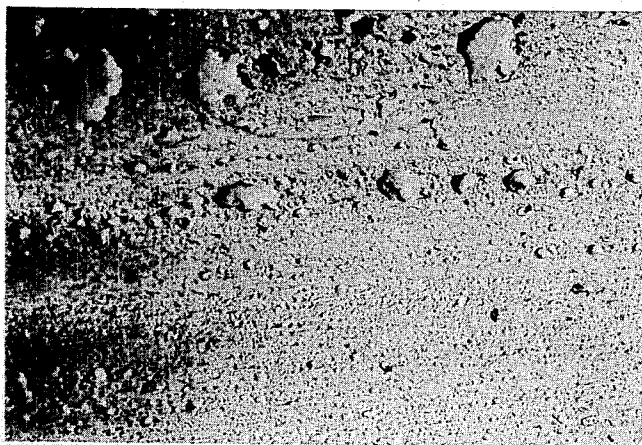
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FIG. 2



FIG. 3



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METHOD FOR IMPROVING POLYACRYLONITRILE FIBER BY PEELING OFF THE FIBER SURFACE WITH SOLVENTS

Hiroyuki Yamaguchi, Kyoto, Katsuyoshi Tuji, Osaka, Kenji Maki, Kyoto, and Isoo Shimonishi, Sakai-shi, Japan, assignors to Asahi Kasei Kogyo Kabushiki Kaisha, Osaka, Japan

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U.S. Cl. 8—130.1

10 Claims

ABSTRACT OF THE DISCLOSURE

An acrylic fiber article is improved by treating it with a solution of a solvent having a concentration higher than that at which the solution begins to dissolve the fiber and lower than that at which the swelling velocity of the solution on the fiber surface is equal to the dispersing velocity of the surface of the swelled layer to peel the fiber. Examples of such solvent are dimethylformamide, dimethylacetamide, dimethylsulfoxide, sodium thiocyanate, zinc chloride, sulfuric acid, nitric acid, etc.

This invention concerns a method for improving acrylic fibers by peeling a surface layer of the fibers by the treatment thereof with a solvent having a specific function.

There have been provided various methods for the improvement of acrylic fibers, but none of them have resulted in remarkable improvement. It has been considered to be utterly difficult to semipermanently change the properties of once formed acrylic fiber into desirable ones.

A known method for treating an acrylic fiber article with a solvent, comprises treating acrylic fibers with a low concentration solution of a solvent, drying and heating the treated fibers. However, according to this method, the solvent solution is concentrated on the fibers due to the drying and when the solution becomes concentrated enough to dissolve a part of the fibers, the resultant dissolved polymer layer acts as an adhesive between fibers and causes the adhesion of fibers themselves, whereby the fibers display hard hand due to the same principle as that of starched fibers becoming hard. As mentioned above, the conventional solvent treatment of acrylic fibers imparts stickiness to the fiber surface and causes adhesion of the fibers to each other. Thus, said conventional treatment has been mainly used for stiff finishing of the fiber article and is not used for positively peeling the fibers.

When acrylic fibers are treated by dipping them in a solvent therefor in such a manner that the action of the solvent acts only on the surface layer of the fibers and the thus treated fibers are water washed to remove the solvent in many cases, reduction in the weight of the fibers is observed. However, the surface layer of the treated fibers is covered with a relatively thick recoagulated polymer which strongly adheres to the surface layer. When such treatment is applied to yarns or knitted fabrics, adhesion of fibers resulted in the formation of recoagulated polymer and the fiber article is stiffened as in the above case.

The inventors have done research on the improvement of acrylic fibers and accomplished the peeling treatment of acrylic fibers by solvent treatment using a multi-step process which has never before been successful. That is, this peeling treatment results in unexpected changes in the properties of the fiber surface, physical properties of the fibers and structure of the fiber article, whereby excellent improvements such as the formation of a silk-like soft hand and improvements in luster, dyeability etc., were attained,

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which have never been attained by conventional methods. (Japanese patent application No. 59,462/66, now Japanese patent publication 24,716/70).

Conventionally, as a means for studying structures of cellulose fibers or polyamide fibers, peeling of fiber surface layers has been carried out, but has never been employed for improving fiber articles. Regarding polyester fibers, the treatment of the surface thereof with an alkali has been known. This method is based on a saponification reaction of ester bonds in the fiber molecules. Said chemical reaction has been widely utilized because the reaction progresses with ease. However, acrylic fibers are not easily peeled by any of said methods employed for cellulose fibers, polyamide fibers or polyester fibers because of acrylic fibers' peculiar structure. Thus, no attempts were made for peeling of acrylic fibers before the invention mentioned in said Japanese patent and the properties of peeled acrylic fibers were also unknown.

The purpose of this invention is to attain the improvement of acrylic synthetic fibers by peeling them by a one-step solvent treatment using a solvent having a specific function, not by the multi-step solvent treatment process of the above-mentioned invention.

The effects to be expected in this invention are obtained only when the surface layer of fibers is successively and approximately uniformly removed and ideally a fresh and smooth surface having the same property as the inner portion of the fibers is exposed, namely, the fibers are peeled. As mentioned above, no effects and advantages of this invention can be obtained by the usual solvent treatment, according to which the treated fiber surface is covered with a large amount of recoagulated polymer.

Generally, the process in which acrylic fibers react with a solvent and are dissolved thereby is as follows: First, the swelling action of the solvent rapidly progresses from fiber surface to inner portion. The swelling of the surface layer gradually becomes higher and polymer molecules of fibers slowly disperse into the solvent, whereby the dissolution of fibers progresses. Thus, it has been found that the dissolution of acrylic fibers comprises two stages of swelling and dispersing, and the swelling velocity is always extremely higher than the dispersing velocity. Due to this fact, a swelled layer is always present regardless of the time at which fibers are transferred to a step for removing the solvent and the swelled layer is deswelled to form a recoagulated polymer layer. Further, the recoagulated polymer layer of acrylic fibers strongly adheres to the fibers and does not easily fall off from the fibers.

The inventors have studied the relation between the concentration of the solvent, and swelling and dispersion and found that there is a relatively narrow range of concentration in which the swelling velocity of the fiber surface is extremely low and the dispersing velocity is higher than the swelling velocity. That is, when fibers are treated with a solvent solution having a concentration within said range, no recoagulated polymer layer is formed on the fiber surface regardless of the time at which the deswelling treatment is given, and so-called peeling is possible.

That is, this invention relates to a method for treating acrylic fibers with a solvent solution, which comprises treating the acrylic fibers with a solvent solution having a concentration higher than that at which the solution begins to exhibit its dissolving action on the fibers and lower than that at which the swelling velocity of the solution on the fiber surface is equal to the dispersing velocity of the surface of said swelled layer, thereby to peel the fiber.

Acrylic fibers referred to in this specification include synthetic fibers made of polyacrylonitrile, so-called acrylic fibers made of a copolymer of more than 85%

by weight of acrylonitrile and up to 15% by weight of a monomer polymerizable therewith, and so-called moda-acrylic fibers made of acrylonitrile and another monomer. Conjugated fibers made of polymers whose copolymer components are different and yarns whose cross section is non-circular are naturally included in said definition of acrylic fibers. Further, acrylic fiber article means filaments, bulky finished yarns, tow, cut fiber, sliver, rove, spun yarn, web, non-woven fabric, knitted fabric, woven fabric, etc., all of which are composed of the acrylic fibers defined above. It is not required that said articles should be made of only acrylic fibers and a mixed article composed of the acrylic fibers and natural fibers, semi-synthetic fibers, or synthetic fibers other than acrylic fibers, or a mixed spun article, a mixed woven article, a mixed stranded article or a mixed knitted article with other acrylic fibers may be treated according to this invention.

FIG. 1 is a schematic graph showing the relation between the concentration of a solvent, and the swelling and dispersing velocities of dipping-treated acrylic fibers. FIG. 2 is an electro microscopic photograph of the surface of the usual acrylic filament yarns (75 deniers, 38 filaments). FIG. 3 is an electro microscopic photograph of the surface of said acrylic filament yarns peeled by the method of this invention.

In this invention, the relation between the concentration of a solvent and its dissolubility of fibers is the most important. This relation is shown in FIG. 1. In FIG. 1, when the concentration of the solvent reaches a specific value A, the solvent swells the surface of fibers and begins to dissolve the fibers. In this invention, the solvent is required to have a concentration higher than said value A. With an increase in the concentration of the solvent, the dissolving action becomes stronger and the velocity of swelling at the fiber surface sharply increases as shown in FIG. 1. The surface of fibers which are already swelled begins to disperse at a concentration of C which is lower than A. With an increase in the concentration, the velocity of dispersion increases. (When the swelled layer contacts a solution having a concentration lower than C, the layer does not disperse, but is re-coagulated.) However, the increase in dispersion velocity with the increase in the concentration is not so large as the increase in the swelling velocity. Therefore, the two curves of velocities intersect at a specific concentration B. That is, in the range of concentration higher than B, the dispersion velocity is lower than the swelling velocity. Said area has been conventionally recognized, and in this area, fibers cannot be peeled for the reasons mentioned hereinbefore. Within the area between A and B, the swelling velocity is equal to or is lower than the dispersion velocity, namely, the fibers can be peeled. The conventional research in this field has been incomplete and such an area of concentration which is extremely narrow has not been known. According to the inventor's experiments, for example, regarding nitric acid at 25° C., A is 49.2%, B, 51.3% and C, 47.7%.

Said swelling velocity can be approximately measured by the following method. A fiber whose weight is known is dipped in a tested solution of a solvent having a certain concentration and, after a certain period of time, is immersed in water to discontinue the swelling. Water is completely removed from the fibers, which are then sufficiently treated with a solvent capable of dissolving only the re-coagulated polymer layer. (Generally, a solvent having a concentration between C and A can dissolve only said layer, but a 90% aqueous solution of dimethyl formamide is especially suitable.) Thereafter, thus the treated fiber is dried and then weighed to determine the weight reduction percentage. The dipping time of fiber in the tested solution is preferably such that results in a 5% weight reduction. Thus, the swelling velocity of the solution can be shown by

Weight reduction percentage
time

On the other hand, the approximate dispersion velocity can be obtained as follows. A fiber whose weight is known is dipped in a solution having a concentration higher than B for a suitable period of time to form a swelled layer and then dipped in a tested solution for a certain period of time. The fiber is immediately immersed in water to coagulate and discontinue the dispersion. Then, the fiber is dried and weighed to obtain the weight reduction percentage W. Another fiber whose weight is known is solvent treated under the same conditions as for the formation of the swelled layer mentioned above, and immediately immersed in water, dried, and weighed to obtain the weight reduction percentage W'. W' indicates the amount of polymer dispersed when the swelled layer is formed. Accordingly, the dispersion velocity of the tested solution can be obtained by

$$\frac{(W-W')}{\text{time}}$$

In this case, it is necessary to know previously the conditions under which the amount of the swelled layer is larger than that of dispersion by preliminary experiment. Further, the treating time is preferably such that results in about 5% of (W-W').

The values of C, A and B of the preferred solvents are as follows:

Solvent	Percent		
	C	A	B
Dimethylformamide	83.4	91.7	95.3
Dimethylacetamide	92.6	95.0	98.5
Dimethylsulfoxide	84.3	89.5	96.7
Sodium thiocyanate	39.6	44.6	50.7
Zinc chloride	50.2	54.4	57.7
Sulfuric acid	64.6	69.5	71.5
Nitric acid	47.7	49.2	51.3

NOTE.—(1) The treating temperature is 25° C. except that in case of dimethyl acetamide, the temperature is 50° C. (2) The values C, A and B change somewhat depending upon the composition of the polymers, spinning conditions, setting conditions, temperature, stirring conditions, etc. The numerical values in the above table were obtained by the method mentioned herein. That is, an article to be treated was dipped in the solvent and stirred by hand. The treated article is an acrylic long fiber article, which is produced from a copolymer composition comprising 92 weight percent of acrylonitrile, 3 weight percent of methyl acrylate, and 5 weight percent of acrylamide. The denier thereof is 100 d./50 f. (d. is denier and f. is filament.) (3) The percentage of peeling of the surface of the fiber with said treatment, namely, o.w.f. (over weight of fiber) is usually 5-30%. The percentage may be varied according to the use and purpose of the article to be produced. When an article having a silky touch is desired, the percentage of peeling should be within a range of 0-20%.

The range of the concentration in which peeling of fibers is possible in this invention shifts from the low concentration side at a high temperature to the high concentration side at a low temperature. The peeling treatment may be effected at a temperature from several tens centigrade degrees below zero to several tens centigrade degrees. The dissolubility of the fiber, especially the dispersion velocity is greatly affected by mechanical conditions such as shaking, stirring, etc. of the solution or fiber during the treatment. Such stirring and shaking accelerate the dispersion velocity and the increase of the dispersion velocity results in an increase of the range in which peeling is possible.

The peeling percentage, that is, the weight reduction percentage varies depending upon the purpose for improvement and the nature of the fiber article, but preferably is 2-30%. The range of concentration in which peeling is possible is the range in which the dissolving action is mild. Therefore, the time required for peeling of

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2-30% depends on the kind of solvent, but generally is more than 30 seconds, and preferably 3 minutes to 3 hours.

The solvents for acrylic fibers used in this invention include inorganic compounds such as inorganic acids, salts, etc. and various organic compounds. Examples of the inorganic acids are nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, chlorosulfonic acid, etc. Examples of the salts are thiocyanates such as sodium thiocyanate, potassium thiocyanate, calcium thiocyanate, ammonium thiocyanate, and zinc thiocyanate, halides such as calcium 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, etc. Further, examples of the organic solvents are amide compounds such as N,N-dimethyl formamide, N,N'-dimethyl acetamide, N-methyl pyrrolidone, and 2-oxazolidone, nitrile compounds such as malononitrile, adiponitrile, and β -hydroxypropionitrile, sulfone and sulfoxo compound such as dimethyl sulfoxide, and ethyl methyl sulfone, thiocyanate compounds such as methylene dithiocyanate, nitrobenzene, nitrophenol, and nitroethanol, amino compounds such as phenylene diamine, and triaminotoluene, phosphorous compounds such as tris(dimethyl amide) phosphate, and dimethyl phosphite, and carbonates such as γ -butyrolactone, maleic anhydride and ethylene carbonate, etc. In addition, acetone, dimethyl cyanoacetamide, tetrachloroethane, etc. may be used. The materials listed above are merely examples of the materials which may be used. All other materials which can dissolve acrylic fibers may be used in this invention. Further, mixtures thereof may be used.

The dissolving action of the solvent solution varies depending upon jointly used material which is added to the solution. Therefore, the peeling may be more advantageously effected by choosing the suitable material to be jointly used. Further, the range of the concentration in which the peeling of fibers is possible and the degree of effects obtained by peeling also vary depending upon the previous treatment of the fibers and material to be treated, such as scouring condition, heat set condition, surfactant used and sizing material.

Thus, treatment of acrylic fiber article according to this invention results in remarkably soft hand and refined lustre. Further, according to this invention, the levelling dyeability of the fiber article is raised and dyeing spots are improved, whereby the fibers can be clearly dyed.

This invention is applicable to all acrylic fibers, but is especially an excellent treating method for improvement of acrylic filament yarn article. That is, acrylic filament yarn articles have defects in that they have a hard hand and dyeing spots easily occur when dyed. These defects can be eliminated by application of the method of this invention and silk-like hand and lustre, and clear dyeing are attained. Such excellent improvements are obtained due to smoothening of the fiber surface and changes of fiber properties by peeling the surface layer of fibers. Furthermore, there are formed proper spaces in the structure of the fiber article, and hand and drapability of the article are improved because the fibers constituting the fiber article are peeled.

This invention will be further illustrated with reference to the following examples, in which all percentages are expressed by weight.

EXAMPLE 1

Acrylic fiber spun yarns (single yarn 48 metric count) were dipped in 50.5% aqueous solution of nitric acid maintained at 5° C. for 10 minutes, thereafter washed with water and dried. This treatment resulted in the reduction of weight of the yarns by about 15.0%. Two

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jerseys were produced by knitting thus treated yarns and usual yarn 54 metric count, respectively. The jersey knitted from the treated yarns felt remarkably soft in comparison with that knitted from usual yarns and was level dyed.

EXAMPLE 2

Acrylic synthetic fiber filament yarns (trade name: PEWILON, 75 deniers, 38 filaments) were covered on a frame and dipped in 92.5% aqueous solution of dimethylformamide at 25° C. for two hours. Thereafter, the yarns were water-washed and dried. The weight of yarn was reduced by 7.3% by this treatment. Tricot obtained by knitting said yarns and silk-like lustre and hand, and gave no dye-spots when dyed.

FIG. 2 is an electron microphotograph of the surface of a usual filament yarn and FIG. 3 is that of the surface of the treated yarn. From these photographs, it is clear that by the treatment according to this invention, the diameter of fibers was reduced and the peeling of the surface layer of the fibers was carried out.

EXAMPLE 3

Acrylic fiber spun yarns (single yarn 52 metric count) were dipped in aqueous solutions (20° C.) of sodium thiocyanate having concentrations as indicated in the following table for 6 minutes and then water-washed and dried. The weight reductions of yarns are shown in Table 1.

TABLE 1

Fabric:	Concentration of sodium thiocyanate, percent	Weight reduction percentage
A-----	43.0	0
B-----	45.5	2.4
C-----	50.2	32.0
D-----	51.5	10.3

The spun yarns B and C became softer than non-treated yarn, but A showed no change in softness and D became extremely hard. Tricots made by knitting B and C yarns had silk-like lustre and hand and gave no spots when dyed. Tricot made of A had the same properties as that made of non-treated yarn. Breaking of yarns often occurred in knitting D yarns and the tricot produced had hard hand and gave many spots when dyed. Thus, the tricot made of D yarns had no utility.

EXAMPLE 4

Plain woven fabric made of fiber spun yarns (two folded yarn 80 metric counts) was dipped in 48.0% aqueous solution of sodium thiocyanate at 15° C. for one hour, and the fabric was sometime stirred in the solution. Then, the fabric was water-washed and dried. This treatment resulted in the reduction of weight of the fabric by 12.7%, and the fabric had a soft hand.

EXAMPLE 5

Plain woven fabric made of acrylic filament yarns of 100 deniers (non-twisted yarns) was dipped in 71.0% aqueous solution of sulfuric acid at 50° C. for 10 minutes, during which the fabric was continuously stirred. Then, the fabric was water-washed and dried. The weight of the fabric was reduced by 23.0%. The treated fabric had silk-like hand and lustre and had drapability. No spots were seen when dyed.

EXAMPLE 6

Fabrics made of acrylic filament yarns of 40 deniers (non-twisted yarns) were dipped in aqueous solution of nitric acid having the concentrations mentioned in Table 2 at 20° C. for 5 minutes, water-washed and dried. The

weight reduction percentage and other properties of each fabric treated are shown below.

TABLE 2

Symbol of fabric	Concentra- nitric acid	Weight reduction, percentage	Softness		Tear strength, kg.	
			Direction of warp	Direction of weft	Direction of warp	Direction of weft kg.
A	47.0%	0	2.23	4.01	1.37	1.54
B	50.0%	20.0	16.4	8.5	1.42	1.60
C	52.0%	7.0	1.04	2.11	1.20	1.34
	Nontreated		2.21	4.01	1.36	1.52

Regarding fabric C, the weight reduction was observed, but it became harder than non-treated fabric and therefore was outside this invention. Fabric B was the fabric treated in accordance with this invention and had silk-like hand.

EXAMPLE 7

Acrylic fiber cotton (3 deniers and the length of cutting 50 mm.) was dipped in 93.0% aqueous solution of dimethylsulfoxide at 10° C. for one hour, water-washed and dried. The weight of the cotton was reduced by 8.0% according to said treatment. The Young's Modulus of fiber of raw cotton was 374 kg./mm.², but that of the treated fiber was 405 kg./mm.².

EXAMPLE 8

Dechine fabric was manufactured using acrylic filament yarns of 40 deniers (200 times/m. S twist yarn) as a warp and filaments of 75 denier (1500 times/m. S twist yarn and Z twist yarn) using as weft, scoured, creped, and then heat set at 130° C. for 30 seconds. This fabric was dipped in 52.0% aqueous solution of zinc chloride at 50° C. for 60 minutes, water-washed and dried. The weight of the fabric thus treated was reduced by 12.0% and the fabric had silk-like excellent hand. The comparison of the properties of the treated fabric and non-treated fabric was shown in Table 3.

TABLE 3

	Softness		Crease resistance, direction of warp plus weft	Tear strength, kg.	
	Direction of weft	Direction of warp		Direction of weft	Direction of warp
Treated fabric	7.3	14.1	211°	1.51	1.36
Nontreated fabric	3.7	2.0	193°	1.34	1.25

The softness of fabrics in Tables 2 and 3 was measured according to Canti Laver method of ASTM, D1388-64. The greater the value measured, the higher the softness. The crease resistance was shown by crease recovery angle measured according to the method based on AATCC, 66-1959T. The greater the measured value, the better the crease resistance. Further, the greater said value, the higher the tear strength.

EXAMPLE 9

Koma rinzu (figured stain) fabric was woven using acrylic filament yarns of 75 deniers (about 400 times/m. S twist yarn) as warp and acrylic filament yarns of 75 deniers (about 600 times/m. S twist yarn was Z twisted about 600 times/m. in the form of two folded yarn) as weft. This fabric was dipped in an aqueous solution containing 50.0% of nitric acid and 0.5% of urea at 10° C. for 20 minutes while unceasingly stirring, then water washed and dried. The weight of the fabric thus treated was reduced by 6.2%. The hand of the fabric became silk-like and no spots were seen when dyed.

EXAMPLE 10

Mixed spun yarn fabric comprising 70.0% of acrylic fibers, and 30.0% of polyester fibers was dipped in an aqueous solution containing 95.0% of ethylene carbonate and 1.0% of polyvinyl alcohol at 30° C. for 3 hours, then water washed and dried. The weight of the fabric

thus treated was reduced by 4.2% and the fabric had soft hand.

EXAMPLE 11

A twill fabric made of acrylic filament yarns of 75 deniers as warp and viscose rayon yarns of 75 deniers as weft was dipped in 93.0% aqueous solution of dimethyl sulfoxide at 5° C. for 40 minutes, then water-washed and dried. The weight of the fabric thus treated was reduced by 6.2%. The fabric had silk-like hand and refined lustre in comparison with non-treated fabric.

EXAMPLE 12

A plain fabric made of moda-acrylic fiber (single yarn 48 metric counts) (acrylonitrile 60% and vinyl chloride 40%) was dipped in 98.0% aqueous solution of dimethylformamide at 20° C. for one minute, then water-washed and dried. The weight of the fabric thus treated was reduced by 8.0%.

EXAMPLE 13

A jersey was produced by knitting crimped yarn made of acrylic filament conjugated yarn having different copolymer components (75 deniers). This knitted article was dipped in 95.0% aqueous solution of dimethylformamide at 20° C. for 1.5 minutes, then water-washed and dried. The weight of this article thus treated was reduced by 30.0%. The article had silk-like refined hand, lustre and drapability.

EXAMPLE 14

A plain woven fabric made of acrylic filament yarns of 150 deniers was dipped in a solution containing 94.3% of dimethyl acetamide and 0.3% of polyethylene glycol (average molecular weight is 1000) at 70° C. for 30 minutes, then water-washed and dried. This treatment resulted in the reduction of weight of the fabric by 10.4% and the fabric had silky touch in comparison with the untreated fabric.

What is claimed is:

1. A method for improving a polycrylonitrile fiber article containing at least 60% acrylonitrile therein by peeling the fiber with asolvent therefor, which comprises (1) dipping the article in a solution of the solvent having a concentration higher than that at which the solution begins to swell the fiber and lower than that at which the swelling velocity of the solution on the fiber surface is equal to the dispersing velocity of the swelled layer until the incident swelled layer is peeled from the fiber and (2) rinsing the article in water to remove the solvent.
2. A method according to claim 1, wherein the article is treated with the solvent for 3 minutes to 3 hours.
3. A method according to claim 1, wherein the weight reduction percentage of the fibers treated is 2-30%.
4. A method according to claim 1, wherein the acrylic fiber article is treated with a solution of dimethylformamide having a concentration of 91.7-95.3% at 25° C.
5. A method according to claim 1, wherein the acrylic

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fiber article is treated with a solution of dimethylacetamide having a concentration of 95.0%–98.5% at 50° C.

6. A method according to claim 1, wherein the acrylic fiber article is treated with a solution of dimethylsulfoxide having a concentration of 89.5%–96.7% at 25° C.

7. A method according to claim 1, wherein the acrylic fiber article is treated with a solution of sodium thiocyanate having a concentration of 44.6%–50.7% at 25° C.

8. A method according to claim 1, wherein the acrylic fiber article is treated with a solution of zinc chloride having a concentration of 54.4%–57.7% at 25° C.

9. A method according to claim 1, wherein the acrylic fiber article is treated with a solution of sulfuric acid having a concentration of 69.5%–71.5% at 25° C.

10. A method according to claim 1, wherein the acrylic fiber article is treated with a solution of nitric acid having a concentration of 49.2%–51.3% at 25° C.

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GEORGE F. LESMES, Primary Examiner

H. WOLMAN, Assistant Examiner

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