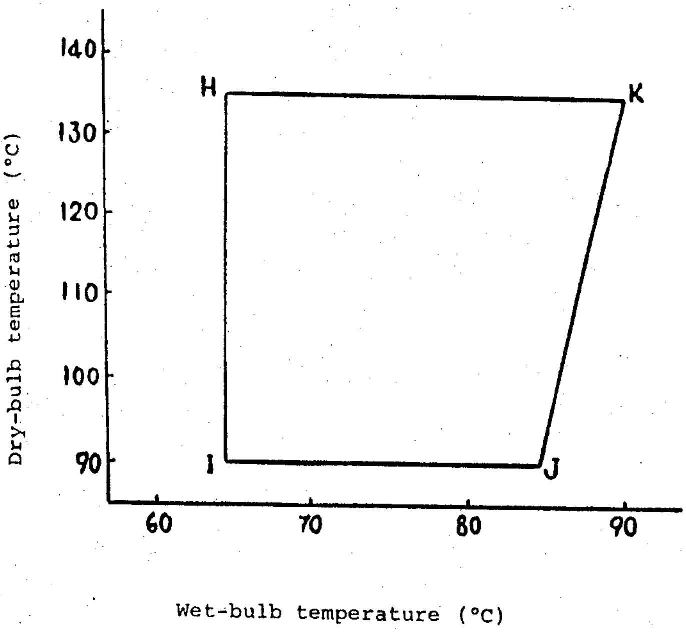
June 24, 1969 KAZUMI NAKAGAWA ETAL 3,451,140

PRODUCTION OF ACRYLIC SYNTHETIC FIBERS

Filed Aug. 16, 1967 Sheet 1 of 3

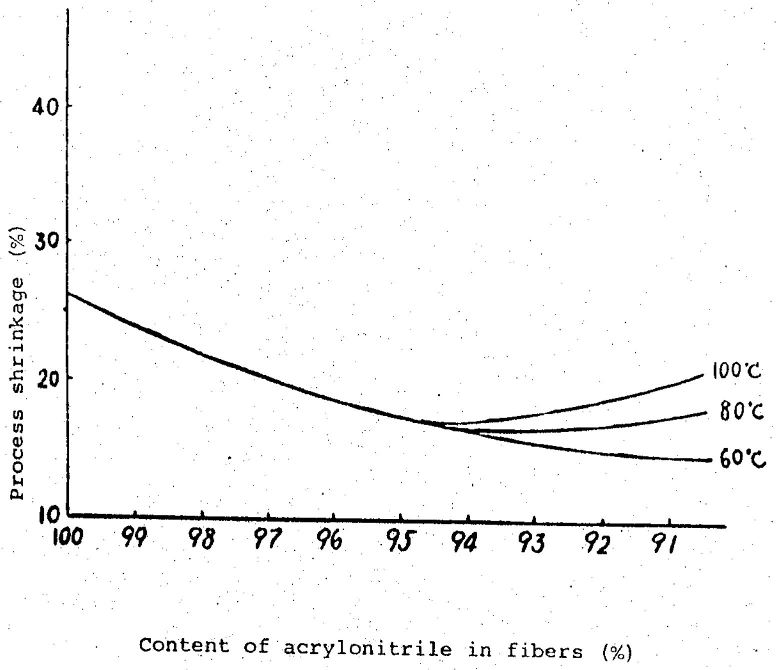
FIG. 1



INVENTORS: KAZUMI NAKAGAWA
NOBUHIRO TSUTSUI
TAKEHIKO SUMI

By Wenderoth, Lind & Ponack,
Attorneys

FIG. 2



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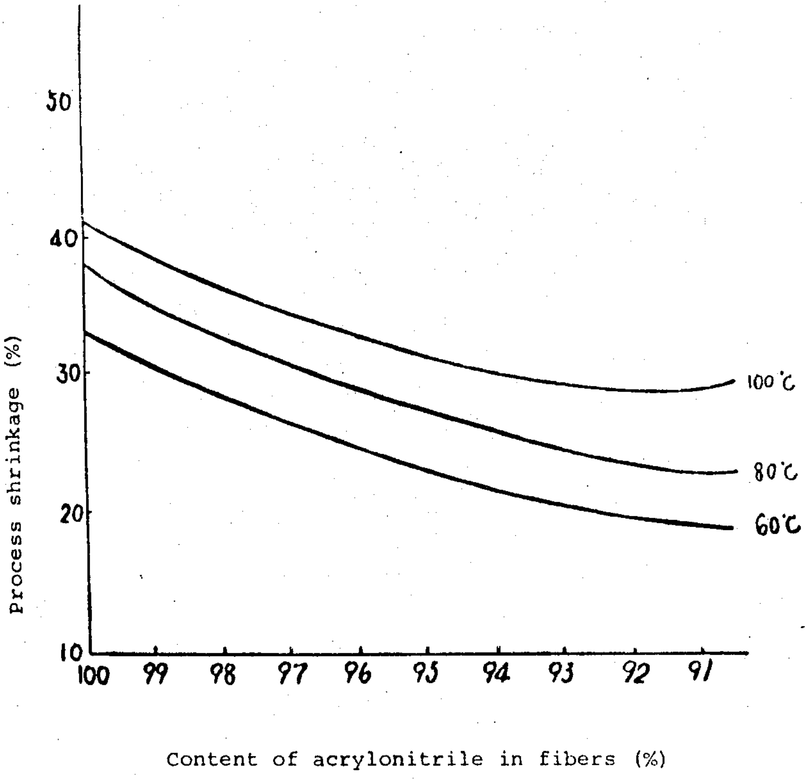
Filed Aug. 16, 1967 Sheet 3 of 3

FIG. 3



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PRODUCTION OF ACRYLIC SYNTHETIC FIBERS

Kazumi Nakagawa, Saidaiji, Nobuhiro Tsutsui, Okayama, and Takehiko Sumi, Saidaiji, Japan, assignors to Japan Exlan Company Limited, Osaka, Japan

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Int. Cl. F26b 21/10, 21/08
U.S. Cl. 34—12 5 Claims

ABSTRACT OF THE DISCLOSURE

Fibers of acrylonitrile polymer are produced by spinning a solution, in the concentrated aqueous solution of a thiocyanate, of an acrylonitrile homopolymer or of an acrylonitrile copolymer of at least 91% by weight of acrylonitrile, the balance being at least one monomer copolymerizable with acrylonitrile, into an aqueous coagulating bath to form filaments, washing the latter with water and then stretching the filaments to obtain swollen gel filaments containing at least 40% by weight of water, relaxing the gel filaments in non-tensioned state in a wet medium (hot water or steam) at 60° to 100° C., and then drying the relaxed filament under correlated temperature and humidity conditions defined by the line H—I—J—K of FIG. 1 of the drawings.

This invention relates to an improved method of producing fibers of acrylonitrile polymers by aqueous wet-spinning.

It is known in U.S. Patent No. 2,984,912 to produce fibers of acrylonitrile fibers with improved properties such as uniform and improved dyeability, improved wear-resistance, hand, less tendency to fibrillation, etc. by wet-spinning an acrylonitrile polymer into filaments, which are stretched and then dried under particular conditions of temperature and humidity until substantially all of the water is removed from the filament and its structure is collapsed.

It is also known in British Patent No. 776,678 to produce acrylic fibers with improved knot strength by wet-spinning an acrylonitrile polymer into filaments, which are stretched and then dried and densed until the water content in the filament is reduced to 9–60% by weight based on the total weight of the filament, followed by the relaxation at 105° C.

Thus it has been conventional, in order to obtain acrylic synthetic fibers by wet-spinning, to conduct relaxation of acrylic fibers after they have been spun, washed with water, stretched and dried. In such method, if swollen gel fibers obtained after stretching for orientation are directly heated to be relaxed they will be devitrified, and therefore it has been possible to heat and relax them only after the fibers have been substantially completely dried.

However, generally, in acrylic synthetic fibers, with the increase of the content of acrylonitrile, the glass transition temperature will rise and therefore the thermal motion of fiber molecules will be suppressed to some extent. As a result, in case the content of acrylonitrile in the fibers is high, the fibers after being spun, water washed, stretched and then once dried will reduce so much in the shrinkage in the heating and relaxing treatment that it will be difficult to obtain satisfactory relaxing effect. Thus, for example, as shown in FIG. 3, the total of the shrinkages in the drying and heat-relaxing treatments or the so-called process shrinkage will reduce so remarkably that no satisfactory knot strentgh or elonagtion will be obtained. Further, in case the temperature of the heat-relaxing treatment is elevated to rectify these defects, the whiteness of the resulting fibers will reduce so much and the dyeing rate will increase so much that uneven dyeing will occur in the dyeing step.

It is also known in U.S. Patent No. 2,743,994 to produce a shaped article of an acrylonitrile polymer by preparing a solution of a copolymer consisting of at least 80% by weight of acrylonitrile and at most 20% by weight of a mono-olefinic monomer copolymerizable with acrylonitrile, extruding the solution into a coagulating medium to form a coagulated shaped article, which is then stretched for molecular orientation at a temperature of 100° C. or less within 15 seconds, then relaxed, followed by crystallization by heat-treating the article at a temperature of at least 100° C. for at least 15 seconds. In this method, however, the relaxation is conducted at such a high temperature of at least 100° C. and no special consideration is paid in respect of drying after the relaxation. Therefore, the resulting fibers are not satisfactorily densed and contain a considerable extent of voids. Further, this method has a drawback that, since the relaxation is conducted at such high temperature, there will be caused discoloration in the resulting fibers so that the whiteness is very low.

Therefore, the primary object of the present invention is to obtain sufficiently relaxed and densed acrylic synthetic fibers by wet-spinning process from an acrylonitrile homopolymer or copolymer containing at least 91% by weight of acrylonitrile.

The second object of the present invention is to obtain acrylic synthetic fibers high in the whiteness by carrying out the relaxing treatment at a comparatively low temperature.

The third object of the present invention is to obtain acrylic synthetic fibers having improved physical properties.

The fourth object of the present invention is to obtain acrylic synthetic fibers comparatively low in the dyeing rate and high in the level dyeability.

The other objects of the present invention will become apparent from the following description which will be made partly by referring to the accompanying drawings wherein:

FIG. 1 is a graph of temperature and humidity conditions which are employed in drying gel fibers for densing according to this invention;

FIG. 2 is a graph showing the relation between process shrinkage and acrylonitrile content in fibers prepared according to the method of this invention; and

FIG. 3 is a graph similar to FIG. 2 but in respect of fibers prepared according to conventional method.

Briefly, the above mentioned objects of this invention are accomplished by preparing a solution of an acrylonitrile homopolymer or copolymer containing at least 91% by weight of acrylonitrile dissolved in a concentrated aqueous solution of a thiocyanate, spinning the solution into an aqueous coagulating bath of a low temperature to form filaments, washing the so formed filaments with water, thermal-stretching the filaments to obtain swollen gel fibers containing at least 40% by weight of water, relaxing the gel filaments in a wet medium (hot water or steam) of a temperature from 60° C. to 100° C., and then drying and densing the relaxed filaments in an atmosphere under correlated conditions of temperature and humidity defined hereinlater.

Noticing that, in the wet-spinning of acrylic synthetic fibers, the acrylonitrile homopolymer or the acrylonitrilic copolymer will become the final fiber product through the state of swollen gel fibers, we have found that, when the wet-heat-relaxing treatment is carried out in respect of swollen gel fibers of an acrylonitrile homopolymer or an acrylonitrilic copolymer containing at least 91% acrylonitrile, it is possible to give a sufficient shrinkage to the fibers at a comparatively low temperature of 60 to 100° C. without devitrifying them. Such phenomenon is presumed to be caused by the facts that the swollen gel fibers are plasticized by a large amount of the swelling agent or water and consequently the apparent glass transition temperature is consisiderably lowered. When said relaxed fibers are further dried in heated air meeting such moisture controlled condition as is shown in FIG. 1, compacted or densed fibers are obtained. When such treatment is carried out, as shown in FIG. 2, according to the method of the present invention, the process shrinkage of the fibers becomes larger then the process shrinkage by the conventional method (relaxed after stretching and drying) shown in FIG. 3. Thus, according to the method of the present invention, in case that the acrylonitrile content in the polymer is more than about 91% by weight, the process shrinkage will remarkably increase and a high relaxing effect not obtainable in the conventional method will be obtained.

The method of the present invention will be described in more detail.

Polymers to be used in carrying out the method of this invention are acrylonitrile homopolymers and acrylonitrilic copolymers containing at least 91% by weight acrylonitrile and at least one monomer compound copolymerizable with acrylonitrile. These polymers and copolymers may be obtained by any well known method. If desired, a mixture of two or more of these polymers may be employed. Examples of the monomer compounds copolymerizable with acrylonitrile include methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, methoxyethyl acrylate, phenyl acrylate, cyclohexyl acrylate and dimethylaminoethyl acrylate, the corresponding esters of methacrylic acid, acrylamides and methacrylamides and their alkyl substituted products and nitrogen substituted products; such unsaturated carboxylic acids as acrylic acid, methacrylic acid and itaconic acid; such unsaturated ketones as methyl vinyl ketone, phenyl vinyl ketone and methyl isopropenyl ketone; such vinyl carboxylates as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl thiolacetate and vinyl benzoate; esters of such ethylene alpha, beta carboxylic acids as maleic acid, fumaric acid, citraconic acid, mesaconic acid and aniconic acid: N-alkylmaleinimides; N-vinyl carbazol; N-vinyl succinimide; N-vinyl phthalimide; vinyl ether; N-methylol acrylamide; such vinyl pyridines as 2-vinyl pyridine, 4-vinyl pyridine and 2-methyl-5-vinyl pyridine; styrene and its alkyl substituted products; allyl alcohol; vinyl chloride; vinylidene chloride and vinylidene cyanide; such unsaturated organic sulfonic acids as allyl sulfonic acid, methallyl sulfonic acid, allyoxyethyl sulfonic acid, methallyloxyethyl sulfonic acid, allylthioethyl sulfonic acid, allylthiopropanol sulfonic acid, isopropenylbenzene sulfonic acid, vinyl bromobenzene sulfonic acid, vinyl fluorobenzene sulfonic acid, vinyl methylbenzene sulfonic acid, styrene sulfonic acid and methyl styrene sulfonic acid and their water-soluble salts.

A solvent to be used for dissolving such acrylonitrile polymer to prepare a spinning solution is a concentrated aqueous solution of a thiocyanate. Usually the concentration of thiocyanate is 42 to 55% by weight.

The thiocyanates to be used in the present invention are such thiocyanates of alkali metals as lithium thiocyanate, sodium thiocyanate and potassium thiocyanate and ammonium thiocyanate. They may be used alone or as mixed. Further, such thiocyanates of alkaline earch metals as, for example, calcium thiocyanate and barium thiocyanate may well be added.

The concentration of polymer in the spinning solution varies depending on the molecular weight of the polymer to be used but is generally 8 to 15% by weight. The spinning solution may be obtained directly by solution polymerization. The conditions required in such case are also exactly the same as are described above. The spinning solution is deaerated and filtered in the usual manner and is then conveyed to the spinnerette.

The above mentioned spinning solution is spun into a coagulating bath at a low temperature of −5 to 20° C. consisting of water or a dilute aqueous solution (0–25% concentration) of a thiocyanate which is well known in the art of aqueous wet-spinning of acrylic fibers. Swollen gel fibers coming out of the coagulating bath are then well washed with water in a water-washing bath. By the water-washing, the remaining thiocyanate and impurities are removed. Then, the fibers are stretched 3–20 times the initial length in hot water above 80° C. so as to be oriented so that the properties of the fibers are improved to practical strength and elongation ranges. Such heat-stretching may be conducted in a single stage. However, it is also possible to slightly (e.g. 1.1–4 times) stretch the fibers at the normal temperature in a water bath by utilizing the cold-stretchability and then heat-stretch the same so that the total stretch ratio becomes 3–20 times. It is also possible to multistep-stretch them by dividing the heat-stretching into several stages. It is also possible to stretch them while steam heating at 100–140° C. In any case the stretching is conducted about 3 to 20 times the initial length.

The important feature of this invention is in relaxing the so stretched and oriented swollen gel fibers by heating them with hot water or steam in a nontensioned state so that the elongation and knot strength are increased and at the same time the fibers are homogenized and become to have a high level dyeability.

The stretched and oriented swollen gel fibers to be relaxed in wet hot condition should have never been dried and should be of a water content of at least 40%. There is no upper limit in the water content, but usually it is up to about 400%.

If the water content in the stretched and oriented swollen gel fibers is less than 40%, the plasticization with water will decrease and the apparent glass transition temperature will rise so that the effect of the wet-heat-relaxing treatment will not be fully obtained, the fibers will not be perfectly densed by the subsequent drying treatment and devitrified fibers will result.

The medium in which the wet-heat-relaxing treatment is to be carried out is hot water or steam. The temperature is in the range of 60 to 100° C. In order to fully obtain the effect of the wet-heat-relaxing treatment, it is preferable to carry out the treatment for about 5 to 15 minutes.

If the treating temperature is less than 60° C., the fibers will not be able to be sufficiently relaxed and therefore fibers high in the knot strength and elongation will not be able to be obtained, while when the treating temperature exceeds 100° C., the swollen gel fibers will be discolored and the resulting fibers will become yellow. Further, the dyeing rate depends on the wet-heat-relaxing temperature. Therefore, if the wet-heat-relaxing temperature is made too high, the dyeing rate will remarkably increase and the level dyeing will become difficult.

The wet-heat-relaxed swollen gel fibers are then dried to be dense under specific conditions so that characteristics required for textile fibers are imparted. Thus, the fibers are dried in a hot air under the temperature and humidity conditions defined by the line H—I—J—K shown in FIG. 1 wherein the points H, I, J, and K are as follows:

	Dry bulb temperature (° C.)	Wet bulb temperature (° C.)
H	135	65
I	90	65
J	90	85
K	135	90

The fibers are dried until substantially all of the water has been evolved from the fiber and its structure collapses.

If these fibers are dried outside the above mentioned moisture temperature range, the above mentioned wet-heat-relaxed swollen gel fibers will not be able to be made compact or dense and the object of the present invention will not be attained.

In the present invention, the swollen gel fibers of a water content of not less than 40% mean swollen gel fibers not substantially subjected to any drying. When such swollen gel fibers are immediately wet-heat-relaxed, there will be an advantage that one drying step will be able to be omitted as compared with conventional methods.

In order to have the present invention better understood, examples of the present invention will be given in the following. In the examples, unless otherwise specified, the percentages and parts are by weight.

This whiteness of fibers mentioned in these examples was calculated by arranging the fibers in the same direction, determining their reflection rates for lights of wave lengths of 453, 553 and 595 mμ on the basis of a magnesium oxide plate with a spectrophotometer and using the following formula:

$$\text{Fiber whiteness} = \frac{R_{595} - R_{453}}{R_{553}} \times 100$$

The smaller the value, the higher the fiber whiteness.

The dyeing rate of fibers were determined by dyeing the fibers in a bath of Sumiacryl Orange 3R (trademark of Sumitomo Chemical Co., Ltd., Osaka, Japan) in an amount of 4% on the weight of the fibers (which shall be abbreviated as "OWF" hereinafter), 3% OWF acetic acid, a bath ratio of 1/100, a dyeing bath temperature of 90° C. and a dyeing time of 60 minutes, and measuring the dye exhausting rate. The larger the value, the higher the dyeing rate.

EXAMPLE 1

A copolymer ($[\eta_i]=1.4$ as measured with a dimethyl formamide solution at 30° C.) consisting of 91% acrylonitrile and 9% methyl acrylate was dissolved in an aqueous solution of 46% sodium thiocyanate to prepare a spinning solution of a copolymer concentration of 11%. This spinning solution was spun into a spinnig bath consisting of an aqueous solution of 12% sodium thiocyanate at −3° C. through a spinnerette having 50 orifices of a diameter of 0.09 mm. to form filaments. The filaments were then well washed with water by being passed through a water-washing bath, stretched 2.5 times the length in said water-washing bath, further stretched 4 times the length in boiling water at about 100° C. and the stretched filaments (water content 96%) were immediately wet-heat-relaxed for 15 minutes in a nontensioned state under the condition shown in Table 1. The thus wet-heat-relaxed swollen gel fibers were then dried in an atmosphere at a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. The properties of the resulting fibers are shown in Table 1. For comparison, the properties of fibers produced by a conventional method, that is, fibers obtained by once drying swollen gel fibers after being spun, water-washed and stretched in the same manner as is mentioned above, under the conditions of a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. and then wet-heat-relaxing them in a nontensioned state are shown in Table 2.

TABLE 1

No.	Wet-heat-relaxing conditions (° C.)	Compacting drying conditions		Process shrinkage (percent)	Denier (d.)	Strength (g./d.)	Elongation (percent)	Knot strength (g./d.)	Knot elongation (percent)	Fiber whiteness (percent)	Dyeing rate (percent)	Devitrification of fiber
		Dry bulb temperature (° C.)	Wet bulb temperature (° C.)									
1	60; Hot water	110	75	20.3	2.45	4.32	25.0	2.10	13.1	1.1	8.9	Not devitrified.
2	70; Hot water	110	75	24.5	2.59	4.11	32.0	2.80	20.8	1.1	8.9	Do.
3	80; Hot water	110	75	26.8	2.80	4.16	33.3	2.92	25.7	1.1	9.0	Do.
4	90; Hot water	110	75	28.9	3.03	3.81	40.3	3.16	35.8	1.1	10.0	Do.
5	100; Hot water	110	75	31.2	3.12	3.42	45.6	2.98	38.4	1.1	14.0	Do.
6	105; Saturated steam	110	75	34.0	3.15	3.40	49.3	2.89	39.8	1.9	15.0	
7	do	110	60	32.0	3.13	3.20	46.0	2.78	38.9	1.4	16.0	Devitrified.
8	115; Saturated steam	110	75	38.2	3.21	3.08	51.4	2.84	40.6	2.5	26.4	Not Devitrified.

TABLE 2

Number	Compacting drying conditions		Wet-heat-relaxing conditions (° C.)	Process shrinkage (percent)	Denier (d.)	Strength (g./d.)	Elongation (percent)	Knot strength (g./d.)	Knot elongation (Percent)
	Dry bulb temperature (° C.)	Wet bulb temperature (° C.)							
9	110	75	80; Hot water	18.8	2.49	4.50	29.8	1.62	11.1
10	110	75	105; Saturated steam	20.6	2.52	4.31	32.6	2.24	19.0

As shown in Tables 1 and 2, according to the method of the present invention, even when a comparatively lower temperature than in the conventional method was used for the wet-heat-relaxing, fibers having a sufficient knot strength and elongation could be obtained. Further, as shown in Nos. 6 and 8, in case the relaxing temperature was high, the whiteness of the fibers reduced and the dyeing rate increased. Further, as shown in No. 7, when the compacting drying conditions were outside the range of Table 1, the fibers could not be made compact or dense.

Example 2

An acrylonitrile homopolymer (of $[\eta_i]=2.1$ as measured with a dimethyl formamide solution at 30° C.) was spun under the same conditions as in Example 1. The formed filaments were stretched 2.5 times the length in a water-washing bath, were further stretched 4 times in boiling water at about 100° C. The stretched filaments (water content 170%) were immediately wet-heat-relaxed for 5 minutes in a nontensioned state under the conditions shown in Table 3 and were then dried for densing in an atmosphere at a dry bulb temperature of 100° C. and a wet-bulb temperature of 80° C. The characteristic values of the resulting fibers are shown in Table 3.

TABLE 3

Wet-heat-relaxing condition (° C.)	Process shrinkage (percent)	Denier (d.)	Strength (g./d.)	Elongation (percent)	Knot strength (g./d.)	Knot elongation (percent)
80; Hot water	28.8	2.91	4.97	35.5	3.90	30.7
90; Hot water	29.3	3.01	4.84	38.7	3.82	31.8
100; Hot water	31.6	3.19	4.82	42.6	3.75	33.2
105; Saturated steam	33.1	3.20	4.41	45.2	3.70	34.4
115; Saturated steam	34.8	3.24	4.21	42.3	3.55	35.0

Example 3

Each of acrylonitrilic copolymers (of $[\eta_1]=1.8$ as measured with a dimethyl formamide solution at 30° C.) containing acrylonitrile and methyl acrylate in such proportions as shown in Table 4 was spun and the formed filaments were water-washed and stretched in the same manner as in Example 1. The filaments were immediately wet-heat-relaxed for 5 minutes in a nontensioned state. The relaxed swollen gel fibers were then dried in an atmosphere of a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. The properties of the resulting fibers are shown in Table 4. For comparison, the properties of fibers produced by a conventional method, that is, fibers after having been spun, water-washed, stretched and oriented in the same manner as is mentioned above, were once dried in an atmosphere of a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. and then wet-heat-relaxed in a nontensioned state are shown in Table 5.

TABLE 4

Polymer composition									
Acrylonitrile (percent)	Methyl acrylate (percent)	Water content in stretched filaments (percent)	Wet-heat-relaxing condition (° C.)	Process shrinkage (percent)	Denier (d.)	Strength (g./d.)	Elongation (percent)	Knot strength (g./d.)	Knot elongation (percent)
100	0	317	90; Hot water	32.2	3.01	4.34	45.0	3.32	35.8
98	2	263	do	33.6	3.44	4.13	48.1	3.21	37.1
96	4	170	100; Hot water	33.7	3.49	4.48	50.1	3.28	35.8
94	6	133	do	28.4	3.28	4.53	39.4	3.61	31.5
92	8	100	do	28.2	2.90	4.71	37.8	3.60	28.4

TABLE 5

Polymer composition								
Acrylonitrile (percent)	Methyl-acrylate (percent)	Wet-heat-relaxing condition (° C.)	Process shrinkage (percent)	Denier (d.)	Strength (g./d.)	Elongation (percent)	Knot strength (g./d.)	Knot elongation (percent)
100	0	140; Saturated steam	27.2	3.62	2.89	28.7	1.55	12.9
98	2	do	23.8	3.03	4.30	28.0	2.24	14.4
96	4	do	23.0	3.30	4.52	32.6	2.56	17.5
94	6	do	25.7	3.34	4.73	34.8	3.31	23.6
92	8	110; Saturated steam	21.8	2.86	5.02	30.6	2.88	16.6

As is clear from the above, according to the method of the present invention, by employing a lower temperature than in the conventional method for the wet-heat-relaxing, fibers of a sufficient quality were obtained. Specifically, in case the content of acrylonitrile was high, fibers of properties never obtainable by the conventional method were obtained.

EXAMPLE 4

An acrylonitrile copolymer (viscosity $[\eta_1]=1.8$ in dimethylformamide at 30° C.) consisting of 91% of acrylonitrile and 9% of vinylidene chloride was dissolved in a 52% aqueous solution of sodium thiocyanate to prepare a spinning solution of a polymer content of 10%. The spinning solution was extruded into a coagulating bath of 12% aqueous solution of sodium thiocyanate at −3° C. through a spinnerette having 50 orifices of 0.09 mm. diameter to form filaments. The filaments were washed with water in a water bath and were stretched 2 times the length in said water bath. The filaments were further stretched 5 times in boiling water of about 100° C. Immediately thereafter, the stretched filaments (water content 178%) were subjected to wet-heat-relaxing treatment in a nontensioned state for 15 minutes in a hot water of 80° C. The resulting relaxed swollen gel filaments were then dried for 15 minutes in an atmosphere of a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. The properties of the fibers thus obtained are shown in Table 6.

Table 6

Process shrinkage, percent	30.0
Denier (d.)	3.65
Strength (g./d.)	3.91
Elongation, percent	42.6
Knot strength (g./d.)	2.93
Knot elongation, percent	31.2

For comparison similar fibers were produced in conventional manner. Thus, the swollen gel filaments after having been spun, washed with water and stretched in the above mentioned manner were dried in an atmosphere of a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. and then subjected to wet-heat-relaxation in nontensioned state with steam of 143° C. The properties of the resulting fibers are as indicated in Table 7.

TABLE 7

Process shrinkage, percent	22.5
Denier (d.)	3.26
Strength (g./d.)	4.01
Elongation, percent	27.4
Knot strength (g./d.)	1.66
Knot elongation, percent	8.3

EXAMPLE 5

An acrylonitrile copolymer (viscosity $[\eta_1]=1.4$ in dimethylformamide at 30° C.) consisting of 91% of acrylontirile, 4% of methyl acrylate and 5% of vinylidene chloride was spun, washed with water and stretched in the same manner as in Example 4. Immediately after stretching the filaments (water content 140%) were subjected to wet-het-relaxation in nontensioned state for 15 minutes in hot water of 85° C. and the so relaxed swollen gel filaments were then dried for 15 minutes in an atmosphere of a dry bulg temperature of 110° C. and a wet bulb temperature of 75° C. The properties of the resulting fibers are as indicated in Table 8.

TABLE 8

Process shrinkage, percent	31.1
Denier (d.)	3.65
Strength (g./d.)	3.35
Elongation, percent	41.4
Knot strength (g./d.)	2.86
Knot elongation, percent	35.6

For camparison similar fibers were produced in conventional manner. Thus, the swollen gel filaments after having been spun, washed with water and stretched in the above mentioned manner were dried in an atmosphere of a dry bulb temperature of 110° C. and a wet bulb temperature of 75° C. and then subjected to wet-heat-relaxation in nontensioned state with steam of 143° C. The properties of the resulting fibers are shown in Table 9.

TABLE 9

Process shrinkage, percent	24.7
Denier (d.)	3.01
Strength (g./d.)	3.76
Elongation, percent	34.8
Knot strength (g./d.)	2.20
Knot elongation, percent	19.5

EAXMPLE 6

An acrylonitrile copolymer (viscosity $[\eta_i]=1.8$ in dimethylformamide at 30° C.) consisting of 91% of acrylonitrile, 6% of methyl acrylate and 3% of diethylaminoethyl methacrylate was dissolved in a 46% aqueous solution of sodium thiocyanate to prepare a spinning solution of a polymer content of 11%. The spinning solution was spun, washed with water and stretched in the same manner as in Example 4. Immediately after stretching the gel filaments (water content 121%) were subjected to wet-heat-relaxation treatment in nontensioned state for 15 minutes in boiling water of about 100° C. and then dried for 15 minutes in an atmosphere of a dry bulb temperature of 115° C. and wet bulb temperature of 75° C. The properties of the fibers obtained are shown in Table 10.

TABLE 10

Process shrinkage, percent	30.1
Denier (d.)	3.12
Strength (g./d.)	3.24
Elongation, percent	4.03
Knot strength (g./d.)	2.76
Knot elongation, percent	37.0

For comparison similar fibers were produced in conventional manner. Thus, the swollen gel filaments after having been spun, washed with water and stretched in the above mentioned manner were dried in an atmosphere of a dry bulb temperature of 110° C. and wet bulb temperature of 75° C. then subjected to wet-heat-relaxation treatment in nontensioned state in boiling water at about 100° C. The properties of the resulting fibers are as shown in Table 11.

TABLE 11

Process shrinkage, percent	21.0
Denier (d.)	2.89
Strength (g./d.)	3.51
Elongation, percent	29.8
Knot strength (g./d.)	1.57
Knot elongation, percent	8.8

What we claim is:

1. A method of producing fibers of an acrylonitrile copolymer of at least 91% by weight of acrylonitrile with at least one monomer copolymerizable therewith by spinning a solution of the copolymer dissolved in a concentrated aqueous thiocyanate solution into an aqueous coagulating bath to form filaments, which are washed with water and stretched, which comprises subjecting the swollen gel filaments resulting from the stretching and which contain at least 40% by weight of water to wet-heat-relaxation treatment in nontensioned state in hot water or steam of 60–100° C. and then drying the fibers which have not yet been dried in any way in an atmosphere under correlated temperature and humidity conditions defined by the line H—I—J—K shown in FIG. 1.

2. A method as claimed in claim **1** wherein the thiocyanate is at least one selected from the group consisting of sodium thiocyanate, potassium thiocyanate, calcium thiocyanate and ammonium thiocyanate.

3. A method as claimed in claim **1** wherein the acrylonitrile polymer is a homopolymer of acrylonitrile.

4. A method as claimed in claim **1** wherein said monomer is selected from the group consisting of methyl acrylate, vinyl acetate, allyl sulfonic acid, vinylidene chloride and diethylaminoethyl methacrylate.

5. A method as claimed in claim **1** wherein the wet-heat-relaxation is conducted for 5–15 minutes.

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JOHN J. CAMBY, *Primary Examiner.*