

[54] **CONTINUOUS WET SPINNING
METHOD OF PRODUCING USEFUL
FILAMENTARY MATERIALS OF AN
ACRYLONITRILE COPOLYMER**

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[58] Field of Search ..8/130.1; 264/182, 342, 342 RE

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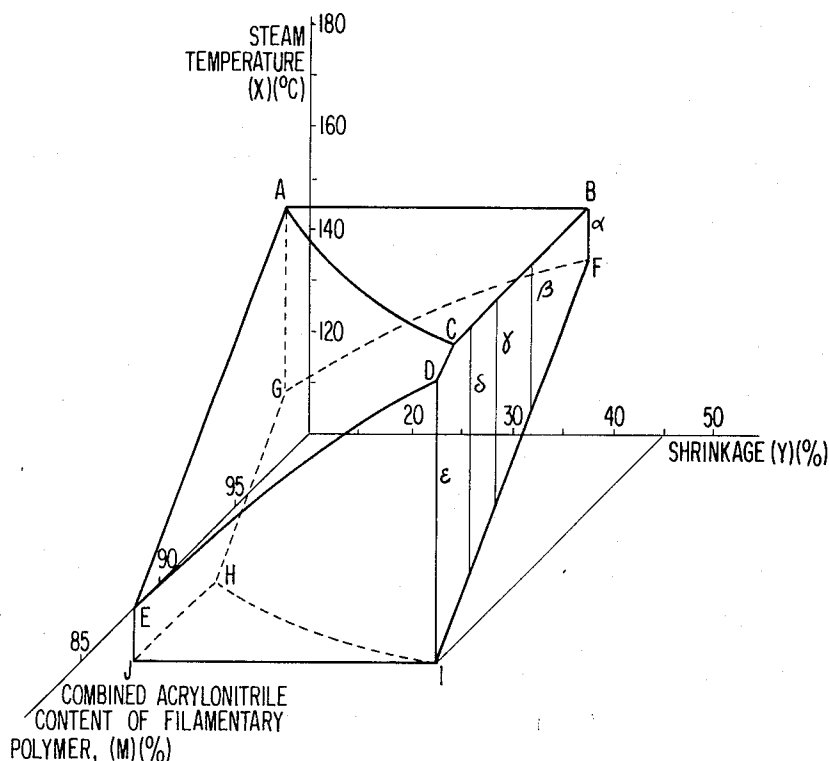
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[57] **ABSTRACT**

A continuous wet-spinning method for producing a useful filamentary material, such as multi-filaments or a tow, from a spinning solution of an acrylonitrile copolymer in an aqueous saline solvent consisting essentially of zinc chloride. In this method, an aquagel filamentary material obtained by spinning the spinning solution is taken up from an aqueous coagulating bath, continuously stretched in water and continuously dried so as to form a dried filamentary material having a moisture content of less than 5 weight percent and a transparency of at least 70 percent, measured under specific conditions. Subsequently, the dried filamentary material is continuously relaxed under a tension of at least 2 mg. per denier in substantially saturated steam at a temperature, $X(^{\circ}\text{C})$, such that the following expression is satisfied: $55 \log Y + 5M - 417 \leq X \leq 100 \log Y + 5M - 434$ wherein $160^{\circ}\text{C} \leq x \leq 100^{\circ}\text{C}$, 45 percent $\leq Y \leq 15$ percent and Y is the percent of shrinkage.

17 Claims, 6 Drawing Figures



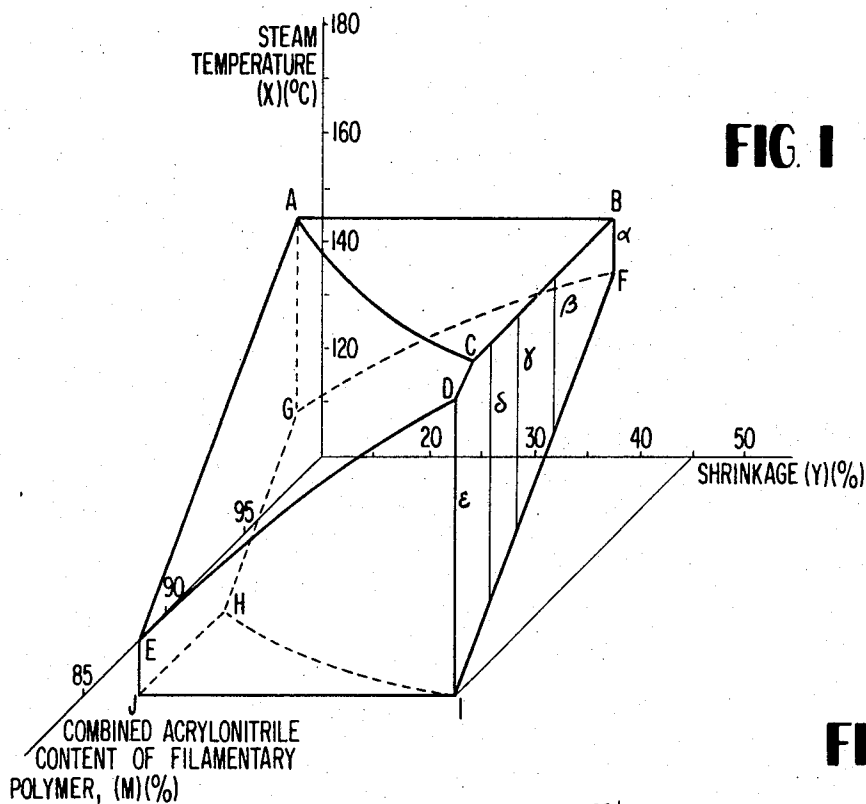


FIG. 2

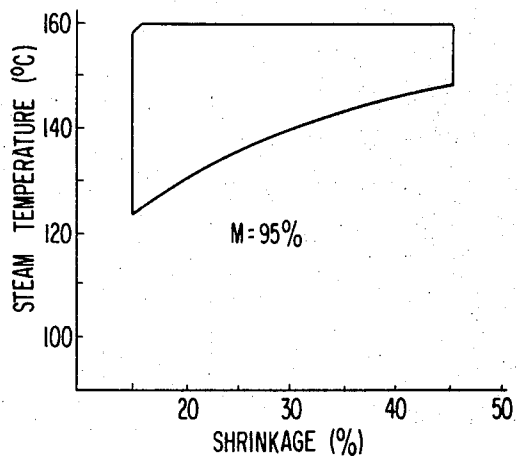
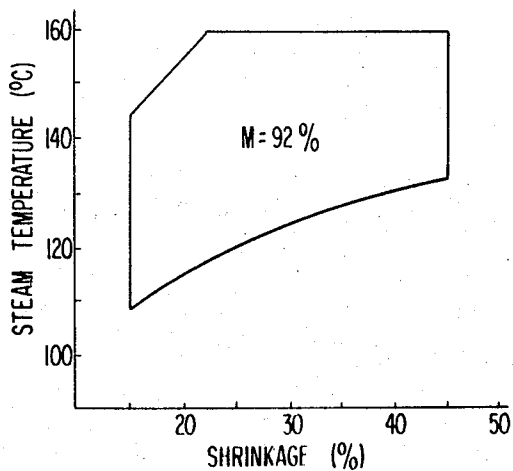


FIG. 3



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FIG. 4

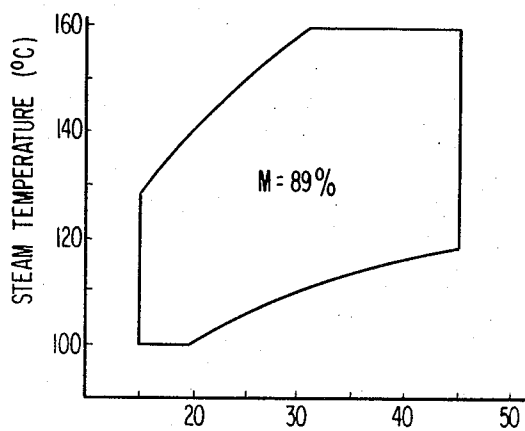


FIG. 5

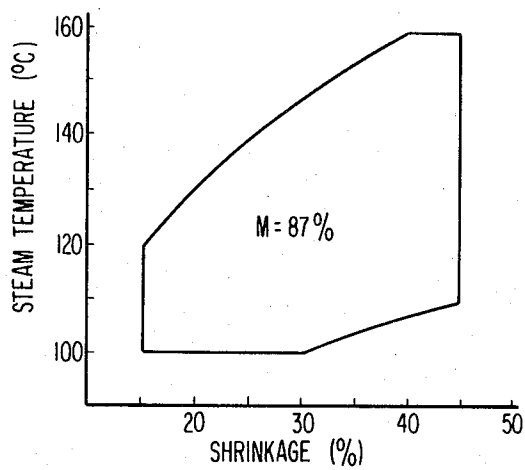
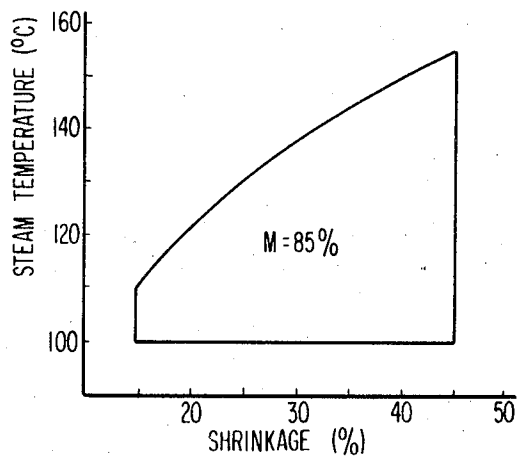


FIG. 6



CONTINUOUS WET SPINNING METHOD OF PRODUCING USEFUL FILAMENTARY MATERIALS OF AN ACRYLONITRILE COPOLYMER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for the production of acrylonitrile-copolymer filamentary materials, in particular to a continuous wet spinning method of producing such materials from a spinning solution of an acrylonitrile-copolymer containing from 85 to 95 percent by weight of combined acrylonitrile in an aqueous saline polyacrylonitrile-dissolving solvent consisting essentially of zinc chloride. More particularly, it relates to a new continuous method for treating an aquagel filamentary material that has been obtained by spinning the above-described spinning solution into an aqueous coagulating bath to prepare an acrylic filamentary material having improved properties.

2. Description of the Prior Art

As has been well known, a wet spinning process for producing acrylonitrile polymer filaments, particularly in the case of using an aqueous saline polyacrylonitrile-dissolving solvent, generally comprises extruding a spinning solution of an acrylonitrile polymer in the afore-said saline solvent through a spinnerette, or spinnerettes, into an aqueous coagulating bath consisting of a non-polymer-dissolving composition of the same solvent, washing the spun, gelled filaments with water and subjecting the washed, gelled filaments to a so-called aftertreatment, which generally comprises procedures such as hot-stretching, hot-relaxing, putting a surfactant emulsion, crimping and drying. In addition, it has been well known that the properties or qualities of the wet-spinning products are substantially or considerably dependent on the specific methods and operating conditions of the after-treatment, even if the same washed, gelled filaments are used. As a result, many studies directed toward the methods and conditions of the after-treatment have been undertaken, in connection with the composition and properties of the polymer solution to be spun out, the coagulating method and conditions of the wet extruding step and/or other similarly important technical factors, in order to produce acrylic filamentary materials having useful properties or to improve the methods of after-treatment from an economical view-point.

The primary object of the present invention is to provide a method of continuous treatment of aquagel filamentary materials (which have been spun out from an aqueous saline solution of an acrylonitrile copolymer) useful for preparing acrylic filamentary materials having improved properties, particularly excellent knot strength and knot elongation and an improved resistance to brittleness when hot-stretched with a hot-stretching machine such as a Turbo-stapler.

It has been well known that, in the preparation of shrinkable acrylic yarn, the material filaments of the acrylic polymer are hot-stretched in their dry state and rapidly cooled with an air steam under tension sufficient to cause no relaxing, before being subjected to cutting and yarn spinning, so as to have such a shrinkable property that the treated fiber is easily shrunk to its original length before the hot-stretching when it comes in contact with steam or hot water in a freely relaxed

condition. In this case, the percentage shrinkage, in steam or hot water, of the prepared shrinkable yarn as well as the shrinkable filaments and staple thus-obtained depends mainly on the degree of the hot-stretching. However, the fiber obtained as the intermediate material in the method of forming the shrinkable yarn, which has been subjected to the dry-stretching treatment, tends to become more brittle and poorer in knot strength and elongation as the degree of hot-stretching increases. An extreme increase in brittleness or a very weak knot strength and elongation of the fiber will lead to great difficulties in the yarn spinning process and also will result in the production of only spun yarn of a poor quality.

The interrelationships between the methods and procedures of producing the acrylic filaments themselves, the process conditions of preparing shrinkable filaments or fibers from original non-shrinkable filaments, the production efficiency in yarn spinning and the quality of the shrinkable yarn prepared are very complicated in detail, but one of the most important matters for preparing useful acrylic shrinkable yarn may be dependent on the specific method and conditions of the after-treatment of the coagulated, gelled filaments in the process of producing the original filaments. One of the objects of the present invention is to provide a continuous method for the production of acrylic filaments and tow having not only good physical properties, but also, which are suitable for preparing useful shrinkable fibers and yarns.

It is the second object of the present invention to provide a continuous method for producing acrylic filamentary materials having good whiteness and showing no devitrification. Among the so-called after-treatments of spun, gelled filamentary materials of an acrylic polymer, there have been disclosed several methods in which the relaxing operation is carried out in superheated steam or air at high temperatures of over 180° to 200°C. Such a procedure may be simple in operation but will lead to the production of filamentary materials of poor whiteness due to heat-discoloration, so that a relaxing procedure in saturated steam or in an aqueous liquid at temperatures considerably lower than 180°C and preferably lower than 160°C will be better in order to obtain white products. On the other hand, performing the wet relaxing procedure in saturated steam or in an aqueous liquid under a pressure considerably over atmospheric, may possibly result in the production of acrylic filamentary material showing undesirable devitrification, particularly in wet spinning of acrylonitrile polymer fibers from an aqueous inorganic saline solution into an aqueous coagulating bath. The present invention provides an improved method for producing acrylic filamentary materials showing no devitrification in spite of the application of a wet relaxing procedure in substantially saturated steam, over 100°C, to wet spun filamentary materials.

Other and related objects will become evident from an understanding the following specification.

SUMMARY OF THE INVENTION

The present method comprises stretching the aquagel filamentary material in water to a length of from 1.5 to four times its unstretched length after withdrawal from the coagulating bath; continuously

drying the resulting aquagel filamentary material until it has a water content of less than 5 percent by weight and a transparency, which is defined hereinafter, of not less than 70 percent; continuously stretching the dried filamentary material in a hot aqueous medium (e.g., hot water or steam) to a length of from four to eight times its length after the drying but immediately prior to the hot stretching; and continuously relaxing the hot-stretched filamentary material in substantially saturated steam and under an applied tension of at least 2 mg. per denier during its relaxation; the temperature, $X(^{\circ}\text{C})$, of the saturated steam and the shrinkage, $Y(\text{percent})$, to be applied to the hot-stretched filamentary material being selected such that the following expression is satisfied:

$$55 \log. Y + 5M - 417 \leq X \leq 100 \log. Y + 5M - 434,$$

wherein

$$160^{\circ}\text{C} \geq X \geq 100^{\circ}\text{C},$$

$$\text{and } 45 \text{ percent} \geq Y \geq 15 \text{ percent}$$

wherein M indicates the combined acrylonitrile content, in percent by weight, of the copolymer filamentary material to be relaxed.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the relationship between steam temperature, acrylonitrile content of the filamentary material and percent of shrinkage.

FIGS. 2-6 show the relationship between steam temperature and percent of shrinkage when the acrylonitrile content in the filamentary material is 95 weight percent, 92 weight percent, 89 weight percent, 87 weight percent and 85 weight percent, respectively.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

By "filamentary material" is meant a single filament, multi-filaments or two e.g. bundle) filaments.

The "transparency" of a filamentary material used as a characteristic parameter in the present method is defined as follows: A sample of a filamentary material is cut so as to form a staple fiber of about 15 mm. in length. 80 mg. of the staple fiber sample is placed in a transparent glass or quartz cell for measuring the light absorption of liquid samples, wherein the light-pass distance between the two parallel inner walls of the cell is designed so as to be just 20 mm. long. Then, 15 ml. of a homogeneous liquid mixture comprised of 72 percent by weight of liquid paraffin and 28 percent by weight of α -bromo-naphthalene is poured into the cell, and agitated slowly so as to form a homogeneous suspension of the staple fiber sample in the liquid mixture without generation of any air foam. The difference in light transmission between the suspension sample and the homogeneous liquid mixture itself is measured, while the fiber sample is homogeneously suspended in the liquid, using light having a wavelength of 610 m μ . The light transmission, on the basis of the organic liquid, represented in percent, is defined as the transparency of the sample filamentary material. The present method is based on the following:

1. The stretching procedure consists of two independent steps. The first step is applied in water to the aquagel filamentary material which has been wet spun and withdrawn from a coagulating bath,

while or after the material is washed substantially free from residual salts. The second step is applied in a hot aqueous medium after drying the aquagel material which has been washed and stretched in water. One of the characteristics of the present method is to dry an aquagel filamentary material between the first and second stretching operations.

2. It is important in the drying step to control the water content of the dried filamentary material to less than 5 percent by weight and the transparency to not less than 70 percent. Maintaining the drying condition is indispensable for the production of a filamentary material showing no devitrification.

3. The relaxation of the filamentary material which has been dried and stretched in a hot aqueous medium is continuously carried out in substantially saturated steam at temperature of at least 100°C , under a tension of at least 2 mg. per denier of the filamentary material to be relaxed. It may be generally said that a stretched filamentary material tends to be more easily relaxed as the tension applied to the filamentary material decreases, particularly when the tension is substantially zero. However, in the case of a continuous relaxing treatment of passing a filamentary material through a medium of saturated steam above atmospheric pressure, the practice of the treatment has been often found to be difficult when the applied tension is less than about 2 mg. per denier. A very weak tension of less than 2 mg. per denier leads to an unstable relaxing operation or results in the production of a filamentary material of poor quality. The present inventors have found that the temperature of the saturated steam medium used in the continuous relaxation step should be kept within a specific range, which is limited in accordance with the percentage of the combined acrylonitrile content of the filamentary material to be relaxed, in order to stabilize the continuous relaxing operation under a tension of at least 2 mg. per denier and in order to attain the above-mentioned objects of the present invention. The steam temperature range has been indicated hereinabove and it is further illustrated in FIG. 1.

4. While the present method is characterized by the combination of the above-mentioned 1-3, the effects achieved by the practice of the present method will be enhanced by subjecting the washed, stretched aquagel filamentary material to intimate contact, immediately before drying, with an aqueous emulsion of any one of the surfactants which will be indicated hereinafter.

The acrylonitrile copolymer which may be employed in the practice of the present invention may be any of the well-known fiber-forming copolymers that contain polymerized in the polymer molecule, 85 to 95 weight percent of acrylonitrile with at least one other ethylenically unsaturated monomer that is copolymerizable with acrylonitrile. Blends of at least two kinds of the above-mentioned copolymers may also be utilized.

The polyacrylonitrile-dissolving solvent utilized in the present method is an aqueous concentrated solution of zinc chloride or of a salt mixture of zinc chloride with a lesser amount of a chloride of an alkali or alkaline-earth metal, wherein the total salt concentration

of the aqueous solvent is controlled to be not less than 54 weight percent, preferably not less than 57 weight percent. The spinning solution to be utilized is prepared by dissolving a powder of an acrylonitrile copolymer in the solvent or by homogeneously polymerizing acrylonitrile with at least one other ethylenically unsaturated monomer in the solvent.

In practicing the present method, an aquagel filamentary material of an acrylonitrile copolymer is produced by wet extruding the afore-said spinning solution through at least one spinnerette into an aqueous coagulating bath consisting of a non-polymer-dissolving composition of the same salt constituent. The aquagel filamentary material is withdrawn from the coagulating bath, washed with water substantially free from any residual salts and stretched in water to a length of from 1.5 to four times its unstretched length. This stretching can be also carried out during the washing step, and it may be effective to stretch the filamentary material in several steps while passing it through a series of washing baths. The stretching ratio, 1.5 to 4, of this first stretching is defined as that equivalent to the speed ratio of the filamentary material immediately before drying to that immediately after withdrawing the material from the coagulating bath. It is not desirable according to the present method to practice this first stretching outside of the range of 1.5 to four times. In case of a stretching ratio of less than 1.5, the stretched aquagel filamentary material is substantially weakened and tends to be partially cut off during the after-treatment. When the ratio is over 4, the properties of the resulting product have been found to render the product not suitable for preparing a shrinkable fiber or yarn of good quality.

The aquagel filamentary material is subjected to drying after being washed and stretched in water. This drying should be done so as to control the water content of the resulting filamentary material to less than 5 weight percent, preferably less than 3 weight percent; and the transparency to not less than 70 percent, preferably over 80 percent. Transparency has been described hereinbefore. In producing a filamentary material containing some amount of an opaque substance such as a dulling agent, a colored pigment or a dyestuff, the transparency is assumed to be equivalent to that for a filamentary material which will be produced without such additional substances. According to the results obtained when drying acrylic, aquagel filaments, there seems to be no simple numerical relationship between the water content and the transparency of the resulting dried filaments. For example, when acrylic, aquagel filaments are dried very slowly at a moderate temperature of below about 70°C until they have a water content of less than 5 weight percent, the resulting filaments are often opaque and their transparency does not reach 70 percent. On the other hand, when they are dried rapidly at a relatively high temperature of above about 120°-130°C, their transparency, after dried to a water content below 5 weight percent, is always higher than 70 percent. In the present method, the aquagel filamentary materials are preferably dried at a temperature between about 100°C and 160°C for a period of between about 5 to 30 minutes. Maintaining the above-mentioned conditions in the drying procedure is very important for the production of acrylic filamentary

materials showing no devitrification and having an improved resistance to brittleness when hot-stretched.

The filamentary material which has been stretched in water and dried in accordance with the above-mentioned procedure is then subjected to a second stretching in a hot aqueous medium, i.e., hot water or steam. The amount of stretch should amount to from four to eight times the length of the filamentary material immediately after the drying step. The stretching procedure can be divided among several subsequent steps, for example, the dried filaments may be stretched in hot water near 95°C to two times their original length and again stretched in substantially saturated steam at 115°C to 3.5 times the length of the filaments stretched in hot water. Also, it is preferable in the practice of the present method that the total stretch (consisting of the first stretch in water and the second stretch in a hot aqueous medium) may amount to at least 10 times the length of the aquagel filamentary materials immediately before the first stretching step.

The filamentary material subjected to the second stretching step is continuously relaxed in substantially saturated steam. In this procedure, we have found that it is essential to relax the filamentary material under a combination of conditions, as hereinafter set forth, in order to produce a totally acceptable acrylic filamentary material. That is to say, the relaxing treatment is accomplished by maintaining the tension applied to the dried, hot-stretched filamentary material at 2 mg. per denier or higher during relaxation and the temperature, X°C, of the substantially saturated steam in a range which satisfies the following expression, wherein M is the percentage combined acrylonitrile content of the copolymer filamentary material to be relaxed and Y is the percentage of relaxation:

$$55 \log Y + 5M - 417 \leq X \leq 100 \log Y + 5M - 434$$

where X and Y are limited within 100°-160°C and within 15 to 45 percent, respectively.

It has been well known that in a process of preparing acrylic fibers the practice of including a hot-setting or hot-relaxing treatment after hot-stretching is necessary for improving the properties of the product fibers. According to the experiments conducted by the present inventors of wet spinning acrylic polymer filaments from an aqueous saline solution, a hot-relaxation of at least 15 percent and not over 45 percent of the length of the hot-stretched filaments has been found to be necessary in order to prepare useful acrylic filaments. The product was too brittle to be commercially usable when a low relaxation far below 15 percent was employed, while a relaxation much in excess of 45 percent led to the production of only unusual filaments having a low strength but an excess elongation. In the practice of the present invention, the percentage of relaxation is controlled preferably to be within the range of 15 to 45 percent, and more preferably between 20 and 30 percent.

One of the characteristics of the present method is, as mentioned above, to relax the filamentary material subjected to the second stretching step in substantially saturated steam at a temperature between 100° and 160°C, in a continuous manner. The pressure of the saturated steam increases beyond atmospheric pressure with an increase in the steam temperature over 100°C,

so that in the practice of such a continuous relaxation, pressure equipment is necessary, such as a machine provided with a steam chamber for relaxation, a slit or a set of sealing-rollers for drawing filamentary material into the chamber and another slit or set of sealing-rollers for drawing the relaxed material out of the chamber. For example, a pressure tube provided with a set of guiding rollers and having both ends provided with a slit of the labyrinth seal type will be advantageously used, together with two sets of driving rollers which are installed near each end of the slits.

In the practice of the present invention, various types of relaxing equipment may be used, but the present inventors have found that it is always essential to keep the tension of the filamentary material to be relaxed at least 2 mg. per denier during their continuous relaxation, regardless of the type of relaxing equipment employed, in order to obtain a filamentary product of constant physical properties and uniform shape (i.e., without any irregularity in paralleling filaments). Relaxation under a very weak tension or substantially no tension would be advantageous in a batch-wise operation, but in a continuous operation such as that disclosed above, it is not operable because of the reason either that a filamentary product of non-uniform quality is often obtained or that the filamentary material to be relaxed can not smoothly pass through the relaxing equipment without being disturbed by a current of steam.

The temperature of the substantially saturated steam utilized for the relaxation treatment in accordance with the present invention should be selected so that the expression described above is satisfied. The present inventors have found that the relaxing tendency of an acrylic filamentary material depends not only upon its production history to a point immediately prior to its relaxation, such as the spinning, washing, drying and hot-stretching conditions, but also sensitively upon its chemical composition. Also, it is evident that the relaxing tendency will become remarkable, at least qualitatively, with an increase in the relaxation temperature. However, it seems that no substantial relationship among these controlling factors has been disclosed in connection with a continuous wet spinning method for preparing acrylic filamentary materials having improved properties, particularly acrylic filaments and tows suitable for making shrinkable fibers and yarns of good qualities.

The limiting conditions with respect to the relaxation temperature, which have been discovered by the present inventors, will be more fully understood by the ensuing description and the attached drawings.

With reference to FIG. 1, the surface consisting of the plane A-B-C and the curved surface A-C-D-E indicate the upper limit of the steam relaxation temperature, while the surface consisting of the plane H-I-J and the curved surface F-G-H-I indicate the lower limit of the steam relaxation temperature. Also, the lines (α), (β), (γ), (δ), and (ϵ) show the positions at which *M* is equivalent to 95, 92, 89, 87 and 85 percent, respectively.

Continuous relaxation treatments at temperatures above and below the temperature range illustrated in FIGS. 1-6 are not desirable according to the present invention. It will be difficult at a temperature below the

lower limit to achieve a relaxation near or over 15 percent shrinkage, while the application of a relaxation temperature higher than the upper limit will cause frequent break-downs of filaments or lead to the production of abnormally stiff filaments.

The practice of the present invention is facilitated and optimum results are obtained when the aquagel filamentary material is continuously subjected, immediately prior to drying, to intimate contact with an aqueous emulsion of a surfactant selected from the group consisting of diethanol-amine monoester of fatty acid phosphate, poly-oxyethylene-alkylamine, alkyl phosphate, poly-alkylene-glycol, derivatives of alkyl-polyamines and a mixture of polyoxyethylene alkyl ether with polyalkylene glycol, so as to absorb from 0.2 to 2.0 percent by weight of the surfactant, based on the weight of the resulting dried filamentary material. Such an emulsion treatment has been found to be remarkably effective not only for preventing trouble in the subsequent drying operation due to static electricity but also for improving, even more, the physical properties of the product obtained by the practice of the present invention. The absorbed surfactant content should not be over 2 weight percent, otherwise the product will show an undesirable devitrification. When the content is less than 0.2 percent, no substantial effect is obtained.

The following examples will serve to further illustrate the present invention but are not to be construed as limiting its scope. All parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

Three 9 percent solutions of acrylonitrile copolymers A, B and C, dissolved in an aqueous saline solvent comprised of 54 percent zinc chloride, 4 percent sodium chloride and 42 percent water, were prepared by a direct solution-polymerization method, wherein A is a copolymer of 7 percent vinyl acetate, 1 percent sodium allyl-sulfonate and 92 percent acrylonitrile; B is a copolymer of 9.5 percent methyl acrylate, 1.5 percent sodium methallyl-sulfonate and 89 percent acrylonitrile; and C is a copolymer of 8 percent methyl acrylate, 4 percent acrylamide, 1 percent sodium methallyl-sulfonate and 87 percent acrylonitrile.

Each of the three polymer solutions was extruded through 1,200-hole spinnerettes with 0.10 mm. hole diameter into an aqueous coagulating bath at 20°C, which was prepared by mixing one part of the aforesaid saline solvent with one part of water, and the aquagel filaments thus obtained were successively stretched to 2.43 times their unstretched length, in total, while they were being washed with water. In this case, the aquagel filaments were passed through four washing baths, and the stretching procedure was carried out under the conditions indicated in Table 1.

	Washing bath Composition	Washing bath Temperature	Stretch Ratio
1st bath	About 5% aqueous solution of the salt constituent of the saline solvent	30°C	1.2
2nd bath	About 1% aqueous solution of the salt constituent of the saline solvent	40°C	1.2
3rd bath	Water (containing a trace of zinc chloride)	60°C	1.3
4th bath	Water	75°C	1.3

The aquagel filaments thus washed and stretched were then continuously dried, at an air temperature of 150°C and for a period of 10 minutes, until their water content decreased to 1 percent and their transparency reached 94 percent, and the dried filaments were continuously stretched to a length of 5.5 times in substantially saturated steam at 115°C (about 0.7 kg/cm², gauge pressure) by means of pressure stretching equipment provided with a steam chamber and inlet and outlet slits of a labyrinth seal type, wherein the surface speed of the stretching rollers adjacent to the outlet slit was 90 meters/minute.

The filaments thus hot-stretched were continuously fed to a second pressure apparatus similar in structure to that of the first except that the second apparatus was provided with a set of guide rollers in its steam chamber, and relaxed under a tension of about 5 mg. per denier. The filaments, after being relaxed, were continuously contacted with an aqueous emulsion of a surfactant having an anti-electrostatic property, squeezed with press-rollers, crimped with a crimper of the nip-roller type, dried in a hot air stream and then collected as product filaments.

In this experiment, the relaxation treatment was examined to retract each of the three hot-stretched filaments of the copolymers A, B and C by 20, 30 and 40 percent in length, respectively, at steam temperatures of 105°, 115°, 130°, 140° and 150°C. The results obtained are summarized in Table 2, where the designations XX indicate such poor results that it was difficult or impossible to stably continue the relaxation of a given sample to an expected shrinkage, X indicates a poor result such that while a given sample could be easily retracted by an expected shrinkage, the resulting product was devitrified, stiff and unsuitable for making shrinkable fibers and yarns of commercial quality, and 0 indicates a good result in both continuous operation and the properties of the product.

TABLE 2

Kind of filamentary Copolymer	A			B			C		
	20%	30%	40%	20%	30%	40%	20%	30%	40%
Shrinkage Steam Temp. ↓									
105°C (about 0.7 kg/cm ² G)	XX	XX	XX	0	XX	XX	0	0	XX
115°C (about 0.7 kg/cm ² G)	/	XX	XX	0	0	XX	0	0	0
130°C (about 1.8 kg/cm ² G)	0	0	XX	/	0	0	0	/	/
140°C (about 2.7 kg/cm ² G)	0	/	0	0	/	0	X	0	0
150°C (about 3.7 kg/cm ² G)	0	0	0	X	0	0	X	X	/

In this experiment, for example, the product filaments prepared by relaxing the hot-stretched filaments of Turbo-silver B by 30 percent in length at 130°C had a dry strength of 3.6 grams per denier (g/d), a dry elongation of 42 percent, a knot strength of 3.0 g/d and a knot elongation of 32 percent. They were not devitrified and were very white in color. Furthermore, they could be treated with Turbo-stapler, without any trouble, to have a shrinkage of 23 percent in boiling water in a relaxed, free-to-shrink condition, and a shrinkable yarn of good quality could be prepared from

the Turbo-silver thus obtained, wherein the component fiber of the sliver had a knot strength of about 1.2 g/d and a knot elongation of about 5 percent before steaming.

In comparison with the above results, the aquagel filaments of copolymer B, after being washed and stretched to a length of 2.43 times, were dried, at about 150°C and for about 1 minute, to a water content of about 12 percent and a transparency of about 80 percent, in one case (case 1) and also, at about 80°C and for about 20 minutes, to a water content of about 5 percent and a transparency of about 55 percent (case 2). Each of the two dried filaments was then subjected to hot-stretching, retracting and subsequent treatments, under the same conditions as those selected in the former experiment. Both of the product filaments, in case 1 and case 2, were markedly devitrified, and the component fibers of the resulting Turbo-slivers in case 1 and case 2 were too brittle to form shrinkable yarns of commercial quality.

EXAMPLE 2

A 9 percent solution of a ternary polymer of 8.7 percent methyl acrylate, 1.3 percent sodium methallyl sulfonate and 90 percent acrylonitrile dissolved in a 58 percent aqueous solution of zinc chloride was prepared by a direct solution-polymerization method and extruded through a 10,000-hole spinnerette with 0.12 mm. hole diameter into a coagulating bath of a 25 percent aqueous zinc chloride solution at 20°C.

The aquagel filaments thus obtained were withdrawn from the coagulating bath, washed free of zinc chloride with water, stretched about three times in water at about 70°C and then dried in an air stream at about 150°C, for a period of 10 minutes, to a water content of about 2 percent and a transparency of about 89 percent. After leaving the dryer, the filaments were stretched about two times in water at about 95°C, and again stretched about 2.2 times in substantially saturated steam at 108°C (about 1.4 kg/cm²G) by means of stretching equipment similar to that used in Example 1. The linear velocity of the filaments leaving the stretching equipment was kept at about 105 meters per minute. The filament thus stretched was then relaxed by about 25 percent in length in substantially saturated steam at about 135°C by means of relaxing equipment similar to that used in Example 1, wherein their tension during the relaxation was kept at about 10 mg per denier and wherein the length of time necessary to pass through the relaxing equipment was about 5 seconds.

The product obtained had about 5 denier per filament, a dry strength of about 3.9 g/d, a dry elongation of about 36 percent, a knot strength of about 2.8 g/d, a knot elongation of about 28 percent and a whiteness of about 0.86, according to measurements followed by the Japan Industrial Standard. They were not devitrified and the shrinkable yarns prepared through Turbo-processing were very good in quality.

What is claimed is:

1. A wet-spinning method for producing acrylic filamentary material having good whiteness from a spinning solution of an acrylonitrile copolymer of from 85 to 95 percent by weight of acrylonitrile with at least one ethylenically unsaturated monomer copolymerizable therewith in an aqueous saline solvent consisting es-

essentially of a member selected from the group consisting of zinc chloride and a mixture of zinc chloride with a lesser amount of a chloride of an alkali or alkaline earth metal, said method comprising:

- a. spinning said spinning solution into an aqueous coagulating bath to produce an aquagel filamentary material;
- b. stretching said aquagel filamentary material in water to a length of from 1.5 to four times the length of said aquagel filamentary material after withdrawal from said coagulating bath;
- c. continuously drying the resulting stretched aquagel filamentary material to obtain a dried filamentary material having a water content of less than 5 percent by weight and a transparency of at least 70 percent;
- d. continuously hot-stretching said dried filamentary material in a hot aqueous medium to a length of from four to eight times the length of said material immediately prior to said hot-stretching, and
- e. continuously relaxing the resulting stretched filamentary material under a tension of at least 2 milligrams per denier in substantially saturated steam at a temperature of from 100° to 160° C. and within a range satisfying the limited condition:

$$55 \log Y + 5M - 417 \leq X \leq 100 \log Y + 5M - 434,$$

wherein *M* varies from 85 to 95 and represents the content of combined acrylonitrile, in percent by weight, in the acrylonitrile copolymer forming said filamentary material, *Y* is the shrinkage, in percent by length, to be applied to said hot-stretched filamentary material and varies from 15 to 45 percent and *X* varies from 100 to 160 and represents the temperature, in degrees centigrade, of said substantially saturated steam.

2. A method as in claim 1 wherein said aquagel filamentary material stretched in water is continuously dried to form a dried filamentary material having a water content of less than 3 weight percent and a transparency of at least 80 percent.

3. A method as in claim 1 wherein the total stretch applied to said aquagel filamentary material withdrawn from said coagulating bath and to said dried filamentary material is at least 10 times that of the original length of said aquagel filamentary material.

4. A method as in claim 1 wherein: *Y* ranges from 20 to 30 percent.

5. A method as in claim 1 wherein the relaxation of the dried and hot-stretched filamentary material is continuously carried out by passing said filamentary material through relaxing equipment provided with a chamber filled with substantially saturated steam, an inlet port for drawing said hot-stretched filamentary material into said steam chamber and an outlet port for drawing out the relaxed filamentary material from said steam chamber.

6. A method as in claim 1 wherein the aquagel filamentary material is continuously treated, at a stage immediately prior to the drying operation, with an aqueous emulsion of a surfactant selected from the group consisting of diethanol-amine monomer of fatty acid phosphate, poly-oxyethylene-alkylamine, alkyl phosphate, poly-alkylene-glycol, alkyl-polyamine derivatives and a mixture of poly-oxyethylene alkyl-ether with poly-alkylene-glycol, so as to absorb from

0.2 to 2.0 percent by weight of the surfactant, based on the weight of the resulting dried filamentary material.

7. A method as in claim 1 wherein the total proportion in said aqueous saline solvent of said members selected from the group consisting of zinc chloride and a mixture of zinc chloride with a lesser amount of a chloride of an alkali or alkaline earth metal is not less than 54 weight percent.

8. A method as in claim 7 wherein the proportion is not less than 57 weight percent.

9. A method as claimed in claim 1 wherein said aquagel filamentary material is washed subsequent to said spinning but prior to said initial stretching.

10. A method as in claim 1 wherein said aquagel filamentary material is washed with water prior to spinning into said aqueous coagulating bath and subjected to said first stretching in said aqueous coagulating bath.

11. A method as claimed in claim 1 wherein said aqueous saline solvent consists essentially of zinc chloride.

12. A method as claimed in claim 1 wherein said hot aqueous medium is hot water.

13. A method as claimed in claim 1 wherein said hot aqueous medium is steam.

14. A method as claimed in claim 1 wherein the aquagel filamentary material is continuously treated, at a stage not later than the drying operation, with an aqueous emulsion of a surfactant, so as to absorb from 0.2 to 2.0 percent by weight of the surfactant, based on the weight of the resulting dried filamentary material.

15. A method as in claim 1 where said drying is at about 100° to 160°C for from about 5 to 30 minutes.

16. A wet-spinning method for producing acrylic filamentary material having good whiteness from a spinning solution of an acrylonitrile copolymer of from 85 to 95 percent by weight of acrylonitrile with at least one ethylenically unsaturated monomer copolymerizable therewith in an aqueous saline solvent consisting essentially of a member selected from the group consisting of zinc chloride and a mixture of zinc chloride with a lesser amount of a chloride of an alkali or alkaline earth metal, said method consisting of:

- a. spinning said spinning solution into an aqueous coagulating bath to produce an aquagel filamentary material;
- b. stretching said aquagel filamentary material in water to a length of from 1.5 to four times the length of said aquagel filamentary material after withdrawal from said coagulating bath;
- c. continuously drying the resulting stretched aquagel filamentary material to obtain a dried filamentary material having a water content of less than 5 percent by weight and a transparency of at least 70 percent;
- d. continuously hot-stretching said dried filamentary material in a hot aqueous medium to a length of from four to eight times the length of said material immediately prior to said hot-stretching, and
- e. continuously relaxing the resulting stretched filamentary material under a tension of at least 2 milligrams per denier in substantially saturated steam at a temperature of from 100° to 160° C. and within a range satisfying the limited condition:

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$$55 \log Y + 5M - 417 \leq X \leq 100 \log Y + 5M - 434$$

wherein M varies from 85 to 95 and represents the content of combined acrylonitrile, in percent by weight, in the acrylonitrile copolymer forming said filamentary material, Y is the shrinkage, in percent by length, to be applied to said hot-stretched filamentary material and varies from 15 to 45 percent and X varies from 100 to

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160 and represents the temperature, in degrees centigrade, of said substantially saturated steam.

17. A method as claimed in claim 16, further consisting of washing said aquagel filamentary material subsequent to said spinning step, but prior to said initial stretching step.

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