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3,706,828

WET SPINNING NON-CIRCULAR POLYACRYLONITRILE FIBERS BY UTILIZING
CIRCULAR ORIFICES AND SEQUENTIAL COAGULATION

Filed Aug. 19, 1969

3 Sheets-Sheet 1

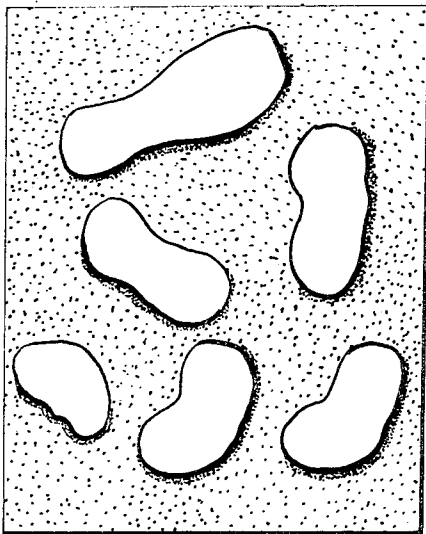


FIG. 1

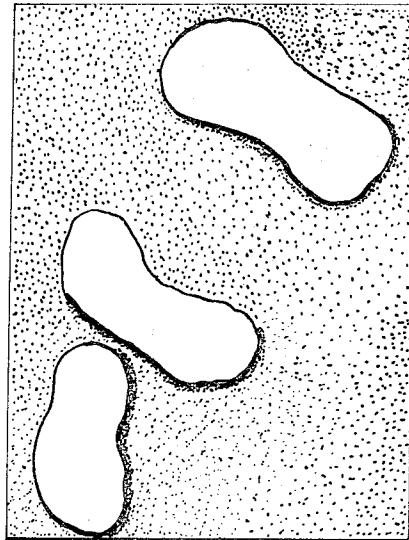


FIG. 2

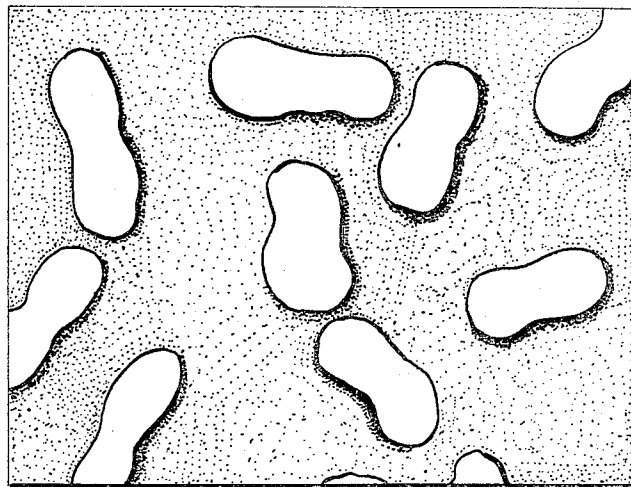


FIG. 3

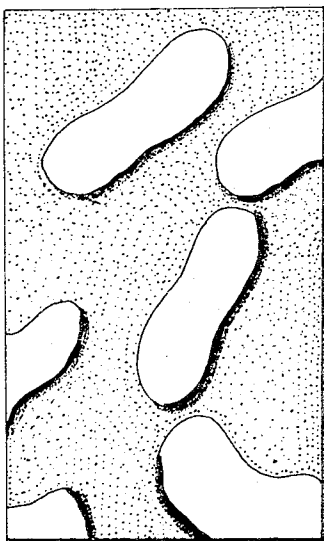


FIG. 4

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3 Sheets-Sheet 2

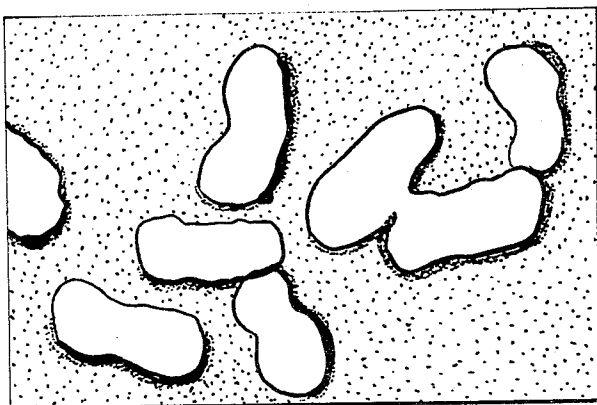


FIG. 5

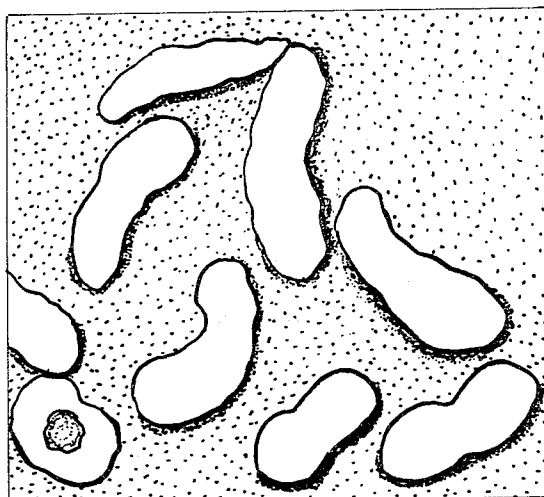


FIG. 6

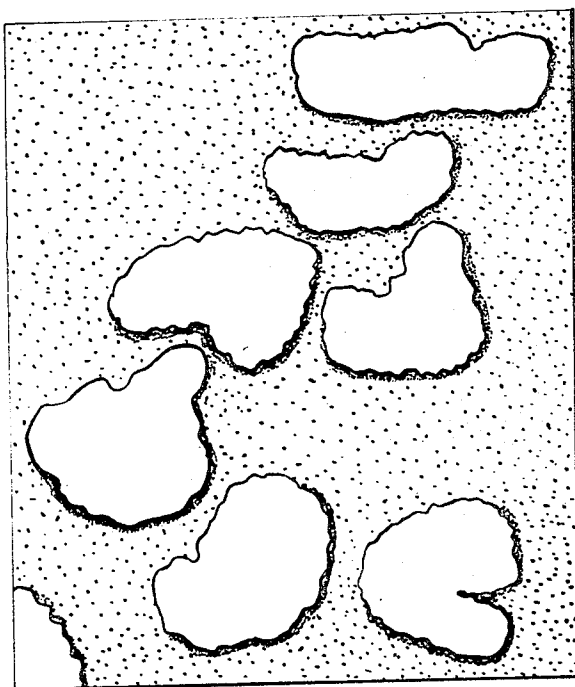


FIG. 7

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3 Sheets-Sheet 3

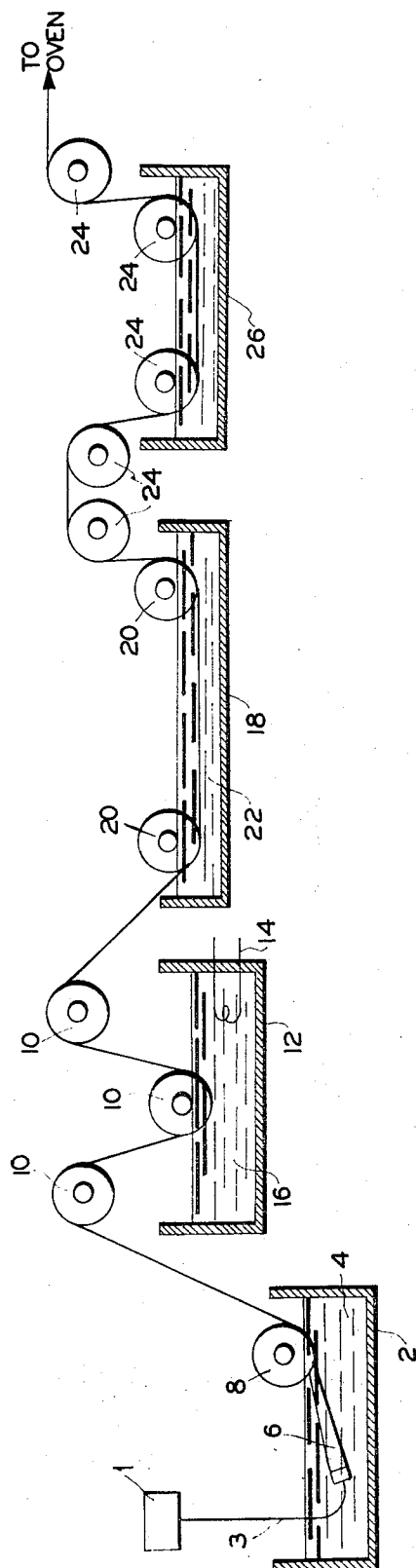


FIG. 8

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**WET SPINNING NON-CIRCULAR POLYACRYLO-
NITRILE FIBERS BY UTILIZING CIRCULAR
ORIFICES AND SEQUENTIAL COAGULATION**
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U.S. Cl. 264—182

10 Claims

ABSTRACT OF THE DISCLOSURE

A method of producing synthetic fibers having tough outer skins and dog-bone or other non-circular cross-sections which comprises spinning said fiber and subjecting the spun fiber to sequential coagulation treatments whereby the outer core is coagulated and shrinks to a tough shell, surrounding the inner core which is incompletely coagulated and collapsed. The fibers may be used in conventional textile materials.

This invention relates to synthetic fibers, particularly to polyacrylonitrile homopolymers, copolymers, or terpolymers in fibrous form. More specifically, the invention relates to a method of producing such fibers of noncircular cross-section.

The production of synthetic filaments has been the subject of considerable inquiry since these fibers have been found to be particularly susceptible to treatment with coloring materials such as dyes, flame retardants, anti-static materials, etc., while retaining structural stability and flexibility when used in textiles.

Non-circular filaments have generally been prepared by melt spinning a polymeric material using a complicated spinnerette or by dry spinning. Typically, the spinnerettes are provided with orifices adapted to suitably mold the fiber. Additionally, laminating techniques have been used wherein shaped orifices separately extrude sections of the fiber which are laminated while still in a flowable condition prior to coagulation. These spinnerettes are bulky and expensive and it is, therefore, desirable to devise a process adapted for use with conventional circular hole spinnerettes.

It has now been discovered that wet spun non-circular synthetic fibers, particularly acrylonitrile fibers, can be produced having irregular shapes and collapsed cores by a sequential coagulation treatment conducted under such conditions as to produce a strong skin and weak collapsible core.

With respect to acrylonitrile fibers, irregular shapes have been produced by such methods as solution spinning from organic solvents into an aqueous coagulation bath as disclosed in 3,180,845 and 3,088,188 or solution spinning from nitric acid into a coagulation bath containing nitric acid as disclosed in U.S. 2,907,096. The former methods require collapsing the voids which form while the latter must avoid the collapse of the voids. These patents do not allow controlled production of non-circular cross-section fibers.

The use of certain coagulating baths is undesirable in treating synthetic fibers since it is found to detract from the physical properties of the ultimate fibers, such as the flexibility and extensibility. Additionally, the conditions under which coagulation occurs are found to produce variable characteristics in the fibers so that a coagulating bath which works satisfactorily under some conditions is unsatisfactory when those conditions are varied. This invention provides treatments which give useful fibers having the requisite strength.

It is, therefore, a primary object of this invention to

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provide a method which is adapted to produce synthetic polymer fibers having a non-circular cross-section by extruding from circular orifices.

A further object is to produce the subject fibers having improved properties, particularly increased cover in yarns and fabrics.

These and other objects and advantages of the invention will be apparent from a consideration of the following drawings and description. In the drawings, FIGS. 1-7 are photomicrographs showing cross-section of fibers produced by the present invention;

FIG. 8 is a schematic diagram illustrating a process for producing the fibers of FIGS. 1-7.

The method of the present invention may be described generally as comprising the steps of wet-spinning polymeric acrylonitrile material from an aqueous medium containing an inorganic salt or from an organic medium through orifices of circular cross-section, passing the filament into a mild first coagulation bath containing a solvent or salt corresponding to the solvent or salt present in the spinning dope, which bath contains 35-95% coagulant and is maintained at a temperature of -20° to +25° C., preferably about 15° C., for a residence time of 1-12 seconds, optionally stretching the fibers therein, passing the initially coagulated fiber into a harsh second coagulation bath containing a like solvent or salt in an amount of less than 35%, preferably less than 15%, which bath is maintained at a temperature of 30°-120° C., preferably 35°-100° C., for an average residence time of 20-75 seconds, washing, stretching, and drying. Fibers thus produced have a dense inner core which is integrally bound to a relatively tough skin producing non-circular cross-section fibers.

Reference to FIG. 8 shows a schematic flow diagram wherein spin dope 3 is extruded initially to produce fibers 6 which are spun from a spinnerette 1 through a first bath 2 wherein first coagulation bath 4 is provided. The fibers 6 are removed from the bath across adjustable roller 8 onto a series of rolls 10 adapted to maintain tension on the fibers into second bath 12 containing heating coil 14 and second coagulation bath 16. Following this treatment, the fibers are washed in tank 18 wherein guide rolls 20 keep the fibers submerged in wash liquid 22, generally comprising water. After washing, a cold stretching treatment is provided by passing over movable rolls 24 and then a hot stretching treatment is provided using a boiling liquid such as water maintained in tank 26. Finally, the fibers are dried in an oven (not shown). These steps are conventional in producing fibers and those skilled in the art will be aware of variations of this treatment which may be utilized depending upon the particular polymer being treated. For example, the stretching operations can be modified to provide more than one cold stretching operation and/or more than one hot stretching operation. Likewise, the washing treatment may occur in more than one stage.

More specifically, the process of this invention comprises spinning a solution or dispersion of an acrylonitrile containing polymer through a circular hole spinnerette. The term "acrylonitrile polymer" as used in this invention includes homopolymers, copolymers, and interpolymers of acrylonitrile wherein the acrylonitrile is present in the polymer in a quantity of approximately 80% by weight or more. Suitable comonomers for preparation of copolymers useful in this invention include vinyl monomers such as acrylic and methacrylic acid esters, particularly the lower alkyl esters; other suitable vinyl compounds are vinyl acetate, vinyl chloride, vinyl bromide, and vinyl pyridine, and sulfo-containing vinyl compounds such as ethylene sulfonic acid, mineral salts thereof, sulfoethyl acrylate or methacrylate compounds and salts thereof. Ad-

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ditional comonomers and methods of preparation will be apparent to those skilled in the art.

While acrylonitrile polymers are preferred, other polymers can be used provided the rate of coagulation is slow enough to allow a two-stage treatment. Likewise, the fibers can be formed by blending the acrylonitrile polymer with minor (2-5%) proportions of compatible polymers, e.g. polyethylene glycol or different acrylonitrile polymers. Spinning dope is formed by dissolving the polymer in a suitable carrier, e.g., an aqueous solution carrier containing an inorganic salt or an organic solvent, or both or by solution polymerizing the monomers in the spinning solvent. An aqueous zinc chloride solution may be utilized. Other aqueous saline solutions, that is, solutions containing an ionizable salt, may be used, which contain mixed inorganic salts such as zinc chloride, sodium chloride, calcium chloride, magnesium chloride, etc. Generally, any highly water-soluble salt may be utilized and this further includes the alkali metal thiocyanates, alkali earth metal thiocyanates, ammonium thiocyanate, guanidine thiocyanate, lithium bromide, lithium iodide, sodium iodide. The aforementioned systems may be termed "inorganic solutions;" however, the invention should be understood to include organic spinning dopes wherein the polymer is dissolved in, or formed by solution polymerization in, e.g., dimethyl acetamide or other organic spinning liquids. Mixed organic and inorganic systems may be used wherein the solvent system consists essentially of water containing at least one water-miscible, aliphatic liquid containing one alcoholic hydroxyl group and not more than six carbon atoms in the molecule, and at least one highly water-soluble salt as described above. For example, a system which has been used with satisfactory results comprises 48% zinc chloride, 28% water, and 24% methyl alcohol (weight percents are used). These and other systems are adequately described in the art as exemplified by U.S. Pats. 2,648,646 and 3,284,555.

The coagulation baths comprise a coagulation medium, generally water, and an organic solvent such as dimethyl acetamide or inorganic salts such as zinc chloride, or mixed organic-inorganic solutions containing water, alcohol, and inorganic salt. The specific bath depends upon the spinning dope and generally the bath should contain ingredients corresponding to those in the spinning dope. Naturally the compositions and temperatures will vary.

In the first coagulation bath, relatively mild coagulation conditions are used, e.g., the temperature is maintained at -20° to $+25^{\circ}$ C., preferably -10° to 15° C., and the spun fibers are allowed a dwell time of 1-12 seconds, preferably 5-10 seconds. When the bath comprises an aqueous inorganic system, the inorganic salt or mixture of salts should be present in a weight quantity of 20-50%, preferably 25-45%, giving from 50-80% coagulant. When a mixed inorganic-organic system of an organic system is used, the organic component should be present in a quantity of 5-60%, giving 40-90% coagulant. In the first coagulation bath, rapid coagulation of the outer skin only is desirable and, therefore, tension and temperature extremes should be avoided since these tend to increase the rate of complete coagulation of the fibers. Thus, the low temperatures and the tension should be maintained throughout the fiber travel through the first bath.

When the fibers are introduced in the second bath, the outer skin will already be coagulated; however, the dwell time and condition in the first bath will have been insufficient to allow migration of the coagulation medium to the inner core of the fiber. Thus, the inner core will remain soft and uncoagulated. In the second bath, it is desirable to substantially increase the migration of coagulating mediums to the inner portion of the core. To accomplish this purpose, high temperatures and concentrations of coagulant are utilized in a coagulating bath having greater proportion of coagulant than the first bath. For example, the second bath should contain (in organic systems) approximately 0-10% of the organic medium and

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in inorganic systems, approximately 0-35% of the inorganic salt. The temperature in the second bath should be maintained at $30-120^{\circ}$ C., preferably about 50° C. It is generally unnecessary to apply tension to fibers in the second bath since high temperature accomplishes sufficient coagulation to yield the desired bistructured fibers. A dwell time in the second bath should be maintained at approximately 20-75 seconds, preferably 35-40 seconds, which will depend upon the exact conditions and ingredients used. This time is generally more than used in the first bath.

While excessive stretching should generally be avoided in the coagulation baths, it is possible and sometimes desirable to apply tension in and between the baths and after the second baths. Thus, for example, a stretch may be applied to the fibers in the first bath at a ratio of 1-6:1, between the first and second baths, up to a 3:1, ratio, and after the second bath, the fibers can be stretched at a 15:1 ratio or can be shrunk, depending upon the ultimate product desired. This stretching can be accomplished in a series of stretching steps by conventional techniques: for example, a three-stage stretch wherein a stretch ratio of approximately 3:1 is applied in each step. Stretching also orients the fiber molecules and increases the strength of the fibers in coagulated fibers. A stretch ratio of 1:1 indicates no elongation of fibers was produced and a ratio of less than 1:1 indicates shrinkage.

Following the second bath, the fibers are washed to eliminate the coagulating medium and any remaining solvent. Washing is generally accomplished in hot water at about $20-50^{\circ}$ C. and can be a sequential stage-like treatment or a one-bath treatment.

The weak inner core of the fibers can be collapsed by the stretching and drying steps. Essentially, the inner walls remain weak, while the outer skin is relatively tough due to the different rate of coagulation. To collapse the inner core and allow the skin to conform to the core contours, the preliminary timed coagulations under specified conditions are required. The fibers are dried in an oven, e.g., a hot air ($100-150^{\circ}$ C.) type oven of conventional construction.

The invention will be more fully understood by reference to the following illustrative examples. In the examples, parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A homopolymer of acrylonitrile was spun from a zinc chloride solution through a 30-hole spinnerette having circular holes 15 mils in diameter into a first coagulation bath containing a 41% zinc chloride aqueous solution maintained at 15° C. The spinnerette pressure drop was 20 p.s.i.g., and the polymer temperature issuing from the spinnerette was 35° C. While passing through the first bath, a 5.86:1 stretch ratio was applied by conventional adjustable driven rollers and the fibers were lead to a second bath maintained at 30° C. and containing 41% zinc chloride aqueous solution. The residence time in the first bath was approximately 8.4 seconds, while in the second bath, the residence time was about 35 seconds. The fibers were washed at 30° C. and were removed from the wash bath and subjected to a 2-stage stretching operation, the first stage being on cold rollers at a ratio of 1.6:1, the second being on hot rollers (80° C.) at a ratio of 7.5:1. Following the stretching, the fibers were passed through an oven wherein hot air at approximately 130° C. was blown over the fibers until dry. The dried fibers produced a cross-section corresponding to the photomicrograph of FIG. 1 wherein the cores and skin shrink. The fibers were 14 denier, and upon subjection to the conventional testing techniques, the elongation was 47%, the yield strength was 1.09 grams per denier, the tenacity was 3.4 grams per denier, and the elastic modulus was 36. On looping, 14.6 denier fibers tenacity measured 2.1, and elongation 22%. The luster was measured as 62.8 and an average shape index of 1.30 was measured.

5 EXAMPLE 2

The procedure of Example 1 was repeated using a terpolymer of acrylonitrile comprising 80% acrylonitrile and 20% of a mixture of methyl acrylate and methyl methacrylate. The fibers were stretched in the first bath at a ratio of 3.75:1 and after the second bath in a 2-stage treatment comprising one cold (1:1) and one hot (16.8:1) stretch. The residence time in the first bath was about 7 seconds and in the second bath was about 36 seconds. The fibers produced are shown in FIG. 2 and were 14.5 denier with an elongation of 4%, tenacity of 4.1 grams/denier, a yield strength of 1.18 grams/denier, and an elastic modulus of 42. Upon looping, 14.9 denier fibers measured tenacity 3.2, and elongation 28%. The luster was measured as 57.7 and a shape index of 1.52 was measured.

EXAMPLE 3

Procedure of Example 2 was repeated using a 12 mil 60-hole spinnerette with the temperature in the first bath being 14.9° C. and ZnCl₂ concentration of 40.1%. The stretches after the second bath were cold (1.8:1) and hot (6.6:1). This produced the fibers shown in FIG. 3 which are 14.1 denier with an elongation of 29%, a tenacity of 2.8 grams/denier, a yield strength of 1.0 gram/denier, and an elastic modulus of 36. When looped, 13.6 denier fibers had tenacity 1.8, and elongation 17%. The luster was 64 and an average shape index was 1.40.

EXAMPLE 4

The procedure of Example 2 was repeated using a 60 mil 60-hole spinnerette, a first bath temperature of -8° C., a concentration of 32%, a stretch ratio of 1.82:1, and a residence time in the first bath of about 5 seconds. In the second bath, the residence time was about 36 seconds, the wash bath temperature was at 44° C., and the hot stretch ratio was 10:1. The fibers produced are seen in FIG. 4 and were 18.3 denier with tenacity of 4.0 grams/denier, elongation of 42%, yield strength of 0.98, and elastic modulus of 39. When looped, the tenacity was 1.9 and elongation was 22%. The shape index was between 1.45 and 1.65.

EXAMPLE 5

The procedure of Example 4 was repeated using a 6 mil 60-hole spinnerette, a first bath stretch of 3.0:1, and temperature of -9° C. The hot stretch ratio after the second bath was 4.0:1. The fibers were passed through boiling water before washing at 50° C. The fibers produced are shown in photomicrograph of FIG. 5, and were 28.7 denier with an elongation of 66%, a tenacity of 1.8 grams/denier, a yield strength of 0.94 gram/denier, an elastic modulus of 26. When looped, the elongation was 27% and the tenacity was 1.3 grams/denier. The shape index was between 1.25 and 1.4.

EXAMPLE 6

The procedure of Example 5 was repeated using a first bath temperature of -6.5° C. and stretch of 2.0. The stretch ratios after the second bath were cold (1:1), and hot (10:1). The wash was at 31° C. This produced the fibers shown in FIG. 6 which were 57.9 denier with an elongation of 38%, a tenacity of 2.1 grams/denier, a yield strength of 1.0 gram/denier, and an elastic modulus of 34. When looped, the tenacity was 1.3 grams/denier, and the elongation 18%. The shape index was between 1.5 and 1.7.

EXAMPLE 7

The procedure of Example 6 was repeated using a 65-hole spinnerette and a first bath temperature of 0° C. The stretch ratios after the second bath were cold (2:1) and hot (7.8:1), respectively. The fibers produced are shown in FIG. 7. They were 72.2 denier with a tenacity of 1.6 grams/denier, elongation of 40%, yield strength of 0.88, and elastic modulus of 28. When looped, the tenacity was

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0.33 and elongation was 24%. The shape index was between 1.25 and 1.45.

EXAMPLE 8

An acrylonitrile homopolymer dissolved to 10% solids in a 50-60% aqueous sodium thiocyanate solution was spun through a spinnerette having 15 holes of 8 mil diameter wherein a pressure drop of 10 p.s.i.g. occurs. These fibers were led into a first bath containing 10% sodium thiocyanate and maintained at 5° C. for a dwell time of 7.8 seconds. The fibers were not stretched therein. The second bath contained 22% sodium thiocyanate maintained at 30° C. and the fibers' dwell time was 36 seconds. Following the second bath, the fibers were washed at 30° C., and hot stretched at a ratio of 12:1. After stretching, the fibers were conducted to an oven wherein air at 125° C. was blown across the fibers until dried. The fibers produced were 20 denier/filament and correspond in structure to those shown in FIG. 1.

EXAMPLE 9

An acrylonitrile copolymer containing a combination of methyl acrylate and methyl methacrylate in a total quantity of less than 20% was dissolved to 25% solids in 100% dimethyl acetamide. This solution was spun through a spinnerette having 15 holes of 8 mil diameter into a first bath containing 55% dimethyl acetamide maintained at 10° C. for a dwell time of 5.15 seconds. The fibers were conducted without stretching to a second bath containing 20% dimethyl acetamide maintained at 30° C. for a residence time of 36 seconds. The fibers were then washed at 30° C. and were hot stretched at 8:1 ratio and then dried at an oven temperature of 125° C. to produce 23.5 denier/filament having structure corresponding to that shown in FIG. 2.

EXAMPLE 10

An acrylonitrile homopolymer dissolved in dimethyl sulfoxide to 25% solids was spun through a spinnerette having fifteen 8-mil holes into a first bath containing 50% dimethyl sulfoxide maintained at 20° C. for a dwell time of 11.3 seconds. The fibers were conducted to a second bath containing boiling water for a residence time of 36 seconds. The fibers were then washed at 30° C., hot stretched at an 8:1 ratio, and then dried at 125° C. to yield 30 denier/filament, corresponding in structure to those of FIG. 1.

EXAMPLE 11

The procedure of Example 10 was repeated, substituting dimethyl formamide for the dimethyl sulfoxide and using dwell times in the first bath of 7.9 seconds, and in the second bath of 7.2 seconds with 50% dimethyl formamide in the first bath and 0% in the second bath. A hot stretch ratio of 8:1 was used after the second bath. The fibers were 60 denier/filament and corresponded to those of FIG. 1.

EXAMPLE 12

A spinning solution is prepared using 15% of a copolymer containing 90% acrylonitrile and 10% methyl acrylate (M.W. about 100,000) and dissolved in a solution consisting of 35% sodium thiocyanate dissolved in 65% of a mixture of 20 parts water and 80 parts methyl alcohol.

Fibers produced by this invention are highly flexible and show improved strength for non-circular fibers. They are useful in all lengths and in all diameters although diameters beyond the initial range of 3.3-50.0 mils are difficult to coagulate properly.

As an effective means of determining the non-circular shape of the ultimate fibers a shape index is calculated as follows:

$$\text{Shape Index} = \frac{(\text{Cross Sectional Perimeter})^2}{4\pi \times (\text{Cross Sectional Area})}$$

As can be seen if the fiber is round, the shape index is 1.0. The fibers of this invention preferably exhibit a shape index between 1.25 and 1.65, however, it is readily appreciated that widely varied shape indices can be produced and the preferred range merely designates those presently preferred.

The other testing procedures used in the examples are conventional in the art and are available from such publications as Encyclopedia of Polymer Technology, (John Wiley & Sons—1960), or from the American Society for Testing and Materials and the American Association of Textile Chemists and Colorists.

Having described the invention, what is desired to be protected is as follows:

What is claimed is:

1. In the known process comprising solution spinning polyacrylonitrile homopolymers or copolymers containing at least 80% by weight acrylonitrile and up to 20% by weight of one or more vinyl monomers through a round orifice into a first bath to superficially coagulate the fiber; passing the superficially coagulated fiber into a second bath; washing the fibers; stretching the fibers; and drying the fibers; wherein the spinning solution and said first and second baths all contain a member selected from the group consisting of an aqueous saline solvent, an aqueous saline solvent containing an aliphatic alcohol, dimethyl acetamide, dimethyl formamide, and dimethyl sulfoxide, the improvement which comprises forming shaped fibers by spinning said solution into said first bath wherein the concentration of the selected member is maintained in an amount of 15 to 65% by weight in 85 to 35% by weight water and the temperature of said first bath is maintained at -20 to $+25^{\circ}$ C. and maintaining the fiber in said first bath for from about 1 to about 12 seconds and thereafter passing the superficially coagulated fiber into said second bath wherein the concentration of the selected member is maintained in an amount less than 35% by weight in more than 65% by weight water and the temperature of said second bath is maintained at 30 to 120° C. and maintaining said fiber in said second bath from about 20 to 75 seconds.

2. Method of claim 1 wherein the member is an aqueous saline solvent containing an aliphatic alcohol.

3. Method of claim 1 wherein the polymer is an acrylonitrile homopolymer.

4. Method of claim 1 wherein the member is dimethyl acetamide.

5. Method of claim 1 wherein the member is dimethyl formamide.

6. Method of claim 1 wherein the member is dimethyl sulfoxide.

7. Method of claim 1 wherein an aqueous saline solvent member is used.

8. Method of claim 7 wherein the member is an aqueous solution of ZnCl_2 .

9. Method of claim 2 wherein the member is an aqueous solution of ZnCl_2 containing a lower alcohol.

10. The method of claim 1 wherein an acrylonitrile copolymer is used which contains vinyl monomers in an amount less than 20% by weight selected from the group consisting of acrylic acid lower alkyl esters, methacrylic acid lower alkyl esters, vinyl acetate, vinyl chloride, vinyl bromide, vinyl pyridine, and sulfo-containing vinyl monomers.

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PHILIP E. ANDERSON, Primary Examiner

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