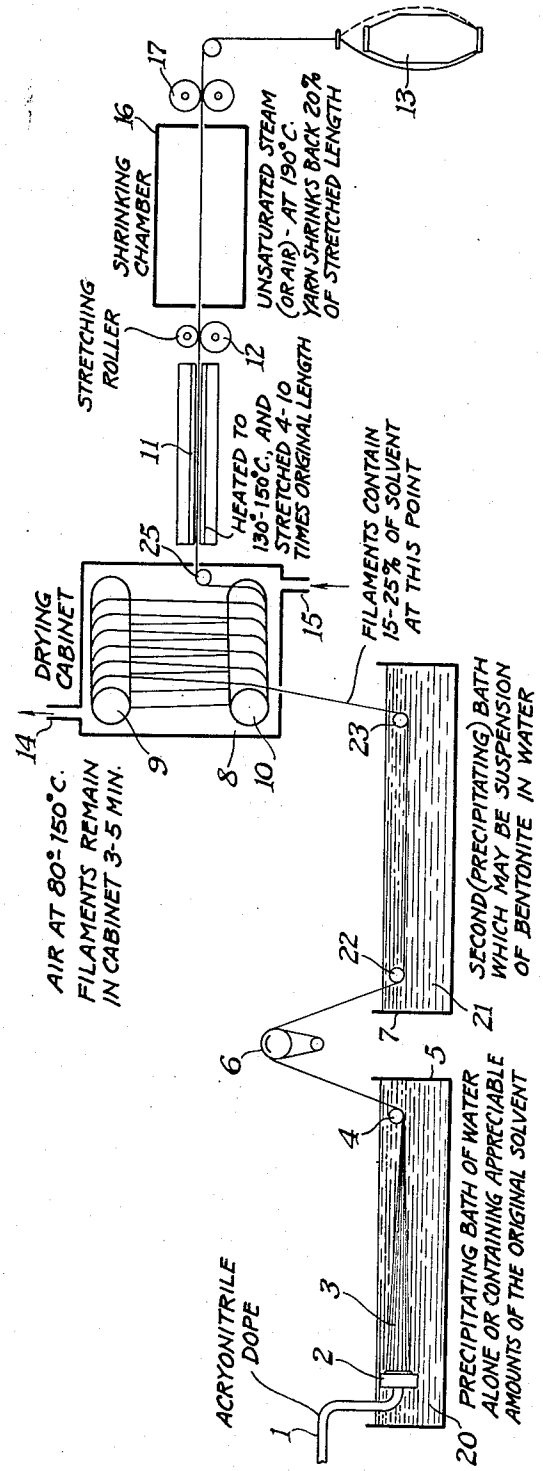
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SPINNING ACRYLONITRILE

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SPINNING ACRYLONITRILE

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This invention relates to spinning of acrylonitrile in order to form filaments or the like shaped objects therefrom. More particularly this invention concerns an improved process for spinning acrylonitrile materials whereby shaped articles such as filaments, fibers and the like are obtained almost completely free of voids, having a lustrous appearance and possessing high tenacity and extensibility.

The production of this type object such as filaments, fibers and yarn, generally known in the industry as acrylonitrile textiles, has in recent years become of substantial interest. In certain preliminary work on the spinning of acrylonitrile materials into shaped articles, it was attempted to spin the materials into aqueous baths. However, the resultant products thus spun into aqueous baths were unsatisfactory. Therefore, a number of methods have been proposed wherein the acrylonitrile materials are spun into baths comprised of various different chemical compositions. These chemical baths may contain various ionizable salts or other chemicals such as polyhydroxy alcohols.

It is apparent that such chemical baths are more costly and complicated than a simple aqueous bath and otherwise adds to the complexity of processes for forming acrylonitrile materials into shaped articles.

After extensive investigations, I have found a process whereby acrylonitriles of various compositions may be spun into relatively simple aqueous baths with the ultimate production of excellent products, provided the shaped articles thus produced are processed by the steps of the instant invention as described in detail hereinafter.

This invention has for one object to provide a process for forming acrylonitrile materials into shaped objects. Another object is to provide an improved process for the wet spinning of acrylonitrile polymeric materials into filaments which are substantially free of voids and have a lustrous appearance. Still another object is to provide a spinning process for acrylonitriles wherein relatively simple aqueous baths may be used. A still further object is to provide an improved spinning process for acrylonitrile materials wherein filaments formed in relatively simple aqueous baths are substantially immediately subjected to a relatively high temperature drying treatment. Still another object of this invention is to provide a process for spinning acrylonitrile materials which does not require the use of special chemical baths or the like. Another object is to provide new and improved acrylonitrile filaments characterized by their freedom from voids, lustrous appearance, freedom from contaminating chemicals, and exhibiting high density and extensibility. Other objects will become apparent from the description of the invention hereinafter set forth.

For assistance in understanding my invention, reference will be made to the attached drawing forming a part of the present application. The attached drawing is a side elevation view, somewhat in the nature of a flow sheet showing in a diagrammatic manner an apparatus arrangement of the type which may be used in carrying out the process of the present invention.

In the drawing, 1 indicates the supply pipe through which the acrylonitrile materials to be formed are forced under pressure through a multi-hole spinneret 2. This spinneret 2 and any associated parts may be of conventional construction and of a construction well known in the spinning art; hence, detailed description appears unnecessary.

As shown in the drawing the spinneret 2 may be positioned in some convenient manner in the end of a vessel 5, which vessel is deep enough and of such construction as to contain a precipitating or coagulating bath 20. While not shown on the drawing, the container or vessel 5 may be provided with means as known in the art for continuously supplying to or removing therefrom precipitating solution and means for securing circulation of the solution in the container 5.

The yarn 3 emerging from spinneret 2 is led through bath 20 past guide 4 to a positively driven roller 6. From roller 6 the yarn filaments 3 pass under guides 22 and 23, submerged in a second bath 21. This second bath 21 is contained in vessel or tank 7.

As indicated above, the present drawing is diagrammatic in nature and generally illustrative. Therefore, it will be understood that while 2 baths have been illustrated and described, it is quite possible to employ three or more baths, or even a single bath. In addition, while, for simplicity of description ordinary guides 22 and 23 have been referred to and simple open tanks 5 and 7 mentioned, closed containers, motor driven rollers and the like may be used in place of these parts. In other words, the exact construction of the apparatus for conducting the filaments through the baths is not an undue limitation upon the present process.

The yarn emerging from the last bath passes to the positively driven rollers 9 and 10 whose axes are inclined at an angle to each other so that the yarn passes gradually from one end of the rollers to the other. These delay rollers 9 and 10 are enclosed in a cabinet 8 through which hot air or other suitable heating medium at a temperature from 70° C. to 150° C. is circulated, the heating medium, for example, entering the port 15 and leaving through port 14.

It is desired to mention at this point that the legends on the drawing indicate that the yarn contains 15–25% solvent, and this is merely illustrative depending upon the number of washing baths through which the yarn has been passed prior to its entering the high temperature drying cabinet 8. It is an important feature of the present invention that the washed yarn will be substantially immediately subjected to a relatively high temperature drying step as will be described in detail hereinafter.

When the high temperature dried yarn emerges from cabinet 8 it may be withdrawn over a roller or a guide 25 and then the dried yarn passes through another chamber designated 11. This chamber 11 is also a relatively high heat chamber containing heating liquids such as mineral oil or the various commercial heating chemicals, electric heat or the like for heating chamber 11 to a temperature within the range of 100° C. to 300° C. This step at point 11 is for heating the already hot dried yarn sufficiently to render it plastic to a slight extent in order that it may be stretched or drafted many times its original length. This drafting may be accomplished by means of positively driven rollers given the overall designation 12. In other words, by operating stretching rollers as known in the art at a higher rate of rotation than the speed of movement of the yarn at point 25 the yarn may be drafted or stretched to a substantial extent.

Upon emerging from stretching rollers 12 the yarn passes into another heating environment designated 16. This chamber 16 may be of a generally similar construction to the constructions already described and is heated in some suitable manner so that the yarn may be relaxed under warm conditions. The yarn is withdrawn through and from the shrinking means 16 by means of a set or sets of rollers given the overall designation 17. In general, these rollers 17 are operated at a lower speed than rollers 12 in order to permit the shrinking or relaxing of the filaments in the environment 16.

It is desired to point out that in connection with the drafting and relaxing operations just described from 11 to 16 it is not necessary to use heating chambers as such to accomplish this, although the arrangement shown is relatively simple and effective. For example, suitable heating may be applied by radiant heat or by means of heated rollers, the heated rollers being suitably enclosed for the conservation of heat.

In any event the yarn emerging from the rollers at

17 may then be wound up in any conventional manner such as on the bobbin or the like as indicated at **13**.

Referring now to the general aspects of my process, it will be noted that various polymeric compositions may be handled in accordance with the present invention. That is, the well-known polymeric material polyacrylonitrile as conventionally prepared or procured commercially may be regarded as the primary material processed by the present invention. However, I contemplate not only processing spinning dopes consisting essentially of polyacrylonitrile but various mixture or copolymers or the like may be similarly processed. Generally these various other combinations would not contain more than about 35% of the other components. Examples of such combinations are acrylonitrile with proteins such as zein or soya bean protein. Other combinations comprise acrylonitrile with varying amounts of cellulose derivatives such as the cellulose esters or cellulose compounds such as ethyl cellulose. Also, combinations such as acrylonitrile with the various resins exemplified by polyvinyl acetate resins, isopropenyl acetate or alkyl alpha acetamido acrylate may be sprung.

The particular acrylonitrile compound chosen, of course, influences to some extent the choice of the solvent which is used for preparing the dope solution injected from supply pipe **1** to the spinneret **2**. Since all of my compositions contemplate a preponderance of acrylonitrile (as contrasted to some of the compositions in the prior art where vinyl compounds and the like constitute the major ingredient) in general the solvent chosen will be a solvent which favors the dissolution of the acrylonitrile component. Certain materials such as dimethyl formamide, dimethyl acetamide, and the like are suitable. However, there are numerous other solvents such as the various butyro and valero lactones as well as succinonitrile and tetramethylene cyclic sulfone which may be used. It is sufficient at the present point of description to state that the polyacrylonitrile compound is dissolved in a suitable solvent to form a flowable dope. In general the dope is comprised of 10 to 35 parts of the polymeric materials in one hundred parts of solvent. This dope is pumped through conduit **1** so that filaments are extruded through spinneret **2**.

Referring to the drawing, the filaments emerging through spinneret **2** are submerged in bath **20** which bath is preferably maintained at a temperature between about 18° C. and 50° C.

In contrast to prior art procedure I have found that it is not necessary to make bath **20** of any complicated or special composition. I have found that an aqueous bath in vessel **5** is quite satisfactory. This aqueous bath may contain some of the solvent corresponding to the solvent used in preparing the dope that is being spun. In other words, there is considerable latitude in the precipitating or coagulating of bath **20** of my invention in that it may be comprised of water varying from 25 to 100%, the balance being a solvent of the type contained in the dope. As mentioned, there is no need of incorporating special salts or alcohols into this bath when operating in accordance with the present invention. However, it is apparent that the incorporation of small amounts of some of these salts and chemicals, while not required, are not injurious.

The extruded filaments **3** in passing through the aqueous bath **20** would preferably be passed through the bath for a sufficient time and distance to substantially or nearly completely coagulate or set the filaments. However, it is apparent if several separate baths are employed such a great degree of coagulation is not required in the first bath as further coagulation and hardening may be accomplished in subsequent baths.

Referring now to bath **21** contained in vessel **7**, this bath in accordance with my invention may also be principally or entirely of water. In the bath shown on the drawing, there is included a small amount of bentonite. However, various other components for the purpose referred to below may be included. The purpose of using an aqueous solution in this second bath is to cause a deposit on the yarn of a small amount of solid material which prevents the yarn from adhering or otherwise sticking together during subsequent processing.

Turning now to one of the principal features of my invention, the yarn emerging from the final aqueous bath (either one of several) at the particular point of emergence still may contain a few per cent of solvent, and at this particular point in my process may not represent too satisfactorily a yarn because of voids and other defects therein. However, I have found that if this aqueous-spun yarn is immediately given a relatively high temperature drying treatment that an excellent quality yarn is procured, particularly when this yarn is further treated by stretching and relaxing as will be apparent under the specific examples set forth hereinafter.

Heretofore, no one has found a means whereby solutions of acrylonitrile polymers could be spun in water to form shaped articles without the shaped articles containing so many voids that the articles were delustered, weak, and rather brittle, and generally unsuited for use as yarns or films. The present invention provides a means for spinning acrylonitrile polymer yarns into water and, thereafter forming a yarn without voids therein.

A measure of the total space occupied by voids in the yarns is given by the ratio of the actual cross-section area of the yarn filaments to the area calculated from the denier of the yarn and the density of polyacrylonitrile. The actual area of the filaments was determined by direct measurement with a planimeter (magnification 1250 times), and the density of the polyacrylonitrile was taken as 1.165. The ratio of the measured area to calculated area of the yarn of Example I below was found to be 1.05, indicating the presence of very few voids.

This invention provides a process by which solutions of acrylonitrile polymers in volatile organic solvents can be extruded into water or mixtures of water and solvent to produce yarns almost completely free of voids and having other desirable properties. Use of the high temperature dryer (**8** in the accompanying drawing) is an important part of this process. The temperature of the air in this dryer must be at least 70° C. and may be as high as 150° C., preferably 80° C. to 110° C. It is also desirable that the filaments contain an appreciable quantity of solvent when they enter the dryer, usually 5% to 25% of the solvent associated with the polymer in the spinning solution. The high temperature of the dryer permits rapid removal of the water and most of the residual solvent, and at the same time the presence of the solvent permits the polymer to flow slightly, thus removing voids in the yarns produced in the spinning baths. Under proper conditions, the yarn emerges from the dryer without any appreciable number of voids, and dry enough to permit stretching to produce greater strength. The filaments show very little tendency to adhere to each other. The use of heat in the dryer is essential, since these freshly spun yarns, if dried at temperatures appreciably less than 70° C., say from 25° C. to 50° C., can be stretched only with difficulty and will contain numerous voids and be generally unsuited for use in the textile art.

The two important features of the drying step, namely, elevated temperature and the presence of solvent in the yarn filaments are utilized in all instances, whether the spinning bath is water only, a mixture of water and solvent, or is a series of baths of different concentrations of water and solvent.

The use of precipitating baths (**20** and **21**) containing some quantity of solvent is generally preferred over pure water for three reasons: First, the length of the bath required is longer in the former case and hence less critical; and second, the problem of recovery of solvent from the precipitating bath in the former case is not nearly so great as in the latter. In recovering one liter of solvent from a mixture of 50% water and 50% solvent, it is necessary to distill off only one liter of water (assuming water boils at a lower temperature than the solvent), while in recovering one liter of solvent from water containing only 1% solvent, it is necessary to distill off 99 liters of water. Hence, with certain solvents there may be a definite economical advantage in spinning into aqueous baths containing a relatively high percentage of solvent. The third advantage of spinning into mixtures of water and solvent is that the filaments can be stretched 50 to 100% while in the bath. The advantage in this stretching at this stage in the process resides in the fact that the yarn, after the final high temperature stretching to produce strength, can be shrunk in a relaxed state in steam at 180° C. to produce a yarn having from 2% to 5% greater extensibility than yarn spun into a pure water bath but otherwise similarly treated.

The foregoing sets forth a general understanding of my invention. A further understanding will be had by a consideration of the following specific examples.

Example I

A solution of 130 grams of polyacrylonitrile possessing an average molecular weight of about 100,000, as determined from viscosity measurements by the Staudinger formula, in one liter of dimethyl formamide at 25° C. is extruded through a 30-hole spinneret (hole diameter 0.100 mm.) into a precipitating bath consisting of water at 28° C. After traveling about 2½ inches in this bath, the yarn thus formed is led over a guide into a second bath of water containing a 1% suspension of bentonite. After a travel of about ½ inch in this second bath, the yarn is led to the positively driven rolls in the drying cabinet, through which air at 82° C. was circulating. The yarn is passed around these rollers 20 times (total length of yarn on rollers at one time was 70 ft.).

The peripheral speed of these rollers is 30 feet per minute. At this point the yarn is nearly dry and lustrous. The yarn next passes through an air chamber maintained at 155° C. to a positively driven roller whose peripheral speed is 180 feet per minute. The yarn is then collected on a rotating bobbin of a cap spinner. This yarn is soft, lustrous, 65 denier and has a tenacity of 3.6 grams per denier and an extensibility of 8%. It has a knot tenacity of 2.4 grams per denier. This yarn is not brittle and is suitable for use in the textile art. If desired, the extensibility of the yarn can be increased to about 16% without appreciable loss in tenacity by shrinking the yarn in a relaxed state in unsaturated steam at 180° C. for perhaps two minutes.

Example II

A solution of 130 grams of polyacrylonitrile having an average molecular weight of about 100,000, as determined from viscosity measurements by the Staudinger formula, in one liter of dimethyl formamide at 25° C. is extruded through a 30-hole spinneret (hole diameter 0.100 mm.) into a precipitating bath consisting of a mixture of 625 parts by volume of dimethyl formamide and 375 parts of water at 30° C. The yarn is led through this bath for a distance of 48 inches to a positively driven roller having a peripheral speed of 192 inches per minute. The yarn passes from this roll without slippage to a second precipitating bath consisting of 500 parts dimethyl formamide and 500 parts water at 24° C. After traveling a distance of 32 inches in this second bath, the yarn passes over a guide into a third bath consisting only of water at 24° C. After a travel of a distance of 2 inches in the third bath, the yarn is led over guides to the positively driven rollers in the drying cabinet. These rollers have a peripheral speed of 326 inches per minute, thereby stretching the yarn during its travel through the second precipitating bath. The drying cabinet has air circulating through it at a temperature of 88° C. After 20 turns around the delay rollers, the yarn is led through an air chamber at a temperature of 135° C. to a positively driven roller having a peripheral speed of 1630 inches per minute. The yarn is then collected on the bobbin of a cap spinner. The yarn is then lustrous, soft, 113 denier, and has a tenacity of 3.4 grams per denier and an extensibility of 12%. After being shrunk in steam at 180° C. for 5 minutes, the tenacity is 3.6 grams per denier and the extensibility is 20%, while the knot tenacity is 1.9 grams per denier and the knot extensibility is 11%.

Example III

A solution of 100 grams of polyacrylonitrile having an average molecular weight of approximately 100,000 in one liter of dimethyl acetamide at 25° C. is extruded through a 30-hole spinneret (hole diameter 0.125 mm.) into a precipitating bath consisting of water at 35° C. The yarn is led through this water bath a distance of 9 inches, and upon leaving the bath, it enters the drying cabinet where it passes around these rollers 30 times in moving air at a temperature of 88° C. In the dryer the yarn travels at a speed of 240 inches per minute. Upon leaving the dryer, the yarn is drawn through an air chamber maintained at a temperature of 160° C. by means of a positively driven roller having a peripheral speed of 1920 inches per minute, thereby stretching the yarn to 8 times its original length. This yarn is 65 denier, lustrous, almost completely without voids, has a tenacity of 3.1 grams per denier and an extensibility of 9%. After being shrunk in steam, relaxed at 180° C., the tenacity is 3.0 grams per denier and extensibility is 18%.

Example IV

A solution of a mixture of 120 grams of polyacrylonitrile and 30 grams of a copolymer of vinyl acetate and isopropenyl acetate (equimolar proportions in the monomeric mixture) in 1 liter of dimethyl formamide at room temperature was extruded through a 52-hole spinneret (hole diameter 0.100 mm.) into a precipitating bath consisting of 53 parts water and 47 parts dimethyl formamide at room temperature. After a travel of 39 inches in this bath, the yarn was led over a guide to a second precipitating bath consisting of 90 parts water and 10 parts dimethyl formamide at room temperature. After a travel of 58 inches in this second bath, the yarn was led into the dryer, which was maintained at 88° C. The peripheral speed of the rollers in the dryer was 150 inches per minute. After passing 14 turns around these rollers, the yarn was led through an air chamber at 155° C. to a positively driven roll with peripheral speed of 1350 inches per minute, then through an air chamber at 185° C. to a driven roller with peripheral speed of 1120 inches per minute, thus permitting the yarn to shrink 17% in length during its travel through the second heated chamber. The yarn was then wound on a bobbin on a cap spinner. The final yarn of 140 denier was soft, had good luster, and possessed strength of 4.3 grams per denier, and 19% elongation at break.

Example V

A solution of 225 grams of a copolymer of 88% acrylonitrile and 12% isopropenyl acetate in 1 liter of dimethyl acetamide at room temperature was extruded through a 52-hole spinneret (0.100 mm. diameter holes) into a precipitating bath consisting of 84 parts water and 16 parts dimethyl acetamide at room temperature. After a travel of 36 inches in this bath, the yarn was led over a guide into a second precipitating bath consisting of water only at room temperature. After a travel of 9 inches in this bath, the yarn was led to the dryer which was maintained at 82° C. The rollers in the dryer had a peripheral speed of 240 inches per minute. After passing 35 times around the rollers in the dryer, the yarn was led through an air chamber at 160° C. to a positively driven roller with a peripheral speed of 2120 inches per minute, then through an air chamber at 185° C. to a roller with peripheral speed of 1700 inches per minute, thus permitting the yarn to shrink 20% in length in the second heated air chamber. The final yarn was 180 denier, showed no sticking together of the filaments, was substantially free of voids, and had a tenacity of 1.9 grams per denier and 23% extensibility.

From the foregoing description, it may be seen that I have provided a relatively simple and direct process for spinning acrylonitrile materials into relatively simple aqueous spinning baths.

The acrylonitrile polymer, of which the shaped articles are formed, is preferably prepared by the persulfate catalyzed polymerization of monomeric acrylontrile dissolved in water, although it can be prepared by any other suitable type of polymerization reaction. The polymer used in accordance with this invention should, of course, be of sufficiently high molecular weight to have film- or filament-forming properties. Since the monomeric material is an article of commerce and since polymerization thereof is a known art, further details in this respect appear unnecessary.

The preferred polymers employed possess an average molecular weight within the range 25,000 to 500,000 or even higher, and preferably within the range of 50,000 to 200,000 as calculated from viscosity measurements by the Staudinger equation.

As already mentioned, the polymer employed may be a simple polymer of acrylonitrile or a copolymer or a mixture of acrylonitrile and another substance such as the various vinyl compounds, esters or other derivatives of acrylic or methacrylic acid styrene, isobutylene, or other polymerizable substances. However, for the final yarn to have the desirable properties of polymerized acrylonitrile (such as fairly high softening temperature and resistance to chemicals), the polymer should contain a substantial proportion of acrylonitrile. These polymers containing

no more than 35% of another substance are preferred.

The polymer can be dissolved in any suitable volatile organic solvent. The term "volatile organic solvent" is meant to include those organic substances that are capable of forming stable homogeneous solutions with an acrylonitrile polymer and that can be distilled without decomposition at atmospheric pressure. Suitable solvents for use with this invention include dimethyl formamide, dimethyl acetamide, succinonitrile, γ-valerolactone, and tetramethylene cyclic sulfone and the like as already mentioned. Dependent upon the temperature of the dryer 8, the amount of solvent in the yarn and the like details, the yarn will be held in dryer 8 for a period of time varying from 1 to 10 minutes.

I claim:

1. A process for spinning polymeric material comprised predominantly of acrylonitrile which comprises preparing a dope containing the acrylonitrile, forcing this dope through a shaped orifice into a bath predominantly of water which contains no added ionizable salt, withdrawing the shaped object of acrylonitrile from this bath and immediately subjecting it to a relatively high temperature drying operation at a temperature in excess of 70° C.

2. A process for the wet spinning of polymeric material comprised principally of acrylonitrile which comprises extruding a dope of said acrylonitrile through a spinneret into several spinning baths in series, the spinning baths being characterized in that they are essentially comprised of water and contain no added ionizable salt, withdrawing the spun product from the last bath and immediately subjecting it to a relatively high temperature drying operation at between 70° C. and 150° C., said drying operation being applied to the spun product for a sufficient period that the product becomes lustrous and substantially dry.

3. A process for spinning polymeric material predominantly of acrylonitrile which comprises dissolving said polymeric material in a solvent therefor to form a spinning dope, spinning said dope into an aqueous spinning bath, said bath being characterized in that it consists of water and said solvent used in preparing the dope and contains no added ionizable salt, withdrawing the spun product from the bath and immediately subjecting the spun product to a relatively high temperature drying step at between 70° C. and 150° C. until the product becomes lustrous and nearly completely dry.

4. The process which comprises preparing a spinning dope by dissolving a material comprised predominantly of acrylonitrile in a solvent for the acrylonitrile, spinning said dope into a plurality of spinning baths in a series, the spinning baths being characterized in that they are predominantly aqueous baths substantially free of ionizable salts, withdrawing the spun product from the last bath and into and through a relatively high temperature drying step whereby the spun product is heated to a temperature between 70° C. and 150° C. for a sufficient period to cause the spun product to become substantially free of voids and substantially dry, thereafter conducting the spun product to and through stretch drafting at elevated temperatures, relaxing the drafted product and thereafter winding up the product.

5. The process of spinning a material principally comprised of acrylonitrile, but containing up to 35% of other yarn forming materials, dissolving these materials in a solvent to prepare a spinning dope, extruding said dope through a spinneret to form filaments, passing the filaments through a series of baths, the baths being characterized in that they consist essentially of water and the solvent used in preparing the dope and contain no added ionizable salt, withdrawing the spun filaments from the last bath while still containing some solvent and while the filaments still contain a substantial portion of this solvent subjecting the filaments to a relatively high temperature drying treatment between 80° C. and 150° C. whereby substantially dry yarn free from voids is obtained, immediately subjecting this hot dried yarn to stretch drafting at a temperature in excess of the drying temperature, relaxing the drafted yarn and winding it into a suitable package.

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