

March 5, 1963

P. A. UCCI

3,080,210

SPINNING OF ACRYLONITRILE POLYMERS

Filed Dec. 1, 1961

3 Sheets-Sheet 1

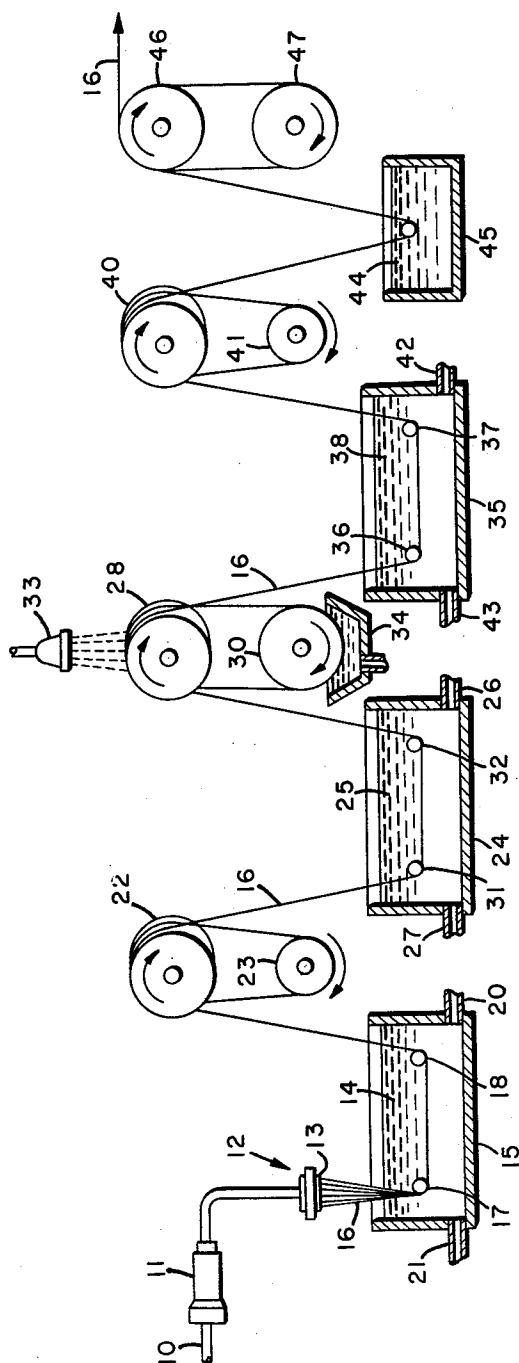


FIG. 1.

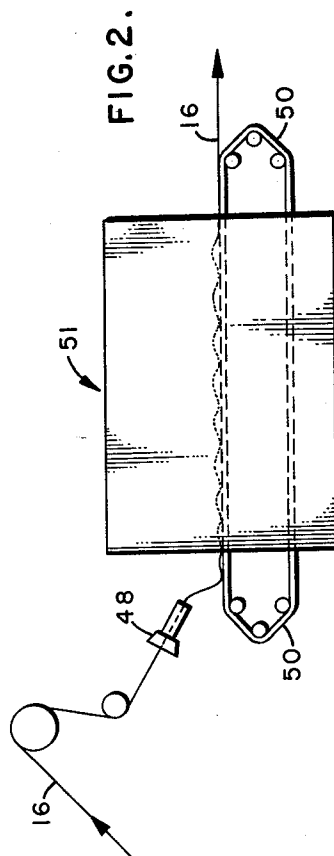


FIG. 2.

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SPINNING OF ACRYLONITRILE POLYMERS

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3 Sheets-Sheet 2

ACRYLONITRILE POLYMER
SPINNING SOLUTION

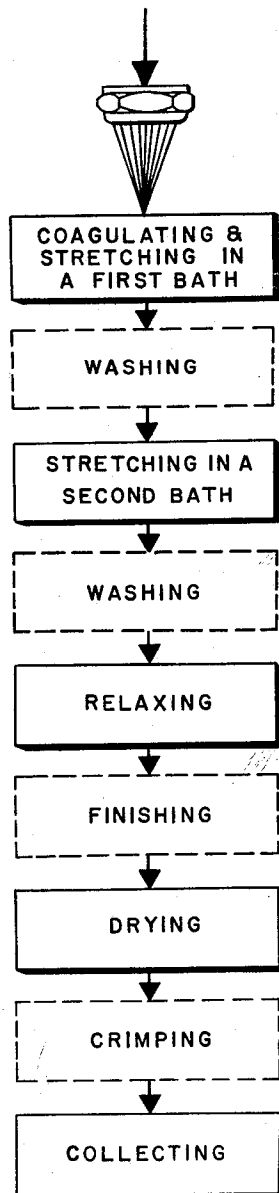


FIG. 3

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SPINNING OF ACRYLONITRILE POLYMERS

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FIG. 4.

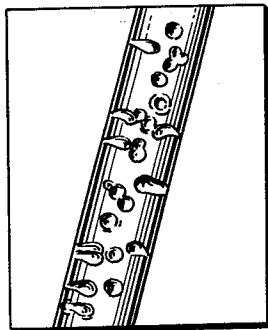


FIG. 5.

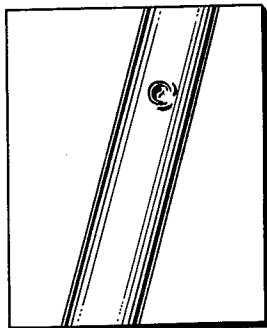


FIG. 6.

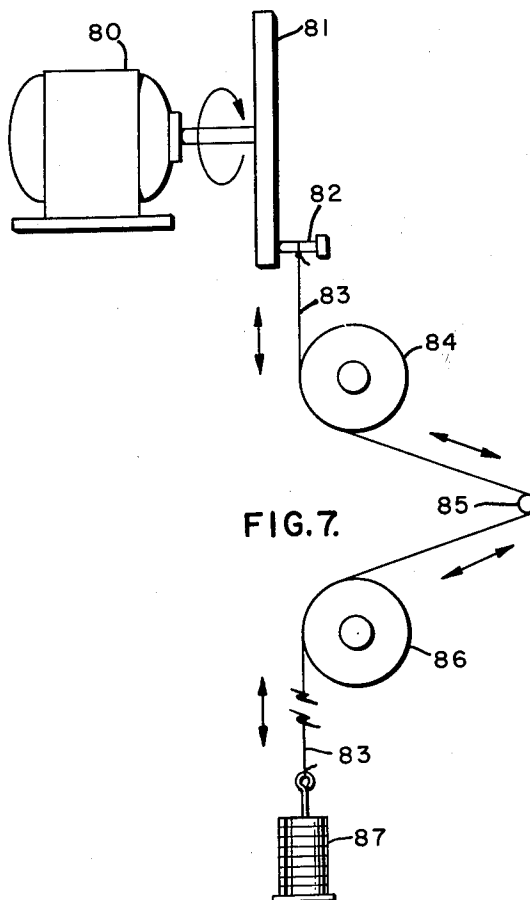


FIG. 7.

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SPINNING OF ACRYLONITRILE POLYMERS

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Filed Dec. 1, 1961, Ser. No. 156,368

11 Claims. (Cl. 18-54)

This invention relates to the manufacture of improved shaped articles such as fibers, filaments, yarns and the like produced from acrylonitrile polymers. More particularly, this invention concerns said shaped articles characterized by having a normally lustrous appearance and possessing an optimum balance of longitudinal and lateral properties and a process for producing same.

In view of the thermal instability of acrylonitrile polymers, filaments of such polymers are formed by dissolving the polymers in a suitable solvent and then removing the solvent from a flowing stream of the solution to form filaments therefrom. Commercially, filaments of acrylonitrile polymers are prepared either by the dry spinning process or by the wet spinning process, as is well known. The specific technique chosen results in a compromise among yarn properties, the economic aspects of the technique involved, and other considerations. There are advantages and disadvantages associated with the employment of each process. For example, dry spinning has the advantage of considerably higher spinning speeds than those which can be attained with wet spinning. In addition, a greater percentage of solids can be tolerated in the spinning solution used in dry spinning as compared with that which can be used in wet spinning since, inter alia, the solution is spun at relatively high temperatures. Unfortunately, the better solvents for acrylonitrile polymers are not as volatile as would be desired for use in the dry spinning process wherein the solvent is removed to a great extent by evaporation into air or other suitable inert gas. In view of the fact that at least 75 percent of the solvent is removed as a gas in the dry spinning process, large amounts of heat must be applied to the spinning solution, as well as to the extruded filaments, to facilitate removal of such a quantity of solvent within a reasonable time. The amounts of heat so required can affect adversely the properties of the produced filaments, particularly in regard to color.

When the solvent is extracted from an extruded stream of spinning solution in a coagulating bath during wet spinning, solidification of the polymer in filamentary form results. Normally, during coagulating there is an inward diffusion of coagulating bath liquid into the filaments undergoing coagulation, as well as a corresponding outward movement of solvent into the coagulating bath. The solvent and bath liquid can interchange in such a manner that the resulting filaments contain many voids or cavities along their lengths which can be seen clearly with an optical phase microscope. Filaments containing these voids or unfilled spaces do not possess the requisite physical properties desired for some end uses. For example, such filaments exhibit a delustered appearance, lower tenacity, and lower abrasion resistance than filaments not containing voids.

To overcome this physical weakness inherently formed in the filaments, positive aftertreatment steps during the processing of the filaments normally are taken. The tenacity of the filaments is improved greatly by various modes of stretching that molecularly orient the polymer molecules but which in addition tend to collapse these voids. To collapse fully these voids, the filaments may be dried at rather high temperatures under tension, thereby forming a more dense filamentary structure. The prior art has found that the tenacity of the filaments is

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satisfactory with such aftertreatment of the filaments. However, tenacity is primarily a longitudinal property of the filaments; and satisfactory tenacity is not the full answer to the attainment of filaments having an optimum balance of properties. In many end uses the abrasion resistance and the resistance to break upon being flexed (flex life) are most important. Such properties may be regarded as lateral properties as distinguished from longitudinal properties. While drying under tension gives the illusion of forming filaments without voids therein, the voids merely are crushed together. Although the crushed voids do not detract from the longitudinal properties of the filaments to any significant extent, it has been found that lateral stresses cause the filaments to splinter or break. In other words, filaments having voids which are merely crushed together are laterally weak. The art has found that the lateral properties of the filaments can be improved substantially by subjecting the filaments to an annealing operation. One such annealing procedure includes a series of elevated and reduced pressure treatments applied to the filaments. More specifically, annealing can be accomplished by placing the acrylonitrile polymer filaments in a closed chamber, subjecting them to a high temperature and pressure in the presence of wet steam and then evacuating the chamber. This treating cycle is repeated as many times as needed. It will be appreciated that this annealing operation as just described is expensive and time consuming. Omitting the annealing step in the aftertreatment of the wet spun acrylic filaments results in a filament having a tendency to splinter or fibrillate; and hence, the filaments have a low abrasion resistance. This tendency to fibrillate is minimized by annealing the filaments. The improvement is thought to result from the interface surfaces of the collapsed voids being rendered less separable.

In addition to the possible presence of the voids which are visible under an optical phase microscope and occur in filaments of acrylonitrile polymers coagulated in an aqueous coagulating bath, electron microscopy has shown the existence of a reticulate structure in the filaments displaying a network of submicroscopic pores or interstitial spaces most of which intercommunicate with each other. These pores in freshly spun filaments, that is filaments which have been coagulated without having been subjected to any aftertreatment producing a pronounced change in the structure thereof, are quite observable under an electron microscope. The polymers comprising the filaments appear to take the form of a latticework of integrally joined strings. The polymer lattice has a pattern resembling that of a fine, extremely small meshwork, although the interstices are usually somewhat irregular in size and shape. The micropores present in filaments produced by ordinary wet spinning techniques as they leave the coagulating bath are more or less spherical with the polymer lattice defining such interstitial spaces. The distances across these spaces are ordinarily about 250 A. to 3000 A. or greater. The frequency of occurrence of the micropores in the filaments produced by ordinary wet spinning techniques employing aqueous coagulating baths can be estimated under an electron microscope and is usually around $35-90 \times 10^{14}$ per gram of polymer. The presence of these pores is believed to explain the anomalously low density of normal filaments as they leave the coagulating bath. At this point the apparent density of the filaments produced by ordinary wet spinning techniques employing aqueous coagulating baths is usually about 0.4 to 0.5 gram per cubic centimeter.

It will be appreciated that the voids that are visible under the optical phase microscope are quite different from the micropores or interstitial spaces not visible under an optical phase microscope but readily apparent under an electron microscope. Hence, the term "voids"

as used herein signifies enclosed spaces or surface pits of the filaments which are visible under an optical phase microscope and which do not contain acrylonitrile polymer, whether or not the enclosed spaces contain a fluid or are collapsed. The term "micropore" as used herein signifies extremely diminutive enclosed spaces or surface pits of the filaments that are not visible under an optical phase microscope but visible under an electron microscope and that do not contain acrylonitrile polymer, whether or not the enclosed spaces contain a fluid or are collapsed.

When the freshly spun filaments are stretched, these micropores as would be expected assume the geometric configuration of ellipsoids. Subsequent collapsing of the porous structure of the filaments due to the presence of these micropores can be accomplished by drying the filaments under tension at an elevated temperature. Annealing the filaments renders the interstitial interface surfaces of the micropores less separable. Hence, annealing has been regarded as an important step in the attainment of acceptable lateral physical properties in the filaments.

It is an object of this invention to provide a process for producing filaments and the like of acrylonitrile polymers that possess an advantageous combination of lateral and longitudinal physical properties by modification of the conventional acrylonitrile polymer filament forming processes. Other objects will become apparent from the following description of the invention and the claims.

In general, these objects are accomplished in accordance with the invention by continuously extruding a solution of an acrylonitrile polymer through a desired number of orifices in a spinneret disposed in air or other inert gaseous medium and continuously directing the thus-formed streams of the solution for a short distance through the medium, wherein only a very small amount of the solvent, if any, is evaporated into the ambient medium as a gas. The streams then are passed into a liquid which is a precipitant for the polymer and an extractant for the solvent, such as an aqueous coagulating bath. In the liquid bath the streams of polymer are coagulated into filaments by the substantial removal therefrom of the solvent as a liquid. The solvent employed is preferably N,N-dimethylacetamide, N,N-dimethylformamide or the like; and the coagulating bath preferably is composed essentially of the solvent and water. By employing such preferred solvent and bath composition while maintaining the bath temperature between the critical temperature range of $+10^{\circ}\text{C.}$ to -40°C. , preferably between $+10^{\circ}\text{C.}$ and -15°C. , the filaments produced possess most advantageous physical properties and differ in structure from other acrylonitrile polymer filaments heretofore known in the art. The extrusion rate of the polymer and the speed of withdrawal of the filaments from the coagulating bath are correlated so that the filaments are subjected to a draw ratio usually of 0.8-20. However, the filaments may be stretched at this point up to just short of the point at which filamentary breakage occurs. Preferably the draw ratio is between 0.5 and 5.0 times. Often higher draw ratios are desired whereby to obtain higher spinning speeds. Draw ratio is a convenient term for designating the attenuation or shrinkage that often occurs during various steps in the production of man-made filaments. Draw ratio is the number resulting from the division of the speed of withdrawal by the speed of feed of the filaments between two given points. In the production of wet-spun filaments draw ratio as applied to the attenuation or shrinkage in the coagulating bath is the number derived by dividing the measured length of filaments produced by the length that should have been produced as calculated from the extrusion rate of polymer through the spinneret. Most of the attenuation, if attenuation of the filaments is desired, occurs while the streams of polymer pass through the short air gap separating the face of the spinneret and the upper surface of the liquid in the coagulating bath, with little, if any, stretch

taking place in the coagulating bath. After being passed through the coagulating bath for a sufficient distance, the filaments are continuously removed therefrom and directed through a second bath. This bath is preferably composed of hot water wherein additional solvent remaining in the coagulated filaments is removed therefrom and a considerable stretch is imparted thereto to orient the polymer molecules thereof. Following this operation, the filaments are permitted to relax continuously under a low tension in a hot liquid or hot gaseous atmosphere and/or then continuously dried. The necessity of the continuous relaxation depends upon the spinning conditions employed. It has been found that when N,N-dimethylacetamide or N,N-dimethylformamide is employed as the solvent for the acrylonitrile polymer and when an aqueous coagulating bath consisting primarily of water and solvent and maintained within the critical temperature range of $+10^{\circ}\text{C.}$ and -40°C. is used, the relaxing step unexpectedly can be omitted and yet produce filaments of textile grade. Moreover, it is not necessary to dry the filaments under tension since the filaments are substantially free of voids and when dried at room temperature, whether relaxed or under tension, display densities corresponding to normally produced filaments dried under tension to insure that the voids and micropores therein are collapsed.

To further understand the invention, reference will be made to the attached drawing that forms part of the present application.

In the drawing, FIGURE 1 is a side elevational view partly in section showing schematically an apparatus arrangement of the type which can be used in carrying out the process of the present invention;

FIGURE 2 is a schematic view showing the produced filaments being dried by a different drying means;

FIGURE 3 is a flow sheet illustrating the manipulative steps used in carrying out the process of the invention;

FIGURE 4 is a reproduction of a photomicrograph at a magnification of about 100 times of acrylonitrile polymer filaments of textile grade which give the appearance of smooth, glassy rods;

FIGURE 5 is a reproduction of a photomicrograph of greater magnification of an acrylonitrile polymer filament that contains numerous voids along the length thereof;

FIGURE 6 is a reproduction of a photomicrograph of an acrylonitrile polymer filament substantially free of voids; and

FIGURE 7 is a schematic view of a simple laboratory abrasion testing apparatus.

By acrylonitrile polymer is meant polyacrylonitrile, copolymers, and terpolymers of acrylonitrile, and blends of polyacrylonitrile and copolymers of acrylonitrile with other polymerizable mono-olefinic materials, as well as blends of polyacrylonitrile and such copolymers with small amounts of other polymeric materials, such as polystyrene. In general, a polymer made from a monomeric mixture of which acrylonitrile is at least 70 percent by weight of the polymerizable content is useful in the practice of the present invention. Besides polyacrylonitrile, useful copolymers are those of 80 or more percent of acrylonitrile and one or more percent of other mono-olefinic monomers. Block and graft copolymers of the same general type are within the purview of the invention. Suitable other monomers include vinyl acetate, and other vinyl esters of monocarboxylic acids, vinylidene chloride, vinyl chloride and other vinyl halides, dimethyl fumarate and other dialkyl esters of fumaric acid, dimethyl maleate and other dialkyl esters of maleic acid, methyl acrylate and other alkyl esters of acrylic acid, styrene and other vinyl-substituted aromatic hydrocarbons, methyl methacrylate and other alkyl esters of methacrylic acid, vinyl-substituted heterocyclic nitrogen ring compounds, such as the vinyl imidazoles, etc., the alkyl-substituted vinylpyridines, vinyl chloroacetate, allyl chloroacetate, methallyl chloroacetate,

allyl glycidyl ether, methallyl glycidyl ether, allyl glycidyl phthalate, and the corresponding esters of other aliphatic and aromatic dicarboxylic acids, glycidyl acrylate, glycidyl methacrylate, and other mono-olefinic monomers copolymerizable with acrylonitrile.

Many of the more readily available monomers for polymerization with acrylonitrile form copolymers which are not reactive with some dyestuffs and may therefore be impossible or difficult to dye by conventional techniques. Accordingly, these non-dyeable fiber-forming copolymers may be blended with polymers or copolymers which are in themselves more dye-receptive by reason of their physical structure or by reason of the presence of functional groups chemically reactive with the dyestuff, whereby the dyestuff is permanently bonded to the polymer in a manner which lends resistance to removal thereof by the usual laundering and dry cleaning procedures. Suitable blending polymers may be polyvinylpyridine, polymers of alkyl-substituted vinylpyridine, polymers of other vinyl-substituted N-heterocyclic compounds, the copolymers of the various vinyl-substituted N-heterocyclic compounds and other copolymerizable monomers, particularly acrylonitrile.

Of particular utility are the blends formed of polyacrylonitrile or a copolymer of more than 90 percent acrylonitrile and up to 10 percent vinyl acetate, and a copolymer of vinylpyridine or an alkyl-substituted vinylpyridine and acrylonitrile, the said acrylonitrile being present in substantial proportions to provide heat and solvent resistance, and a substantial proportion of the vinylpyridine or derivatives thereof to render the blend receptive to acid dyestuffs. Of particular utility are the blends of copolymers of 90 to 98 percent acrylonitrile and 10 to 2 percent vinyl acetate and sufficient copolymer of 10 to 70 percent acrylonitrile and 90 to 30 percent vinylpyridine to produce a blended composition with a total of 2 to 10 weight percent vinylpyridine.

The polymers just described may be prepared by any conventional polymerization procedure, such as mass polymerization methods, solution polymerization methods, or aqueous emulsion methods. The polymerization is normally catalyzed by known catalysts and is carried out in equipment generally used in the art. However, the preferred practice utilizes suspension polymerization wherein the polymer is prepared in finely divided form for immediate use in the filament-forming operations. The preferred suspension polymerization involves batch procedures, wherein monomers are charged with an aqueous medium containing the necessary catalyst and dispersing agents. A more desirable method involves the semi-continuous procedure in which the polymerization reactor containing the aqueous medium is charged with the desired monomers gradually throughout the course of the reaction. Entirely continuous methods involving the gradual addition of monomers and the continuous withdrawal of polymer can also be employed.

The polymerization is catalyzed by means of a water-soluble peroxy compound, for example, the potassium, ammonium and other water-soluble salts of peroxy acids, sodium peroxide, hydrogen peroxide, sodium perborate, the sodium salts of other peroxy acids, and other water-soluble compounds containing the peroxy group:



A wide variation in the quantity of peroxy compound is possible. For example, from 0.1 to 3.0 percent by weight of the polymerizable monomer may be used. The so-called redox catalyst system also may be used. Redox agents are generally compounds in a lower valent state which are readily oxidized to the higher valent state under the conditions of reaction. Through the use of this reduction-oxidation system, it is possible to obtain polymerization to a substantial extent at lower temperatures than otherwise would be required. Suitable "redox" agents are sulfur dioxide, the alkali metal and ammonium bisulfites,

and sodium formaldehyde sulfoxylate. The catalyst may be charged at the outlet of the reaction, or it may be added continuously or in increments through out the reaction for the purpose of maintaining a more uniform concentration of catalyst in the reaction mass. The latter method is preferred because it tends to make the resultant polymer more uniform in regard to its chemical and physical properties.

Although the uniform distribution of the reactants throughout the reaction mass can be achieved by vigorous agitation, it is generally desirable to promote the uniform distribution of reagents by using inert wetting agents, or emulsion stabilizers. Suitable reagents for this purpose are the water-soluble salts of fatty acids, such as sodium oleate and potassium stearate, mixtures of water-soluble fatty acid salts, such as common soaps prepared by the saponification of animal and vegetable oils, the "amino soaps," such as salts of triethanolamine and dodecylmethylamine, salts of rosin acids and mixtures thereof, the water-soluble salts of half esters of sulfonic acids and long chain aliphatic alcohols, sulfonated hydrocarbons, such as alkyl aryl sulfonates, and any other of a wide variety of wetting agents, which are in general organic compounds containing both hydrophobic and hydrophilic radicals. The quantity of emulsifying agent will depend upon the particular agent selected, the ratio of monomer to be used and the conditions of polymerization. In general, however, from 0.1 to 1.0 weight percent based on the weight of the monomers can be employed.

The emulsion polymerizations are preferably conducted in glass or glass-lined vessels provided with means for agitating the contents therein. Generally, rotary stirring devices are the most effective means of insuring the intimate contact of the reagents, but other methods may be successfully employed, for example, by rocking or rotating the reactors. The polymerization equipment generally used is conventional in the art and the adaptation of a particular type of apparatus to the reaction contemplated is within the province of one skilled in the art.

The optimum methods of polymerization for preparing fiber-forming acrylonitrile polymers involve the use of polymerization regulators to prevent the formation of polymer units of excessive molecular weight. Suitable regulators are the alkyl and aryl mercaptans, carbon tetrachloride, chloroform, dithioglycidol and alcohols. The regulators may be used in amounts varying from 0.001 to two percent, based on the weight of the monomer to be polymerized.

The polymers from which the filaments are produced in accordance with the present invention have specific viscosities within the range of 0.10 to 0.40. The specific viscosity value, as employed herein, is represented by the formula:

$$N_{sp} = \frac{\text{Time of flow of polymer solutions in seconds} - 1}{\text{Time of flow of the solvent in seconds}}$$

Viscosity determinations of the polymer solutions and solvent are made by allowing said solutions to flow by gravity at 25° C. through a capillary viscosity tube. In the determinations herein, a polymer solution containing 0.1 gram of the polymer dissolved in 100 ml. of N,N-dimethylformamide was employed. The most effective polymers for the preparation of filaments are those of uniform physical and chemical properties and of relatively high molecular weight.

Referring now to FIGURE 1, a water coagulable solution comprising an acrylonitrile polymer and a solvent therefor is passed under pressure from a supply tank (not shown) through a conduit 10 and thence through a candle filter 11 wherein undissolved particles and foreign materials in the solution are removed. Ordinarily, gear pumps are used to propel the solution through the filter 11 and to meter same to the spinneret assembly 12. This assembly is suitably mounted and positioned such that the face 13 of the spinneret is horizontally disposed preferably along a plane substantially parallel to the upper sur-

face of the coagulating liquid 14 contained in an open-top spinning trough or bath 15. The solution may be extruded through a single orifice or a plurality of orifices in the spinneret to form a filament or a bundle of filaments 16 as desired. The extruded streams of polymer are directed substantially vertically downward and under filament guide 17 disposed in said trough 15. A second filament guide 18 is suitably positioned in said trough so that the filaments directed thereunder will pass through the liquid 14 for a predetermined distance sufficient to cause the solution to coagulate as desired. Fresh liquid 14 is supplied to trough 15 through pipe 20 (which may be water or water containing a desirable quantity of solvent) and is withdrawn therefrom through pipe 21.

The coagulated filaments are withdrawn by employment of a positively driven roller 22 or other thread advancing means, the peripheral speed of which preferably is synchronized with the extrusion speed so that the filaments during their travel between the spinneret and the rollers may be attenuated, and if desired attenuated up to the point just short of where filamentary breakage occurs. As indicated above, most of the attenuation will take place between the face of the spinneret and the upper surface of the coagulating bath. After passing around roller 22 and an idler roll 23, the filaments are directed into a second spinning trough 24 containing a liquid 25. Fresh liquid is supplied to trough 24 through pipe 26 and is withdrawn therefrom through pipe 27. While it is quite possible to employ three or more liquid-containing troughs, only two have been illustrated and described in the interest of simplicity. The filaments before emerging from the liquid in second trough 24 and being directed around a set of positively driven rollers identified by numerals 28 and 30 are passed under guides 31 and 32. The peripheral speed of rollers 28 and 30 can be adjusted so that a predetermined orientation stretch will be imparted to the filaments 16 during their travel in second trough 24.

To roller 28 a washing liquid such as hot water is supplied from a spray or shower head 33, the liquid being collected in a container or tray 34. It will be recognized that the washing operation can be accomplished in more than one stage of the process and by employment of other known washing means. After leaving rollers 28 and 30, the filaments are directed through a liquid in a third trough 35 by being passed under guides 36 and 37. The liquid 38 in this trough is normally water at an elevated temperature. The filaments are withdrawn therefrom by means of a driven roller 40 and associated idle roller 41 operated at a peripheral speed less than that of the peripheral speed of rollers 28 and 30 so that the filaments are permitted to relax substantially completely and thereby to shrink during their travel in trough 35. Fresh water is supplied to trough 35 through an inlet pipe 42 and is withdrawn through an outlet pipe 43. It will be appreciated that other equivalent means may be used to permit the shrinking or relaxing of the filaments. For example, the filaments may be directed around a tapered roller or rollers and progressively led from the end having the larger circumference to the end having the smaller circumference, the rollers being immersed in a liquid or having a liquid applied thereto. Following the relaxing operation the filaments are passed through a finish bath liquid 44 contained in a vessel 45 and composed of a lubricant or like beneficial treating agent. The filaments after being withdrawn from liquid 44 are dried. As illustrated in FIGURE 1, the filaments are continuously directed around a pair of driven drying drums 46 and 47 heated internally with steam or the like. Thereafter, the filaments are subjected to additional operations such as crimping, cutting, and then are collected in the form of staple fiber, continuous filament yarn, or tow.

In accordance with a second embodiment relative to the drying operation as illustrated in FIGURE 2, the filaments after being stretched and washed are laid by means of a traversing piddler 48 or like guide means onto

a moving endless belt 50 (in a zig-zag pattern). This belt passes through a drying cabinet 51 in which hot air or other suitable drying gas at an elevated temperature is directed onto the filaments therein. In this embodiment, it is seen that the filaments are continuously dried in a tension-free condition. An advantage of this embodiment is that the filaments are permitted to relax and are dried; thus the relaxing and the drying of the filaments are accomplished in one step. It should be understood that it is entirely possible to dry the filaments while not being tensioned by the employment of other drying means. For example, the filaments may be dried suitably by being conveyed by and suspended in a stream of air.

FIGURE 3 is a flow sheet illustrating a preferred arrangement of the manipulative steps used herein. As seen there, a prepared spinning solution is extruded from a spinneret into air to form a bundle of filaments that are then coagulated. The filaments may be stretched a substantial extent, if desired, between the spinneret and the means used to withdraw them from the coagulating bath. From the coagulating bath the filaments so produced are passed through a second bath where they are stretched and thence through a third bath in which the filaments are permitted to relax. The filaments may be washed free or substantially free of solvent either before or after they have been stretched in the second bath. After the relaxing operation, the filaments may be directed through a bath containing a suitable finish, if desired, and thereafter are dried by conventional means. Optionally, the filaments are crimped. Finally, the filaments are reduced to staple size and baled, or alternatively they are collected as continuous filaments by employment of a suitable take-up device.

FIGURE 5 is a drawing prepared from a photomicrograph showing a view of part of a filament containing voids or cavities. Enclosed voids in the filament also can be seen by observing a cross section of the filament. Due to the presence of the voids, the light rays impinging thereon are scattered, imparting a dull or subdued luster to the filament.

FIGURE 6 is a drawing prepared from a photomicrograph showing a corresponding view of part of a filament substantially free of voids or cavities. Due to the substantial absence of voids, the filament has a lustrous appearance. The novel filaments of the present invention are substantially free of voids and hence have a normally lustrous appearance. However, when desired, delustrants, pigments, and the like can be incorporated in the filaments to produce dull filaments. The marked differences of the novel filaments herein and those heretofore known become more apparent when a comparison of the reticulate filamentary structures is made at magnifications obtainable by the use of an electron microscope.

In general, the spinning solution can be prepared by heating and stirring a mixture of a finely divided acrylonitrile polymer of the type described above with a suitable solvent until the polymer is dissolved. To some extent the selection of the solvent is influenced by the particular polymer chosen. Certain materials such as N,N-dimethylformamide, butyrolactone, dimethyl sulfoxide, N,N-dimethylacetamide and the like are particularly suitable solvents. While ethylene carbonate and the like, concentrated solutions of certain water-soluble inorganic salts, such as zinc chloride, calcium chloride, lithium bromide, cadmium bromide, sodium thiocyanate, etc. may be employed in accordance with the broadest aspects of the invention, such solvents are not preferred for use in producing the novel filaments herein or for use in the embodiment of the invention employing the low temperature coagulation bath of +10° C. to -40° C. The percentage of polymer based on the weight of the solution will depend upon the particular polymer and solvent employed, as well as upon the temperature at which the polymer is spun. It is desirable to employ a solution containing a high percentage of polymer for obvious reasons.

An advantage of the present invention is the fact that spinning solutions having much higher temperatures can be employed than ordinarily used in wet spinning. Hence, a greater percentage of polymer in the solution can be used with success. The spinning solution may be maintained prior to and at extrusion at temperatures from about 20 to 180° C. Room temperature is highly satisfactory from an operational standpoint. Ordinarily a solution containing at least 10 percent acrylonitrile polymer is desirable.

Since the viscosity of the acrylonitrile polymer solution varies directly with its temperature, advantage of employing the high spinning temperatures permitted in the instant process may be taken with the result that low extrusion pressures are required for a given percentage of polymer. Normally, the polymer solution temperature for successful wet spinning should be closely correlated with the temperature of the coagulating bath. In order to spin acrylonitrile polymer solution by the conventional wet spinning method, it is necessary to avoid elevated coagulating bath temperatures, since such temperatures substantially reduce the solvent extraction efficiency to a point where it is not possible or feasible to utilize the advantage of spinning a solution containing a high percentage of polymer.

The spinneret used in accordance with the instant invention can be of the type ordinarily used in dry spinning operation. An important variable in any spinning process is the orifice diameter of the spinneret. From practical aspects it is of ten desirable to employ the largest diameter consistent with good spinning. By increasing the orifice size the filtration of the spinning solution becomes less important and the number of spinneret changes due to clogging thereof is reduced. In the present invention one may employ orifices having relatively large diameters due to the fact that the filaments may be given a considerable attenuation immediately after extrusion of the spinning solution. This in practical terms means a reduction in operating cost. Among other benefits derived by employing a large orifice opening are the higher spinning speeds and the improvement in the physical properties by the attenuation of the filaments that can be attained. In conventional wet spinning this is not possible because the maximum jet stretch that can be imparted to the freshly spun filaments is usually less than two times, and in most cases is less than one time due to the anisotropic condition of normally wet spun filaments. On the other hand, it is possible to stretch the freshly spun filaments of the present invention to the extent of as high as 15 times. That is to say, that the first take-up linear velocity may be up to 15 times the extrusion velocity of the polymer. By disposing the spinneret above the coagulating bath, it is possible to attain spinning speeds as high as 100-1500 feet per minute using apparatus with which a maximum speed of only 75 to 150 feet per minute can be attained in normal wet spinning. Moreover, filament deniers below 1.0 can be spun readily without difficulty whereas 1.2 to 2.0 denier per filament is generally the least that can be spun in the ordinary wet spinning process. Another advantage of the present process is that a wide range of filament denier can be spun from a single spinneret. For example, filament deniers from 0.8 to 22 and higher having satisfactory textile properties may be spun from a single spinneret having an orifice diameter of 0.005 inch. This means that filaments having various deniers may be spun conveniently without shut down being required to change from production of one diameter to another.

The distance that the spinneret is disposed above the coagulating bath may be varied. Ordinarily, the spinneret is positioned so that its face is between 1/8 and 1 1/2 inches above the bath. However, one can increase this distance by taking precaution that adjacent polymer streams do not come in contact with and cohere to each other. For example, a cell through which the streams co-

axially pass may be provided to minimize any disturbance thereof. Ordinarily, the gas between the spinneret and the coagulating bath and through which the streams of polymer travel is air, although any other gaseous medium that does not adversely affect the filaments may be used. The temperature of the gas may be regulated; however, the temperature normally present during spinning is satisfactory. For best results the spinning variables should be correlated so that less than one percent of the solvent based on the weight of the solution is evaporated into the gaseous medium from the extruded stream.

Although the reason why the filaments produced by the instant process can be stretched to a much greater extent between the spinneret and the means used to withdraw the coagulated filaments is not entirely elucidated, it is thought that the extrusion of polymer solution through a spinneret positioned above the surface of the coagulating bath provides a fluid region in each extruded stream of polymer wherein the streams easily yield to a longitudinally applied force without a separation of the mass composing the streams. Therefore, considerable attenuation of the streams of polymer can take place prior to the entry of the streams into the coagulating bath. During their brief passage through the space above the surface of the coagulating bath and below the face of the spinneret only a small amount of the solvent, if any, is removed from the extruded streams of polymer with the result that little or no coagulation takes place when the streams are being attenuated. Because of the high fluidity of the streams of polymer in the zone between the spinneret and coagulating bath, the longitudinal force applied to the coagulating filaments to pull same through and out of the coagulating bath is accepted by the extruded streams of polymer, in the main, in this zone. Apparently, the coagulating filaments as a result are passed through the coagulating bath under a minimum tension; that is, the tension exerted on the coagulating filament would be only that tension required to overcome the viscosity forces within the filaments and drag forces in the coagulating bath. Under these conditions it is believed that isotropic filaments exhibiting only an extremely thin outer skin formation and a reduced susceptibility to skin rupture or fissure to cause undesirable variations in the resulting filaments exist in this zone.

In normal wet spinning a much thicker skin is formed from the very genesis of filament formation; and the longitudinal force necessary to impart even a moderate stretch in the filaments undergoing coagulation can be sufficient to cause ruptures of the filamentary skin. This rupturing also can occur in many instances when the longitudinal force is sufficient only to withdraw the filaments from the coagulating bath. It has been observed that when the skin becomes ruptured during coagulation, an array of voids forms along the line of skin cleavage. Since the longitudinal forces exerted on the filaments in the coagulating bath are minimized in accordance with the present invention, the tendency of the surface of the filaments to crack or rupture accordingly is reduced, resulting in the production of superior filaments.

The coagulating baths suitable for use in the invention normally contain a non-solvent such as water, or a mixture of a solvent and a non-solvent for the acrylonitrile polymer. The solvent used in the coagulating bath is preferably the same as the one used in preparing the polymer solution; however, such need not be the case. Although good spinning can be accomplished while using a coagulating bath composed essentially of water, it is preferred that the bath contain 20 percent to 80 percent solvent. On the basis of available data the temperature range for the coagulating bath is preferred to be from -40° to +80° C. It is preferred that the bath contain 60-70 percent solvent at the lower bath temperatures.

The filaments may be given a travel in the coagulating bath, for example, from 2 to 24 inches or more by employment of the two suitably spaced guides and with-

drawal rolls as illustrated in FIGURE 1. Between the spinneret and the withdrawal rolls, the filaments, as indicated above, are subjected to a stretching operation to attain a desired substantial attenuation thereof.

A second bath is employed following the coagulating bath wherein the filaments are given an additional stretch in order to increase the strength, as well as otherwise to improve the physical properties of the filaments. This improvement results from orientation of the polymer molecules along the filament axis. The second bath may consist simply of water, or it may have the same composition as the coagulating bath but at a greater dilution with water. The temperature of the secondary bath is preferably between 50° and 100° C., the highest feasible temperature being preferred. Draw ratios of up to 10 or higher may be employed, the amount of stretch applied depends on the properties desired for the yarn. Preferred draw ratios are between 1.5 and 8.0.

Following the passage through the coagulating bath and the stretch bath or baths, the filaments are washed substantially free of solvent if desired. This may be accomplished by spraying water on the filaments traveling around positively driven rolls. The water extracts the solvent from the filaments as they pass gradually from one end of the rollers to the other end. Other washing means, of course, can be used. Moreover, the washing can be carried out prior to applying the orientation stretch to the filaments as indicated above.

The next step is important to the proper practice of the present invention and consists of subjecting the filaments to sufficient temperatures at a low tension or zero tension to permit substantially complete relaxation of the filaments. This may be accomplished preferably by continuously passing the filaments through a water bath maintained at a temperature near or at the boiling point of water by means of a thread-advancing device operated at a peripheral speed less than the linear velocity at which the filaments are fed to the water bath. Ordinarily, the filaments may shrink at least 15 percent and up to 40 percent of their original length or more. The resulting filaments which are relaxed in hot or boiling water have higher elongation values as compared to filaments produced in a comparable manner but without being permitted to relax. Surprisingly, the higher elongation values are attained without a sacrifice of tenacity. Moreover, it appears that an inverse relationship exists between the elongation of the resulting filaments and the temperature at which the filaments are given the orientation stretch. That is to say, for a given orientation stretch, filaments having higher elongation are obtained generally where lower stretch temperatures are employed. As indicated, the step of relaxing is not entirely necessary when one follows the low temperature coagulating bath aspect of the invention.

After the filaments are permitted to freely shrink, they are dried in a convenient manner. This may be done either under tension or under no tension. Preferably, the filaments are dried while in a completely relaxed condition so that the filaments are dried and relaxed in one operation.

Quite unexpectedly the filaments produced by the present invention after leaving the relaxation bath have a substantially reduced porosity and have a smooth, mirror-like surface. Hence, the disadvantages associated with drying under tension, such as yellowing of the filaments when subjected to high local temperatures on the drying drums and like apparatus used in a tension drying operation, may be avoided and yet produce filaments that have a luster greater than normal wet-spun filaments dried under tension.

The examples below are illustrative of the practice of the present invention and not limitative thereof. In the examples, all percentages are given on a weight basis unless otherwise indicated.

EXAMPLE I

A spinning solution was prepared by dissolving in N,N-dimethylacetamide a blend of (A) a copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and (B) a copolymer of 50 percent acrylonitrile and 50 percent 2-methyl-5-vinylpyridine, said blend containing 6 percent vinylpyridine based on the total weight of the blend and having a specific viscosity of 0.12 to give a 26 percent solids solution. The solution was extruded at 25° C. through a spinneret containing 90 holes, each being 0.005 inch in diameter, downwardly through air for a distance of ½ inch and into a coagulating bath containing 50 percent N,N-dimethylacetamide and 50 percent water by volume at 25° C. The bundle of filaments thus formed was led through this bath for a distance of 18 inches and then was removed therefrom at a rate of 30.6 feet per minute, the rate of withdrawal being established in relation to the rate of extrusion so that the filaments are subjected to a draw ratio of 0.94 between the spinneret and the means used to withdraw the filaments from the coagulating bath. Next, the filaments were passed into a second stretch bath maintained at 100° C. and containing essentially 100 percent water. After traveling a distance of 24 inches in this second bath, the filaments were withdrawn therefrom at a rate of 186 feet per minute so that a stretch of approximately 6.1 times was imparted to the filaments. Stretch in times, as seen, is the number resulting from the division of the speed of withdrawal by the speed of feed between two points. Then, the filaments were passed around a pair of spaced rollers 30 to 40 times with a total length of the filaments around the rollers at one time being about 120 feet. Water at 50–80° C. was sprayed on the filaments during their travel around said rollers to wash the filaments. Following this washing operation, the filaments were directed into a relaxing bath containing water at 100° C. with the filaments being withdrawn therefrom at a speed of 152 feet per minute. Under these conditions the filaments were permitted to shrink 18 percent. The filaments next were passed through a bath containing a yarn lubricant and then around a heated drying drum assembly to dry the filaments. Thereafter, the filaments were crimped, cut into staple lengths, and baled. The fibers so-produced were lustrous with an excellent resistance to abrasion and had a tenacity of 2.5 grams per denier, an elongation of 26.0 percent, and a denier of 3.1.

Additional samples of filaments were prepared in the same manner except that polymer blends having various specific viscosities were used to prepare spinning solutions having various percentages of solids as shown in Table 1 where the yarn properties are also given.

Table 1

Specific viscosity	Solids, Percent	Tenacity, gms./den.	Elongation, Percent
0.16	22.0	2.79	27.0
0.25	18.0	2.97	23.7
0.29	15.5	2.97	23.5
0.33	14.5	2.87	22.0

It can be seen readily from the above data that wide variations in regard to the specific viscosity of the polymer and to the percentage of polymer in the spinning solution are permitted in the instant process.

EXAMPLE II

A spinning solution was prepared in N,N-dimethylacetamide containing 22 percent polymer and 0.1 percent sulfuric acid based on the weight of the solution. The polymer employed was the polymer blend used above in Example I and had a specific viscosity of 0.16. The spin-

ning solution was extruded at 25° C. through a spinneret containing 100 holes, each having a diameter of 0.009 inch, into air for a distance of one inch and into a coagulating bath containing 40 percent N,N-dimethylacetamide and 60 percent water by volume at a temperature of 25° C. The bundle of the thus-formed filaments was removed from the coagulating bath at a rate of 38.4 feet per minute, the rate being correlated to stretch the filaments 6.6 times between the spinneret and the means used for withdrawing the filaments from the coagulating bath. Then, the filaments were passed into a stretch bath maintained at a temperature of 100° C. and containing water. The filaments were withdrawn from the second bath at a rate of 186 feet per minute so that an additional stretch of approximately 4.9 times was imparted to the filaments by employing a thread advancing reel assembly. Water was sprayed on the filaments during their storage on the assembly to wash same. Following this washing operation, the filaments were relaxed thereby causing them to shrink 5 percent in air at room temperature. A yarn lubricant was applied in a continuous fashion to the filaments, and then the filaments were dried in a tension-free condition by laying the filaments on an endless belt conveyor moving through a drying cabinet. The dried filaments were crimped, cut into staple lengths, and baled. The fibers so-produced were lustrous with an excellent resistance to abrasion and had a tenacity of 2.7 grams per denier and an elongation of 16.4 percent.

EXAMPLE III

A spinning solution was prepared in N,N-dimethylacetamide containing 18 percent polymer based on the weight of the solution. The polymer employed was the polymer blend used in Example I and had a specific viscosity of 0.16. Samples of the spinning solution were extruded at 25° C., 120° C., and 180° C., respectively, through a spinneret containing 40 holes, each having a diameter of 0.005 inch into air for a distance of ¼ inch and then into a coagulating bath containing 40 percent N,N-dimethylacetamide and 60 percent water by weight and maintained at a temperature of 28° C. The filaments were processed then into staple fibers in the manner described in Example II. However, the filaments were given a jet stretch of 1.3 times and an orientation stretch of 4.9 times in the second bath. The fibers so-produced were highly lustrous with an excellent resistance to abrasion. The textile data of these spinnings are tabulated below in Table 2.

Table 2

Solution temperature, ° C.	Tenacity, gms./den.	Elongation, Percent
25	2.8	19.5
120	2.8	19.7
180	2.7	20.3

EXAMPLE IV

The spinning solution of Example II was extruded through various spinnerets having orifices of various diameters as indicated in Table 3. Diverse temperatures and concentrations of the coagulating bath were employed, also as indicated in the table. The filaments so-formed were passed through the air above the bath for ½ inch and thence through the bath. The filaments were withdrawn from the bath at a speed such that the filaments were stretched just short of the point at which breaking thereof occurred. The maximum stretch that could be imparted to the filaments is given below.

Table 3

Sample	Spinneret		Coagulating bath		
	Holes	Diameter, inches	Solvent/water, percent	°C.	Maximum stretch, times
A-----	60	0.003	70/30	36	9.1
B-----	60	0.003	60/40	35	4.8
C-----	60	0.003	40/60	28	1.9
D-----	60	0.003	20/80	25	1.6
E-----	60	0.003	0/100	19	1.6
F-----	100	0.005	70/30	30	9.2
G-----	100	0.005	60/40	30	5.4
H-----	100	0.005	40/60	30	4.4
I-----	100	0.005	20/80	30	4.1
J-----	100	0.005	0/100	30	4.6
K-----	100	0.007	70/30	30	10.5
L-----	100	0.007	60/40	30	8.0
M-----	100	0.007	50/50	30	6.6
N-----	100	0.007	40/60	30	6.1
O-----	100	0.007	20/80	30	5.6
P-----	100	0.007	0/100	30	5.6
Q-----	100	0.009	70/30	30	15.4
R-----	100	0.009	60/40	30	9.6
S-----	100	0.009	50/50	30	8.0
T-----	100	0.009	40/60	30	7.3
U-----	100	0.009	20/80	30	6.6

It can be noted from the above data that a significant increase in maximum stretch values occurred when the solvent content of the coagulating bath was above 50 percent. Stretches above 10 times were obtainable. Unlike in normal wet spinning where the opposite relationship holds, the maximum jet stretch of the subject invention decreased with increasing amounts of water in the coagulating bath and increased with decreasing amounts of water in the coagulating bath.

EXAMPLE V

A spinning solution was prepared in N,N-dimethylacetamide containing 18 percent polymer of the type employed above in Example I but having a specific viscosity of 0.25. The spinning solution was extruded at 25° C. through a spinneret containing 40 holes, each having a diameter of 0.005 inch, into air for a distance of ½ inch and then into a coagulating bath containing 10 percent N,N-dimethylacetamide and 90 percent water by volume at a temperature of 27° C. The thus-formed filaments were stretched 1.3 times and then passed through a second bath containing water at 100° C. During their travel through the second bath the filaments were stretched 5.0 times. The filaments were washed and then dried while in a tension-free condition.

Additional spinnings were carried out at temperatures of 90° C., 80° C., and 70° C. in the second stretch bath. At these various temperatures the filaments were stretched to different extents as indicated from Table 4.

Table 4

Sample	Second bath, temp., ° C.	Stretch in second bath, times	Percent shrinkage during relaxation	Denier	Tenacity, gms./den.	Elongation, percent
1-----	90	5	22	288	2.7	31.4
2-----	80	5	29	289	2.5	36.3
3-----	70	5	39	284	2.3	47.0
4-----	100	6	20	285	2.7	26.9
5-----	90	6	24	298	2.6	23.3
6-----	80	6	29	289	2.6	31.3
7-----	100	7	21	315	2.7	25.5
8-----	90	7	24	323	2.6	27.0
9-----	80	7	18	282	2.6	30.0

From the data above it is seen that the percent elongation increased for a given stretch in the second bath as the temperature in the bath was decreased without an appreciable sacrifice in tenacity.

For comparison purposes the spinneret was immersed in the coagulating bath and the same spinning solution was spun into filaments under like conditions. It was found that a second bath temperature of 95° C. or above was required to attain stretches of up to 4 to 5 times.

Furthermore, stretches greater than 5 times were impossible; below this temperature the maximum stretch obtainable was even less than 4.

Hence, it is seen that in the present method the filaments can be given an orientation stretch in the second bath over a relatively wide temperature range without sacrifice of yarn properties. From practical considerations this wide latitude of temperature assumes considerable significance, since there is no necessity of rigid temperature control and since more energy is required to maintain the bath at the high temperature required in regular wet spinning.

EXAMPLE VI

Samples Q, R, and T above in Example IV were washed with water and permitted to relax and not to relax in an aqueous bath. The resulting filaments were dried on heated rotating rolls and their physical properties determined. These results are given in Table 5 below.

Table 5

	Tenacity, gms./den.	Elongation, percent
Sample Q, relaxed.....	2.41	29.0
Sample Q, unrelaxed.....	2.48	19.8
Sample R, relaxed.....	2.52	27.6
Sample R, unrelaxed.....	2.53	20.6
Sample T, relaxed.....	2.70	28.5
Sample T, unrelaxed.....	2.65	16.4

These data show that the relaxed samples had a significantly higher elongation as compared with the unrelaxed samples, but unexpectedly tenacities remained substantially unchanged. The fibers having the greater elongation and produced by employing the relaxation step had considerably less breaks on the card when processed on the cotton system than the fibers with the low elongations.

EXAMPLE VII

The effect of various orientation stretches in the second bath and continuous relaxation on the physical properties of the formed filaments in regard to tenacity and elongation was studied while employing a coagulating bath having a relatively low temperature.

A spinning solution was prepared in N,N-dimethylacetamide containing 18 percent polymer based on the weight of the solution. The polymer employed was the polymer blend used in Example I above and had a specific viscosity of 0.25. Samples of the spinning solution were extruded through a spinneret containing 100 holes, each having a diameter of 0.0035 inch into air for a distance of 1/8 inch. The extruded streams of polymer were directed into a coagulating bath containing 70 percent N,N-dimethylacetamide and 30 percent water by volume. The coagulating bath was maintained at 5° C. ± 1°. The extruded streams were directed through this bath for 24 inches; the bundle of filaments thus-formed was then removed therefrom at a rate of 22 to 44 feet per minute, the rate of withdrawal being established in relation to the rate of extrusion so that the filaments were subjected to a draw ratio of 0.8 between the spinneret and the means used to withdraw the filaments from the coagulating bath. Next, the filaments were passed through a water bath at 60° C. so as to remove residual solvent from the filaments.

The filaments were next directed through a water bath at about 100° C. and stretched therein a predetermined extent. Various stretches were given the samples at this stage. Some of the samples were directed into a relaxing bath containing water at about 100° C. and other samples were not. The filaments were collected on cones and dried in air. The tenacity and elongation were measured on the filaments. These results are given in Table 6 below.

Table 6

Sample	Stretch in second bath, times	Percent shrinkage during relaxation	Denier	Tenacity, gms./den.	Elongation, percent
1.....	6.0	None	2.8	4.5	13
2.....	6.0	15	3.2	3.9	26
3.....	5.0	None	2.8	4.1	14
4.....	5.0	15	3.2	3.4	25
5.....	4.0	None	2.8	3.7	16
6.....	4.0	15	3.2	3.2	27
7.....	3.0	None	2.7	3.1	18
8.....	3.0	15	3.1	2.8	30

Thus, from the above data, it is indicated that satisfactory textile properties are obtained by employing relatively low coagulating bath temperatures even though the yarn is not permitted to relax after being stretched to induce molecular orientation therein.

EXAMPLE VIII

Additional spinnings were carried out following the procedure outlined above in Example VII. The acrylonitrile polymer in this instance was a binary copolymer of 94 weight percent acrylonitrile and 6 weight percent vinyl acetate. The effect of various orientation stretches in the second bath and continuous relaxation on the physical properties of the formed filaments in regard to tenacity and elongation while employing coagulating baths having various relatively low temperatures as set forth in Table 7 below was demonstrated. The final filaments had a denier of about 3.1 when permitted to relax and a denier of about 2.7 when not so permitted.

Table 7

Sample	Coagulating bath temp., °C.	Stretch in second bath, times	Percent shrinkage during relaxation	Tenacity, gms./den.	Elongation, percent
1.....	-10	6.0	None	4.1	18
2.....	-10	6.0	16	4.5	25
3.....	-10	4.0	None	3.3	17
4.....	-10	4.0	16	3.6	24
5.....	-10	2.0	None	2.9	19
6.....	-10	2.0	16	2.8	27
7.....	0	6.0	None	4.0	18
8.....	0	6.0	16	4.2	24
9.....	0	4.0	None	3.6	20
10.....	0	4.0	16	3.6	32
11.....	0	2.0	None	2.8	21
12.....	0	2.0	16	2.6	35
13.....	10	6.0	None	4.0	18
14.....	10	6.0	16	4.0	25
15.....	10	4.0	None	3.3	16
16.....	10	4.0	16	3.4	25
17.....	10	2.0	None	2.7	27
18.....	10	2.0	16	2.5	36

The following indications may be read into the above data: A gradual reduction in bath temperature results in a corresponding increase in tenacity. Furthermore, a higher tenacity is obtained when greater stretches are imparted to the filaments in the second bath. In addition, the yarn not permitted to relax has physical properties comparable to the yarn permitted to relax. Hence, while relaxation is important to obtain optimum properties when relatively high temperature coagulating baths are employed, the step of relaxing may be omitted with low temperature coagulating bath spinning without a substantial sacrifice of properties.

EXAMPLE IX

The effect of various bath temperatures on tenacity, elongation and abrasion resistance was studied, the value for abrasion resistance being tabulated as cycles to break at a 100 gram load.

Spinning solutions were prepared in N,N-dimethylacetamide containing 18 percent polymer based on the weight of the solution. In one instance the polymer employed was the polymer blend used in Example I; in the second instance, the polymer was a copolymer of 94 weight per-

cent acrylonitrile and 6 weight percent vinyl acetate. These samples in the data which follow in Table 8 are identified as A and B, respectively. Samples of the spinning solution were extruded into filaments by the spinning technique described in Example VII. The coagulating bath was composed of 70 percent N,N-dimethylacetamide and 30 percent water and was maintained at the temperature indicated in Table 8. The filaments were collected without permitting same to relax.

Table 8

Sample	Coagulating bath temp., °C.	Stretch in second bath, times	Tenacity, gms./den.	Elongation, percent	Cycles to break 100 gm. load
1A.....	-10	5.0	4.7	12	14
2A.....	0	5.0	4.6	13	23
3A.....	10	5.0	4.3	15	47
4A.....	20	5.0	4.2	16	18
5A.....	30	5.0	4.0	16	5
6A.....	50	5.0	3.8	16	2
1B.....	-10	6.0	4.4	13	30
2B.....	0	6.0	4.4	15	27
3B.....	10	6.0	4.2	15	15
4B.....	50	6.0	3.6	18	5

The study indicates a general improvement in abrasion resistance as coagulating bath temperature is decreased. The abrasion resistance was measured by using the simple laboratory device disclosed in FIGURE 7. As seen, the device comprises a synchronous motor 80 adapted to drive wheel 81. Near the periphery of wheel 81 is a rotatably mounted peg 82. One end of the yarn 83 which is to be tested for abrasion resistance is attached to the peg as shown. The yarn is threaded around pulley 84 and around one side of a stationary horizontally disposed pin 85. To complete the threading-in the yarn is passed around pulley 86 with a weight 87 being tied to the other end of the yarn. The pin 85 is a round long rigid metal wire having a smooth surface and a diameter of about 0.006 inch. During the test the motor is operated at 60 revolutions per minute and the revolutions are counted until the yarn breaks. The denier of the yarn in each case was the same. The weight, as indicated above, in the test was 100 grams.

EXAMPLE X

The abrasion resistance when the yarn is dry and when the yarn is saturated with water was studied.

A spinning solution was prepared by dissolving a copolymer of 94 weight percent acrylonitrile and 6 weight percent vinyl acetate in N,N-dimethylacetamide in an amount that the solution contained 25 percent polymer. The solution was extruded into a short air gap and spun into acrylic filaments as described in Example VII. However, the coagulating bath had a composition of 70 percent N,N-dimethylacetamide and 30 percent water and was maintained at a temperature of -10° C. The orientation stretch was 5.5 times and the filament yarn before drying and collecting was not permitted to relax. The resulting yarn was up-twisted to a twist of 3-5 turns per inch and knitted into a narrow tape 14 ends wide on a tricot knitting machine. The resulting tape was then tested on the Stoll Abrader until failure occurred. To break the knitted tape by the use of the Stoll Abrader, 506 cycles were required when wet, and 365 cycles were required to break the tape when dry.

In an additional spinning the polymer solution was extruded through a short air gap and into a coagulating bath composed of 30 percent N,N-dimethylacetamide and 70 percent water and maintained at a temperature of -5° C. The orientation stretch was 5.5 times and the filament yarn before drying and collecting was not permitted to relax. The yarn was knitted into tricot tape as described above and tested on the Stoll Abrader. To break the wet tape required 635 cycles on the Stoll Abrader whereas dry tape broke at 414 cycles.

The present invention makes possible the production

of acrylonitrile polymer filaments that have an optimum balance of longitudinal and lateral properties and that are eminently suitable for use in the textile art. The filaments have increased elongation realized without sacrifice of tenacity, the higher elongation enabling the filament to be tougher and to be able to absorb more energy without breakage. In addition, the speed at which the filaments may be produced is notably high. Moreover, filaments that are substantially free from voids and have a high lustrous appearance can be produced. It is not necessary according to the present invention to dry the filaments under tension in order to produce a satisfactory dense fiber structure. Also, the present process lends itself readily to employment on a commercial scale without substantial modification of conventional spinning equipment. Numerous other advantages of the present invention will be apparent to those skilled in the art.

Any departure from the description herein that conforms to the present invention is intended to be included within the scope of the claims.

This application is a continuation-in-part application of copending application Serial No. 315, filed January 4, 1960, the latter application being a continuation-in-part application of application Serial No. 783,226, filed December 29, 1958 (now abandoned).

What is claimed is:

1. A process for producing a shaped article from an acrylonitrile polymer which comprises the steps of preparing a solution containing said polymer, extruding the resulting solution into a stream by forcing said solution through a shaped orifice into a gaseous evaporative medium in which only a small amount of the solvent used in the preparation of said solution is evaporated from the stream as a gas, directing said stream through said medium for a short distance and into a coagulating bath comprising a liquid that is a precipitant for the polymer and an extractant for the solvent, withdrawing the thus-formed article from said coagulating bath, stretching said article between the point of extrusion and point of withdrawal to attenuate same, passing the article through a second liquid and stretching same in the presence of said second liquid to orient the polymer molecules thereof, and then permitting the article to relax and thereby to shrink.

2. The process as defined in claim 1 wherein the acrylonitrile polymer is a copolymer containing at least 80 percent by weight acrylonitrile and up to 20 percent of another mono-olefinic monomer.

3. The process as defined in claim 1 wherein the polymer is polyacrylonitrile.

4. The process as defined in claim 2 wherein the mono-olefinic monomer is vinyl acetate.

5. The process as defined in claim 1 wherein the acrylonitrile polymer is a blend of a copolymer of 80 to 99 percent acrylonitrile and 20 to 1 percent of another mono-olefinic monomer and a copolymer of 10 to 70 percent acrylonitrile and 90 to 30 percent of a vinyl-substituted tertiary heterocyclic amine, said blend having an overall vinyl-substituted tertiary heterocyclic amine content of 2 to 10 percent, based on the weight of the blend.

6. A process for producing a filament from an acrylonitrile polymer which comprises the steps of preparing a solution containing said polymer by dissolving a copolymer of at least 80 percent by weight of acrylonitrile and up to 20 percent of another mono-olefinic monomer in a solvent therefor, extruding the resulting solution into a stream by forcing said solution through an orifice of a spinneret whose face is disposed in a gaseous evaporative medium, directing said stream through said medium and into a coagulating bath comprised of water and the solvent after the stream has passed through said medium for a short distance and after a small amount of the solvent has evaporated from the stream as a gas, withdrawing the thus-formed filament from the coagulating bath,

stretching the filament between the point of extrusion and point of withdrawal to attenuate same a considerable extent, passing the filament through a second liquid and stretching same in the presence of said second liquid to orient the polymer molecules thereof, washing said filament by passing the same through a water bath, then subjecting the filament in water to a sufficient temperature at a low tension to permit the filament to relax substantially completely and thereby to shrink at least 15 to 40 percent in a substantially tension-free condition while being dried.

7. A process for producing a filament from an acrylonitrile polymer which comprises the steps of preparing a solution containing said polymer by dissolving a copolymer of at least 80 percent by weight acrylonitrile and up to 20 percent of another mono-olefinic monomer in a solvent therefor, extruding the resulting solution into a stream by forcing said solution through an orifice in a spinneret horizontally disposed in air, directing said stream through said air and into a coagulating bath comprised of water and the solvent after the stream has passed substantially vertically downward through the air and after a small amount of solvent has evaporated from the stream as a gas, withdrawing the thus-formed filament from the coagulating bath, stretching the filament between the point of extrusion and point of withdrawal by at least three times but short of the breaking point of the filament, passing the filament through a second liquid and stretching same in the presence of said liquid to orient the polymer molecules thereof, then relaxing the filament substantially completely and to shrink same, and thereafter drying the filament in a substantially tension-free condition.

8. The process as defined in claim 7 wherein the mono-olefinic monomer is vinyl acetate.

9. The process as defined in claim 7 wherein the acrylonitrile polymer is a blend of a copolymer of 80 to 99 percent acrylonitrile and 20 to 1 percent of another mono-olefinic monomer and a copolymer of 10 to 70 percent acrylonitrile and 90 to 30 percent of a vinyl-substituted tertiary heterocyclic amine, said blend having an overall vinyl-substituted tertiary heterocyclic amine content of 2 to 10 percent, based on the weight of the blend.

10. A process for producing a filament from an acrylonitrile polymer which comprises the steps of preparing a solution containing said polymer by dissolving a copolymer of at least 80 percent by weight acrylonitrile and up to 20 percent of another mono-olefinic monomer in N,N-dimethylacetamide, extruding the resulting solu-

tion into a stream by forcing said solution through a shaped orifice in air, directing said stream through air and into a coagulating bath comprising a liquid that is a precipitant for the polymer and an extractant for N,N-dimethylacetamide after the stream has passed a short distance through the air and after only a small amount of N,N-dimethylacetamide has evaporated from the stream as a gas, withdrawing the thus-formed filament from the coagulating bath, stretching the filament between the point of extrusion and point of withdrawal to attenuate same a considerable extent, passing the filament through a second liquid and stretching same in the presence of said second liquid to orient the polymer molecules thereof, then relaxing the filament substantially completely to shrink same, and thereafter drying the filament.

11. A process for producing a filament from an acrylonitrile polymer which comprises the steps of preparing a solution containing said polymer by dissolving a copolymer of at least 80 percent by weight acrylonitrile and up to 20 percent of another mono-olefinic monomer in N,N-dimethylacetamide, extruding the resulting solution at a temperature of 20 to 180° C. into a stream by forcing said solution through an orifice in a spinneret whose face is horizontally disposed in air, directing said stream through air and into a coagulating bath composed of 100 to 20 percent non-solvent for the polymer and 0 to 80 percent N,N-dimethylacetamide after the stream has vertically passed downward through the air for a distance of 1/8 to 1 1/2 inches and after at most one percent of N,N-dimethylacetamide has evaporated from the stream as a gas, withdrawing the thus-formed filament from the coagulating bath, stretching the filament just short of its breaking point between the point of extrusion and point of withdrawal, passing the filament through a second liquid and stretching same in the presence of said second liquid to orient the polymer molecules thereof, washing the filament by contacting it with water, then subjecting the filament in water to a sufficient temperature at a low tension to permit the filament to relax substantially completely and thereby to shrink at least 15 to 40 percent, and thereafter drying the filament in a substantially tension-free condition.

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