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MANUFACTURE OF SHAPED OBJECTS OF ACRYLONITRILE
POLYMER BY WET SPINNING
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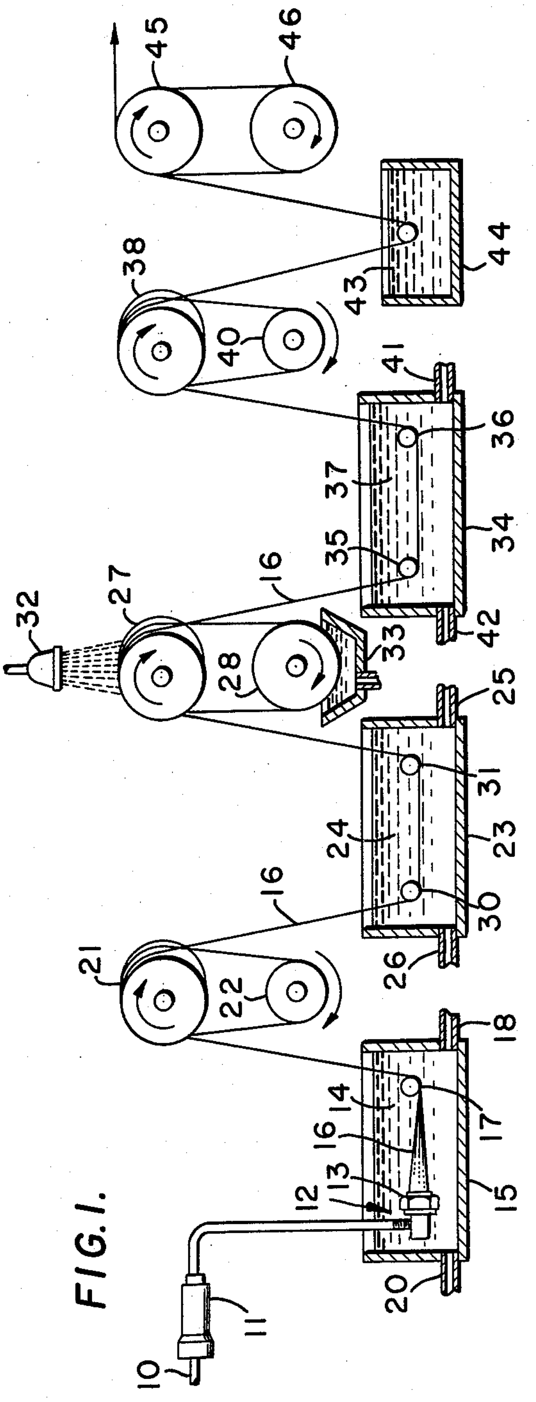

FIG. 1.

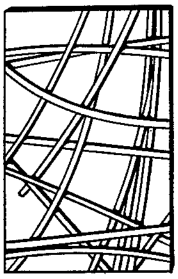

FIG. 2.

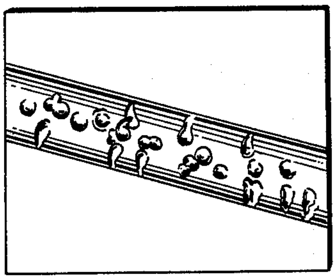

FIG. 3.

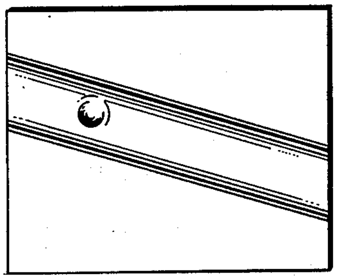

FIG. 4.

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MANUFACTURE OF SHAPED OBJECTS OF ACRYLONITRILE POLYMER BY WET SPINNING

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Original application Jan. 4, 1960, Ser. No. 314, now Patent No. 3,088,188, dated May 7, 1963. Divided and this application Nov. 14, 1961, Ser. No. 152,263
5 Claims. (Cl. 264—182)

This invention relates to improved shaped objects such as fibers, filaments, yarns and the like manufactured from acrylonitrile polymers and to an improved process of producing same. More particularly, this invention concerns such shaped objects 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 the yarn properties, the economic aspects of the technique involved, and other considerations. There are advantages and disadvantages associated with the employment of each process.

The present invention is particularly concerned with the wet spinning process. Ordinarily, in a wet spinning operation coagulation is accomplished by extruding the polymer solution into an aqueous bath sometimes containing a percentage of solvent or dissolved salt. As used herein an aqueous or water bath refers to a composition having water as one of its main components. When the solvent is extracted from the extruded stream of spinning solution in a coagulating bath during wet spinning, solidification of the polymer in filamentary form results. Normally, during coagulation 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 the bath liquid may interchange in such a manner that the resulting filaments contain 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 as compared with 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 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 filaments 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 $35–90 \times 10^{14}$ 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 are 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 an ellipsoid. 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 is regarded as an important step in the attainment of acceptable lateral physical properties in the filaments.

In accordance with one aspect of the present invention the size and frequency of the interstitial spaces are correlated with each other so as to produce filaments offering an optimum combination of longitudinal and lateral properties. Therefore, a method is provided whereby the size and frequency of the normally occurring micropores are changed substantially to produce filaments having such properties.

It is an object of this invention to provide filaments and the like of acrylonitrile polymers that possess an advantageous combination of lateral and longitudinal physical properties.

Another object is to provide a process for producing such filaments by modification of the conventional acrylonitrile polymer filament forming processes.

Other objects will become apparent from the following description of the invention and 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 a liquid medium composed of polyalkylene glycol and continuously directing the thus-formed streams of the solution for a short distance through the medium to coagulate the polymer in the form of filaments. The solvent employed is N,N-dimethylacetamide, N,N-dimethylformamide or the like. The coagulating bath preferably is composed essentially of polyalkylene glycol although during spinning the solvent concentration will build up in the bath with certain concentrations of solvent being completely tolerable. Fresh coagulating bath composition should be supplied to the coagulating bath when the solvent concentration therein becomes excessively high. The solvent is recovered from the bath by conventional methods. Up to at least 20% concentration by weight of solvent can ordinarily be tolerated in the coagulating bath without adversely affecting the filament appearance or properties. Although the coagulating bath is preferably free of water, nevertheless, water may be present in the coagulating bath in minor amounts without inducing the formation of inferior filaments. For best results, it is necessary to maintain the water concentration in the coagulating bath below 10%. When greater amounts of water are present in the coagulating bath, inferior filaments may be produced. By employing the spinning composition composed of acrylonitrile polymer dissolved in N,N-dimethylformamide, N,N-dimethylacetamide or the like and spinning such composition into a polyalkylene glycol coagulating bath, the filaments produced possess advantageous physical properties and differ in structure from other acrylonitrile polymer filaments heretofore known in the art. During their travel from the spinneret to the means used to withdraw the filaments from the coagulating bath, a stretch may be imparted to the filaments in order to attenuate same, if desired. After being removed from the coagulating bath the filaments are stretched to obtain a desired orientation according to various techniques in order to increase the tenacity, as well as otherwise to improve the physical properties of the filamentary material. Although the orientation stretch may be accomplished in various ways, it is preferred that the filaments after being withdrawn from the coagulating bath be continuously directed through a second bath and stretched therein. This second bath is preferably composed of hot water; additional solvent remaining in the coagulated filaments is removed therefrom in the second bath. Following this operation the filaments optionally may be continuously permitted to relax under low tension or in a hot liquid or hot gaseous atmosphere and/or then continuously dried. In addition to the stretching operation other treating and processing steps may be given the filaments, such as for example, washing, crimping, cutting into staple lengths. The filaments may be collected in continuous form or in staple form. Of course, various lubricants and other beneficial treating agents may be advantageously placed on the fibers during the manufacturing operation.

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 elevation view partly in section showing schematically an apparatus arrangement of a type which can be used in carrying out the process of the present invention;

FIGURE 2 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 3 is a reproduction of a photomicrograph of greater magnification of an acrylonitrile polymer filament that contains numerous voids along the length thereof; and

FIGURE 4 is a reproduction of a photomicrograph of an acrylonitrile polymer filament substantially free of voids.

The present invention provides novel filaments which differ markedly from previous wet-spun acrylonitrile polymer filaments.

The novel filaments of the present invention are of textile grade quality and are molecularly oriented. The term "textile grade quality" refers to the characteristics required of textile filaments, fibers, and the like with respect to strength, elongation, etc. in order that the same can be converted into an acceptable fabric. The filaments also are manufactured from an acrylonitrile polymer and are substantially free of porosity. To be substantially free of porosity means that the density of the filaments closely approaches or corresponds with the density of the acrylonitrile polymer from which the filaments are produced. The filaments are particularly characterized by displaying an internal fiber surface area in the range of about 150–500 square meters per gram of filament. The inner surface area of the filaments is the total surface area thereof less the geometric external surface area thereof and is measured as described more fully below. The inner surface area is therefore an indication of the number of the micropores in the reticulate filamentary structure. This area is best seen and measured by analyzing a sample of the coagulated filaments as they leave the coagulating bath. In view of the fact that the micropores in the final filamentary structure appear to be matted together, the inner surface area is actually a measure of the total area of the engaging sufraces defining collapsed submicroscopic interstitial spaces. In addition the filaments are characterized by having the interstitial spaces spaced apart at a distance of from 10 A. to at most about 300 A. as measured before the filaments are oriented and before said spaces are collapsed. That is to say, that assuming the micropores take the form of a sphere, the average diameter of the micropores before orientation and collapsing is 300 A. or less as can be measured visually under an electron microscope. Furthermore, the frequency of the interstitial spaces in the filaments is in the range of about $200–2000 \times 10^{14}$ per gram of filament which can be calculated from internal surface area and diameter data or estimated by visual analysis. The average number of interstitial spaces in the filaments is at least 40,000 per millimeter of length. The filaments may be further characterized by having at least as good and in most instances a higher resistance to abrasion when wet than dry. The novel filaments require a relatively high tension in order to be elongated. For example, a tension of at least one gram per denier has been found to be necessary to elongate a given filament 5 percent in water at 100° F. Comparably high tensions are required at other temperatures to elongate the filaments. The apparent density of the filaments leaving the coagulating bath is unusually high in that they exhibit densities of about 0.7 to almost 1.0 gram per cubic centimeter. Also at this point the filaments have an area ratio of 1.5 to 1.1. Hence, by having such a high density, ab initio, i.e. early in the production of the filaments, some of the conventional aftertreating steps that induce the formation of a denser structure, such as relaxing and annealing described above can be omitted, if desired, without substantial loss of properties.

It is known that all solids have adsorbed gases on their surfaces at all temperatures and pressures. As the temperature is lowered and the pressure is increased, the amount of gas adsorbed thereon increases. The amount of gas adsorbed can be quantitatively measured if it is large enough. Hence, methods of low temperature gas adsorption for the determination of the surface area of porous solid samples are known. The usual studies of gas adsorption are isothermal rather than isobaric because of the relative ease of maintaining constant temperature and variable pressure conditions.

The experimental determination of the isothermal volume of gas adsorbed as a function of pressure gives rise to one of five classical types of isotherms. The shapes of the isotherms are a function of the size of the adsorbing molecule. In the gaseous adsorption method the gas condenses on the surfaces of the sample whose surface area is being measured and gradually covers the surface as the pressure is increased until a monolayer of gas is adsorbed thereon. Further increases in pressure result in progressive increases in the thickness of the adsorbed layer until at a partial pressure of one, the adsorbed phase is indistinguishable from the liquid phase of the gas.

Provided that the volume of gas adsorbed at the monolayer point and the cross sectional area of the gas molecule are known, the surface area can be calculated. The advantage of using gas molecules is that the individual gas molecules are small enough to fill the micropores of the novel filaments herein, the diameter of which is only a few angstroms larger than that of the gas molecule.

The Brunauer-Emmett-Teller (BET) theory of multilayer physical adsorption described in numerous printed papers is regarded to be the most generally applicable theory explaining the isothermal adsorption of a gas on a free surface of a solid. The following expression for such isothermal adsorption is obtained by application of the BET theory:

$$V=\frac{V_{\mathrm{m}}CP}{[P_0-P]\left[I+(C-1)\frac{P}{P_0}\right]} \qquad (1)$$

wherein V is the volume of gas adsorbed at a particular pressure P, C is a constant related to the heat of adsorption, V_m is the volume of gas adsorbed for a monolayer, P_0 is the saturation pressure of the gas at the temperature of the experiment, and P/P_0 is defined as the relative pressure.

Of the terms appearing in (1) V, P, and P_0 are experimental; V_m and C are characteristic of the system under study. By rearrangement, Equation 1 can be put in the form:

$$\frac{P}{V(P-P_0)}=\frac{1}{V_{\mathrm{m}}C}+\frac{C-1}{V_{\mathrm{m}}C}\,\frac{P}{P_0} \qquad (2)$$

so that a plot of

$$\frac{P}{V(P-P_0)}\text{ vs. }\frac{P}{P_0}$$

should give a straight line with a slope (S) of

$$\frac{C-1}{V_{\mathrm{m}}C}$$

and an intercept (I) of

$$\frac{1}{V_{\mathrm{m}}C}$$

These two equations can be solved to give

$$V_{\mathrm{m}}=\frac{1}{S+1}$$

and

$$C=\frac{S}{I}+1$$

For most isotherms a linear plot is obtained only for the region of 0.05 to 0.40 relative pressure units. This range is more than sufficient for a satisfactory determination of V_m.

The cross sectional area of the gas molecule can be calculated from:

$$A=4\times 0.355\left[\frac{M}{4}\sqrt{2}Nd1\right]2/3 \qquad (3)$$

In this Equation M is the weight of the molecule, N is Avagadro's number and *d* is the liquid density. By knowing V_m and the cross sectional area of the adsorbed molecule, the surface area of the sample easily can be calculated.

If an isotherm is started at zero pressure, continued to a relative pressure of one and then desorbed, that is starting at a relative pressure of one and working down toward zero pressure, a hysteresis is often found. The presence of the hysteresis loop is interpreted as showing that the sample has a porous structure. From various analyses of these loops, the size and distribution of the micropores can be obtained.

In brief, the procedure for determining the surface area per unit weight of filament is to determine volumetrically the amount of gas adsorbed on the sample as a function of pressure at the temperature the gas liquifies. The amount of gas required to form a monolayer is calculated by the use of the Brunauer-Emmett-Teller equation. Then, by knowing the cross sectional area of the molecule of the gas, one can calculate the surface area of the filament. The internal surface area of acrylonitrile polymer filaments has been found to be considerable. The ratio of the total surface area to the geometric external area is roughly 500 which indicates a relatively large internal porosity.

The density (apparent) of the filaments either as finished filaments or as they leave the coagulating bath can be determined by mercury displacement. The density data indicate the total porosity of the filaments, including the porosity attributable to the presence of voids and micropores. This void volume data, together with the surface area data and diameter data of the micropores, can be used to calculate the size and frequency of the micropores. At least two techniques are known for determining the density of a filament, these being a pycnometer procedure and a buoyancy procedure. The pycnometer method involves determining the volume of mercury excluded from a calibrated pycnometer by a filament sample. The second procedure comprises determining the loss in weight of a calibrated platinum bob in mercury with and without a filament sample. From the data obtained one may calculate conveniently the density of the sample.

The term "area ratio" refers to the ratio of the measured cross-sectional area of the individual filaments as spun to the cross-sectional area of those filaments as calculated from the denier of the filaments and the known density of the polymer. The filaments prepared in accordance with the present invention possess an unusually low area ratio when the filaments leave the coagulation bath. It is thought that such initially low area ratio is related to the final improved properties of the filaments.

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 acrylonitrille 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 methods 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 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:

(—O—O—)

A wide variation in the quantity of peroxy compounds 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 outset of the reaction, or it may be added continuously or in increments throughout 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:

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

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 dissolved in N,N-dimethylacetamide, N,N-dimethylformamide, or the like 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 pump the solution through the filter **11** and to meter same to the spinneret assembly **12**. This assembly includes a spinneret **13** and is suitably disposed below the upper surface of the coagulating liquid **14** composed primarily of polyalkylene glycol and 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 **13** to form a filament or bundle of filaments **16**. The extruded streams of polymer are directed through the liquid **14** for a predetermined and sufficient distance to cause the solution to coagulate as desired. A guide **17** may be employed to define the path taken by the filaments in bath **15**. Fresh liquid **14** is supplied to trough **15** through pipe **18** (which may be polyalkylene glycol or polyalkylene glycol containing a desirable quantity of solvent) and is withdrawn therefrom through pipe **20**.

The coagulated filaments are withdrawn by employment of a positively driven roller **21** 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. After passing around roller **21** and an idler roll **22**, the filaments are directed into a second spinning trough **23** containing a liquid **24**. Fresh liquid is supplied to trough **23** through pipe **25** and is withdrawn through pipe **26**. 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 **23** and being directed around a set of positively driven rolls identified by numerals **27** and **28** are passed under guides **30** and **31**. The peripheral speed of rollers **27** and **28** can be adjusted so that a predetermined orientation stretch will be imparted to the filaments **16** during their travel in second trough **23**.

To roller **27** a washing liquid such as hot water is supplied from a spray or shower head **32**, the liquid being collected in a container or tray **33**. 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 **27** and **28**, the filaments are directed through a liquid in a third trough **34** by being passed under guides **35** and **36**. The liquid **37** in this trough is normally water at an elevated temperature. The filaments are withdrawn therefrom by means of a driven roller **38** and associated idle roller **40** operated at a peripheral speed less than that of the peripheral speed of rollers **27** and **28** so that the filaments are permitted to relax substantially completely and thereby to shrink during their travel in trough **34**. Fresh water is supplied to trough **34** through an inlet pipe **41** and is withdrawn through an outlet pipe **42**. 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 **43** contained in a vessel **44** and composed of a lubricant or like beneficial treating agent. The filaments after being withdrawn from liquid **43** are dried. As illustrated in FIGURE 1 the filaments are continuously directed around a pair of driven drying drums **45** and **46** 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.

As can be seen, the acrylonitrile polymer selected is dissolved in N,N-dimethylacetamide, N,N-dimethylformamide or the like to form a spinning solution. This solution is extruded through a spinneret into a coagulating bath composed of polyalkylene glycol.

As pointed out above, the improvement herein is obtained by spinning the polymer solution into a bath composed of polyalkylene glycol. The term "polyalkylene glycol" as used throughout the specification and claims refers to polyethers which may be derived from alkylene oxides or glycols or from other heterocyclic ethers such as dioxolane, and which may be represented by the formula $HO(RO)_nH$ in which R stands for an alkylene radical such as methylene, ethylene, propylene, etc., and n is an integer of at least four. It will be appreciated that the polyglycol may contain inert substituents; for example, methoxypolyethylene glycol may be employed. Not all of the alkylene radicals present need be the same. Glycols containing a mixture of radicals such as in block polymers and copolymers are also useful. Similarly, mixtures of polyglycols of differing compositions or molecular weights can be employed. The glycols which are useful in the process of this invention have molecular weights of at least 200 and may have molecular weights as high as 6000. The preferred glycols are the polyethylene glycols which preferably have molecular weights of 600–2000. These glycols as just defined are either viscous liquids or waxy solids at room temperature. However, they become less viscous at higher temperatures and permit spinning at these temperatures. Although wide variations in the spin bath temperatures are permitted, it is preferred that the temperatures be of the order of 50 to 150° C. depending on which glycol is employed.

FIGURE 2 is a drawing prepared from a photomicrograph. This illustrates the normal appearance of acrylonitrile polymer filaments heretofore known at a magnification of 100 times. At this magnification no visible differences between the filaments of the present invention and the known filament are noticeable since the voids or cavities on the surfaces of the filaments are not apparent.

FIGURE 3 is a drawing prepared from a photomicrograph showing a view of part of a filament containing voids or cavities. Enclosed voids of 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 subdued luster to the filament.

FIGURE 4 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 or colored products. The marked differences of the novel filament herein and those heretofore known become apparent when the 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 solvent selected from the group consisting of N,N-dimethylacetamide, N,N-dimethylformamide, or the like. The percentage of polymer based on the weight of the solution depends upon the particular polymer or solvent employed as well as the temperature at which the polymer is spun. It is desirable to employ a solution containing a high percentage of polymer for obvious reasons. Ordinarily a solution containing at least 10 percent acrylonitrile is desirable. The spinning solution may be maintained prior to and at extrusion at temperatures from about 20 to 150° C.

Although it is not fully understood how the coagulating bath contributes to the formation of the improved fiber structure, it is believed that the relatively large size of the polyalkylene glycol molecules is such that inflow thereof into the coagulating filaments is minimized whereby denser and more compact filaments are obtained.

Filaments may be given a travel in the coagulating bath, for example, from 2 to 24 inches or more by the employment of a suitably spaced guide and withdrawal rolls as illustrated in FIGURE 1. Between the spinneret and withdrawal rolls, the filaments as indicated above may be subjected to a stretching operation to obtain a desired attenuation thereof, if desired.

A second bath is employed following the coagulating bath wherein the filaments are given a stretch in order to increase the strength as well as otherwise to improve the physical properties of the filaments. This improvement results from an 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 second bath is preferably between 50° and 100° C., the highest feasible temperature being preferred. Draw ratios up to 10 or higher may be employed; the amount of stretch applied depends on the properties desired for the yarn. Preferred draw ratios lie 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 equivalent 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.

Next the filaments may be permitted to relax, if desired. 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 obtained 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 in accordance with the present invention although in some cases it is to be recommended. Next, the filaments are dried in a conventional manner. This may be done either under tension or under no tension.

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 having a luster greater than normal wet-spun filaments dried under tension. Moreover, the present process enables one to produce filaments of very fine deniers. Owing to the high jet stretch permitted by the process as pointed out above, filaments having individual filaments as low as 0.25 can be successfully spun.

The following examples in which parts and percentages are given by weight unless otherwise indicated illustrate preferred methods of preparing filaments in accordance with the principles of this invention. The invention is not to be limited by the details set forth in the following examples.

EXAMPLE I

A 20 percent solution of a copolymer of 95 percent acrylonitrile and 5 percent vinyl acetate was prepared by intimately mixing the copolymer in powdered form with the solvent, N,N-dimethylacetamide, until a clear liquid resulted. The resulting solution was cooled to a temperature of 50° C., filtered, and extruded through a spinneret submerged in a coagulating bath composed of polyethylene glycol having an average molecular weight of 1000. The filaments so formed were withdrawn from the coagulating bath after a travel therein of 20 inches and thereafter directed through a bath of boiling water where a stretch of 6.0 times was imparted to the filaments. Next, the filaments were dried by passing same around rotating drying cans maintained at a temperature of 125° C. Samples of the filaments were taken at the point where they emerged from the coagulating bath and were centrifuged for 60 seconds to remove excess surface liquids. Analyses for several typical samples are presented below in Table 1. Additional spinnings were conducted using polyethylene glycol having a molecular weight of 600 as the coagulating liquid. This lower molecular weight glycol was employed in the presence of varying amounts of the dimethylacetamide solvent. Also, filaments were produced using an aqueous coagulating bath having the composition of 55 percent N,N-dimethylacetamide and 45 percent water. The results of these spinnings are also given in Table 1.

Table 1

Coagulating Bath Composition	Percent Polymer in Sample	Percent Solvent in Sample	Percent Glycol or water in Sample	Percent Original Solvent Extracted
Polyethylene glycol (M.W.=1000)	70	22	8	90
Polyethylene glycol (M.W.=600)	69	23	8	89
95% polyethylene glycol (M.W.=600)+5% Solvent	61	30	9	83
90% polyethylene glycol (M.W.=600)+10% Solvent	60	25	15	86
80% polyethylene glycol (M.W.=600)+20% Solvent	60	23	17	87
55% Solvent +45% Water	35	35	30	67

The higher polymer content of the filaments spun using the polymeric glycol baths of the present invention is evident; and it can be seen from the above data that the solvent and coagulating liquid contents thereof accordingly are lower. Furthermore, there seems to be very little difference between the solvent content of the filaments spun into a bath of 100% glycol as compared to the solvent content of those filaments spun into baths containing up to 20 percent solvent; and no substantial difference is seen in regard to the solvent content when the molecular weight of the polyethylene is varied. The fact that no significant differences in coagulation rates are indicated when the glycol baths are diluted with 20 percent solvent shows that the solvent level of the coagulating bath can be maintained at a level up to at least 20 percent.

Results comparable to those above were obtained by spinning a 20 percent solution of a copolymer blend composed of 85–90 percent of a copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and a sufficient amount of a copolymer of 50 percent acrylonitrile and 50 percent 2-methyl-5-vinylpyridine to give a total vinylpyridine content by weight in the blend of about 6 percent.

EXAMPLE II

To determine the effect of the molecular weight of the polymeric glycols and of the coagulating bath temperatures on the jet stretch and coagulation of the acrylonitrile polymer filaments, a series of spinnings using various coagulating bath compositions and coagulating bath temperatures were conducted. The copolymer of 95 percent acrylonitrile and 5 percent vinyl acetate was dissolved in N,N-dimethylacetamide to form an 18 percent solution. The solution was extruded through a spinneret having orifices with a diameter of 0.0035 inch.

The effect of increasing bath temperatures and molecular weight of the glycol on the jet stretch can be seen in Table 2 in which the results of using various glycol-containing baths are compared with the results when baths of water and a solvent/water mixture are used.

Table 2

Bath Composition	Bath Temp., ° C.	Yarn appearance	Max. Jet Stretch
Water	40	Opaque	1.8
Do	60	do	2.5
Do	80	do	3.3
Ethylene glycol	30	Clear	1.5
Do	60	Cloudy	2.5
Do	80	Opaque	3.3
Do	100	do	5.7
Do	120	do	11.5
55/45 solvent/water	40	do	1.7
Do	60	do	2.5
Do	80	do	3.7
Do	100	do	4.9
Polyethylene glycol 600	40	Clear	1.5
Do	60	do	3.0
Do	80	Slightly cloudy	4.0
Do	100	Cloudy	6.0
Do	120	Opaque	15.0
Polyethylene glycol 1000	60	Clear	3.0
Do	80	do	5.0
Do	100	do	8.0
Do	120	Cloudy	15.0

There appears to be a general increase in maximum jet stretch as a function of temperature. For low molecular weight baths (water, solvent/water, and ethylene glycol), temperature and not bath composition appears to be the important variable whereas in the polyethylene glycol-containing bath, the effect of bath composition is additive with the thermal effect to give higher stretches with increasing molecular weight at a given temperature.

An opaque appearance of the yarn indicates an internal spongy structure whereas a clear appearance indicates a denser, more homogeneous structure.

Cross sections of the filament were cut and observed under an optical phase microscope to determine the influence thereon by both the temperature and molecular weight of the polyethylene glycol used in the coagulating bath. For a given bath temperature there is a progressive improvement in the uniformity and surface smoothness of the filaments as the molecular weight of the bath is increased. There is a less pronounced, but still detectable, trend to greater irregularity with increases in temperature for a given glycol bath composition. The typical cross section of yarn spun into the polyethylene glycol bath is somewhat in the shape of a horseshoe, and the filament is suggestive of a flat ribbon which has been rolled lengthwise until its edges nearly meet.

It was found that the afterstretch is less affected by the bath compositoin than is the jet stretch. The maximum afterstretch obtainable for the polymer solutions spun in the polymeric glycol bath was in the range of from 7.5 to 10 times and on the average, 8.5 times. The same polymer solution spun in solvent/water mixtures generally gave a maximum afterstretch of less than 7.0 times regardless of bath temperature or solvent-water ratio. This shows that the filamentary structures obtained by the use of the glycol bath are capable of accepting higher stretches than can normally be obtained by employing aqueous coagulating baths.

EXAMPLE III

A 20 percent solution of the copolymer of 95 percent acrylonitrile and 5 percent vinyl acetate in N,N-dimethylacetamide was prepared and extruded into coagulating baths composed of polyethylene glycol of 1000 and 4000 molecular weights to determine the effect of the baths on spinning speeds and denier range.

At 95° C. spinning speeds of up to 500 ft./min. were easily obtained. By taking advantage of the wide latitude in jet stretch afforded by the polymeric glycol baths, it was possible to spin deniers from as high as 8 denier per filament down to 0.5 denier per filament and less with the same spinneret. Deniers as low as 0.25 denier per filament were produced from a spinneret having orifices with diameters of 0.002 inch at spinning speeds of 200–250 ft./min. These spinnings caused no unusual spinning problems. With an aqueous bath it was not possible to spin filaments having an individual denier of less than 1.5 under like conditions.

EXAMPLE IV

The acrylonitrile polymer solution of Example III was spun into a coagulating bath composed of equal parts of mixed polyethylene glycols having molecular weights of 400 and 1000. A portion of the resulting filaments were passed through a bath containing a yarn lubricant and an anti-static agent; filaments which had not been so treated compared favorably therewith. It was found that even without the application of finish the filaments have a soft, pleasant hand and required only the application of anti-static finish to give satisfactory processability into fabric.

EXAMPLE V

A series of spinnings were conducted in which a 20 percent solution of the copolymer of 95 percent acrylonitrile and 5 percent vinyl acetate in N,N-dimethylacetamide was extruded in various coagulating baths as indicated below in Table 3. The values of tenacity and elongation for various fibers spun in the glycol baths, together with data of comparative controls spun in aqueous baths, are also given in the table.

Table 3

Bath Composition	Bath Temp., ° C.,	Stretch, Times	Filament, Dernier	Tenacity, g./den.	Elongation, Percent
55% solvent +45% water	55	5.0	2.60	3.08	16
Polyethylene glycol (M.W.=200)	100	5.0	2.62	2.72	23
Polyethylene glycol (M.W.=400)	100	5.0	2.55	3.69	24
Polyethylene glycol (M.W.=600)	100	5.0	2.43	3.76	24
Polyethylene glycol (M.W.=1000)	100	5.0	2.55	3.84	23
Do	100	6.0	2.68	4.07	19
Do	100	8.0	2.84	4.48	17
55% solvent+45% water	50	4.4	3.00	2.67	17
Polyethylene glycol (M.W.=600)	95	2.0	2.82	1.98	42
Do	95	3.0	2.88	2.80	32
Do	95	4.0	2.90	3.08	26
Do	95	5.0	2.94	3.97	23

As might be expected, the tenacity of the filaments spun into the polymeric glycol baths depends upon the degree of orientation stretch applied to the fiber. Similarly, elongation shows a characteristic inverse relationship to the amount of stretch.

It can be seen from the above data that for a given stretch ratio, filaments spun into the polymeric glycol baths generally show higher values for both elongation and tenacity than the aqueous controls. It is also apparent that the filaments spun into the polymeric glycol baths have a better balance of elongation and tenacity than do the controls.

EXAMPLE VI

The acrylonitrile polymer solution of Example III was spun into a coagulating bath composed of polyethylene glycol having an average molecular weight of 4000. The resulting filaments were processed as in Example I with an afterstretch of 7.0 times being imparted to the filaments. The finished filaments had deniers ranging from 4–9 with tenacities of 2.7–3.2 g./den. and elongations of 17–27 percent.

EXAMPLE VII

A homopolymer of acrylonitrile was dissolved in N,N-dimethylformamide to form an 18 percent solution of the polymer. The resulting solution was spun into a bath containing polyethylene glycol having an average molecular weight of 1000. Samples were collected with a variety of afterstretches and had physical properties as given in Table 4.

Table 4

No.	Stretch, Times	Filament, Denier	Tenacity, g./den.	Elongation, Percent
1	3.5	3.0	2.6	32
2	4.5	3.2	3.3	26
3	5.5	3.2	4.3	23
4	6.5	3.7	4.4	21

EXAMPLE VIII

The acrylonitrile polymer solution of Example III was extruded in a series of coagulating baths composed of polypropylene glycol of varying molecular weight. The results of these spinnings are summarized in Table 5 below.

Table 5

No.	Molecular Weight of Bath	Stretch, Times	Filament, Denier	Tenacity, g./den.	Elongation, Percent
1	1,025	9.3	3.0	3.0	28
2	425	7.5	2.5	4.5	19
3	425	4.5	2.5	3.8	25
4	425	5.5	2.5	4.2	23
5	425	6.5	2.5	4.5	20

EXAMPLE IX

The acrylonitrile polymer solution of Example III was spun into a coagulating bath at 90° C. containing methoxypolyethylene glycol having an average molecular weight of 750. The resulting filaments were aftertreated as in Example I with afterstretches of 4–6 times. The finished filaments had tenacities of 3–4 g./den. and elongations of 20–30 percent.

EXAMPLE X

Eighty-eight parts of a copolymer of 95 percent acrylonitrile and 5 percent vinyl acetate were blended with 12 parts of polyvinylpyrrolidone with the resulting blend being dissolved in N,N-dimethylacetamide to form a 20 percent solution. This solution was extruded into a bath composed of polyethylene glycol having an average molecular weight of 1000. The resulting filaments were processed in the manner described in Example I with an afterstretch of 6 times being imparted to the filaments. The finished filaments contained in excess of 10 percent polyvinylpyrrolidone and had improved dye takeup with most dyestuffs. The filaments had a tenacity of 3.9 g./den. and an elongation of 21 percent.

EXAMPLE XI

A spinning solution was prepared by dissolving a copolymer of 94 weight percent acrylonitrile and 6 weight percent of vinyl acetate in N,N-dimethylacetamide. Samples of the spinning solution at 30° C. were extruded through a spinneret into a coagulating bath consisting essentially of polyethylene glycol having a molecular weight of 1000 and maintained at 93° C. The filaments were withdrawn from the coagulating bath after the same were directed therethrough for a distance of 24 inches. At this point it was found that the filaments were composed of 42.2 percent acrylonitrile polymer, 9.2 percent N,N-dimethylacetamide, and 48.6 percent of polyethylene glycol. The filaments were then passed through a water wash bath. It was found that the filaments were composed of 47.6 percent acrylonitrile polymer, 2.1 percent N,N-dimethylacetamide, and 50.3 percent water.

For comparison purposes, the same acrylonitrile polymer spinning solution was likewise extruded into an aqueous coagulating bath composed of 55 percent N,N-dimethylacetamide and 45 percent water at 50° C. The filaments removed from the coagulating bath in this instance were composed of 28.7 percent acrylonitrile polymer, 40.0 percent N,N-dimethylacetamide and 31.3 percent water. The filaments were then passed through a water wash bath as above. It was found that the filaments were composed of 26.9 percent acrylonitrile polymer, 0.0+ percent N,N-dimethylacetamide, and 73.1 percent water.

These data indicate that in accordance with the present invention the filaments immediately after coagulation contain a higher percentage of polymer and accordingly are more dense. Moreover, it is manifest that drying of the washed filaments produced by the present invention could readily be accomplished and would require less heat and drying time, as compared with aqueous spun controls. This is due to the lower moisture content in and the initially denser structure of the filaments.

EXAMPLES XII

The improvement of the present invention in regard to the abrasion resistance of the filaments when converted into fabric was studied.

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 with (B) a copolymer of 50 percent acrylonitrile and 50 percent 2-methyl-5-vinylpyridine, said blend containing 6 percent vinylpyridine based on the weight of the blend. The polymer blend had a specific viscosity of 0.25 and the spinning solution contained 18 percent solids. The solution was extruded at 50° C. through a spinneret containing 1000 holes, each being 0.003 inch in diameter, into a coagulating bath composed essentially of polyethylene glycol having a molecular weight of 1000. The temperature of the coagulating bath was maintained at 100° C. The bundle of filaments formed was led through the bath for a distance of 36 inches and then was removed therefrom at a rate of 40 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 1.1 between the spinneret submerged in the coagulating bath 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 water. After they had traveled a distance of 12 inches in the second bath, the filaments were withdrawn at a rate of 140 feet per minute so that a stretch of approximately 3.5 times was imparted to the filaments. The filaments were then passed around a pair of spaced apart rollers 30 to 40 times with a total length of 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 rolls to wash same. Following the washing operation, the filaments were dried by being passed around a heated drum assembly.

In like manner additional filaments were produced under the same conditions as just described except in this instance the filaments were given an orientation stretch of 6.5 times and before drying were directed into a relaxation bath composed of water at 100° C. with the filaments being withdrawn therefrom at a rate such that the filaments are permitted to shrink 10 percent in length.

For additional comparison purposes the polymer spinning solution was spun into an aqueous coagulating bath having the composition of 55 percent N,N-dimethylacetamide (DMA) and 45 percent water. This bath was maintained at 55° C. The filaments were given an orientation stretch of 4.5 times and subjected to an annealing operation as above described.

In each case the resulting filaments were uptwisted 3–5 turns per inch and knitted into a narrow tape 14 ends wide on a tricot knitting machine. The resulting tapes were then tested on a Stoll abrader until failure occurred. The abrasion resistances are tabulated below in Table 6.

Table 6

Bath Comp.	Percent Relaxation	Cycles to Break	
		Wet	Dry
PEG 1000	0	892	620
PEG 1000	10	1,122	766
DMA+H_2O		316	358

This study above indicates that one obtains a general improvement in the abrasion resistance when the acrylonitrile polymer filaments are produced in accordance with the present invention. Moreover, the resistance to abrasion of the filaments when wet is somewhat better than that of dry filaments. However, it is to be noted that filaments produced using a conventional aqueous bath had a greater resistance to abrasion when dry than when wet.

EXAMPLE XIII

Samples of the spinning solution described above in Example XII were spun into a coagulating bath at 95° C. Baths composed of polyethylene glycols of molecular weights of 1000 and 400 were used. In each instance the filaments were withdrawn from the coagulating bath after the same were directed therethrough for a distance of 24 inches. The rate of withdrawal was established in relation to the rate of extrusion so that the filaments were subjected to a draw ratio of 0.8. The filaments were then washed, collected, frozen, and dried under vacuum without additional aftertreatment. In Table 7 below fiber surface area data for the filaments so formed are given.

Table 7

Bath Comp.	Inner Fiber Surface Area, m.^{2}/g.	Fiber Density, gm./cc.	Area Ratio	Pore Diameter, A.	Pore Frequency[1]
PEG 1000	180	0.81	1.48	120	$3,650\times10^{14}$
PEG 400	141	0.62	1.89	315	440×10^{14}

[1] Number of pores per gram of fiber.

For comparison purposes the same spinning solution was spun into an aqueous coagulating bath consisting of approximately 50 percent water and 50 percent N,N-dimethylacetamide. The inner surface area of these filaments produced in accordance with the conventional wet spinning method was 100 m.^{2}/gram. Other comparative data were as follows: Fiber density—0.49 gm./cc.; area ratio—2.42; pore diameter—340 A. and pore frequency—62×10^{14}.

EXAMPLE XIV

In accordance with a known method the polymer blend described in Example XII was dissolved in ethylene carbonate. The resulting solution contained 19 percent solids. The solution was extruded at 100° C. through a spinneret containing 100 holes, each being 0.0035 inch in diameter, and into a bath containing polyethylene glycol of 1000 molecular weight and maintained at 100° C. The filaments thus formed were washed free of solvent, collected, frozen, and dried under vacuum without additional aftertreatment. The fiber inner surface area was 12.5 m.^{2}/gram. Other comparative data were as follows: Fiber density—0.6 gm./cc.; area ratio—1.95; pore diameter—4000 A. and pore frequency—2.5×10^{13}. Finished filaments gave a very dull appearance.

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, higher elongation enabling the filaments to be tougher and to be able to adsorb more energy without breakage. Moreover, the filaments are substantially free from voids and have a highly lustrous appearance. By proper selection of stretch ratios, it is possible according to the present invention to produce a filament equivalent in elongation-tenacity balance to the normally aqueous spun filaments that have been annealed. Consequently by using the high molecular weight glycol bath of the present invention, the annealing step may be eliminated without sacrificing the physical properties of the yarn in regard to balance of elongation and tenacity. It is not necessary according to the present invention to dry the filaments under tension in order to produce a satisfactorily dense fiber structure. Also the present process lends itself readily to employment on a commercial scale without substantial modification of conventional equipment. The surface of filaments spun into a high molecular weight polyalkylene glycol bath of the present invention is relatively smooth and substantially free from the surface pits which characterize filaments spun in aqueous baths. The smooth surface of the filaments results in a very high gloss. The addition of a delustrant, such as titanium dioxide, opaques the filaments but does not mask the surface gloss. Boiling or annealing usually has little affect on the appearance of the filaments.

Drying of the filaments produced for the present invention is readily accomplished and requires little heat. Of importance is the fact that the filaments show less tendency to fibrillate as determined by standard fibrillation tests and as compared with aqueous spun filaments. Without being annealed filaments produced in accordance with the present invention have resistances to abrasion comparable to or greater than that of aqueous spun filaments that have been annealed. 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 division of copending application Serial No. 314, filed January 4, 1960, (now U.S. Patent 3,088,188) the latter application being a continuation-in-part of application Serial No. 755,372, filed August 18, 1958 (now abandoned).

What is claimed is:

1. A process for producing a filament from an acrylonitrile polymer which comprises dissolving said polymer in a solvent selected from the group consisting of N,N-dimethylacetamide and N,N-dimethylformamide, extruding the resulting solution through a shaped orifice immersed in a coagulating bath consisting essentially of polyalkylene

glycol having a molecular weight of 200–6000, less than 10 percent water, and up to 20 percent of the selected solvent, thereby precipitating said polymer from its solution in the form of a filament, withdrawing said filament from said coagulating bath, stretching said filament to a substantial extent, and drying said filament, whereby a dense filament having a smooth surface is formed.

2. A process for producing a filament from an acrylonitrile polymer which comprises the steps of preparing a spinning solution containing said polymer by dissolving said polymer into a solvent selected from the group consisting of N,N-dimethylacetamide and N,N-dimethylformamide, extruding the resulting solution into a stream by forcing said solution through an orifice of a spinneret disposed in a coagulating bath composed essentially of polyalkylene glycol having a molecular weight of 200–6000, less than 10 percent water and up to 20 percent of the selected solvent, stretching the thus-formed filament between the face of the spinneret and the point of withdrawal from the coagulating bath to attenuate same, withdrawing the thus-formed filament from the coagulating bath, passing the filament through a hot water bath and stretching same in the presence of the hot water to orient

molecules thereof, washing said filament by contacting it with water, and thereafter drying and collecting the filament.

3. The process of claim 2 wherein the solvent is N,N-dimethylacetamide.

4. The process of claim 2 wherein the solvent is N,N-dimethylformamide.

5. The process of claim 2 wherein the polyalkylene glycol in the coagulating bath is polyethylene glycol.

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