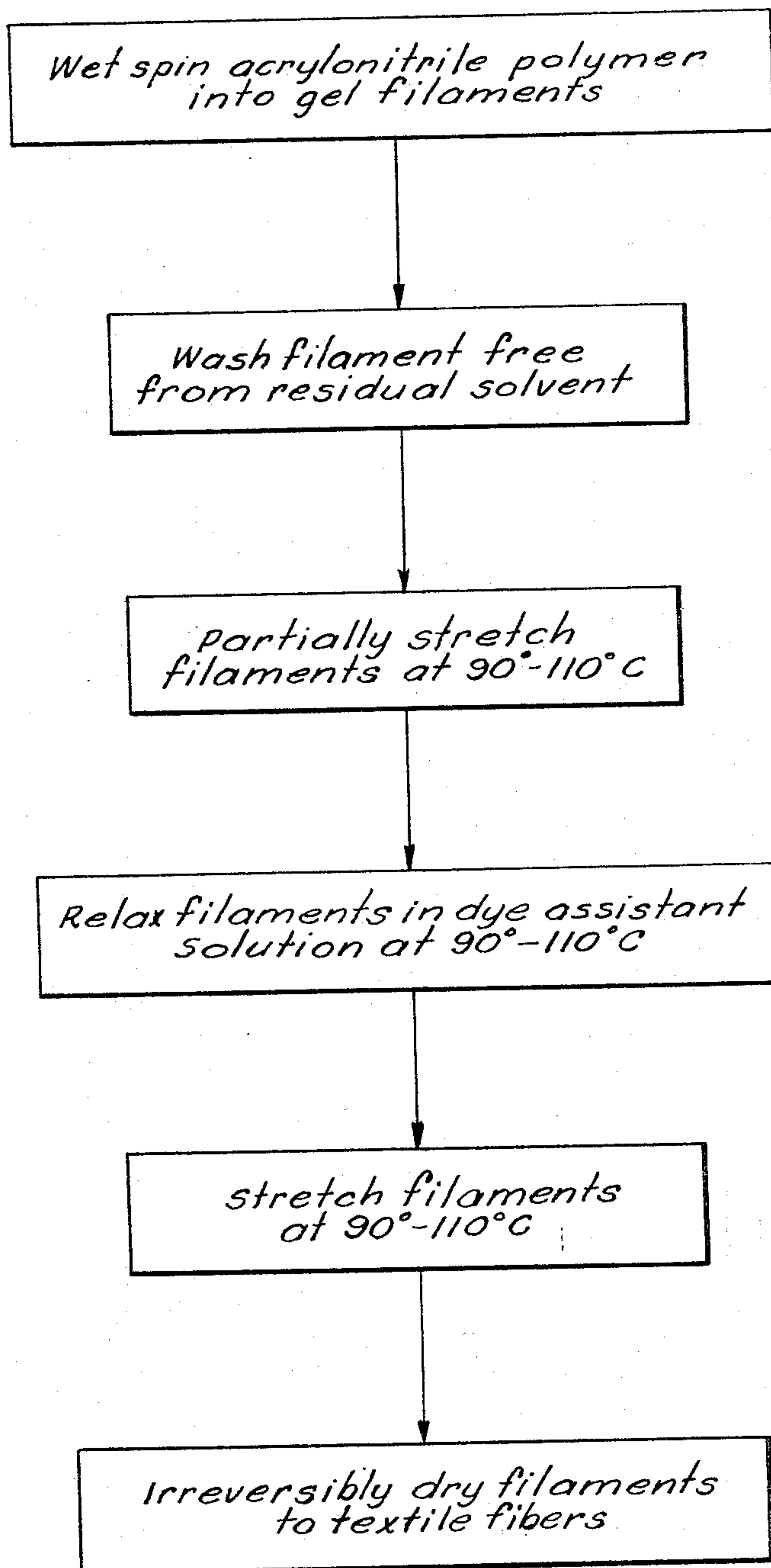


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METHOD FOR IMPREGNATING ACRYLONITRILE POLYMER  
FIBERS TO IMPROVE DYEABILITY  
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**METHOD FOR IMPREGNATING ACRYLONITRILE**  
**POLYMER FIBERS TO IMPROVE DYEABILITY**  
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This invention contributes to the synthetic fiber art and has particular reference to enhancing the dyeability of synthetic fibers. Particularly, it relates to a method for impregnating wet-spun acrylonitrile polymer fibers while they are in a freshly formed gel condition with a dye assistant to improve the dyeability of the fiber.

Synthetic fibers, including acrylonitrile polymer fibers, have always been difficultly dyeable in contrast to the commonly available natural fibers, e.g., cotton and wool. Several methods have been pursued in attempting to solve the inherent and attendant difficulties encountered with acrylonitrile polymer or acrylic fiber dyeability. Among these have been the development of dyestuffs or particular dyeing procedures specifically designed for or especially suited to the polymer structure. Other schemes include building into the polymer structure sites which are receptive to dyestuffs such as might be accomplished by certain additaments that are copolymerized with acrylonitrile to fiber forming polymers, or by incorporating in the acrylonitrile polymer a dye receptive polymer by blending the two polymers prior to extruding or spinning the polymer composition to form the filament or fiber.

Although the foregoing means have frequently led to better dyed or dyeable fibers, there are certain attendant disadvantages associated with each. For instance, when dyestuffs are especially synthesized for polyacrylonitrile, the dyestuffs are apt to be quite expensive, and additionally, the range of shades and colors is usually limited or lacking in desirable fastness properties. Or, particularly when dye receptive sites are built into the polymer chain through copolymerization of another monomer with acrylonitrile there is most always observed a sacrificial loss in some of the inherent properties so desirable in the polyacrylonitrile backbone, such as tensile strength. Blending a dye-receptive polymer with the polyacrylonitrile prior to spinning presents mixing problems to attain uniformity and may require rather large energy requirements. Another method sometimes employed, is to add color, generally in the form of a pigment, into the spinning solution, frequently called spinning dope. This method, however, has the inherent disadvantage of contaminating the polymer handling and conveying systems with colored bodies which must be dealt with when plain white fibers are subsequently to be manufactured in the same equipment.

One means that has been rather successfully employed to overcome some of the above-indicated disadvantages when acrylonitrile polymers are wet-spun is to impregnate the freshly spun fiber while it is in a gel condition with a dye receptive additive, such as a polymer (which will hereinafter be referred to as dye assistant). One difficulty that has been observed with this method is that frequently the running length of fibers are not uniformly impregnated along the length of the fibers, and additionally, the dye assistant does not penetrate the gel structure but remains only on the periphery of the fiber surface or at best only slightly penetrates the gel structure. This results in ring dyeing of the fiber, i.e., dyeing on the surface. This in itself is not always bad since often times good coloration is achieved when the fiber is dyed. The deficiencies of the method ordinarily make themselves known when the dyed fibers are subjected to abraid-

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ing forces, such as those induced during the wearing by an individual of a garment made of the fibers, or those induced during some of the textile processing treatments. The result is that the fibers tend to objectionably whiten or become lighter in shade, particularly at wear points. This may be a result of the color lying on the surface of the fiber being worn off and exposing the undyed portions of the fiber underneath, or, sometimes, it may be a result of the dye assistant build-up on the fiber surface weakening, as for instance by tending to plasticize the acrylonitrile polymer, such that actual fibrils may peel back from the surface. This has the dual effect of exposing the undyed portions of the fiber and of the fibrils dispersing the incident light so that a frosted appearance is presented. A secondary drawback of any surface build-up of the dye assistant on the gel fiber surface is that oftentimes the adjacent fibers will fuse during the drying of the fibers causing objectionable large fibers or "sticks" to form.

Accordingly, it is the chief aim and primary object of the present invention to provide an improved and highly efficient method for incorporating a dye assistant in acrylonitrile polymer gel fibers whereby the dye assistant is uniformly and deeply and frequently thoroughly penetrated throughout the cross-section of the fiber and uniformly distributed along the fiber length so that the fibers in an irreversibly dried form can be dyed to excellent shades of coloration having good resistance to whitening and fibrillation.

In accordance with the present invention, a method is provided for incorporating a dye assistant in acrylonitrile polymer gel or aquagel filaments comprising spinning a solution of a polymer of an ethylenically unsaturated monomeric material containing at least about 80 weight percent polymerized acrylonitrile into an aqueous coagulating bath to form acrylonitrile polymer filaments; washing the filaments essentially free of any residual acrylonitrile polymer solvent, partially stretching the washed filaments in an aqueous medium at 90–110° C., immersing the washed and partially stretched filaments in a liquid bath at between about 90–110° C. containing dye assistant agent capable of enhancing the dyeability of the filaments and relaxing the filaments therein, stretching the impregnated filaments at between about 90–100° C., and subsequently, irreversibly drying the impregnated and stretched filaments to a textile fiber.

The sequence of steps of the invention is schematically illustrated in the sole figure of the drawing.

The fibers prepared in accordance with the present invention possess excellent physical properties in addition to being made through dyeable to excellent deep shades of coloration throughout the cross section as well as along the length of the fibers. They exhibit outstanding resistance to fading from exposure to washing and light as well as to whitening and fibrillation. The present inventive method provides a highly expedient and efficient means for continuously, rapidly, uniformly and reproducibly preparing acrylonitrile fibers that can be dyed with a wide variety of dyestuffs.

The residence time of the gel fiber in the impregnating bath is extremely short, i.e., usually on the order of  $\frac{1}{20}$  to  $\frac{1}{10}$  second, although much longer times can be employed if desired. Despite this unusually short cycle, the fiber is uniformly impregnated frequently throughout the cross-section of the fiber as well as lineally. Not only is each filament uniformly impregnated throughout, but the complete tow which may consist of thousands of filaments and be of 100,000 or so total denier is uniformly impregnated throughout. That is, fiber-to-fiber variation is usually minimal.

The reasons for the marked improvement in penetration



of the dye assistant into the gel filament structure with practice of the present invention is not fully understood. It is evidently related to the morphological phenomena that take place during the transformation of the polymer in solution to the stretched gelled filament. Thus, the combination of pre- and post-impregnation stretch combined with the intermediate relax in the dye assistant solution allows for and enhances uptake and penetration of the assistant even when the dye assistant itself is a high molecular weight polymer. There are apparently several factors that may influence the uptake and penetration of the dye assistant. It has been noted that stretching the gel filament to the point where it has normally acceptable physical properties, i.e., stretched 10 to 20 times, that a rather dense structure including outer skin, is presented which tends to inhibit penetration. Likewise, if the gel filament is not stretched at all the structure is likely to be in a "skin-core" state with a semi-soft core, but tight skin again resisting penetration. If impregnation is carried on during stretching other unknown factors tend to prohibit penetration. The present invention takes advantage of the finding that the particular sequence of steps employed provides a gel structure excellently adapted for the purpose of accepting a dye assistant throughout the structure.

Another feature that points up the novelty of the invention is that, strange as it may seem, if the dye assistant is present in the first stretch bath, i.e., the pre-impregnation stretch bath, in addition to being in the relaxing impregnation bath, the penetration of the dye assistant is apparently interfered with so that inferior results are obtained.

The pre-impregnation stretch is carried out in aqueous medium, which may be steam, but preferably water, at about 90–110° C. Higher temperatures can be employed but ordinarily do not materially enhance the results of the invention and may introduce deleterious effects. Penetration of the dye assistant tends to decrease quite readily when temperatures of much less than 90° C., e.g., 70° C., are maintained in the pre-impregnation stretch. Depending somewhat on the composition of the acrylonitrile polymer and spinning conditions, e.g., solvent, coagulant and temperature, the stretch imparted to the gel filament in the pre-impregnation stretch may be from about 2 to about 12 times, beneficially a stretch between about 4 and 8 times, i.e., a stretch ratio of 4:1 to 8:1, is utilized. Any suitable means may be employed to effect the stretch which is most conveniently accomplished by stretching the filaments between two sets of pinch rolls with the down-stream set of rolls being driven at a faster rate than the up-stream rolls.

After the pre-impregnation stretch the gel filaments are ordinarily passed directly to the relaxing impregnation bath. As indicated, the impregnation bath is advantageously an aqueous bath maintained at between 90 and about 110° C. Pressure may be applied to attain the higher temperatures or other solvents inert to the acrylonitrile polymer may be added to raise the boiling point or aid in dissolution of the dye assistant, or the dye assistant itself may elevate the boiling point of the solution. Beneficially, temperatures near the boil of the solution are employed. While the gel filaments are in the impregnation bath they are completely relaxed, that is, they are maintained at zero tension. The degree of relax will depend somewhat on the composition of the gel and the dye assistant, and the time it is desired to keep the gel filament in the impregnating solution. The relax can be expressed in terms of stretch ratios and, beneficially, a stretch of between about 0.2 and 0.9 times is used. This means that the gel filaments are removed from the impregnating bath at 0.2 to 0.9 times as fast as they enter.

Following the impregnation of the filaments with the dye assistant they are generally passed directly to the post-impregnation stretch and there given an ultimate stretch.

This stretch influences the impregnation, but is principally directed to impart the final orientation to the filament molecules to the point where they will have acceptable physical properties. This will be determined in large part on the amount of stretch given in the pre-impregnation step. Ordinarily, this stretch will range from greater than one up to 6 to 8 times so that the filament will have a total stretch from about 8 to 20 times its washed length. As with the pre-impregnation stretch, the post-impregnation stretch is carried out in an aqueous medium which may be steam but is preferably a water bath maintained at 90 to 110° C.

The invention is applicable to treating acrylonitrile polymer fibers which are fabricated from fiber forming acrylonitrile polymers that contain in the polymer molecule at least about 80 weight percent of polymerized acrylonitrile, and is especially applicable to the treating of homopolymeric acrylonitrile, which are wet spun in and with systems, that are adapted to utilize aqueous coagulating liquids in the spinning operation, such as systems wherein ethylene glycol, dimethylformamide, dimethylsulfoxide, butyrolactone and the like or the various saline polyacrylonitrile-dissolving solvents are employed as spinning solution solvents for the polymer and are also present in non-polymer dissolving quantities in the aqueous coagulating liquid used in the spin bath.

The utile, known aqueous saline solvents for the various fiber forming acrylonitrile polymers and polyacrylonitrile include zinc chloride, the various thiocyanates such as calcium and sodium thiocyanate, lithium bromide, salt mixtures of the so-called "lyotropic" series, and others recognized by the art as has been disclosed, among other places, in United States Letters Patent Nos. 2,140,921; 2,245,192; 2,648,592; 2,648,593; 2,648,646; 2,648,648; 2,648,649; and 2,949,435. Advantageously, aqueous zinc chloride solutions are used for the purpose.

Exemplary of some of the monomeric material that may be employed with the acrylonitrile in the preparation of the acrylonitrile polymer and copolymer fiber forming systems and treated in accordance with the practice of the present invention include allyl alcohol, vinyl acetate, acrylamide, methacrylamide, methyl acrylate, vinyl pyridine, ethylene sulfonic acid and its alkali metal salts, vinyl benzene sulfonic acid and its salts, 2-sulfoethylmethacrylate and its salts, vinyl lactams such as vinyl caprolactam and vinyl pyrrolidone, etc. and mixtures thereof.

As indicated, after acrylonitrile polymer fibers have been wet spun they are most frequently water washed or washed with an aqueous inert solution to remove any residual polymer solvent from the freshly formed filaments, thus forming an intermediate fiber product often referred to as a gel or aquagel filament. Thoroughly washed acrylonitrile polymer aquagel fibers, incidentally, are usually found to contain up to about 6 parts by weight of water (including residual extrinsic or exterior water associated therewith) for each part by weight of dry polymer therein. More frequently, washed acrylonitrile aquagel polymer fibers are found to contain from about 3 to 4 parts by weight of water for each part by weight of polymer.

The present invention can be carried out conveniently in standard spinning trains. That is, no major alterations to a conventional fiber forming process need be undertaken except to provide the necessary stretch and dye assistant impregnation baths. Because of the extreme speed at which the fibers can be impregnated in practicing the present invention, the ordinary and commercially useful spinning speeds can be employed while simultaneously obtaining an excellent dye receptive fiber.

Essentially any additive that will enhance the dyeability of the acrylonitrile polymer fiber can be incorporated in the gel in accordance with the present invention. Beneficially, the dye assistant is water soluble or at least water dispersible so that it can be applied from a water



bath; however, other solvents or mixtures of solvents may be employed for dissolving or dispersing the dye assistant. If the dye assistant is a liquid itself, it can be used at full strength, although more dilute solutions are preferred. Any suitable temperature can be employed for the impregnation, for example, from room temperature up to the boiling temperature of the particular solution in use. When water is used, advantageously, the impregnation bath is maintained at about 90–100° C.

The amount of the dye assistant that is applied to and impregnated in the acrylonitrile polymer gel is usually about at least 1.0 weight percent, based on dry fiber weight. Preferably, between about 2 and 15 percent of the additive is impregnated in the fiber, based on dry fiber weight, but amounts up to 30–40 percent can be utilized in some instances without deleterious effects. The impregnation bath usually contains relatively dilute solutions of the dye assistant. For most purposes, between about 1 and 10 weight percent of the assistant, based on solution weight, is adequate to obtain the desired level of additive in the fiber, but concentrations up to the saturation point of the assistant in the solvent can be used. Any conditions that tend to cause agglomeration of the dye assistant should be avoided for obvious reasons.

Exemplary of the types of dye assistants that can be impregnated in the gel fiber in accordance with the invention include:

(1) Water-soluble amine salts, including:

Octadecyl ammonium acetate  
Octadecyl ammonium chloride  
Di-n-amyl ammonium chloride  
Tri-n-amyl ammonium chloride  
N-2-[2-(2,2,3,3-tetramethylbutyl phenoxy) ethoxy] ethyl-N,N-dimethyl ammonium chloride  
N-2-(octadecyloxy)ethyl-N,N-dimethyl ammonium chloride  
N-2-(decyloxy)ethyl-N,N-dimethyl ammonium chloride  
N-2-(heptoxy)ethyl-N,N-dimethyl ammonium chloride  
N-octadecyl-N,N-di-(2-hydroxyethyl)ammonium chloride  
N-dodecyl-N,N-di-(2-hydroxyethyl)ammonium chloride  
2-n-nonyl pyridine hydrochloride  
5-ethyl-2-n-nonyl pyridine hydrochloride  
N-n-octadecylpiperidine hydrochloride  
2-heptadecyl-3-(2-hydroxy ethyl)glyoxalidine hydrochloride  
2-heptadecyl-3-butyl glyoxalidine hydrochloride  
2-heptadecyl glyoxalidine hydrochloride  
Di-(carboxymethyl)dodecyl ammonium chloride

(2) Quaternary ammonium salts, including:

n-Nonyltrimethyl ammonium bromide  
n-Decyltrimethyl ammonium bromide  
n-Dodecyltrimethyl ammonium chloride  
n-Hexadecyltrimethyl ammonium chloride  
n-Octadecyltrimethyl ammonium chloride  
n-Dodecylbenzyltrimethyl ammonium chloride  
n-Dodecyltolylmethyltrimethyl ammonium chloride  
n-Decyloxyethyltrimethyl ammonium iodide  
n - [2 - (2,2,3,3-tetramethylbutylphenoxy)ethoxy] ethyl-trimehtyl ammonium iodide  
Carboxymethyl dimethyl tetradecyl ammonium chloride  
Benzylhexadecyldimethyl ammonium chloride  
Benzyl - (2,2,3,3 - tetramethylbutylphenoxy)ethyldimethyl ammonium chloride  
2-hydroxyethyl-n-octadecyldimehtyl ammonium bromide  
n-Dodecyl-bis-(2-hydroxyethyl)methyl ammonium bromide  
Bis-(2-hydroxyethyl)methyl-n-octadecyl ammonium bromide  
Benzyl-2-[2-(2,3,4,6-tetrachlorophenoxy)ethoxy] ethyl morpholinum chloride  
Ethyl-n-octadecyl morpholinium ethosulfate  
n-Dodecyl pyridinium chloride  
n-Hexadecyl pyridinium chloride  
n-Dodecyl isoquinolinium bromide

Bis-(polyoxyethylene oleate) ethyl methyl ammonium ethosulfate

Trimethylene bis(dimethyl-n-tetradecyl ammonium bromide)

5 Trimethylene bis[n-dodecyl-di-(2-hydroxyethyl) ammonium bromide]

Trimethylene bis[2,2,3,3 - tetramethylbutyl - phenoxyethoxy]ethyl dimmethyl ammonium chloride]

Tetramethylene bis(n-dodecyldimethyl ammonium chloride)

10 Pentamethylene bis(n-dodecyldimethyl ammonium chloride)

Poly-4-methyltrimethyl ammonium stearyl chloride

Dimethyl 2-hydroxyethyl stearamidopropyl ammonium chloride

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(3) Water-soluble sulfonium salts, including:

n-Dodecyl dimethyl sulfonium chloride, bromide or methosulfate

20 n-Dodecyl ethyl methyl sulfonium halide or alkylsulfate

n-Dodecyl methyl octyl sulfonium methosulfate

n-Tetradecyl ethyl methyl sulfonium methosulfate

2[2-(2-biphenyloxy)ethoxy]ethyl butyl methyl sulfonium methosulfate

25 Di-n-dodecyl methyl sulfonium methosulfate

Di-(2-hydroxyethyl)methyl sulfonium methosulfate, dicapric ester

Di-n-dodecyl dimethyl ethylene disulfonium di-methosulfate

30 n-Octadecyl dimethyl sulfonium bromide

n-Dodecyl benzyl methyl sulfonium methosulfate

Cetyl p-tolyl methyl sulfonium methosulfate

n-Octadecyl 2-(diethyl methyl ammonium)ethyl methyl sulfonium dimethosulfate

35 Cetyl dimethyl sulfonium methosulfate

n-Dodecyl 2-chloroethyl methyl sulfonium 2-chloroethyl sulfate

2[2-(4-cyclohexylphenoxy)ethoxy] ethyl diethyl sulfonium ethosulfate

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(4) Water-soluble phosphonium halides, including:

Triethyl n-octyl phosphonium iodide

n-Dodecyl trimethyl phosphonium bromide

Cetyl trimethyl phosphonium chloride

Trimethyl n-octyl phosphonium chloride

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Benzyl tri-n-butyl phosphonium chloride

Benzyl n-dodecyl dimethyl phosphonium bromide

Benzyl cetyl dimethyl phosphonium iodide

Dichlorobenzyl triphenyl phosphonium chloride

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(5) Water-soluble polymers of N-vinyl pyrrolidone and related compounds, including:

N-vinyl n-methyl formamide

N-vinyl N-ethyl formamide

N-vinyl N-methyl acetamide

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N-vinyl N-ethyl acetamide

N-vinyl valerolactam

N-vinyl caprolactam

N-vinyl morpholinone

N-vinyl oxazolidinone

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N-vinyl-5-methyl-oxazolidinone

(6) Polymers of aromatic alkenyl-containing sulfonic acid compounds including:

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Para-styrene sulfonic acid

Sodium para-styrene sulfonate

Methyl para-styrene sulfonate

2-chloro-4-vinyl benzene sulfonic acid

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(7) Polymers of alkenyl sulfonic acid compounds including:

Ethylene sulfonic acid

Sodium ethylene sulfonate

Methyl ethylene sulfonate

75

1-butylene-3-sulfonic acid



(8) Polymers of sulfoalkylacrylate compounds including:

- Sulfomethylacrylate
- 2-sulfoethylacrylate
- 2-sulfoethylmethacrylate, methyl ester

(9) Polymers of acryloyl taurine and homolog compounds including:

- N-acryloyl taurine
- N-methacryloyl taurine, methyl ester
- Methyl N-methacryloyl-aminomethane sulfonate

Preferably, the water soluble or water dispersible polymeric dye assistants are employed in the practice of the invention. The polymeric assistants tend to have better resistance to washing and other processing treatments, and a water solution is more conveniently handled and is less hazardous and expensive than conventional organic solvents. Profitably, polymers of N-vinyl pyrrolidone and N-vinyl morpholinone are used.

Depending on the dye assistant employed, the impregnated fiber can be dyed with one or several of a wide variety of dyestuffs, among those that may be mentioned are the vat, sulfur, direct, metallized, basic acid, azoic, acetate, reactive, ingrain and the like classes of dyestuffs.

As mentioned, when the acrylonitrile polymer particularly polyacrylonitrile, fibers are being manufactured, zinc chloride may most advantageously be utilized as the sole, or at least the principal saline solute in the spinning solvent employed for the polymer. In such instances, the aqueous solution of zinc chloride in the spinning solution may advantageously be in a concentration range of from 55 to 65, preferably about 60 weight percent, based on the weight of the aqueous solution. The quantity of substantially pure water passed countercurrent to the filaments in the coagulation bath, should be sufficient, when such aqueous zinc chloride spinning solutions are employed, so as to maintain the concentration of zinc chlo-

In order to further illustrate the invention, a tow of polyacrylonitrile aquagel fiber, which fibers contained from about 4 to 5 parts by weight of water in the gel phase to each part by weight of dry polymer in the aquagel structure, was obtained by extruding a spinning solution comprised of about 10 parts of polyacrylonitrile dissolved in about 90 parts of a 60 weight percent aqueous solution of zinc chloride into an aqueous coagulating bath that contained about 44 weight percent of zinc chloride dissolved therein at about 12.5° C. A multiple filament tow was prepared by extruding the spinning solution through a spinnerette having about 500 round, 3 mil diameter orifices. The coagulated tow bundle after emerging from the coagulating bath was washed substantially free from salt by passing it through sequential water baths at ambient temperature. It was then wet stretched in a hot water trough, some of which contained a dye assistant, to partially orient the gel fibers. Following the partial orienting or stretching of the fibers, the aquagel tow bundle was passed into and impregnated with a dye assistant solution consisting of an aqueous solution of poly-N-vinyl-2-pyrrolidone, (PVP), maintained at about 100° C. The tow bundle was either allowed to relax, or was stretched while in the impregnating solution.

The tow of aquagel filaments was withdrawn from the impregnation bath and passed directly to the post-impregnation stretch bath where the filaments were stretched in water at about 100° C. Subsequently, the fibers were irreversibly dried in a hot air oven at about 140° C. for 7-9 minutes to textile fibers.

The dried fibers were dyed with a 3% Irgalon Blue RL dye solution (based on dry fiber weight), a 2:1 metal complex dyestuff after which random samples were selected from each group of fibers of which cross-sections were examined under a microscope to determine the penetration of the dyestuff into the cross-section. The conditions used for the fiber preparation and results obtained are set forth in the following table.

Sample	Pre-Impregnation Stretch (and Impregnation)				Impregnation Bath			Post Impregnation Stretch		
	Time (Sec.)	Temp. (° C.)	Stretch	Percent PVP	Time (Sec.)	Stretch 100° C.	Percent PVP	Stretch 100° C.	Total Stretch	Penetration, Percent
A-----	7.0	100.0	16X	None	<sup>1</sup> 10.0	-----	1.5	1.06X	17.0X	75
B-----	13.3	100.0	8X	None	<sup>1</sup> 10.0	-----	1.5	2.12X	17.0X	99
C-----	<sup>2</sup> 1.3	70.0	8X	None	<sup>1</sup> 10.0	-----	1.5	2.12X	17.0X	Ring
D-----	<sup>2</sup> 2.4	70.0	4X	None	<sup>1</sup> 10.0	-----	1.5	4.25X	17.0X	25-50
E-----	24	67	4X	6.0	7.5	3.0X	None	1.04X	12.5X	Ring
F-----	24.0	67	4X	6.0	20.0	0.6X	4.0	5.2X	12.5X	75
G-----	24.0	30	4X	6.0	20.0	0.6X	4.0	4.8X	12.5X	50

<sup>1</sup> Tow samples were taken from pre-impregnation stretch and hand relaxed in impregnation bath, then hand stretched to 17X in post-impregnation stretch to obtain independent times in the second pan.

<sup>2</sup> Short times in pre-impregnation stretch were obtained by utilizing only part of the trough.

ride in the portion of the liquid in the spinning zone at a non-polymer-dissolving coagulation concentration of at least about 25 weight percent; advantageously from about 30 to 50 percent by weight and preferably between about 40 and 45 percent by weight. In such aqueous zinc chloride systems for acrylonitrile polymers, wherein the freshly wet spun polymer is generally obtained in an aquagel form, it is generally desirable for the spinning solution that is extruded to contain between about 4 and 20 percent by weight of dissolved polymer; more advantageously from about 6 to 15 weight percent of dissolved polymer; and preferably particularly when polyacrylonitrile fibers are being manufactured, from about 8.1 to 11.5 percent by weight of fiber-forming polymeric solids in the spinning solution.

Aqueous zinc chloride spinning solutions of fiber-forming acrylonitrile polymers are beneficially extruded at a spinning temperature from 0 to 50° C., preferably from about 10 to 30° C., into an aqueous zinc chloride coagulating liquid that is maintained at a coagulating temperature of 0 to 30° C.; preferably from about 10 to 20° C.

Similar excellent results to the foregoing are obtained when other acrylonitrile polymer and other of the dye assistants are employed in accordance with the invention.

What is claimed is:

1. A method for improving through dyeability of acrylonitrile polymer fibers comprising
  - (a) spinning a solution of a polymer of an ethylenically unsaturated monomeric material containing at least about 80 weight percent of polymerized acrylonitrile into an aqueous coagulating bath to form filaments of said polymer;
  - (b) washing said filaments essentially free of any residual spinning solution solvent;
  - (c) partially stretching said washed filaments in an aqueous medium at about 90-110° C.;
  - (d) relaxing said partially stretched filaments at between about 90° and 110° C. in a liquid bath of a dye assistant agent capable of enhancing the dyeability of said filaments and impregnating said filaments therewith;



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- (e) stretching said impregnated filaments in an aqueous medium at about 90°–110° C.; and,  
 (f) subsequently, irreversibly drying said filaments to textile fibers.
2. The method of claim 1, wherein said acrylonitrile polymer is polyacrylonitrile.
3. The method of claim 1, wherein said solution is an aqueous zinc chloride solution.
4. The method of claim 1, wherein said aqueous medium of (c) is water at 95–100° C.
5. The method of claim 1, wherein said filaments are partially stretched in (c) between about 4 and 8 times their washed length.
6. The method of claim 1, wherein said liquid bath of (d) is an aqueous bath.
7. The method of claim 1, wherein said liquid bath

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of (d) is an aqueous bath and said dye assistant agent is a water soluble polymer.

8. The method of claim 7, wherein said water soluble polymer is poly-N-vinyl pyrrolidone.

9. The method of claim 1, wherein said aqueous medium of (e) is water at about 95–100° C.

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