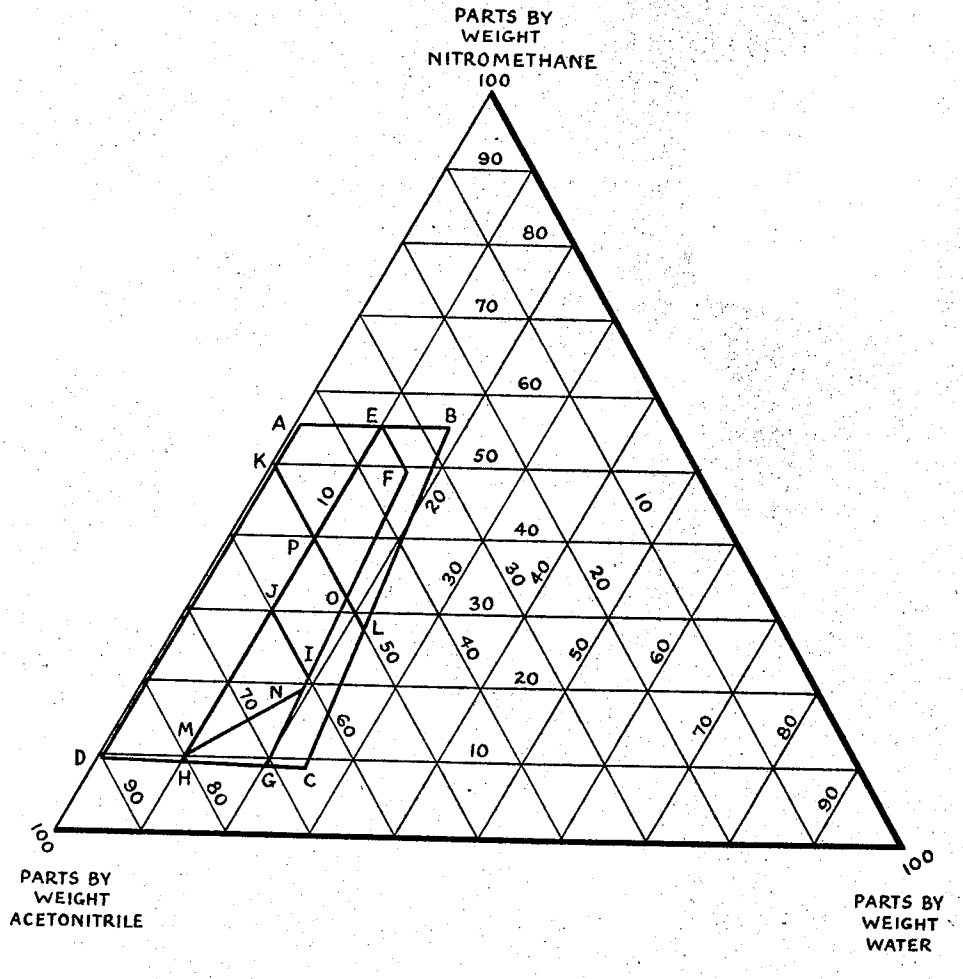
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SPINNING SOLVENT FOR ACRYLIC FIBERS

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SPINNING SOLVENT FOR ACRYLIC FIBERS

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This invention relates to spinning solutions for production of filaments from copolymers of acrylonitrile and at least one other substance having ethylenic unsaturation, and more particularly to such spinning solutions wherein the copolymers contain from 70 to 98 weight percent acrylonitrile based on the starting monomer.

Extruded fibers from copolymers having high (70 weight percent or more) acrylonitrile content are particularly valuable for making a diversity of textiles. However, the high proportion of acrylonitrile generally renders the copolymer incapable of solution in ordinary solvents such as acetone or ethanol for conventional spinning methods.

Therefore, in order to introduce as high a proportion of acrylonitrile in the copolymer as possible and still use common solvents, it has been proposed to incorporate into the copolymer monomers having groups such as hydroxyl radicals which are known to lend it solubility. The disadvantages of this mode of attack on the problem of forming spinnable solutions is the necessity of restricting the copolymer to certain highly specialized types which necessitates obtention of certain less common monomeric materials to produce fiber of limited usefulness.

A more direct mode of attack has been to find new solvents for the general class of polymers having high acrylonitrile content. Thus, it has been proposed to employ dimethyl formamide, dimethyl acetamide, nitromethane, and mixtures of nitromethane with formic acid or water to obtain spinnable solutions of the polymers.

Among the deficiencies of such solvent mediums for making spinning solutions are in some cases their low miscibility with water for rapid solvent removal in aqueous coagulating baths, in other cases their high miscibility resulting in too rapid coagulation of the filaments and necessitating spinning baths of critical composition, their low volatility necessitating high temperatures for solvent removal if dry spinning processes are attempted, their difficulty in recovery, the instability of the spinning solutions made up with them which lead to gel formation if not used promptly after making up, and their inability to making spinning solutions which have viscosity in the range of 1,000 to 30,000 centipoises for moderate power consumption together with a solids content of at least 10, and particularly of 15 or more weight percent copolymer for minimum solvent recovery.

An object of this invention is an improved spinning solvent for use in the production of filaments from copolymers of acrylonitrile with at least one other substance having ethylenic unsaturation, said copolymers containing from 70 to 98 weight percent acrylonitrile, and particularly from copolymers of this type which are difficultly soluble.

Another object of this invention is spinning solutions for production of filaments from copolymers of the type described, which solutions are characterized by their high solids content coupled with moderate spinning viscosity, their stability, their clarity, and their ability to form high quality fibers at moderate temperatures using wet or dry solvent removal techniques.

Still another object of this invention is an improved process for the production of filaments from copolymers of the type described, wherein the filaments formed upon extrusion of the solution into a solvent-removing medium are free of stickiness.

I have now discovered a solvent for acrylonitrile copolymers which has unexpected utility in the manufacture of filaments therefrom and which overcomes many of the objectionable features inherent in previous spinning solvents. The spinning solvent of my invention comprises acetonitrile, nitromethane, and water in the weight ratio range from about 26.5 to about 90 parts acetonitrile, about 9.9 to about 55.5 parts nitromethane, and about 0.1 to about 25 parts water. Broadly, the spinning solution of my invention comprises a solution, in the aforementioned solvent, of a copolymer of acrylonitrile with at least one other substance having ethylenic unsaturation, said copolymer containing from 70 to 98 weight percent acrylonitrile.

In brief, my process comprises dissolving the subject copolymers, at a temperature above 50° C., in a solvent comprising acetonitrile, nitromethane, and water in the weight ratio range from about 26.5 to about 90 parts acetonitrile, about 9.9 to about 55.5 parts nitromethane, and about 0.1 to about 25 parts water; maintaining the solution thus formed at temperatures of at least 50° C.; and extruding said solution through a spinneret into a zone containing a solvent-removing medium.

The drawing is a diagram showing weight ratios of acetonitrile, nitromethane, and water comprising the solvents useful for making the spinning solutions of my invention.

The broad range of the solvent ratios is defined by the area within polygon ABCD, where the approximate coordinates in weight parts are as follows: A=44.4 acetonitrile, 55.5 nitromethane and 0.1 water; B=26.5 acetonitrile, 55.5 nitromethane and 18 water; C=66.5 acetonitrile, 8.5 nitromethane, and 25 water; D=90 acetonitrile, 9.9 nitromethane and 0.1 water. These boundaries define generally the solvent ratios necessary for obtaining the advantages of my invention. Beyond them the valuable low temperature spinning properties of their polymer solutions begin to be adversely affected and/or undesirable haziness is apt to occur in the polymer solution, particularly when the more difficultly soluble acrylonitrile copolymers are used.

Likewise polygons CDKL, EFGH, EFIJ, POIJ, GHJI, and GHMN, circumscribed by the polygon ABCD, define more narrowly various ratios having especially desirable properties for specific applications. Solvent ratios defined by the polygons EFGH, EFIJ, POIJ, GHJI, and GHMN are particularly useful for obtaining clear solutions of high solids content with the more difficultly soluble acrylonitrile copolymers. The approximate coordinates in weight parts of the small polygons are as follows:

	Acetonitrile	Nitromethane	Water
CDKL where:			
C=	66.5	8.5	25.0
D=	90.0	9.9	0.1
K=	50.0	49.9	0.1
L=	50.0	28.0	22.0
EFGH where:			
E=	34.5	55.5	10.0
F=	34.5	49.1	16.4
G=	71.5	8.5	20.0
H=	81.0	9.0	10.0
EFIJ where:			
E=	34.5	55.5	10.0
F=	34.5	49.1	16.4
I=	60.0	21.0	19.0
J=	60.0	30.0	10.0
POIJ where:			
P=	50.0	40.0	10.0
O=	50.0	32.0	18.0
I=	60.0	21.0	19.0
J=	60.0	30.0	10.0
GHJI where:			
G=	71.5	8.5	20.0
H=	81.0	9.0	10.0
J=	60.0	30.0	10.0
I=	60.0	21.0	19.0
GHMN where:			
G=	71.5	8.5	20.0
H=	81.0	9.0	10.0
M=	80.0	10.0	10.0
N=	61.0	19.5	19.5

The acrylonitrile copolymers of special interest for use in my invention are those soluble in nitromethane but negligibly soluble in either water or acetonitrile; e.g. extracted with acetonitrile at about 82° C. for 16 hours, the copolymer formed from 90 parts by weight acrylonitrile monomer and 10 parts by weight of methyl acrylate monomer and having reduced viscosity about 1.2 gave a 0.35 percent by weight solution. Reduced viscosity is a measure of average molecular weight of the copolymer determined by flow from an Ostwald pipette and is computed by the equation: R.V.=(time of efflux of solution—time of efflux of solvent)/(concentration of copolymer in grams per 100 cc. of solvent×time of efflux of solvent. Values presented herein were determined at 40° C. in dimethyl formamide solution using 0.125 gram of copolymer per 100 cc. of solvent.

That spinning solutions with such advantageous properties can be obtained by the use of a solvent mixture containing more than 40 and as much as 90 percent of known non-solvent components (acetonitrile and water) is totally unexpected.

The solvents of this invention must contain acetonitrile, water and nitromethane. Each component is a necessary coacting ingredient without which the special benefits of my invention cannot be obtained. Spinning dopes, which were made up according to the invention principles except that acetonitrile was omitted, were very sticky and adhered strongly to the die, making it practically impossible to draw filaments from the die. In addition, the dopes were unstable to overnight aging at about spinning temperature, a large flocculent precipitate being evident in the mixture after such period. Attempts to make up spinning dopes in which either water or nitromethane were omitted failed because a solution sufficiently concentrated for practical spinning could not be obtained using dissolving procedures disclosed hereinafter.

It is possible to use the solvent mixtures of this invention with appropriate amounts of other known solvents such as dimethyl formamide, but for simplicity, economy of recovery, and efficiency at low spinning temperatures the ternary mixtures of acetonitrile, nitromethane, and water are preferred. It is also possible to dilute the mixture of essential components with small amounts, i.e. 1–15 weight percent, of non-solvents, such as methyl acetate or ethyl formate, or to mix dyes, stabilizers, etc. into the solution for spinning.

For extreme miscibility with aqueous coagulating baths in wet spinning processes, and for highest volatility to obtain rapid drying in dry spinning processes I have found that those solvents containing principally acetonitrile (encompassed by polygon CDKL on the diagram) are the most favorable.

I have also found that the greatest spinning improvement in terms of high permissible solids content with moderate spinning viscosity is obtained using my solvents containing at least 10 percent by weight water, more specifically those having weight ratios of the specific ingredients falling within the polygon EFGH. One feature of solvents in this region is that they permit formation of clear solutions of a very large variety of acrylonitrile copolymers, such solutions being by far the most desirable for spinning and for the production of high quality filaments. Another feature of the solvents in this region is that they allow use of copolymers having comparatively low reduced viscosity, e.g. around 1.0, for formation of high quality filaments.

For dry spinning processes, where solvent removal from the extruded solution is accomplished by means of hot air, solvent mixtures having weight ratios falling within the polygon EFIJ are preferred for their efficacy in making readily spinnable solutions. In this range those having between 50 and 60 weight parts of acetonitrile as defined by the polygon POIJ are especially preferred for their high volatility, having boiling points about 75°–80° C.

In wet spinning processes, where solvent removal from the extruded solution is accomplished by means of an aqueous coagulating bath, I prefer to use the solvent mixtures having weight ratios of the specific ingredients falling within the polygon GHIJ. On a three-component basis these solvents have 60 or more weight percent acetonitrile. The rapid coagulation in aqueous baths of solutions made with these solvents rapidly produces filaments of sufficient strength to resist the stresses inherent in a wet spinning process. On the other hand, coagulation is not so rapid that, in contrast to certain other commonly used systems, high concentrations of solvent must be kept in the bath. Suitable fibers may be spun into water containing no solvent, or into aqueous bath mixtures containing up to about 10–15% of acetonitrile and nitromethane.

Solvent mixtures falling within the polygon GHMN are of interest in that they comprise at least as much water as nitromethane, together with a major proportion of acetonitrile. Spinning solutions formed with them give exceptionally rapid coagulation in aqueous baths. The rate of coagulation in an aqueous bath can be reduced if desired by addition of acetonitrile and nitromethane thereto.

It is often of value to wash the tow with water after it has been coagulated in a spinning bath. This is an effective way for removing residual solvent clinging to the fibers and the solvent can be recovered economically from solution. One simple and effective tow-washing procedure involves countercurrent rinsing with water over a trough as the tow is drawn from the bath. The rinse water can be drained into the bath as makeup therefor, while the solvent-enriched bath water overflows by displacement and is subjected to solvent recovery treatment hereinafter described.

Suitable copolymers for my spinning solutions can contain as much as 98 weight percent acrylonitrile. In some few cases, due to widely different rates of polymerization of the various individual monomers, it is desirable to control individual monomer concentration during polymerization to prevent formation of essentially homogeneous polyacrylonitrile molecules which, because of their insolubility in my spinning solvents at the desirably low spinning temperatures, e.g. 70° C., would give cloudy and unsatisfactory spinning solutions.

Typical acrylonitrile copolymers I have found useful in the practice of my invention are tabulated as follows (copolymer compositions are expressed in parts by weight of starting monomer):

Methyl acrylate-acrylonitrile, 10/90, 8/92, 5/95, 2/98
Vinyl acetate-methyl acrylate-acrylonitrile, 5/5/90, 10/15/75
Vinyl acetate-vinylidene chloride-acrylonitrile, 5/20/75, 10/20/80, 7.5/20/72.5, 10/15/75, 10/20/70
Ethyl acrylate-vinylidene chloride-acrylonitrile, 10/20/70, 5/20/75, 10/15/75
Isopropenyl acetate-vinylidene chloride-acrylonitrile, 10/20/70, 5/20/75
Methyl methacrylate-acrylonitrile, 22/78
Acrylamide-methyl acrylate-acrylonitrile, 5/10/90, 2/10/90
Methallyl alcohol-acrylonitrile, 10/90
Methyl acrylate-vinylidene chloride-acrylonitrile, 10/15/75
N-tertiary butyl acrylamide-vinylidene chloride-acrylonitrile, 5/20/75
N-tertiary butyl acrylamide-methyl acrylate-acrylonitrile, 2/10/90, 5/10/90
Vinyl acetate-ethyl acrylate-acrylonitrile, 5/10/90

Because of its dyeability and other valuable fiber properties, I prefer copolymers having weight compositions close to 90 parts acrylonitrile–10 parts methyl acrylate based on the starting monomers.

For best spinning performance at solids concentration of at least 10 weight percent I prefer to use copolymers having reduced viscosity from about 0.7 to 3.0, and especially those having reduced viscosity from about 1.0 to 2.3. Average molecular weight of a copolymer in the latter range is believed to be roughly about 15,000 to 50,000 while average molecular weight of a copolymer having reduced viscosity in the range from 0.7 to 3.0 is believed to be about 10,000 to 60,000.

Spinning viscosity of the solutions measured at 73–75° C. for effective filament formation and moderate power consumption should be broadly in the range of 1,000 to 50,000 centipoises, preferably between 3,000 and 15,000 centipoises. To attain spinning viscosity in the latter range, the solids content of the solution generally will be in the range 15–25 weight percent. However, spinnable solutions can be made having as much as about 35% solids with many of the copolymers.

Rate of solution and completeness of solution increase with temperature. Other factors affecting the rate of solution are, of course, the particular copolymer and solvent compositions and the final solids concentration desired. The minimum practical dissolving temperature for the practice of my invention is at least 50° C., preferably from about 60 to 75° C. at atmospheric pressure. It is sometimes advantageous to dissolve the copolymer in a sealed system where temperatures above the atmospheric boiling point of the ternary solvent can be used. After solution is completed the solution temperature can be reduced to 70–72° C. for spinning without gel formation.

Deaeration of the spinning solutions of my invention can be accomplished simply, economically, and effectively at atmospheric pressure by maintaining the solution between about 50° and 75° C., thus such operation is preferred. If the solution temperature is allowed to fall below 50° C. some gel formation is likely to occur and cause plugging of the spinneret. In deaerating at atmospheric pressure and temperature above 75° C. vapor losses of the solvent can be appreciable and somewhat variable depending on the amount of air present and the temperature used. It is possible, of course, to use higher temperatures. When deaerating at temperature above 75° C. it is usually less costly to use a slight back pressure for conserving solvent than to use atmospheric pressure and allow excess solvent components to vaporize since the vaporized solvent must either be recovered or lost. Deaeration against pressure, however, is less efficient than the preferred atmospheric pressure deaeration at temperatures between about 50° and 75° C. In respect to maintaining deaeration of the solution when non-condensible gases such as nitrogen are used to transfer the solution to the spinning operation, high gas pressure, i.e. above about 15 pounds per square inch gage, should be avoided to prevent substantial amounts of gas from redissolving in the solution. Gas bubbles in the extruded solution give imperfect yarn formation and filament breakage.

The stability of the spinning solutions of my invention is marked. Retention of the solutions for as long as 24 hours has no effect on them. This excellent stability permits quite elastic scheduling in the manufacture of filaments, and it reduces the investment in standby equipment necessary to prevent raw material loss and reprocessing when down time due to accidents or equipment failures occurs in the plant.

In a dry spinning process I prefer to use a spinning temperature of about 70°–72° C. for maintaining clear, easily-extruded solutions without the danger of solvent vapor bubble formation. In a wet spinning process I prefer to use a spinning temperature about 72° C. for the same reason. When dry spinning, solvent removal can be accomplished by use of hot air between about 140° and 200° C. When wet spinning, solvent removal can be accomplished by extrusion of solution into an aqueous coagulating bath maintained about 70° C.

It is possible to make very light-colored yarn by a dry spinning process using the spinning solutions of my invention because of low temperatures and short times which can be used to dry the filaments. In addition, even while the yarn is still wet with solvent during the spinning, the strength of the yarn is high. This makes possible fast and easy handling with few filament breaks. Spinning behavior is easily reproducible, and minor temperature changes do not affect it since the operation can be carried out at a temperature far below that which will impart undesirable color to the yarn, yet far above that at which gel formation is likely to occur.

A special advantage from the use of my spinning solutions having a very high proportion of acetonitrile for wet spinning processes is the speed with which the filaments are formed and their very high initial strength for easy working.

Another marked advantage of my spinning solutions where the solvent consists of simply acetonitrile, nitromethane, and water for wet spinning is the ease with which the solvent is recovered from the coagulating bath. The solvent can be recovered by distillation from the coagulating liquor at atmospheric pressure to leave most of the bath water as residue without the necessity of evaporating large amounts of water for recovery of residual solvent components. Furthermore, over a considerable range of permissible solvent compositions, the composition of recovered solvents obtained by simple distillation is fairly close to the composition of the solvent used in making up the spinning solutions. Excess water can be readily removed by azeotropic distillation. Solvent recovery of the preferred solvent compositions, i.e. those having at least 10 percent water, is especially economical since considerable water can be left in the recovered solvents.

The following examples show several ways in which my invention has been carried out, but are not to be construed as limiting it. All parts expressed are parts by weight and all solvent composition percentages are weight percentages.

Example 1.—Copolymer having reduced viscosity of 1.20 was prepared by polymerizing for 7 hours in an agitated kettle 10 parts methyl acrylate and 90 parts acrylonitrile at a temperature of 60° C. using 1400 parts of aqueous medium and as catalyst 2.4 parts of ammonium persulfate and 0.4 part of β-mercaptoethanol. The copolymer was then separated, dried and ground.

19 parts of the dried and ground copolymer was dissolved in a closed container in 81 parts of a solvent consisting of 70.8 percent acetonitrile, 17.7 percent nitro-

methane and 11.5 percent water using an inert gas blanket of nitrogen and mechanical agitation at a temperature of 95°–100° C.

The solution was then maintained at a temperature of 80° C. and allowed to deaerate in an enclosed vessel vented periodically.

After 16 hours temperature was adjusted to 73° C. The solution was then extruded through a spinneret which had 104 holes each 0.005 inch in diameter, the spinneret being immersed in an aqueous coagulating bath maintained at 72° C. Filaments were passed through the bath for a distance of three feet, snubbed around feed rolls, and led by draw rolls into an externally heated pipe through which superheated steam was flowing to provide a stretching zone having temperature of about 120° C. The yarn was stretched 15 times its initial extruded length by rotating the draw rolls faster than the feed rolls, and finally wound on the bobbins at rates reaching 450 feet per minute. Filaments were very light colored and possessed tenacity of 4.06 grams per denier at break, said filaments being 1.4 denier/filament. Ultimate elongation of the yarn so made was 8 percent.

Example 2.—21 parts of copolymer material similar to that used in Example 1 was dissolved in 79 parts of a solvent consisting of 38 percent acetonitrile, 55 percent nitromethane and 7 percent water using mechanical agitation and an inert gas blanket at a temperature of 89° C.

The solution was then retained at a temperature of 79° C.

After 20 hours temperature was adjusted to 70° C. The solution was clear and had viscosity at 79° C. of 35,000 centipoises. The solution was then extruded through a spinneret containing forty/0.005 inch diameter holes directed downwardly into an externally heated spinning column through which was passed hot air maintained at 100°–170° C. Yarn was taken out the bottom of the column, snubbed on a take-up roll at a speed of 250 feet per minute, and packaged on a ring twister. The yarn was light colored and was 22 denier per filament. This yarn could then be oriented by stretching, and annealed or relaxed, and packaged.

Example 3.—Copolymer having reduced viscosity of 1.20 was prepared by polymerizing for 4 hours at 60° C. in an agitated kettle 10 parts methyl acrylate and 90 parts acrylonitrile using 1400 parts of aqueous medium and as catalyst 2.4 parts of ammonium persulfate and 0.4 part of β-mercaptoethanol. The copolymer was then separated, dried and ground.

30 parts of the dried and ground copolymer was dissolved in 70 parts of solvent consisting of 35.4 percent acetonitrile, 53.2 percent nitromethane, and 11.4 percent water, using a closed vessel with mechanical agitation and a temperature 85°–93° C. for 2.5 hours.

The solution was then retained at a temperature of 75° C. for 2 hours and deaerated at atmospheric pressure. It had viscosity of 30,000 centipoises at 75° C.

The solution was then extruded through a spinneret containing forty/0.005 inch diameter holes directed downwardly into an externally heated spinning column through which was passed hot air maintained at 120°–185° C. Yarn was taken out of the bottom of the column, snubbed on a take-up roll at a speed increasing from 166 to 401 feet per minute as the test progressed, and packaged on a ring twister. It was light colored.

The yarn was then fed into a stretching zone maintained at 160° C., the unwinding speed being 2.7 feet per minute and the winding up speed being 31 feet per minute. Stretch amounted to 1060 percent. The yarn at this point had ultimate elongation of 8%, tenacity of 4.8 grams per denier, and was 1.8 denier per filament. It was then relaxed 30 percent. After relaxing it had tenacity of 4.5 grams per denier, ultimate elongation of 23 percent, and residual boil shrinkage of 2.4 percent.

Example 4.—10 parts of dried and ground copolymer similar to that used in Example 1 was dissolved in 90 parts of a solvent consisting of 50.5 percent acetonitrile, 46.5 percent nitromethane and 3.0 percent water by heating the mixture to 100° C. in a sealed agitated tube, then cooling to 75° C., at which temperature a stable solution remained.

This solution could be deaerated in the manner of the preceding examples and spun by the wet process essentially as described in Example 1.

Example 5.—24 parts of dried and ground copolymer similar to that used in Example 1 was dissolved in 76 parts of a solvent consisting of 49.6 percent acetonitrile, 33.0 percent nitromethane and 17.4 percent water at a temperature of 75° C. using mechanical agitation. Solution was clear and had a viscosity at 73° C. of 30,000 centipoises.

This solution could be deaerated in the manner of the preceding examples and spun by the dry process essentially as described in Example 2.

Example 6.—20 parts of dried and ground copolymer similar to that used in Example 1 was dissolved in 80 parts of a solvent consisting of 78 percent acetonitrile, 10.5 percent nitromethane and 11.5 percent water at a temperature of 75° using mechanical agitation and an inert gas blanket. Solution viscosity at 73° C. was 1800 centipoises.

After deaerating the solution it was spun into water and the filaments collected on a winder. The unstretched filaments had light color and tenacity of 0.27 gram per denier, ultimate elongation of 5%, and were 16 denier per filament.

Example 7.—The following is a tabular summary of various copolymer solutions suitable for spinning made by using a solvent consisting (unless otherwise designated) of 35.4 percent acetonitrile (A), 53.1 percent nitromethane (N) and 11.5 percent water (W). Copolymer compositions are identified by the ratios of their starting monomers expressed in parts by weight except as indicated.

Copolymer Ratio	Dissolving Temperature, ° C.	Weight Percent solids	Viscosity at 75° C.
Methyl acrylate/acrylonitrile:			
10/90	85	30	30,000
8/92	75	22	1,400
5/95	90	20	116,000
2/98	90	20	----------
(Solvent—53.1A, 35.4N, 11.5W)			
Vinyl acetate/methyl acrylate/acrylonitrile 5/5/90—Solvent (55A, 35N, 10W)	----------	24	----------
Vinyl acetate/vinylidene chloride/ acrylonitrile:			
5/20/75	82–85	29	30,000
9/18/73	80	17	11,000
7.5/20/72.5	85	29	----------
10/15/75	65–75	19	15,000
10/20/70	75	22	24,000
Ethyl acrylate/vinylidene chloride/acrylonitrile:			
10/20/70	80	19	29,000
5/20/75	80	20	20,000
10/15/75	70–80	31	35,000
Isopropenyl acetate/vinylidene chloride/ acrylonitrile:			
10/20/70	85	24	10,000
5/20/75	75	24	49,000
Methyl acrylate/acrylonitrile [1] 9/91	82	24	12,000
Acrylamide-methyl acrylate-acrylonitrile: 5/10/90	81–84	27	14,000
Methallyl alcohol-acrylonitrile: 10/90	75	10	----------
Methyl acrylate-vinylidene chloride-acrylonitrile: 10/15/75	85	28	14,000
N-tertiary butyl acrylamide-vinylidene chloride-acrylonitrile: 5/20/75	87–81	20	21,000
N-tertiary butyl acrylamide-methyl acrylate-acrylonitrile:			
2/10/90	81	25	14,000
5/10/90	86–91	27	20,000
Vinyl Acetate-ethyl acrylate-acrylonitrile: 5/10/90	79	16	50,000

[1] (Proportion of acrylonitrile monomer was controlled during copolymerization to produce a practically homogeneous copolymer and to prevent the formation of molecules which are essentially polyacrylonitrile.)

Example 8.—29 parts of a dried and ground copolymer having composition of 75 parts acrylonitrile, 20 parts vinylidene cloride, and 5 parts of vinyl acetate based on the starting monomer and reduced viscosity of 1.18 was dissolved in a solvent consisting of 35.4 percent acetonitrile, 53.1 percent nitromethane, and 11.5 percent water at a temperature of 70–80° C. using mechanical agitation and an inert gas blanket. Solution was clear and had viscosity at 73° C. of 36,000 centipoises.

After deaerating the solution for 16 hours at about 75° C., it was spun by the dry process described in Example 1.

I claim:

1. A spinning solution comprising a copolymer of acrylonitrile and at least one other substance having ethylenic unsaturation, said copolymer containing from 70 to 98 weight percent acrylonitrile, and a solvent for said copolymer comprising acetonitrile, nitromethane, and water in the weight ratio range indicated in the drawing by the polygon ABCD; said solution having solids concentration of at least 10 weight percent.

2. The spinning solution as defined in claim 1 wherein the copolymer has reduced viscosity between 0.7 and 3.0.

3. The spinning solution as defined in claim 1 wherein the solvent comprises acetonitrile, nitromethane, and water in the weight ratio range indicated in the drawing by the polygon EFGH.

4. The spinning solution as defined in claim 3 wherein the reduced viscosity of the copolymer is between 1.0 and 2.3 and solids content is at least about 15% by weight.

5. The spinning solution defined in claim 4 wherein spinning viscosity at 73° C. is in the range of 3,000 to 15,000 centipoises.

6. The spinning solution as defined in claim 1 wherein the solvent comprises acetonitrile, nitromethane, and water in the weight ratio range indicated in the drawing by the polygon EFIJ.

7. A spinning solution comprising a copolymer of acrylonitrile and at least one other substance having ethylenic unsaturation, said copolymer being soluble in nitromethane and substantially insoluble in water, acetonitrile, and mixtures thereof and containing from 70 to 98 weight percent acrylonitrile, and a solvent for said copolymer comprising acetonitrile, nitromethane and water in the weight ratio range indicated in the drawing by the polygon CDKL, the concentration of said copolymer in the solvent being at least 10 weight percent.

8. The spinning solution as defined in claim 7 wherein the solvent comprises acetonitrile, nitromethane, and water in the weight ratio range indicated by the polygon POIJ.

9. The spinning solution as defined in claim 8 wherein the copolymer composition is about 90 parts by weight acrylonitrile and about 10 parts by weight methyl acrylate, and said copolymer has reduced viscosity from 1.0 to 2.3 and the solvent consists of acetonitrile, nitromethane, and water.

10. The spinning solution as defined in claim 7 wherein the solvent comprises acetonitrile, nitromethane, and water in the weight ratio range indicated in the drawing by the polygon GHJI.

11. The spinning solution as defined in claim 10 wherein the copolymer composition is about 90 parts by weight acrylonitrile and about 10 parts by weight methyl acrylate, and said copolymer has reduced viscosity from 1.0 to 2.3 and the solvent consists of acetonitrile, nitromethane, and water.

12. A spinning solution comprising a copolymer of acrylitrile and at least one other substance having ethylenic unsaturation, said polymer being soluble in nitromethane and substantially insoluble in water, acetonitrile, and mixtures thereof and containing from 70 to 98 weight percent acrylonitrile, and solvent for said copolymer comprising acetonitrile, nitromethane, and water in the weight ratio range indicated in the drawing by the polygon GHMN, the concentration of said polymer in the solvent being at least 10 weight percent.

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