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 spinable 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 spinable 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 make 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 particu-
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% by weight acrylonitrile monomer and 10% 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: 

\[
\eta = \frac{\eta_{sp} - 1}{1 - 10^{-\frac{4.5}{9.7}}}
\]

where: \(\eta_{sp}\) is the specific viscosity of the solution and 1000 cc. of solvent is the concentration of copolymer in grams per 100 cc. of solvent × time of efflux of solution. 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% 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 coating ingredient without which the special benefits of my invention cannot be obtained. Spinning dope, 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 dope 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 a ternary mixture of acetonitrile, nitromethane, and water is preferred. It is also possible to dilute the 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 (encircled 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 EFIG are preferred for their efficacy in making readily spinable solutions. In this range those having between 50 and 60 weight parts acetonitrile as defined by the polygon POI 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 GHN 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 necessary 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. Ternary mixtures of acrylonitrile, acrylamide, and benzyl methyl acrylate are of essentially homogeneous polycarboxylate molecules which, because of their insolubility in my spinning solvents at the desirable 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 (copolymers compositions are expressed in parts by weight of starting monomer):
2,870,342

Methyl acrylate-acrylonitrile, 10/90, 8/92, 5/95, 2/98
Vinyl acetate-methyl acrylate-acrylonitrile, 5/5/90, 10/15/75
Vinyl acrylate-vinylidene chloride-acrylonitrile, 5/20/75, 10/20/90, 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 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. 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 main-
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 70° C. Filaments were passed through the bath for a distance of three feet, snipped 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 spinnning column through which was passed hot air maintained at 100°-170° C. Yarn was taken out the bottom of the column, snipped 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 d -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°-95° C. for 2.5 hours.

The solution was then retained at a temperature of 75° C for 10 minutes 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 spinnning column through which was passed hot air maintained at 120°-185° C. Yarn was taken out the bottom of the column, snipped 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 unwinning 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 percent, tenacity of 4.8 grams per denier, and was 18.8 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 percent water by heating the mixture to 100° C. in a sealed agitation 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 75° 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 11.3 percent water at a temperature of 75° C. 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 percent, 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.

<table>
<thead>
<tr>
<th>Copolymer Ratio</th>
<th>Diminishing Temperature, ° C.</th>
<th>Weight Percent Solids</th>
<th>Viscosity at 75° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acrylate/acrylonitrile:</td>
<td>85</td>
<td>20</td>
<td>80,000</td>
</tr>
<tr>
<td>90/10</td>
<td>75</td>
<td>17</td>
<td>70,000</td>
</tr>
<tr>
<td>75/25</td>
<td>65</td>
<td>20</td>
<td>60,000</td>
</tr>
<tr>
<td>(Solvent—55, 30, 4N)</td>
<td>80</td>
<td>20</td>
<td>75,000</td>
</tr>
<tr>
<td>Vinyl acetate/methyl acrylate/acrylonitrile:</td>
<td>80</td>
<td>20</td>
<td>50,000</td>
</tr>
<tr>
<td>70/10/20</td>
<td>75</td>
<td>22</td>
<td>55,000</td>
</tr>
<tr>
<td>Vinyl acetate/vinylidene chloride/acrylonitrile:</td>
<td>80</td>
<td>20</td>
<td>50,000</td>
</tr>
<tr>
<td>70/20</td>
<td>85</td>
<td>20</td>
<td>55,000</td>
</tr>
<tr>
<td>Ethyl acrylate/vinylidene chloride/acrylonitrile:</td>
<td>80</td>
<td>20</td>
<td>50,000</td>
</tr>
<tr>
<td>70/20</td>
<td>85</td>
<td>20</td>
<td>55,000</td>
</tr>
<tr>
<td>Isobutyronitrile/vinylidene chloride/acrylonitrile:</td>
<td>80</td>
<td>20</td>
<td>50,000</td>
</tr>
<tr>
<td>70/20</td>
<td>85</td>
<td>20</td>
<td>55,000</td>
</tr>
<tr>
<td>Methyl acrylate/n-coacrylonitrile 1/99</td>
<td>85</td>
<td>24</td>
<td>12,000</td>
</tr>
<tr>
<td>Acrylamide-methylacrylate-acrylonitrile:</td>
<td>95/5</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Acrylamide-acrylate-acrylonitrile:</td>
<td>95/5</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

(Proportion of acrylonitrile monomer was controlled during co-polymerization 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 chloride, 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 degassing 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 EFII.

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 POI.

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 GHJ.

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 acrylonitrile 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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