United States Patent Office

2,776,945
Patented Jan. 8, 1957

2,776,945

SPINNING SOLVENT FOR ACRYLIC FIBERS

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No Drawing. Application July 22, 1954,
Serial No. 445,156

10 Claims. (Cl. 260—32.6)

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

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

It has been proposed therefore to incorporate into copolymers of high acrylonitrile content monomers having groups such as hydroxyl radicals which will enhance the solubility of the copolymer in common solvents. Thus the copolymers are restricted to certain highly specific types of limited usefulness, and to produce them it is necessary to use monomeric materials which may be difficult or very costly to obtain.

It has been proposed also to employ N,N′-dimethyl formamide, N,N′-dimethyl acetamide, nitromethane, and mixtures of nitromethane with formamide to obtain spinnable solutions of the copolymers.

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 low volatility necessitating high temperatures for solvent removal if dry spinning processes are attempted; their high cost; 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.

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 at least 70 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 spinning solution temperatures, e. g. 70°–80° C., at which no discoloration or weakening of the fiber product occurs.

Still another object of this invention is an improved process for the production of filaments from the copolymers of the type described.

We 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 our invention consists essentially of 50 to 95 parts by weight acetonitrile and 50 to 5 parts by weight of at least one unsubstituted C_1–C_2 saturated aliphatic amide. The spinning solution of our invention consists essentially of a solution in the aforementioned solvent, of a copolymer of acrylonitrile with at least one other substance having ethylenic unsaturation, said copolymer containing at least 70 weight percent acrylonitrile.

Our process comprises dissolving the subject copolymers at a temperature above 50° C. in a solvent consisting essentially of 50 to 95 parts by weight acetonitrile and 50 to 5 parts by weight of an unsubstituted C_1–C_2 saturated aliphatic amide, and extruding said solution through a spinneret into a zone containing a solvent-removing medium.

By the term "unsubstituted C_1–C_2 saturated aliphatic amide" we mean formamide and acetamide. These amides boil under atmospheric pressures at temperature between 210° and 222° C. Because of the ease with which they dissolve the less soluble copolymers, we prefer to use the solvent mixtures comprising essentially 70 to 90 parts by weight acetonitrile and 30 to 10 parts by weight of the amide. The efficiency of the amide in the practice of our invention decreases as its molecular weight increases. We prefer, therefore, formamide to acetamide.

For simplicity, economy of solvent recovery and efficiency in spinning at low temperatures the binary mixtures of acetonitrile and an unsubstituted C_1–C_2 saturated aliphatic amide are preferred. It is possible, however, to dilute the mixture of essential components with small amounts, i. e. 1–15 weight percent, of extraneous material such as methyl acetate, water, etc.; and to mix dyes, stabilizers, etc. into the solution for spinning. Large amounts of these extraneous materials should not be included in our composition since they tend to lower the dissolving efficiency of the solvent.

The acetonitrile and amide components of our copolymer solvent are both readily soluble in water which makes for rapid coagulation of the fiber in a wet spinning process. Suitable fiber can be spun into water containing little or no solvent; the speed of coagulation can be reduced if desired by incorporating up to about 10–15% by weight of acetonitrile and/or the amide in the aqueous bath.

The acrylonitrile copolymers of special interest for use in our invention are those negligibly soluble in acetonitrile alone or in C_1–C_2 saturated aliphatic amide alone; 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 of about 1.2 gave a 0.35% by weight solution; and heating a similar copolymer with formamide for two hours at 100° C. gave a 0.11% by weight solution. Reduced viscosity (R. V.) 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). The values presented herein were determined at 40° C. in dimethyl formamide solution using 0.125 gram of copolymer per 100 cc. of solvent. The solvent of our invention is practical for making spinning dopes of acrylonitrile copolymers containing up to about 98% acrylonitrile. Dopes containing substantial amounts of polyacrylonitrile itself require an impractically high spinning temperature to stay in clear solution, hence are to be avoided.

Typical acrylonitrile copolymers which we have found useful in practicing our invention are tabulated below. The acrylonitrile content of these copolymers is at least 70% by weight (copolymer compositions are expressed in parts by weight of starting monomer).

Methyl acrylate-acrylonitrile, 2/98, 10/90.
Vinyl acetate-vinylidene chloride-acrylonitrile, 5/20/75.
Methyl acrylate - vinylidene chloride - acrylonitrile, 7.5/12.5/80.
Methyl acrylate - methyl methacrylate - acrylonitrile, 10/10/80.

Because of its dyeability and other valuable fiber properties we prefer to use copolymers having weight composition close to 90 parts acrylonitrile and 10 parts methyl acrylate.

For effective filament formation and moderate power consumption the spinning viscosity of the solutions, measured at 73–75° C., should be broadly in the range of 1,000 to 50,000 centipoises, preferably between 3,000 and 15,000 centipoises. To obtain spinning viscosity in the latter range, the solids content of the solution generally will be in the range 15–25 weight percent. Solutions having 10 or more weight percent solids are generally suitable for spinning. Spinnable solutions can be made having as much as about 30% solids with many of the copolymers in the solvent of our invention.

Rate of solution and completeness of solution increase with temperature. Other factors affecting the rate of solution are the particular copolymer and solvent composition and the final solids concentration desired. The minimum practical dissolving temperature in the practice of our invention is at least 50° C.; for economy and efficiency in our process we prefer to use dissolving temperatures from about 60° to 110° C. and atmospheric pressure. It is sometimes advantageous to dissolve the copolymer in a sealed system where temperatures above the atmospheric boiling point of the binary solvent can be used. After solution is completed, the solution temperature can be reduced to 70°–80° C. for spinning without gel formation.

Deaeration of the spinning solutions of our invention can be accomplished simply 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 should care be not taken to completely redissolve the gel before spinning, e. g. by warming to a temperature above 50° C. In the deaerating at atmospheric pressure and temperature above 75° C. solvent vapor losses can be appreciable and somewhat variable depending upon 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., venting against a slight back pressure for conserving solvent rather than exposing the dope to atmospheric pressure and allowing excessive amounts of solvent components to vaporize. Deaerating against pressure, however, is less efficient than is the preferred atmospheric pressure deaeration at temperatures between about 50° and 75° C. In respect to maintaining deaeration of the spinning solution when non-condensable 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 gauge, 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 our invention is marked. Retention of the solutions for as long as 24 hours at spinning temperatures has no effect on them. This excellent stability permits quite elastic scheduling in the manufacture of filaments, and it enables reduction of investment in standby equipment needed to prevent raw material loss and reprocessing when down time due to accident or equipment failures occurs in the plant.

Our solvent permits use of moderate spinning temperatures, e. g. 70°–80° C. In spinning we prefer to use a spinning solution temperature of about 70–72° C. for maintaining easy extrusion of the solution without the danger of solvent vapor bubble formation. When dry spinning, solvent removal can be accomplished by use of hot air between about 140°–200° C. When wet spinning, solvent removal can be accomplished by extrusion of solution into an aqueous coagulating bath maintained about 70° C. Spinning behavior is easily reproducible, and minor temperature changes do not affect it since the operation can be carried out at a temperature below that which will impart undesirable color to the yarn, yet far above that at which gel formation is likely to occur. It is possible to make very light colored yarn using the spinning solutions of our invention. 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.

In a wet spinning process it is often of value to wash the yarn with water after it has been coagulated in the aqueous bath. This is an effective way for removing residual solvent clinging to the fibers. One simple and effective yarn-washing procedure involves countercurrently rinsing the yarn as it is drawn from the bath, with water over a trough. The rinse water can then 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.

The acetonitrile component can be recovered from an aqueous coagulating liquid by azeotropic distillation and the amide component as a residual material from the distillation. In a dry spinning process solvent vapors can be recovered from the air stream by methods such as adsorption on activated charcoal or low temperature condensation.

The following examples show several ways in which our 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 1.05 was prepared by polymerizing for four hours in an agitated kettle 10 parts methyl acrylate and 90 parts acrylonitrile at a temperature of 35° C. using 1000 parts of aqueous medium and as catalyst 3.2 parts of ammonium persulfate and 1.6 parts of sodium metabisulfite. Copolymer was then separated, dried, and ground. Yield of copolymer was 88.2% of the weight of monomers charged. This copolymer contained more than 70% by weight acrylonitrile, and probably had composition of about 89.2% acrylonitrile with balance of methyl acrylate as estimated from the proportions of monomers used, the yield, and the relative reactivity ratios of the monomers as given in Copolymerization, Alfrey, Bohrer, and Mark, volume VIII, table IV, page 91 (Interscience Publishers Inc., New York, N. Y., 1952).

25 parts of the dried and ground copolymer were dissolved in a closed container in a solvent consisting of 52.5 parts of acetonitrile and 22.5 parts of formamide using a nitrogen gas blanket and mechanical agitation at a temperature of 80° C.

A clear solution having viscosity of 15,000 centipoises at 80° C. was obtained. The solution was then extruded through a spinneret which had 10 holes each 0.005" in diameter, the spinneret being immersed in an aqueous coagulating bath maintained at 72–73° C. Filaments were passed through the bath for 20 inches, snubbed around feed rolls, and led through a 36-inch aqueous stretching bath maintained at 92–94° C. The yarn was stretched 2–4 times its initial extruded length by being taken up on a winding device rotating faster than the feed rolls. Filaments were very light colored and possessed tenacity of 2.02 grams per denier at break, said filaments being 4.7 denier/filament. Ultimate elongation of the yarn so made was 7.8 percent.

In place of the aqueous coagulating bath used in the above example, it is possible to remove solvent from the extruded filaments by drawing them into an externally-heated spinning column through which a flow of hot air at 140°–200° C. is passed.

Example 2.—Copolymer having reduced viscosity of 2.13 was prepared by polymerizing for 4½ hours in an agitated kettle 10 parts methyl acrylate and 90 parts acrylonitrile at a temperature of 35° C. using 1400 parts of aqueous medium and as catalyst 2.8 parts of ammonium persulfate and 1.4 parts of sodium metabisulfite. Copolymer was then separated, dried, and ground. Yield of copolymer was 71% of the weight of monomers charged. This copolymer contained more than 70% by weight acrylonitrile, and probably had composition of about 88% acrylonitrile with balance of methyl acrylate as estimated from the proportions of monomers used, the yield, and the relative reactivity ratios of the monomers as given in Copolymerization, Alfrey, Bohrer, and Mark, volume VIII, table IV, page 91 (Interscience Publishers Inc., New York, N. Y., 1952).

14 parts of the dried and ground copolymer were dissolved in a closed container in a solvent consisting of 68.8 parts of acetonitrile and 12.9 parts of formamide and 4.3 parts of H_2O using a nitrogen gas blanket and mechanical agitation at a temperature of 94° C. in a closed container.

A clear solution having viscosity of 10,000 to 12,000 centipoises at 75° C. was obtained. The solution was then extruded through a spinneret which had 40 holes each 0.005″ in diameter, the spinneret being immersed in an aqueous coagulated bath maintained at 74° C. Filaments were passed through the bath for 24 inches, snubbed around feed rolls, and led through a 36-inch hot air stretching oven at 165° C. The yarn was stretched 7 times its initial extruded length by being taken up on a winding device rotating faster than the feed rolls. Filaments were very light colored and possessed tenacity of 2.91 grams per denier at break, said filaments being 2.13 denier/filament. Ultimate elongation of the yarn so made was 6.5 percent.

Example 3.—The following is a tabular summary of representative copolymer solutions which have been made up with the solvent of our invention. Copolymer compositions are identified by the ratios of their starting monomers expressed in parts by weight. All the resulting copolymers contained at least 70% by weight of acrylonitrile.

Copolymer Ratio	Weight Percent Solids	Solvent Component Weight Ratio	Dissolving Temperature, ° C.
Methyl acrylate/acrylonitrile, 10/90.	10	acetonitrile/formamide at 90/10.	60
Do	22	same at 80/20	82
Do	15	same at 90/10	60–115
Do	15	same at 85/15	60–115
Do	15	same at 80/20	60–115
Methyl acrylate/acrylonitrile, 2/98.	20	same at 70/30	110
Methyl acrylate/vinylidene chloride/acrylonitrile, 7.5/12.5/80.	15	same at 80/20	90
Vinyl acetate/vinylidene chloride/acrylonitrile, 5/20/75.	17	acetonitrile/formamide/water, 80/15/5.	75–78
Methyl acrylate/acrylonitrile, 10/90.	15	same at 80/15/5	94
Do	20	acetonitrile/formamide, 80/20.	70
Do	20	acetonitrile/acetamide, 80/20.	100

We claim:

1. A spinning solution consisting essentially of a copolymer of acrylonitrile and at least one other substance having ethylenic unsaturation, said copolymer containing at least 70 weight percent acrylonitrile, and a solvent for said copolymer consisting essentially of 50 to 95 parts by weight acetonitrile and 50 to 5 parts by weight of an unsubstituted C_1–C_2 saturated aliphatic amide.

2. The spinning solution as defined in claim 1 wherein the reduced viscosity of the copolymer is between 0.7 and 3.0 and solids content is at least 10% by weight.

3. The spinning solution as defined in claim 1 wherein the reduced viscosity of the copolymer is between 1.0 and 2.3 and solids content is at least about 15% by weight.

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

5. The spinning solution as defined in claim 4 wherein said amide is formamide.

6. The spinning solution as defined in claim 4 wherein said amide is acetamide.

7. A spinning solution consisting essentially of a polymer of acrylonitrile and at least one other substance having ethylenic unsaturation, said copolymer being negligibly soluble in acetonitrile alone and formamide alone and containing at least 70 parts by weight acrylonitrile, and a solvent for said copolymer consisting essentially of 70 to 95 parts by weight acetonitrile and 30 to 5 parts by weight of an unsubstituted C_1–C_2 saturated aliphatic amide.

8. The spinning solution as defined in claim 7 wherein the copolymer composition is about 90 parts by weight acrylonitrile and about 10 parts by weight methyl acrylate, the reduced viscosity of said copolymer is from 1.0 to 2.3, the solvent consists essentially of acetonitrile and formamide, and the solids content is at least about 15% by weight.

9. The spinning solution defined in claim 1 wherein said copolymer of acrylonitrile is a copolymer with methyl acrylate as one ingredient thereof.

10. The spinning solution defined in claim 7 wherein said copolymer of acrylonitrile is a copolymer with methyl acrylate as one ingredient thereof.

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