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# ACRYLONITRILE SPINNING SOLUTIONS AND METHOD OF PRODUCING FILAMENTS THEREFROM

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This invention relates to a novel solvent composition and to spinning solutions prepared therefrom. More particularly, this invention relates to spinning solutions for the production of filaments of acrylonitrile polymers.

Fibers, filaments and the like prepared from polymers of acrylonitrile, particularly those polymers having a high content of acrylonitrile (usually 65 percent and higher), have proved highly satisfactory for use in the manufacture of a diversity of fabrics and the like. However, the polymers of acrylonitrile containing in excess of about 65 percent of acrylonitrile are generally incapable of solution in the ordinary solvents commonly employed for preparing conventional spinning solutions.

A number of solvent mediums have been proposed heretofore for use in preparing solutions of the acrylonitrile polymers that are difficultly soluble. For example, it has been proposed to employ N,N'-dimethylformamide, N,N'-dimethylacetamide, nitromethane, and mixtures thereof to obtain spinnable solutions of the polymers of acrylonitrile having an acrylonitrile content of 65 percent by weight and higher.

These solvents are expensive and hence have not enjoyed widespread use in the art. Also, these solvent mediums have relatively low volatility necessitating high temperatures for solvent removal when dry-spinning processes are employed. Further, these solvent mediums have relatively low miscibility with water and hence present a problem of rapid solvent removal in aqueous coagulating baths.

An object of this invention is an improved solvent composition for use in preparing spinning solutions of acrylonitrile polymers, particularly the acrylonitrile polymers containing at least about 65 percent by weight of acrylonitrile, and particularly those acrylonitrile polymers that are difficultly soluble.

Another object of this invention is a spinning solution for the preparation of filaments and fibers of acrylonitrile polymers containing 65 percent by weight of acrylonitrile and higher.

A further object of this invention is an improved process for the fabrication of filaments, fibers, and the like of acrylonitrile polymers containing at least about 65 percent by weight of acrylonitrile.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

For a complete understanding of the nature and the objects of this invention, reference is made to the following detailed description.

In accordance with this invention there is provided a novel solvent composition for use in preparing spinning solutions of acrylonitrile polymers containing at least about 65 percent by weight of acrylonitrile. The solvent composition of this invention is comprised of from about 98 percent to 60 percent by weight of acetonitrile and from about 2 percent to 40 percent by weight of a specific inorganic salt to be detailed hereinafter.

Further, and in accordance with this invention, there is provided a novel spinning solution which is comprised of the novel solvent composition of this invention and an acrylonitrile polymer containing at least about 65 percent by weight of acrylonitrile. The spinning solutions



of this invention will comprise, by weight, from about 10 percent to 30 percent of the acrylonitrile polymer and from about 90 percent to 70 percent of the solvent composition.

It has been determined that a solvent composition comprised of, by weight, from about 2 percent to 10 percent of the inorganic salt and from about 98 percent to 90 percent of acetonitrile is highly satisfactory for preparing spinning solutions of those acrylonitrile polymers containing, by weight, from about 65 percent to 70 percent of acrylonitrile. For those acrylonitrile polymers containing about 90 percent and more of acrylonitrile, it is preferred to employ a solvent composition comprised of, by weight, from about 20 percent to 40 percent of the inorganic salt and from about 80 percent to 60 percent of acetonitrile.

Also, and in accordance with this invention, it has been determined that up to about 15 percent by weight of water based on the weight of the acetonitrile can be incorporated into the novel solvent composition of this invention to improve and hasten the dissolution of the inorganic salt therein.

The inorganic salts employed in preparing the novel solvent composition of this invention are those that are substantially soluble in acetonitrile and will have the formula $C_xA_y$ wherein C is a cation selected from the group consisting of $K^+$, $Pb^{++}$, $NH_4^+$, $Cd^{++}$, $Al^{+++}$, $Na^+$, $Ba^{++}$, $Cu^{++}$, $Cu^+$, $Mg^{++}$, $Ga^{+++}$, $Li^+$, $In^{+++}$, $Tl^{+++}$, $Sn^{++++}$, $Zn^{++}$, $Ag^+$, $Ni^{++}$, $Co^{++}$, and $Mn^{++}$; wherein A is an anion selected from the group consisting of $I^-$, $Br^-$, $NO_3^-$, $SO_4^{--}$, and $SCN^-$; and wherein $x$ and $y$ are integers such that the total charge on the cation portion of the molecule or salt equals the total charge on the anion portion of the molecule or salt.

Specific examples of inorganic salts that can be employed in preparing the novel compositions of this invention include sodium iodide, potassium thiocyanate, sodium thiocyanate, lithium bromide, calcium thiocyanate, silver nitrate, ammonium thiocyanate, and zinc bromide. Mixtures of two or more of the above salts can be employed if desired.

The solvent composition of this invention is particularly useful in providing solutions comprising polymers of acrylonitrile in which the acrylonitrile content is equal to about 65 percent by weight and higher, and particularly polymers of this type that are difficultly soluble in the more common types of spinning solvents. However, the solvent composition can be employed satisfactorily to prepare solutions of acrylonitrile polymers wherein the acrylonitrile content is substantially less than about 65 percent by weight, if desired.

The solvent composition of this invention can be prepared conveniently by dissolving the inorganic salt in acetonitrile in an amount sufficient to provide a solvent composition of desired proportions of the inorganic salt and the acetonitrile. It is preferred to use the inorganic salt in finely divided form in order to hasten dissolution thereof in the acetonitrile. The dissolution of the inorganic salt in acetonitrile can be readily and easily accomplished at room temperature (23° C.); however, heating to a temperature above room temperature, usually not in excess of about 80° C., with stirring, can be employed to hasten dissolution of the salt. As above set forth a small amount of water can be added to the solvent composition to improve the solubility characteristics of the inorganic salt in the acetonitrile.

The acrylonitrile polymer is subsequently added to the solvent composition of this invention in an amount sufficient to provide a spinning solution comprising from about 10 percent to 30 percent by weight of the acrylonitrile polymer and from about 90 percent to 70 percent by weight of the solvent composition. The acrylonitrile poly-

mer is added preferably in finely divided form with rapid stirring followed by heating to complete the dissolution of the polymer in the solvent composition.

The acrylonitrile polymers that can be employed in the practice of this invention are polyacrylonitrile, copolymers of acrylonitrile, including binary and ternary polymers containing at least about 65 percent by weight of acrylonitrile in the polymer molecule. The acrylonitrile polymers of special interest for use in this invention are those that are negligibly soluble in acetonitrile alone.

Examples of acrylonitrile polymers which are particularly adapted for use in carrying out this invention include those polymers comprised of from about 2 percent to 35 percent by weight of methyl acrylate and from about 98 percent to 65 percent of acrylonitrile, a specific example being that polymer having excellent dyeing properties comprised of, by weight, about 10 percent of methyl acrylate and 90 percent of acrylonitrile; a polymer comprised of 5 percent by weight of vinyl acetate, 20 percent by weight of vinylidene chloride, and 75 percent by weight of acrylonitrile; a polymer comprised of about 7½ percent by weight of methyl acrylate, about 12½ percent by weight of vinylidene chloride and about 80 percent by weight of acrylonitrile; and a polymer comprised of about 10 percent by weight of methyl acrylate, about 10 percent by weight of methyl methacrylate, and about 80 percent by weight of acrylonitrile.

The novel solvent composition of this invention permits the use of relatively moderate spinning temperatures of the order from about 70° to 80° C. When dry-spinning techniques are employed in forming filaments from the spinning solution of this invention, solvent removal from the formed filaments can be accomplished by use of hot air maintained at a temperature of from about 140° C. to 200° C. When wet-spinning methods are employed to form filaments, solvent removal from the formed filaments can be accomplished by extrusion of the spinning solution into an aqueous coagulating bath maintained at a temperature of from about 60° C. to 80° C., with a temperature of about 70° C. being preferred. After solvent removal, the thus prepared or extruded filaments are subsequently stretched or drafted to about 300 percent to 600 percent of its original length thereby providing filaments satisfactory for use in the manufacture of textiles.

The following examples are illustrative of this invention. All parts are by weight unless otherwise indicated.

*Example I*

About 10 parts of a 90 percent by weight acrylonitrile-10 percent by weight methyl acrylate polymer having a molecular weight of about 40,000 is dissolved in about 55 parts of a solvent composition prepared by dissolving about 10 parts of sodium thiocyanate in about 45 parts of acetonitrile. The solution thus prepared is extruded through a small orifice into a water bath. The filament that is formed by this extrusion is passed over a hot roll maintained at a temperature of about 150° where it is dried. The filament is subsequently drafted to about 300 percent of its original length. The resulting fiber is strong, tough, and has a high softening temperature.

*Example II*

A solvent composition is prepared by dissolving about 10 parts of silver nitrate in about 40 parts of acetonitrile. Three parts of an acrylonitrile polymer comprised of, by weight, about 92.5 percent of acrylonitrile and about 7.5 percent of methyl acrylate is admixed with about 20 parts of the solvent composition to provide a spinning solution. The spinning solution is tumbled in a container for about 30 minutes. During the tumbling the spinning solution is maintained at a temperature of about 50° C. On cooling to room temperature (about 23° C.) a viscous spinning solution is obtained that can be formed into strong, high-temperature softening fibers in accordance with the method of Example I.



*Example III*

A viscous spinning solution is prepared in substantially the same manner as in Example II with the exception that the solvent composition employed is prepared by dissolving about 10 parts of ammonium thiocyanate in a mixture of about 36 parts of acetonitrile and about 4 parts of water. Filaments spun from this spinning solution are strong and soften only at relatively high temperatures.

*Example IV*

A viscous spinning solution is prepared in substantially the same manner as in Example II with the exception that the solvent composition employed is prepared by dissolving about 10 parts of zinc bromide in a mixture of about 4 parts of water and 36 parts of acetonitrile. Fibers spun from this spinning solution are strong, tough, and have relatively high softening temperatures.

In addition to fibers and filaments, the spinning solutions of this invention can be employed in the preparation of other shaped articles of acrylonitrile polymers wherein the acrylonitrile content is in excess of about 65 percent by weight. Examples of such shaped articles include film, sheets, casings, tubings, rods, and the like. These members can be formed by conventional methods well known in the art.

It is to be understood that the above description and examples are illustrative of this invention and not in limitation thereof.

We claim:

1. A spinning solution consisting essentially of, by weight, (I) from about 10% to 30% of a polymer selected from the group consisting of polyacrylonitrile and a copolymer of acrylonitrile and at least one other substance having ethylenic unsaturation, said copolymer containing at least about 65% by weight of acrylonitrile and (II) from about 90% to 70% of a solvent composition consisting essentially of, by weight, (a) from about 98% to 60% of acetonitrile and (b) from about 2% to 40% of an acetonitrile soluble inorganic salt having the formula $C_xA_y$ wherein C is a cation selected from the group consisting of $K^+$, $Pb^{++}$, $NH_4^+$, $Cd^{++}$, $Al^{+++}$, $Na^+$, $Ba^{++}$, $Cu^{++}$, $Cu^+$, $Mg^{++}$, $Ga^{+++}$, $In^{+++}$, $Tl^{+++}$, $Li^+$, $Sn^{++++}$, $Zn^{++}$, $Ag^+$, $Ni^{++}$, $Co^{++}$, and $Mn^{++}$; wherein A is an anion selected from the group consisting of $I^-$, $Br^-$, $NO_3^-$, $SO_4^{--}$, and $SCN^-$; and wherein $x$ and $y$ are integers such that the total charge on the cation portion of the molecule equals the total charge on the anion portion of the molecule.

2. The spinning solution of claim 1 wherein the (II)(b) inorganic salt is sodium iodide.

3. The spinning solution of claim 1 wherein the (II)(b) salt is potassium thiocyanate.

4. The spinning solution of claim 1 wherein the (II)(b) salt is sodium thiocyanate.

5. The spinning solution of claim 1 wherein the (II)(b) inorganic salt is calcium thiocyanate.

6. The spinning solution of claim 1 wherein the (II)(b) inorganic salt is ammonium thiocyanate.

7. The spinning solution of claim 1 wherein the (II)(b) inorganic salt is lithium bromide.

8. The spinning solution of claim 1 wherein the (II)(b) salt is silver nitrate.

9. The spinning solution of claim 1 wherein the (II)(b) inorganic salt is zinc bromide.

10. In the method of producing filaments from acrylonitrile polymers containing at least about 65% by weight of acrylonitrile the steps which comprise preparing a spinning solution consisting essentially of, by weight, (I) from about 10% to 30% of a polymer selected from the group consisting of polyacrylonitrile and a copolymer of acrylonitrile and at least one other substance having ethylenic unsaturation, said copolymer containing at least about 65% by weight of acrylonitrile and (II) from about 90% to 70% of a solvent composition consisting essentially of, by weight, (a) from about 98% to 60% of acetonitrile and

(b) from about 2% to 40% of an acetonitrile soluble inorganic salt having the formula $C_xA_y$ wherein C is a cation selected from the group consisting of $K^+$, $Pb^{++}$, $NH_4^+$, $Cd^{++}$, $Al^{+++}$, $Na^+$, $Ba^{++}$, $Cu^{++}$, $Cu^+$, $Mg^{++}$, $Ga^{+++}$, $In^{+++}$, $Tl^{+++}$, $Sn^{++++}$, $Li^+$, $Zn^{++}$, $Ag^+$, $Ni^{++}$, $Co^{++}$, and $Mn^{++}$; wherein A is an anion selected from the group consisting of $I^-$, $Br^-$, $NO_3^-$, $So_4^{--}$, and $SCN^-$; and wherein $x$ and $y$ are integers such that the total charge on the cation portion of the molecule equals the total charge on the anion portion of the molecule, forming the solution into the form of filaments, removing from the formed filaments substantially all the solvent composition present therein, and drafting the resulting filaments whereby there are provided filaments suitable for use in the manufacture of textiles.

11. The method of claim 10 wherein the filaments are drafted to from about 300 percent to 600 percent of their originally formed length.

12. The method of claim 10 wherein the filaments are formed by extruding the spinning solution into an atmosphere of air maintained at a temperature of from about 140° C. to 200° C. to remove therefrom substantially all solvent.

13. The method of claim 10 wherein the filaments are formed by extruding the spinning solution into an aqueous coagulating bath maintained at a temperature of from about 60° C. to 80° C.



14. The method of claim 10 wherein the (II)(b) inorganic salt is sodium iodide.

15. The method of claim 10 wherein the (II)(b) inorganic salt is potassium thiocyanate.

16. The method of claim 10 wherein the (II)(b) inorganic salt is sodium thiocyanate.

17. The method of claim 10 wherein the (II)(b) inorganic salt is calcium thiocyanate.

18. The method of claim 10 wherein the (II)(b) inorganic salt is ammonium thiocyanate.

19. The method of claim 10 wherein the (II)(b) inorganic salt is lithium bromide.

20. The method of claim 10 wherein the (II)(b) inorganic salt is silver nitrate.

21. The method of claim 10 wherein the (II)(b) inorganic salt is zinc bromide.

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