

1

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POLYURETHANE SPINNING SOLUTIONS CONTAINING ETHYLENE DIAMINE AND 1-AMINO-3-AMINOMETHYL-3,5,5-TRIMETHYL CYCLO-HEXANE

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ABSTRACT OF THE DISCLOSURE

Spinning solutions for the preparation of spandex fibers are prepared by reacting an NCO terminated polyester-4,4'-diphenylmethane diisocyanate prepolymer in a polar solvent with a mixture of ethylene diamine and 1-amino-3-aminomethyl-3,5,5-trimethyl cyclohexane. The solutions are spun by the wet or dry spinning method to prepare filaments.

This invention relates to the preparation of polyurethane spinning solutions and to rubbery elastic filaments and fibers from segmented polyurethane-polyurea elastomers which are resistant to gel formation when dissolved in polyacrylonitrile solvents.

Numerous processes are already known for producing elastic filaments and fibers based on polyurethanes and which have many uses in the textile industry where they are used alone or are ensheathed in other filaments which are wound or spun around them. They are used mainly in the production of corsets, sportswear, elastic stockings and in the manufacture of elastic bands for underwear and stockings. The material used in the manufacture of elastic filaments and fibers is usually based on high molecular weight, segmented polymers which contain in the molecule urethane and urea groups, which polymers may be prepared by the isocyanate polyaddition process from polyesters or polyethers containing hydroxyl groups, diisocyanates and diamines. The prepolymers are extruded by a process known as "chemical spinning" through spinning nozzles into a coagulating bath which contains ethylene diamine, and possibly also small quantities of polyamines, as reaction components for obtaining the high molecular weight, segmented polyurethane-polyurea filaments. Owing to the prepolymers which contain free isocyanate groups having such high reactivity, they can only be stored for a limited length of time, and it has therefore become desirable to prepare soluble high molecular weight segmented polyurethane-polyurea adducts in solvents and work up these solutions into filaments and fibers by the wet or dry spinning process.

Furthermore, it is already known that polyesters containing hydroxyl groups and diisocyanates may be reacted at elevated temperatures to produce NCO-containing polymers which can then be reacted in polyacrylonitrile solvents with ethylene diamine at temperatures below 20° C. to produce high molecular weight polyurethane-polyurea adducts. The filaments obtainable from these solutions by spinning have good general physical and elastic properties. One feature of the production of filaments on industrial scale is the relatively short time within which these solutions undergo gel formation, and spinning becomes impossible. This process has been found to be particularly advantageous in the case of solutions having viscosities of 600 to 1,000 poises at 20° C. However, one must be able to store solutions having such viscosities

2

for over a week under normal industrial conditions rather than only for the production of filaments by the dry spinning process.

It is therefore an object of this invention to provide improved spinning solutions. It is another object to provide spinning solutions having improved storage characteristics. It is still another object to provide spinning solutions having high resistance to gel formation and degradation. It is a further object of this invention to provide improved spandex fibers.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with the invention generally speaking by providing spinning solutions for the preparation of spandex fibers by reacting in a polar solvent for polyacrylonitrile an NCO containing prepolymer with a mixture of ethylene diamine and 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane. The prepolymer is prepared by reacting a substantially linear polyester having terminal hydroxyl groups and a molecular weight of from about 1,600 to about 2,600 with 4,4'-diphenylmethane diisocyanate in a ratio of NCO to OH of from about 1.5:1 to about 1.95:1. The highly viscous spinning solutions are subsequently formed into elastic filaments by the wet or dry spinning process.

To prepare the spinning solutions according to the invention, a substantially linear polyester containing hydroxyl groups and having a molecular weight of about 1,600 to about 2,600, preferably about 1,700 to about 2,100, is reacted in the melt or in inert solvents, such as, methylene dichloride, tetrahydrofuran, dioxane, benzene or chlorobenzene, and if desired in admixture with low molecular weight diols having one or more tertiary nitrogen atoms, with diphenylmethane-4,4'-diisocyanate at a temperature below 130° C. The ratio of NCO to OH groups in the components used in this reaction should be from about 1.5 to 1 to about 1.95 to 1 in order that prepolymers having free NCO groups will be produced.

The linear polyesters containing terminal hydroxyl groups are prepared by condensing a dicarboxylic acid and one or more diols at elevated temperature. The acid numbers of the polyesters are generally below 8, preferably 0 to 3. The melting point of the polyesters is preferably below about 60° C. because otherwise the elastic properties of the end-products will be impaired, especially at low temperatures, and the tendency of the polymers to gel in solution will also be adversely affected. Any suitable dicarboxylic acid may be used in the production of these polyesters, such as, for example, succinic acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, thiodibutyric acid, sulfonyldibutyric acid and the like. Any suitable diols may be used, such as, for example, ethylene glycol, diethylene glycol, propane-1,2-diol, butane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, hexahydro-p-xylyleneglycol, 2,2-dimethylpropane-1,3-diol, 2,2-diethylpropane-1,3-diol, the hydroxyalkylation products of the above glycols and the like. Polyesters of lactones, e.g. ϵ -caprolactone, may also be used as starting materials. Since the polyesters prepared in this way are highly reactive components, it is quite customary to deactivate them with small quantities of dioxane/SO₂ adduct, benzoyl chloride or traces of hydrogen chloride before they are reacted with diphenylmethane-4,4'-diisocyanate.

Any suitable low molecular weight diols containing one or more tertiary nitrogen atoms may, if desired, be mixed into the polyester, such as, for example, the bis-hydroxyalkylation products of primary and disecundary amines with ethylene oxide, propylene oxide and butylene oxide, and have a molecular weight below 500, such as, for example, N-methyl-diethanolamine, N-butyl-diethanolamine, N-cyclohexyl-diethanolamine, N,N'-di-(b-hydroxyethyl)-N,N'-diethylhexahydro-p-phenylenediamine, N,N'-

di-(b-hydroxyethyl)-N,N'-dimethyl-ethylene diamine, bis-b-hydroxyethylpiperazine and the like. Preferably, however, N-methyl-diisopropanolamine and N,N'-di-(b-hydroxypropyl)-N,N'-dimethyl-ethylene diamine are used. Low molecular weight basic polyethers having tertiary nitrogen atoms, may also be mixed with the polyester. These compounds are obtainable by condensation of the above-mentioned compounds in the presence of phosphorous acid. The quantity of diols having one or more tertiary nitrogen atoms should be so calculated that the amount of tertiary nitrogen atoms, based on the finished elastomer substance, does not exceed 200 milliequivalents/Kg, and preferably only 80 to 150 milliequivalents of tertiary nitrogen are present per kilogram of elastomer product.

In order to prepare the polyurethane-polyurea solutions, the NCO-containing prepolymers obtained in the melt are added slowly, with stirring, at temperatures below about 35° C. and preferably below about 25° C. into a solution of ethylene diamine and 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane (present as a mixture of two stereoisomeric forms), in a polyacrylonitrile solvent. The quantity of solvent is usually so calculated that after termination of the chain lengthening reaction, the polyurethane-polyurea solution is present in the desired concentration. The chain lengthening reaction is accompanied by a rapid rise in viscosity so that viscosities of between 150 and 600 poises at 20° C. are reached. The product is then often adjusted to a desired higher final viscosity by the addition of a small quantity of hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate or biuretriisocyanate which is obtained by reacting 3 mols of hexamethylene-1,6-diisocyanate and 1 mol of water. In most cases, however, the isocyanates are added diluted with a small quantity of solvent.

The solids content of the finished elastomer solution may amount to 18 to 30 percent by weight. The polyacrylonitrile solvents used, such as N,N-dimethylformamide, N,N-dimethyl acetamide and N-methylpyrrolidone, must be free from constituents which are capable of reacting with diisocyanates although these solvents may contain the usual small quantities of water found in commercial solution.

The molar ratio of the chain lengthening mixture of ethylene diamine and 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane employed may be varied between 60:40 and 90:10 but is preferably between 75:25 and 80:20. However, the overall molar ratio of chain lengthening mixture is already partly determined by the ratio of NCO to OH groups used in the preparation of the NCO-containing prepolymer. In general, if the NCO content of the prepolymer is relatively low, one also uses a low proportion of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in the chain lengthening mixture and conversely, a higher NCO content in the prepolymer necessitates the use of a higher proportion of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane for the preparation of stable polyurethane-polyurea solutions. The quantity of ethylene diamine/1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane mixture used for the chain lengthening reaction amounts to 90 to 140 mols percent, depending on the NCO to OH ratio in the prepolymer and the desired final viscosity. The percentage of chain lengthening agents added is based on the free NCO groups-content of the prepolymers.

When preparing the polyurethane-polyurea solutions, it is not absolutely necessary to add the melt of the NCO-containing prepolymer into the solution of chain lengthening mixture. According to another embodiment of the invention, the prepolymer melt may be dissolved in a part of the polyacrylonitrile solvent and rapidly cooled to about 25 to 30° C., this solution then being added as described before, to the solution of chain lengthening mixture. If, however, the prepolymer has been prepared in one of the above-mentioned inert solvents, it is generally

advisable to remove the solvent by distillation before the chain lengthening reaction. The process is in no way, however, impaired by the presence of this inert solvent provided it does not amount to more than 20 percent by weight, based on the total amount of solvent.

Titanium dioxide, talcum or other pigments may, of course, be added to the elastomer solution before further working up, or alternatively these pigmenting agents may already be present during the chain lengthening reaction.

The polyurethane-polyurea polymers which are obtained in solution when carrying out the process according to the invention are of particular importance in industry owing to their high solubility and the resistance of their solutions to gel formation and degradation at room temperature or slightly elevated temperature. The elastic filaments and fibers are produced by known spinning methods, either dry, i.e., by spinning the elastomer solution in air or inert gases at elevated temperatures, or wet, i.e., by injecting the elastomer solution into coagulating baths and winding the resulting filaments which are given a surface treatment with talcum or oily dressings to prevent them from sticking together on the spool. The spun filaments have excellent physical properties such as high elongation on tearing and high mechanical strength, low permanent elongation and high elastic modulus.

The invention is further illustrated by the following examples in which parts are by weight unless otherwise specified.

EXAMPLE 1

About 250 parts of a polyester of adipic acid, hexane-1,6-diol and 2,2-dimethylpropane-1,3-diol (proportion by weight of diols 65/35; OH number 55.5; acid number 0.8) are dehydrated for about one hour at about 120° C. under pressure of about 12 mm. Hg and then reacted with about 50 parts of diphenylmethane-4,4'-diisocyanate at about 90 to about 95° C. for about one hour, with stirring. The melt of the polyester-diisocyanate adduct is dissolved in about 400 parts of N,N-dimethylformamide (H₂O content 0.01 percent) and cooled to 20 to 25° C. in about 10 minutes.

(a) Part of the NCO-containing prepolymer solution is introduced slowly, with stirring, at about 17 to about 22° C. into a solution of about 3.8 parts of ethylene diamine and about 2.55 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in about 428 parts of N,N-dimethylformamide. A spinning solution is obtained which has a solids content of 27 percent and a viscosity of 185 poises/20° C. By observing the spinning conditions given in instructions hereinafter described, filaments having the following properties were obtained by the wet spinning process:

Titre (d.)	640
Strength (g./d.)	0.33
Elongation at break (percent)	620
Permanent elongation (percent)	15
E-modulus (mg./d.)	52

(b) Part of the NCO-containing prepolymer solution is introduced slowly, with stirring, at about 18 to about 25° C. into a solution of about 4.05 parts of ethylene diamine and about 1.3 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in about 425 parts of N,N-dimethylformamide. The viscosity of the resulting spinning solution, which has a solids content of 27 percent, is 210/20° C. Filaments having the following properties can be obtained by observing the general instructions given hereinafter for the wet spinning process:

Titre (d.)	620
Strength (g./d.)	0.35
Elongation at break (percent)	590
Permanent elongation (percent)	15
E-modulus (mg./d.)	63

EXAMPLE 2

About 250 parts of the dehydrated polyester described in Example 1 are reacted with about 56.25 parts of diphenylmethane-4,4'-diisocyanate at about 90 to about 95° C. for about one hour, with stirring, to form a prepolymer which is then dissolved in about 400 parts of N,N-dimethylformamide (H₂O content 0.01 percent) and cooled to about 25° C. in about 10 minutes.

(a) Part of the prepolymer solution is introduced slowly at room temperature, with stirring, into a solution of about 5.7 parts of ethylene diamine and about 1.8 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in about 449 parts of N,N-dimethylformamide. The spinning solution produced by rapid rise is viscosity to 156 poises/20° C., which solution has a solids content of 27 percent, is spun by the wet spinning process according to the instructions given hereinafter to form filaments which have the following properties:

Titre (d.)	630
Strength (g./d.)	0.30
Elongation at break (percent)	670
Permanent elongation (percent)	19
E-modulus (mg./d.)	58

(b) Part of the prepolymer solution is introduced slowly, with stirring, at room temperature into a solution of about 5.0 parts of ethylene diamine and about 3.6 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in about 452 parts of N,N-dimethylformamide. The viscosity of the resulting spinning solution which has a solids content of 27 percent, is about 170 poises/20° C. Filaments having the following properties are obtained from the this spinning solution according to the instructions given hereinafter for the wet spinning process:

Titre (d.)	650
Strength (g./d.)	0.35
Elongation at break (percent)	680
Permanent elongation (percent)	18
E-modulus (mg./d.)	56

EXAMPLE 3

About 3 parts of a 35 percent SO₂/dioxane solution are added to about 200 parts of a mixed polyester of hexane-1,6-diol, 2,2-dimethylpropane-1,3-diol and adipic acid (proportion by weight of diols 65/35; OH number 65.2; acid number 0.9) and the reaction mixture is stirred for about 4 hours at about 100° C. and then freed from dioxane and traces of water by heating for about one hour at about 100° under a pressure of about 12 mm. Hg. About 4.14 parts of N-methyldiisopropanolamine are stirred into the polyester melt, and about 59.1 parts of diphenylmethane-4,4'-diisocyanate are then added and the components are reacted together for about one hour, with stirring, at about 80 to about 85° C. to form an NCO-containing prepolymer. The prepolymer is dissolved in about 400 parts of N,N-dimethylformamide (H₂O content 0.01 percent) and is at the same time cooled to about 25° C. within about 15 minutes. The prepolymer solution is then introduced slowly at room temperature into a dispersion of about 6.8 parts of titanium dioxide (rutile) in a solution of about 4.6 parts of ethylene diamine and about 4.3 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl cyclohexane in about 450 parts of N,N-dimethylformamide. The viscosity of the resulting spinning solution which has a solids content of 27 percent, is 230 poises/20° C. Filaments having the following properties can be obtained from this solution by the wet spinning process described hereinafter:

Titre (d.)	550
Strength (g./d.)	0.49
Elongation at break (percent)	500
Permanent elongation (percent)	21
E-modulus (mg./d.)	103

EXAMPLE 4

About 200 parts of the deactivated and dehydrated polyester described in Example 3 and about 4.14 parts of N-methyldiisopropanolamine are reacted for about one hour at about 75 to about 80° C. with about 65.7 parts of diphenylmethane-4,4'-diisocyanate. The NCO-containing prepolymer is dissolved in about 400 parts of N,N-dimethylformamide (H₂O content 0.01 percent) and at the same time cooled at about 25° C. within about 15 minutes. The solution of the prepolymer is introduced slowly at room temperature into a stirred solution of about 5.8 parts of ethylene diamine and about 5.5 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in about 360 parts of N,N-dimethylformamide. About 7 parts of finely divided titanium dioxide (rutile) are then added to the viscous solution over the course of several hours. When the solids content of the spinning solution is 27.5 percent, stable viscosity is 365 poises/20° C. Filaments having the following properties are obtained under the conditions given hereinafter for the wet spinning process:

Titre (d.)	580
Strength (g./d.)	0.45
Elongation at break (percent)	490
Permanent elongation (percent)	22
E-modulus (mg./d.)	133

EXAMPLE 5

About 3750 parts of the polyester described in Example 1 are deactivated with about 15 parts of a 35 percent SO₂/dioxane solution in a manner analogous to that indicated in Example 3, and dehydrated and thoroughly mixed with about 75 parts of N-methyldiisopropanolamine. The mixture is then reacted for about one hour at about 90 to about 95° C. with about 954 parts of diphenylmethane-4,4'-diisocyanate. The resulting prepolymer is dissolved in about 6000 parts of N,N-dimethylformamide (H₂O content 0.01 percent) and cooled to about 25° C. within about 30 minutes. The NCO-containing prepolymer solution is introduced slowly, with stirring, at 18 to 23° C. into a solution of about 67.8 parts of ethylene diamine and about 63.8 parts of 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane in about 7600 parts of N,N-dimethylformamide which in addition contains about 123 parts of titanium dioxide (rutile) dispersed in it. Addition of about 21 parts of hexamethylene-1,6-diisocyanate causes the viscosity to rise to 920 poises/20° C. The spinning solution obtained, which has a solids content of 27 percent, is spun by the wet spinning process described in detail hereinafter to form filaments having the following properties:

Titre (d.)	500
Strength (g./d.)	0.35
Elongation at break (percent)	680
Permanent elongation (percent)	20
E-modulus (mg./d.)	50

The same solution is worked up by the dry spinning process described hereinafter to produce filaments having the following properties:

Titre (d.)	460
Strength (g./d.)	0.84
Elongation at break (percent)	520
Permanent elongation (percent)	11
E-modulus (mg./d.)	80

EXAMPLE 6

The mixture of polyester and N-methyldiisopropanolamine described in the preceding example is reacted for about one hour at 90 to 95° C. with about 1073 parts of diphenylmethane-4,4'-diisocyanate. The resulting prepolymer is dissolved in about 6000 parts of N,N-dimethylformamide (H₂O content 0.01 percent) and cooled to about 25° C. within about 30 minutes. The NCO-contain-

ing prepolymer solution is introduced slowly, with stirring, at 18 to 24° C. into a solution of about 90 parts of ethylenediamine and about 85.2 parts of 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane in about 8060 parts of N,N-dimethylformamide which in addition contains about 128 parts of titanium dioxide (rutile) dispersed in it. The viscosity is adjusted to 720 poises/20° C. after several hours by adding about 23 parts of hexamethylene-1,6-diisocyanate in about 50 parts of N,N-dimethylformamide. The spinning solution, which contains 27 percent of solids, can be formed into filaments having the following properties by the hereinafter described wet spinning process:

Titre (d.)	570
Strength (g./d.)	0.45
Elongation at break (percent)	540
Permanent elongation (percent)	20
E-modulus (mg./d.)	89

Filaments having the following properties can be produced from the same solution by the dry spinning process described hereinafter:

Titre (d.)	550
Strength (g./d.)	0.79
Elongation at break (percent)	490
Permanent elongation (percent)	15
E-modulus (mg./d.)	100

Spinning of the spinning solutions described in Examples 1-6 into endless filaments.

Before spinning, the solutions are thoroughly filtered by passing them through a filter press and are then degasified in a vacuum to make free from bubbles.

The solutions indicated can be spun both by the wet and the dry spinning process.

(I) Wet spinning process

The filtered and degasified solution is spun via a spinning pump through a multiaperture spinneret with nozzle diameters of 50 to 200 microns into a water bath 2 to 10 meters in length which is heated to from about 20 to about 80° C., preferably about 40 to about 70° C., and which contains 2 to 10 percent N,N-dimethylformamide. The filaments which emerge are drawn off at a speed of 5 to 50 m./min. at a draught of 0.5 to 5. After drying at about 60° C., the filaments are wound. The physical properties indicated for the products obtained in the examples are determined by known methods.

(II) Dry spinning process

The filtered and degasified solution is delivered by a spinning pump to a spinneret which is at a temperature of from about 15 to about 90° C., depending on the viscosity. The solution is injected through a multiaperture nozzle of nozzle diameter 80 to 250 microns into a heated shaft. The temperature of the air blast must be so chosen that the temperature of the air on the spinning nozzle is about 130 to about 230° C. The air which enters the shaft from above and which is meanwhile charged with solvent is withdrawn in front of the end of the shaft. The filaments emerging at the end of the shaft are drawn off at speeds of 200 to 600 m./min., preferably 200 to 400 m./min. The N,N-dimethylformamide content of the filaments is less than 1 percent by weight. Before the filaments are wound, a dressing which prevents adhesion is applied to them. The filament properties are then tested by the known methods.

Explanatory notes on the filament tests

(1) All dynamic tests were carried out at a rate of deformation of the filament of 400 percent per minute.

(2) The permanent elongation is determined after stretching the filament three times by 300 percent of its initial length, allowing a recovery time, in each case of about 30 seconds.

(3) The modulus is determined by elongation of the filament to 300 percent of its initial length.

EXAMPLE 7

About 21,000 parts of a mixed polyester of hexane-1,6-diol, 2,2-dimethylpropane-1,3-diol and adipic acid (molar ratio of diols 65:35; OH number 1.45) are dehydrated in a vacuum at about 120° C. for about one hour, mixed with about 445 parts of N-methyldiisopropanolamine and about 6300 parts of diphenylmethane-4,4'-diisocyanate at about 70° C., and heated to about 90° C. for about 50 minutes with stirring. About 26,500 parts of the NCO-containing prepolymer melt so produced are introduced with intensive stirring into a cold solution of about 540 parts of ethylene diamine and about 380 parts of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane in about 77,000 parts of N,N-dimethylformamide, which contains in addition about 1140 parts of titanium dioxide (rutile) dispersed in it. The viscosity is adjusted to 690 poises by further addition of about 195 parts of hexamethylene-1,6-diisocyanate.

(a) The spinning solution is briefly heated at about 90° C. and directly thereafter spun dry from a 48 aperture spinneret at a shaft temperature of about 200° C. The filaments are wound at a rate of about 300 m./min.

Titre (d.)	460
Strength (g./d.)	0.70
Elongation at break (percent)	490
Permanent elongation (percent)	16.6
E-modulus (mg./d.)	132

(b) The spinning solution is briefly heated to about 65° C. and directly thereafter spun dry from a 12 aperture spinneret at a shaft temperature of about 170° C. The draw-off speed is 450 m./min.

Titre (d.)	78
Strength (g./d.)	0.70
Elongation at break (percent)	360
Permanent elongation (percent)	9.4
E-modulus (mg./d.)	610

It is to be understood that any of the polyester solvents or glycols may be substituted throughout the examples for those specifically used.

Although the invention has been described in considerable detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for this purpose and that variations can be made by those skilled in the art without departing from the spirit and scope of the invention except as is set forth in the claims.

What is claimed is:

1. A spinning solution for the preparation of polyurethane fibers prepared by the process which comprises reacting in a polar solvent for polyacrylonitrile an NCO-terminated prepolymer with a mixture of ethylene diamine and 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane, said prepolymer being prepared by the process which comprises reacting one mol of a substantially linear polyester having terminal hydroxyl groups and a molecular weight of from about 1,600 to about 2,600 with from about 1.5 to about 1.95 mols of 4,4'-diphenylmethane diisocyanate.

2. The spinning solution of claim 1 wherein the ratio of ethylene diamine of 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane is from about 60:40 to about 90:10.

3. The spinning solution of claim 1 wherein the ratio of ethylene diamine to 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane is from about 75:25 to about 80:20.

4. The spinning solution of claim 1 wherein the prepolymer is prepared from an hydroxyl polyester, 4,4'-diphenylmethane diisocyanate and a glycol containing ter-

tiary nitrogen atoms and having a molecular weight less than 500.

5. Polyurethane fibers prepared by the process which comprises spinning the solutions of claim 1.

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