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## POLYURETHANE SPINNING SOLUTIONS CONTAINING ETHYLENE DIAMINE AND BIS-(4-AMINOPHENYL)-ALKANE POLYURETHANES

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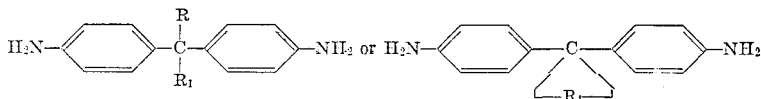
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7 Claims

### 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 a diamine having the formula



where R and R<sub>1</sub> are lower alkyl and R<sub>4</sub> is an alkylene radical of 2 to 6 carbon atoms. 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, which filaments and fibers have a large number of uses in the textile industry in which they are either spun singly or are ensheathed by other filaments wound or spun around them. They are mainly used in the production of corsets, sportswear, elastic stockings and in the manufacture of elastic bands for use in underwear and stockings. The elastic filaments and fibers are usually produced from high molecular weight segmented polymers containing in the molecule, urethane and urea groups, which polymers may be prepared by the isocyanate polyaddition process from polyesters or polyethers containing hydroxyl groups, diisocyanate and diamines. The prepolymers are extruded by a process known as "chemical spinning," through spinning nozzles into a coagulating bath which contains cross-linking agents. For obtaining filaments having a high molecular weight segmented polyurethane-polyurea structure, ethylene diamine and possibly also small quantities of polyamines have been used in the coagulating bath. Owing to the high reactivity of the prepolymers containing isocyanate groups, and owing to the consequent instability during storage of the prepolymers, it has been found desirable to prepare solutions of high molecular weight segmented polyurethane-polyurea adducts in suitable solvents and to work up these solutions into filaments and fibers by the wet or dry spinning process.

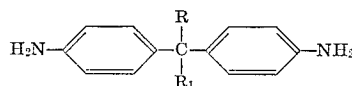
Furthermore, it is already known that polyesters containing hydroxyl groups and diisocyanates may be reacted together at elevated temperatures to produce NCO-containing prepolymers and then to react these in polyacrylonitrile solvents at temperatures below 20° C. with ethylene diamine to form high molecular weight polyurethane-polyurea adducts. The filaments obtainable from these solutions by spinning have good physical and elastic prop-

erties. One factor which is particularly detrimental to the production of filaments on an industrial scale is the relatively short time within which these solutions undergo gel formation, with the result that spinning becomes impossible. This is found to be particularly disadvantageous in solutions having viscosities of 600 to 1000 poises at 20° C. However, while such solutions are suitable for use immediately in the production of filaments by the dry spinning process, stability on storage of over a week are usually required for spinning solutions used under normal industrial conditions.

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 another object to provide spinning solutions having high resistance to gel formation and degradation. It is still another object of this invention to provide improved spandex fibers.

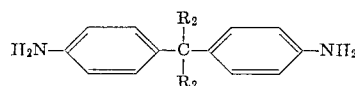
The foregoing objects and others which will become apparent from the following description are accomplished in accordance with this invention, generally speak-

ing, 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 a compound having the formula

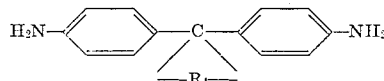


where R and R<sub>1</sub> are lower alkyl or are joined to the methylene carbon atom in a cycloaliphatic radical. The prepolymer is prepared by reacting a substantially linear polyester having terminal hydroxyl groups and a molecular weight of from about 1600 to about 2600 with 4,4'-diphenylmethane diisocyanate 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.

The diamino compounds used in admixture with ethylene diamine and represented by the formula above may also be represented by the formulae



where R<sub>2</sub> is lower alkyl such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, hexyl and the like or



where R<sub>4</sub> is an alkylene radical of 2 to 6 carbon atoms such as ethylene, propylene, butylene, amylene or hexylene, bonded to the carbon atom intermediate the two aromatic rings to form a cycloaliphatic radical.

Any suitable compound within the general formula may be used, such as, for example, 2,2-bis-(4-aminophenyl) propane, 1,1-bis-(4-aminophenyl)-cyclohexane, bis-(4-aminophenyl)-diethylmethane, bis-(4-aminophenyl)-ethyl, isopropyl methane, bis-(4-aminophenyl)-tertiary butyl, hexylmethane, bis-(4-aminophenyl)-dipropylmethane, bis-(4-aminophenyl)-methyl, ethylmethane, 1,1-bis-(4-aminophenyl)-cyclopropane, 1,1-bis-(4-aminophenyl)-cyclobutane, 1,1-bis-(4-aminophenyl)-cyclopentane,

tane, 1,1-bis-(4-aminophenyl)-cyclohexane, 1,1-bis-(4-aminophenyl)-cycloheptane and the like.

To prepare the spinning solutions according to the invention a substantially linear polyester containing hydroxyl groups and having an average molecular weight of from about 1600 to about 2600, preferably from about 1700 to about 2100, is reacted in the melt or in inert solvents such as methylene dichloride, tetrahydrofuran, dioxan, benzene or chlorobenzene, and if desired mixed with low molecular weight diols containing one or more tertiary nitrogen atoms, with diphenyl methane-4,4'-diisocyanate at temperatures below 130° C. The ratio of NCO to OH groups in the components used in the reaction should be from about 1.5:1 to about 1.95:1 in order that prepolymers containing free NCO groups will be produced.

The linear polyesters containing terminal hydroxyl groups are prepared by condensation of dicarboxylic acids and diols at elevated temperatures. The acid numbers are generally below 8, preferably 0 to 3. The melting point of the polyester 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 acids may be used in the preparation of the polyesters such as, for example, succinic acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, thiodibutyric acid, sulphonyl dibutyric acid and the like.

Any suitable diol 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-xylylene glycol, 2,2-dimethylpropane-1,3-diol, 2,2-diethyl-propane-1,3-diol, the hydroxyalkylation products of the above glycols and the like. Polyesters of lactones, e.g.  $\epsilon$ -caprolactone, may also be used as starting materials. Since the polyesters prepared in this way are highly reactive one may deactivate them using small quantities of dioxane/SO<sub>2</sub> adduct, benzoyl chloride or traces of hydrogen chloride before the subsequent reaction with diphenyl methane-4,4'-diisocyanate.

Any suitable low molecular weight diols containing one or more tertiary nitrogen atoms may, if desired, be mixed in with 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 of less than 500 such as, for example, N-methyl-diethanolamine, N-butyl-diethanolamine, N-cyclohexyl-diethanolamine, N,N'-di-( $\beta$ -hydroxyethyl) - N,N'-diethyl-hexahydro-p-phenylene diamine, N,N'-di-( $\beta$ -hydroxyethyl)-N,N'-di-methyl-ethylene diamine, bis- $\beta$ -hydroxyethylpiperazine and the like. However, particularly preferred are compounds such as N-methyldiisopropanolamine and N,N'-di-( $\beta$ -hydroxypropyl)-N,N'-dimethyl-ethylene diamine, although low molecular weight basic polyethers containing tertiary nitrogen atoms, which polyethers are obtainable by condensation of the above mentioned compounds in the presence of phosphorus acid, may also be mixed with the polyester. The quantity of diols containing one or more tertiary nitrogen atoms should always be so calculated that the tertiary nitrogen atoms-content based on the finished elastomer substance, does not exceed 200 millequivalents/kg. but in most cases only 80 to 150 millequivalents of tertiary nitrogen are present per kilogram of elastomer substance.

In order to prepare the polyurethane-polyurea solutions, the NCO-containing prepolymers obtained in the melt are introduced slowly, with stirring, at temperatures below about 35° C., and preferably below about 25° C. into a solution of ethylene diamine and the additional diamine in a polyacrylonitrile solvent. The quantity of solvent used is usually so calculated that the polyurethane-polyurea solution has the desired final concentration after termination of the chain lengthening reaction.

The chain lengthening reaction is accompanied by a rapid rise in viscosity, viscosity values between 150 and 600 poises at 20° C. being reached. In many cases the solution is then adjusted to the desired higher final viscosity by the addition of a small quantity of hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate or biuret triisocyanate which is obtained by reacting 3 mols of hexamethylene-1,6-diisocyanate, with 1 mol of water. In most cases, however, the isocyanates are added diluted with a little solvent.

The solids content of the final elastomer solution may amount to 18 to 30% 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 small quantities of water usually present in the commercial products.

The molar ratio of the chain lengthening mixture of ethylene diamine and additional diamine employed may be varied between 50:50 and 85:15 but is preferably between 75:25 and 80:20. However, the molar ratio of chain lengthening mixture is partly predetermined 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, the proportion of additional diamine used in the chain lengthening mixture will also be low, whereas conversely a higher NCO content in the prepolymer will necessitate a higher proportion of additional diamine when preparing non-yellowing polyurethane-polyurea solutions. The quantity of diamine mixture used in the chain lengthening reaction amounts to 90 to 140 mols percent, depending on the NCO:OH ratio and the desired final viscosity of the prepolymer, the given percentage being based on the free NCO group-content of the prepolymer.

It is not absolutely necessary to add the melt of the NCO-containing prepolymer into the solution of the chain lengthening mixture when preparing the polyurethane-polyurea solutions. According to a further embodiment, the prepolymer melt can be dissolved in part of the polyacrylonitrile solvent and the solution rapidly cooled to about 25° C. to about 30° C. This solution is then added to the solution of chain lengthening mixture described before. If, however, the prepolymer was prepared in one of the above mentioned inert solvents, it is generally advisable to remove the solvent by distillation before the chain lengthening reaction takes place although the process is in no way impaired by the presence of these inert solvents provided they do not amount to more than 20% by weight of the total quantity of solvent. One may, of course, add titanium dioxide, talc or other pigments to these elastomer solutions before further working up, or one may even add these pigmenting agents as early as before the chain lengthening reaction takes place.

The polyurethane-polyurea polymers which may be obtainable in solution under the given conditions are of special importance for working up on an industrial scale owing to their good solubility, and the resistance of their solutions to gel formation and to degradation at room temperature or slightly elevated temperature.

The elastic filaments or fibers are produced by known spinning techniques either dry, i.e., by spinning the elastomer solution into air or inert gases at elevated temperature or wet, i.e. injecting the elastomer solution into coagulating baths and winding the resulting filaments, and surface treating the filaments so formed with talc or oily dressing to prevent their sticking together on the spool. The spun filaments have excellent physical properties such as high elongation on tearing and strength, low permanent elongation and high E-modulus.

The invention will be 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. and under a pressure of about 12 mm. Hg and are then reacted with about 50 parts of diphenylmethane-4,4'-diisocyanate at from about 90 to about 95° C. for about one hour. The melt of the polyesterdiisocyanate adduct is dissolved in about 400 parts of N,N-dimethylformamide and cooled to 20 to 25° C. within about 10 minutes.

This solution is introduced in the course of about 5 minutes at 15 to 20° C., with stirring, into a solution of about 3.8 parts of ethylene diamine, about 3.6 parts of 2,2-bis-(4'-aminophenyl)-propane and about 432 parts of N,N-dimethylformamide, the viscosity of the solution increasing rapidly during this operation.

The spinning solution which contains about 27% of solids has a viscosity of about 390 poises at 20° C. It is spun by the wet spinning process under the spinning conditions described hereinafter to yield filaments having the following properties:

Titre	den	700
Strength	g./den	0.40
Elongation at break	percent	610
Permanent elongation	do	19
E-modulus	mg./den	70

## EXAMPLE 2

About 250 parts of the dehydrated polyester described in Example 1 are reacted at 90 to 100° C. in about 130 parts of anhydrous chlorobenzene with about 50 parts of diphenylmethane-4,4'-diisocyanate in the course of about one hour. The solution of the polyester-diisocyanate adduct is then cooled to about 25° C. and introduced at 15 to 20° C. into a solution of about 3.6 parts of ethylene diamine, about 3.4 parts of 2,2-bis-(4'-aminophenyl)-propane and about 702 parts of N,N-dimethylformamide. The spinning solution produced is accompanied by a rapid rise in viscosity to about 300 poises at 20° C., and the solution having a solids content of about 27%, is spun by the wet spinning process described hereinafter to form filaments having the following properties:

Titre	den	700
Strength	g./den	0.31
Elongation at break	percent	650
Permanent elongation	do	18
E-modulus	mg./den	62

## EXAMPLE 3

About 3 parts of a 36% SO<sub>2</sub>/dioxan solution are added to about 250 parts of the polyester described in Example 1 and this reaction mixture is stirred for about 4 hours at about 100° C. and then allowed to stand for about one hour at about 100° C. and then freed from dioxane and traces of water by keeping it at about 100° C. under a pressure of about 12 mm. Hg for about one hour. About 5 parts of N-methyl-diisopropanolamine are stirred into the polyester melt, and an NCO-containing prepolymer is obtained by further reaction with about 63.6 parts of diphenylmethane-4,4'-diisocyanate at about 80 to about 85° C. for one hour. This prepolymer is dissolved within about 10 minutes in about 400 parts of N,N-dimethylformamide (H<sub>2</sub>O content 0.01%) and is at the same time cooled to about 25° C.

The prepolymer solution is introduced at about 16 to about 22° C. with stirring, in the course of about 25 minutes into a mixture of about 4.95 parts of ethylene diamine, about 7.28 parts of 1,1-bis-(4'-aminophenyl)-cyclohexane, about 8.3 parts of titanium dioxide and about 517 parts of N,N-dimethylformamide. Viscosity of the solution is 237 poises/20° C.

The solids content of the solution is 27% by weight. The elastomer contains 100 millequivalents of tertiary nitrogen per kilogram.

The spinning solution is worked up into filaments under the conditions of the wet spinning process described hereinafter, the following filament properties being obtained.

Titre	den	500
Strength	g./den	0.44
Elongation at break	percent	540
Permanent elongation	do	21
E-modulus	mg./den	90

## EXAMPLE 4

About 250 parts of the polyester described in Example 1 are deactivated in a manner analogous to that described in Example 3 and dehydrated. About 5 parts of N-methyl-diisopropanolamine are then stirred in and an NCO-containing prepolymer is obtained by reaction with about 71.5 parts of diphenylmethane-4,4'-diisocyanate at about 80 to about 85° C. for about one hour. The prepolymer is dissolved within about 15 minutes in about 400 parts of N,N-dimethylformamide (H<sub>2</sub>O content of 0.01%) and is at the same time cooled to about 25° C. and chain lengthened by introduction of the NCO-containing solution into a stirred mixture of about 6.28 parts of ethylene diamine, about 9.3 parts of 1,1-bis-(4'-aminophenyl)-cyclohexane, about 8.6 parts of titanium dioxide and about 548 parts of N,N-dimethylformamide at about 20 to about 27° C. About one part of hexamethylene-1,6-diisocyanate dissolved in about 5 parts of N,N-dimethylformamide is then stirred in. After about four hours, the viscosity is about 340 poises/20° C.

The proportion of elastomer compound in the spinning solution is 27% by weight and the amount of tertiary nitrogen is 97 millequivalents/kg. of solid. The solution is worked up by the wet spinning process described hereinafter, filaments having the following properties being obtained:

Titre	den	600
Strength	g./den	0.53
Elongation at break	percent	510
Permanent elongation	do	20
E-modulus	mg./den	102

## EXAMPLE 5

About 2 parts of a 39 percent SO<sub>2</sub>/dioxane solution are added to about 250 parts of the polyester described in Example 1 and the reaction mixture is stirred for about 2 hours at about 100° C. and then freed from dioxane and traces of water by heating for about one hour at about 100° C. under a pressure of 12 mm. Hg. An NCO-containing prepolymer obtained by reaction of this solution with about 56.25 parts of diphenylmethane-4,4'-diisocyanate for about one hour at about 85 to about 90° C., and this prepolymer is then dissolved in about 400 parts of N,N-dimethylformamide (H<sub>2</sub>O content 0.02 percent) and cooled to about 25° C. within about 15 minutes.

(a) One portion of the prepolymer solution is introduced at room temperature, with stirring, into a solution of about 4.4 parts of ethylene diamine and about 8.25 parts of 2,2-bis-(4'-aminophenyl)-propane in about 473 parts of N,N-dimethylformamide. The final viscosity of the solution is about 180 poises at 20° C. Filaments having the following properties are obtained from this spinning solution by carrying out the instructions given hereinafter for the wet spinning process:

Titre	den	290
Strength	g./den	0.23
Elongation at break	percent	390
Permanent elongation	do	9
E-modulus	mg./den	110

(b) One portion of prepolymer solution is introduced in the course of about 15 minutes at from about 18 to

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about 24° C., with stirring, into a solution of about 5.2 parts of ethylene diamine and about 6.5 parts of 2,2-bis-(4'-aminophenyl)-propane in about 459 parts of N,N-dimethylformamide. The final viscosity of the solution is about 230 poises at 20° C. This spinning solution is worked up into filaments having the following properties by carrying out the instructions given hereinafter for the wet spinning process:

Titre	den	360
Strength	g./den	0.36
Elongation at break	percent	440
Permanent elongation	do	19
E-modulus	mg./den	145

## EXAMPLE 6

About 3750 parts of the dehydrated polyester described in Example 1 are reacted for about one hour at about 82 to about 87° C., with stirring, with about 844 parts of diphenylmethane-4,4'-diisocyanate, the product then being dissolved in about 6000 part of N,N-dimethylformamide and cooled to about 25° C. in about 25 minutes. This NCO-containing prepolymer solution is introduced at 20 to 25° C. into a solution of about 69 parts of ethylene diamine and about 129 parts of 2,2-bis-(4'-aminophenyl)-propane in about 7280 parts of N,N-dimethylformamide which in addition contains about 120 parts of titanium dioxide (rutile) dispersed therein. The resulting spinning solution has a viscosity of 620 poises/20° C. at a solids content of 27 percent. The spinning solution is then worked up by the dry spinning process described hereinafter to form filaments which have the following properties:

Titre	den	210
Strength	g./den	0.77
Elongation at break	percent	510
Permanent elongation	do	19
E-modulus	mg./den	126

## EXAMPLE 7

About 3750 parts of the dehydrated polyester described in Example 1 are reacted for about one hour at 80 to 85° C. with stirring, with about 750 parts of diphenylmethane-4,4'-diisocyanate and product obtained is dissolved in about 6000 parts of N,N-dimethylformamide and cooled to about 25° C. in about 20 minutes. This NCO-containing prepolymer solution is introduced at 18 to 24° C. into a stirred mixture of about 53.1 parts of ethylene diamine, about 67.5 parts of 2,2'-bis(4'-aminophenyl)-propane, about 7000 parts of N,N-dimethylformamide and about 185 parts of titanium dioxide (rutile). About 3 parts of hexamethylene-1,6-diisocyanate, about 27 parts of N,N-dimethylformamide are then introduced dropwise. A spinning solution having a solids content of 27 percent and a viscosity of 690 poises/20° C. is obtained. Filaments having the following properties can be produced from this solution under the spinning conditions given hereinafter for the dry spinning process:

Titre	den	150
Strength	g./den	0.66
Elongation at break	percent	490
Permanent elongation	do	14
E-modulus	mg./den	128

Spinning of the spinning solutions described in  
Examples 1-7 to form endless filaments

Before spinning, the solutions are thoroughly filtered through a filter press and then degasified in vacuo until free from bubbles.

The solutions mentioned hereinabove may be spun either wet or dry.

(I) Wet spinning process.—The filtered and degasified solution is spun by means of a spinning pump through a multiaperture nozzle of nozzle diameter 50 to 200/ $\mu$

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into a water bath 2 to 10 meters in length which contains 2 to 10 percent of N,N-dimethylformamide and is heated to 20 to 80° C., in particular 40 to 70° C.

The emerging filaments are drawn off at a rate of 5 to 50 meters per minute, at a draught of 0.5 to 5. After a drying at about 60° C., the filaments are wound. The physical properties given in the examples are determined by known methods.

(II) Dry spinning process.—The filtered and degasified solution is delivered through a spinning pump to the spinneret which is at a temperature of 15 to 90° C., depending on the viscosity. The solution is injected into the heated shaft through a multiaperture nozzle having a nozzle diameter of 80 to 250 $\mu$ . The temperature of the air blast is so chosen that the air temperature at the spinning nozzle is 130 to 230° C. The air entering the shaft from above, 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 a speed of 200 to 600 meters per minute, preferably 200 to 400 meters per minute. The N,N-dimethylformamide content of the filaments is below 1 percent. Before the filaments are wound, a dressing agent which prevents sticking is applied to them. The filament properties are then determined by known methods.

## Explanatory notes on filament testing

(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 3 times by 300 percent of its initial length, and after a recovery time of 30 seconds.

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

## EXAMPLE 8

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 63.9, acid number 1.45) are dehydrated in vacuo at about 120° C. for about one hour, mixed at about 70° C. with about 445 parts of N-methyldiisopropanolamine and about 6300 parts of diphenylmethane-4,4'-diisocyanate and heated to about 90° C. for about 50 minutes with stirring. About 23,800 parts of the NCO-containing prepolymer melt so obtained are introduced with intensive stirring into a cold solution of about 480 parts of ethylene diamine and about 600 parts of 2,2-bis-(4'-aminophenyl)-propane in about 70,000 parts of N,N-dimethylformamide which contains in addition about 1035 parts of titanium dioxide (rutile) dispersed therein. A spinning solution having a solids content of 27 percent and a viscosity of 610 poises/20° C. is obtained.

(a) A portion of the solution is briefly heated to 90° C and immediately thereafter spun dry from a 48 aperture spinneret at a shaft temperature of about 200° C. When the filaments have left the spinning shaft, a dressing agent for reducing adhesion is applied to them. The filaments are wound at a rate of 300 meters per minute.

Titre	den	450
Strength	g./den	0.68
Elongation at break	percent	480
Permanent elongation	do	20.5
E-modulus	mg./den	134

(b) A further portion of the solution is briefly heated to about 65° C. and immediately thereafter spun dry from a 12 aperture spinneret at a shaft temperature of about 17° C. The draw-off speed is about 450 meters per minute.

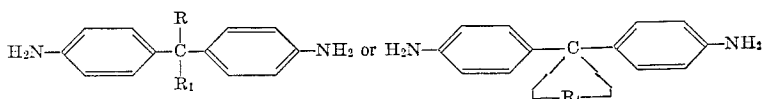
Titre	den	84
Strength	g./den	1.05
Elongation at break	percent	365
Permanent elongation	do	11.4
E-modulus	mg./den	580

It is to be understood that any of the polyesters, solvents, glycols or diamines set forth above 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 a diamine having the formula



wherein R and R<sub>1</sub> are lower alkyl, and R<sub>4</sub> is an alkylene radical containing 2 to 6 carbon atoms joined to the methylene carbon atom to form a cycloaliphatic radical, 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 1600 to about 2600 with about 1.5 to about 1.95 of 4,4'-diphenylmethane diisocyanate.

2. The spinning solution of claim 1 wherein the ratio of ethylene diamine to the diamine represented by the formula is from about 50/50 to about 85/15.

3. The spinning solution of claim 1 wherein the ratio

of ethylene diamine to the diamine represented by the formula 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 tertiary nitrogen atoms and having a molecular weight less than 500.

5. The spinning solution of claim 1 wherein the compound represented by the formula is 2,2-bis-(4-amino-phenyl)-propane.

6. The spinning solution of claim 1 wherein the compound represented by the formula is 1,1-bis-(4-amino-phenyl)-cyclohexane.

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

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