SYNTHETIC FIBERS
AP-42 Section 5.19
Reference Number
51

A-

II-

IT'S ROUND! IT'S RIGHT!
EXTRUDED
LATEX THREAD

Globe
MANUFACTURING CO.
456 BEDFORD STREET · FALL RIVER, MASS. 02720
CODE: 617 674-3585
CABLE ADDRESS: GLOBELAST

June 26, 1980

Mr. Dennis Crumpler
U. S. Environmental Protection Agency
Office of Air Quality Planning & Standards, (M.D.-13)
Research Triangle Park
North Carolina 27711

Dear Mr. Crumpler:

As understood from your discussion with Mr. R. M. Mellom, I am to send the attached information to you.

We have completed the questionaire from Pacific Environmental Services along the lines suggested by Mr. Zerbonia. Also enclosed is a copy of Patent #3,387,071 which describes our process. We believe the information in these documents to be sufficient for your purposes.

Please note that the questionaire includes answers which may reveal proporietary and confidential trade secret information which was developed at great expense to Globe. Accordingly, we are asserting a claim of confidentiality under 40 C F R 2.203 (b) and ask that you notify us before any of the information is passed on to a third party. Such notification will thus enable us to take steps necessary to protect the confidential information.

When you have finished with the information, we ask that you return it to us.

Very truly yours,

GLOBE MANUFACTURING CO.

Richard Legendre

Richard Legendre
Chief Engineer

RL:ok
Enclosures
cc: R. M. Mellom
1000 East North St.

Glospan
GLOBE SPANDEX FIBER

United States Patent Office

3,387,071

Patented June 4, 1968

3,387,071

FIBERS

John W. Cahill, Somerset, Mass., James L. Powell, Barrington, R.I., and Edward A. Gartner, Somerset, Mass., assignors to Globe Manufacturing Company, Fall River, Mass., a corporation of Massachusetts

Continuation-in-part of abandoned application Ser. No. 290,129, June 24, 1963. This application May 5, 1964, Ser. No. 365,082

17 Claims. (Cl. 264—184)

This application is a continuation-in-part of application Ser. No. 290,129, filed June 24, 1963 and now abandoned.

This invention relates to the preparation of spandex, i.e., polyurethane, fibers.

Spandex fibers have been prepared by conventional spinning techniques such as hot melt, wet, dry and reaction spinning. Hot melt techniques require relatively large capital outlays and yield a product with undesirable stress decay characteristics.

Solution spinning requires expensive solvents and elaborate recovery systems. Reaction spinning requires a cumbersome cure under water after coagulation in a dilute aqueous solution of an aliphatic diprimary diamine, e.g., see Kohrn et al. Patent No. 3,009,762 or as a Cacella et al. application Ser. No. 182,575, filed Mar. 26, 1962, now Patent No. 3,115,384, a heat cure after passing the thread through a bath containing at least 50% and preferably 75% of an aliphatic diprimary diamine in a hydroxyl-containing solvent, preferably water maintained at an elevated temperature, e.g., 180° F. The first method of reaction spinning produces a thread having a low modulus and is difficult to dye. The second method produces excellent high modulus thread but is hazardous to use because all of the commercially useful amines possess high volatility and toxicity.

It is an object of the present invention to develope an improved process for making spandex, i.e., polyurethane, fibers.

Another object is to prepare an improved polyurethane thread.

Another object is to prepare a polyurethane thread having good resistance to deteriorate under heating.

An additional object is to develop a process of preparing polyurethanes with increased flexibility as to amine curing agents and polyisocyanates which can be employed, e.g., a process which can be used with secondary amines or aliphatic polyisocyanates, as well as with diprimary amines and aromatic polyisocyanates.

Yet another object is to reduce the toxicity problem in preparing polyurethane threads employing amine curing agents.

Still another object is to prepare polyurethane threads having good tensile strength, ultimate elongation and elastic recovery.

A still further object is to develop a process of curing polyurethane threads which is adaptable to air procedures.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained and excellent spandex fibers can be produced by extruding a liquid polyurethane prepolymer into a cool

amines than are employed in the Cacella et al. procedure and still obtains cured products. With solvents such as alcohols, nitriles and substituted amides which form complexes with amines there is used 5 to 10 normal solutions of the polyamine whereas with non-complexing organic solvents, such as hydrocarbons there is used even less polyamine, normally not over 3 normal and usually as little as 0.05 to 1.5 normal. Even with these lower concentrations of polyamines there is still sufficient to have an excess of polyamine on the thread. The relatively slow reaction rate in hydrocarbon solvents allows the diamine to diffuse into the worm (filament) of the extruded prepolymer rather than form a skin as in the Kohrn et al. procedure. The low concentration of diamine reduces polymer chain termination resulting in high modules and low permanent set. It is also possible to use either primary or secondary aliphatic or heterocyclic amines as chain extenders while Kohrn et al. are limited to primary aliphatic amines. The products of Kohrn are not dyeable whilet those prepared according to the present invention are readily dyeable.

As suitable amines there can be used ethylene diamine, propylene diamine, trimethylene diamine, hexamethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diamino-cyclohexane, 3,3'-diamino-dipropyl ether, diamino dibutyl sulfide, m-xylylene diamine, piperazine, N-aminoethyl piperazine, N,N'-dimethyl ethylene diamine, 2-methyl piperazine, bis tallow amines made by reducing the diamides of dimerized unsaturated fatty acids, e.g., the diamine of dimerized linseed oil fatty acids.

As the organic solvents there can be used ethylene glycol, 1,4-butanediol, 1,3-butylene glycol, propylene glycol, glycerine, hexanetriol, methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, amyl alcohol, acetonitrile, propionitrile, dimethyl formamide, diethyl formamide, dimethyl acetamide, aromatic hydrocarbons, e.g., benzene, toluene, o-xylene, p-xylene, m-xylene, mixed xylenes, ethyl benzene, 1,3,5-trimethyl benzene, propyl benzene, isopropyl benzene and butyl benzene, and aromatic naphtha. Any solvent blend can be used as long as the polyamine is miscible and the concentration is adjusted to yield the desired amount of available amine. Aliphatic hydrocarbons, e.g., hexane, pentane, heptane, octane, kerosene, mineral oils, VM and P naphtha, cyclohexane can be used in combination with other solvents such as alcohols or aromatic hydrocarbons.

The use of 4% of ethylene diamine in toluene is approximately equivalent to the use of 20% of ethylene diamine in isopropanol. The use of secondary diamines and amines containing both primary and secondary groups are suitable when used in hydrocarbon solvents. It is preferred to adjust the filament size to allow complete diffusion of amine and produce a finished product on the extruder. In some cases a hot air post cure can be employed.

Unless otherwise indicated all parts and percentages are by weight.

The material which is extruded into the polyamine reaction bath is either a urethane prepolymer or an equivalent material such as a polyhaloformate, e.g., the bischloroformate of a polyethylene-propylene adipate terminating in alcohol groups. The prepolymer has a molecular weight of 500 to 5,000, preferably between 1,000 and 4,000. The urethane prepolymers are formed by reacting an excess of polyisocyanate with a polyol. The isocyanates can be aromatic or aliphatic. The polyol can be (1) a polyester from either dicarboxylic acids and glycols or by ring opening of lactones, (2) polyethers, (3) polygroups and a hydroxyl number between 20 and 225. In order to lower the viscosity and aid in the spinning of the prepolymer a small amount of a conventional polyurethane solvent, e.g., 1 to 20%, preferably 5%, can be added prior to spinning. Typical solvents include ketones, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, substituted amides, e.g., dimethyl formamide and dimethyl acetamide, carbonates, e.g., ethylene carbonate and propylene carbonate, sulfoxides, e.g., dimethyl sulfoxide, aromatic hydrocarbons, and esters.

As polymeric materials having terminal alcoholic hydroxyl groups suitable for making prepolymers with organic polyisocyanates there can be used chain extended polyesters made from a glycol, preferably a mixture of ethylene and propylene glycols, and a saturated organic dicarboxylic acid, preferably adipic acid. Usually, the glycol contains 2 to 20 carbon atoms. Typical examples of such glycols include ethylene glycol, propylene glycol, trimethylene, glycol, 1,4-butylene glycol, 1,6-hexanediol, 1,4-butenediol, neopentyl glycol, diethylene glycol, thiodiglycol, etc. The acid usually contains 4 to 20 carbon atoms. Typical examples include succinic acid, maleic acid, dihydromucconic acid, thiodipropionic acid, adipic acid, methyl adpic acid, glutaric acid, dimerized linoleic acid, sebacic acid, suberic acid, phthalic acid, and terephthalic acid. Hydroxycarboxylic acids or their lactones can be used, e.g., epsilon caprolactone, in forming the polyesters. As stated, mixtures of various dibasic acids and glycols can be used to form mixed esters.

An excess of the glycol over the acid is used in preparing the polyesters so that the resulting polyester contains terminal hydroxyl groups. Usually such an amount of glycol is used as to give a polyester having a hydroxyl number of 20 to 225 and preferably 30 to 75, and a low acid value, e.g., less than 6 and preferably less than 1. The molecular weight of the polyester usually ranges from 500 to 5,000 and preferably 1,500 to 4,000. In general, the most suitable polyesters having melting point levels of 90° C. or lower and preferably not over 60° C. Less suitably, natural polyesters can be used, e.g., castor oil, as well as blown drying oils, such as blow tung oil, linseed oil and soya oil.

Some functional branching helps. If this is not present in the polyester it is introduced through allophanate formation. Only a small amount is needed, i.e., a functionality above 2.1 but usually not over 2.5.

Other examples of suitable polyesters for use in preparing the prepolymer are polyethylene adipate, polyethylene adipate-phthalate and polyneopentyl sebacate. Small amounts of trialcohols such as trimethylolpropane or trimethylolethane may be included in preparing the glycoldicarboxylic acid polyesters and such modified forms of polyester are included within the term polyester as used herein.

As an alternative to the polyesters there may be used for reaction with the polyisocyanate one or more elastomer-yielding polyesters. Such polyethers are typically anhydrous chain extended polyethers possessing ether linkage separaed by hydrocarbon chains either alkyl or aryl in nature. The ether should also contain terminal groups reactive to isocyanate, such as alcoholic hydroxyl groups. Such polyethers may be linear or branched. Usually, the polyethers are chiefly linear with a melting point of not over 90° C., preferably not over 60° C. The molecular weight may range from 500 to 5,000, hydroxyl number of 225 to 22, but preferably is within the range of 750 to 3,500 (hydroxyl number of 150 to 32). Preferred polyethers have the formula $H(OR)_nOH$ where R is a lower alkylene group (2 to 6 carbon atoms) and n is an integer so that the molecular weight falls within the range specified. Examples of polyethers are polyethylene glycol, polypropylene glycol, mixed polyethylene glycol-polypropylene glycol, polytetramethylene glycol (e.g., of 1,000 molecular weight).

A portion of the polyester or polyether can be replaced by a tris polypropylene glycol phosphite such as tris (dipropylene glycol) phosphite or tris (polypropylene glycol 2025) phosphite as shown in Friedman Patent No. 3,009,939. The phosphite not only serves as a reactant but also imparts improved heat stability to the polyurethane as well as improved dyeing properties. There can be used bis(propylene glycol) hydroxypropoxypropane phosphonate in place of the phosphite to give improved heat stability.

Polyethers not only can be used in place of the polyesters but can be used in conjunction therewith. Examples of such compounds are polydiethylene glycol adipate and polytriethylene glycol adipate. Further examples of polyesters and polyethers which are suitable are set forth in Kohrn Patent No. 2,953,839 and the patents cited therein in column 2, lines 56–68.

The polyester or polyether (including polyether-ester) is reacted or "capped" with a diisocyanate using a considerable molar excess, commonly from a 20 to a 250%, and preferably from a 50 to a 200%, molar excess of the amount of diisocyanate required to react with all of the alcoholic hydroxy groups furnished by the polyester or polyether. The reaction is frequently effected by mixing the polyester or polyether with the diisocyanate either at room temperature or at a moderately elevated temperature, e.g., 70 to 150° C. to form an uncured liquid prepolymer which is soluble in methyl ethyl ketone. The prepolymer is essentially a linear polyurethane having terminal isocyanate groups. The reaction is preferably carried out at 90 to 100° C.

Representative of the preferred aromatic diisocyanates that may be mentioned, by way of nonlimiting examples are m- and p-phenylene diisocyanate, tolylene diisocyanate (65% 2,4 and 35% 2,6 or 80% 2,4 and 20% 2,6 and 100% 2,4), p,p'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, p,p'-diphenyl - methane diisocyanate, 3,3'-bitolylene-4,4' - diisocyanate, 2,4 - tolylene diisocyanate dimer, dianisidine diisocyanate, 4-chloro-1,3-phenylene diisocyanate. Aliphatic and cycloaliphatic diisocyanates can also be used such as 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,4-cyclohexylene disocyanate, 4,4'-methylene-bis (cyclohexylisocyanate) and 1,5-tetrahydronaphthalene diisocyanate. Other diisocyanates can be employed including those set forth in Kohrn Patent No. 2,953,839, as well as those mentioned in the patents set forth in Kohrn. There can be included trisisocyanates or higher isocyanates in order to get added functionality in the coagulating bath. Such isocyanates include PAPI (phenylmethylene isocyanate trimer), 2,4,4'-diphenyl ether triisocyanate, 4,4',4''-trisocyanate triphenylmethane, toluene 2,4,6-triisocyanate.

The single figure of the drawings illustrates in diagrammatic fashion one method of carrying out the invention.

Referring to the drawing a quantity of liquid prepolymer mixture 2 was placed in a supply tank 4 connected to a pump 6 which, in turn, fed the spinnerette 8 immersed in the reaction bath 12 consisting of the polyamine in an organic solvent therefor contained in tank 14. The pump setting was such that a 100 gauge thread was produced at 200 feet per minute take-up speed. The extruded liquid was converted almost immediately to a thread 16. The thread then passed over roll 18 and into oven 20 for solvent and excess extender removal, as well as advancement of the cure. The thread moved through the oven on continuous belt 22. The speed of the belt was regulated by the speed of rotation of rolls 24 and 26. The thread then passed to process rolls and lubricant applicator 28 and 30 and finally to thread take-up spool 32. Talc or other conventional antitack material can be employed as the lubricant.

Curing can be done at 65 to 205° C., usually 80 to 150° C. for a time of 30 minutes to 30 hours, usually 1 to 3 hours at 90 to 120° C. Lower temperatures can be used if longer cure times are employed. At 175° C. a time of 30 seconds is convenient and practical. It is normally not necessary to cure the thread if the solvent and excess diamine are removed rapidly at an elevated temperature, e.g., 175° C. to 220° C., for 30 seconds to a minute.

The cured threads can be stretched 10%, 50%, 100%, 200% or 400% or as high as 700% of their original length by running a second spool 10, 50, 100, 200, 400 or 700% faster than a first spool.

The preparation of suitable prepolymers are given in Examples 1–8.

EXAMPLE 1

A polyester resin of molecular weight 3,700, hydroxyl number of about 35 and an acid number of 0.8 from ethylene glycol, propylene glycol and adipic acid was mixed at a temperature of 90° C. for 1 hour with 17 parts (an excess) of 2,4-toluene diisocyanate. The mixture was then heated for 1 hour at 120° C. A reaction occurred between the hydroxyl groups of the polyester and the diisocyanate groups to form a capped polymer intermediate characterized by the presence of unreacted isocyanate groups. This intedmediate was a viscous liquid urethane prepolymer which was soluble in the common organic solvents for polyurethanes, e.g., acetone.

EXAMPLE 2

Polycaprolactone having a hydroxyl number of 52 was heated with 24 parts of 2,4-toluene diisocyanate at 90° C. for 1 hour and then at 120° C. for 1 hour.

EXAMPLE 3

Polyethylene-propylene adipate, hydroxyl number 35, acid number 0.8 in an amount of 100 parts was heated with 5.2 parts of hexamethylene diisocyanate for 1 hour at 90° C. and then 15.7 more parts of hexamethylene diisocyanate were added and heating continued for 1 hour at 120° C.

EXAMPLE 4

100 parts of polypropylene glycol having a hydroxyl number of 112 (molecular weight 1,000) were heated for 1 hour at 90° C. with 16.7 parts of methylene bis(4-phenylisocyanate) and there were then added 25 parts more of the methylene bis(4-phenylisocyanate) and the mixture heated for 1 hour at 120° C.

EXAMPLE 5

100 parts of polyethylene-polypropylene adipate having a hydroxyl number of 36 and a functionality of 2.3 were heated at 90° C. for 2 hours with 17 parts of 2,4-toluene diisocyanate. The functionality of the polyethylene-propylene adipate was raised from the normal 2 to 2.3 by adding a small amount of trimethylpropane to the starting ethylene glycol, propylene glycol and adipic acid.

EXAMPLE 6

1 mole of a polyol, specifically, polypropylene glycol molecular weight 1,000 was heated with 2 moles of phosgene to produce a polyol capped with chloroformate end groups.

EXAMPLE 7

100 parts of the same polyethylene-propylene adipate having a hydroxyl number of 36 and a functionality of 2.3 employed in Example 5 were heated at 90° C. for 2 hours with a mixture of 13 parts of 2,4-toluene diisocyanate and 5 parts of methyl isobutyl ketone. The ketone was employed to reduce the viscosity of the prepolymer.

EXAMPLE 8

2 moles of polypropylene glycol (molecular weight 2,000), 2 moles of trimethylolpropane and 8 moles of 2,4-toluene diisocyanate were heated for 2 hours at 90° C. Then 2 moles of 2,4-toluene diisocyanate and 1 mole of polypropylene glycol (molecular weight 2,000) were added and the mixture heated for 2 more hours at 90° C.

The materials prepared in Examples 1–8 were metered through a spinnerette into a solution of a primary or secondary amine in an organic solvent. The number of holes in the spinnerette can be varied from one to as many as permitted by the design of the spinnerette, e.g., 200. The polyamine can be varied in structure as set forth above to alter ultimate properties and the concentration can also be varied. The length of the spinning bath can be varied from less than one inch to several yards but is preferably about one foot. The temperature of the spinning bath can be varied, e.g., from 5 to 100° C., but is preferably kept at room temperature. After the fiber is removed from the spinning bath, it is drawn through an oven where excess solvent and extender are removed and the cure is advanced to full or partial completion. The thread is taken up on a spool and cured in an oven if further advancement is desired. This post cure is time-temperature dependent, i.e., the higher the temperature the shorter the time of cure. In the preferred form of the invention using an elevated temperature of, for example, 175° C. or higher, there is no need to take up the thread on the spool and cure in an oven, but instead the thread is simply lubricated and taken up on a package without any further curing.

In the following examples the fibers were prepared with a spinning bath which was at room temperature and had a length of one foot. The extruder oven in Examples 9 to 16 was at 116° C. and post curing was done at 116° C. for 2 hours.

EXAMPLE 9

The polyurethane prepolymer prepared in Example 1 was extruded into a bath containing 20% of ethylene diamine in isopropanol. After the curing the properties of the thread were

Tensile strength	p.s.i.	9,000
Ultimate elongation	percent	625
300% modulus	p.s.i.	1,500
Elastic recovery	percent	90

EXAMPLE 10

The polyurethane prepolymer of Example 2 was extruded into a bath containing 4% of ethylene diamine in toluene. After the curing the properties of the thread were

Tensile strength	p.s.i.	10,500
Ultimate elongation	percent	575
300% modulus	p.s.i.	1,300
Elastic recovery	percent	88

EXAMPLE 11

The polyurethane prepolymer of Example 3 was extruded into a bath containing 19% of ethylene diamine in acetonitrile. After curing the thread had the following properties

Tensile strength	p.s.i.	8,500
Ultimate elongation	percent	625
300% modulus	p.s.i.	1,400
Elastic recovery	percent	90

EXAMPLE 12

The polyurethane prepolymer of Example 4 was extruded into a bath containing 20% of ethylene diamine in dimethyl formamide. After curing the thread had the following properties

Tensile strength	p.s.i.	5,000
Ultimate elongation	percent	525

EXAMPLE 13

The polyurethane prepolymer of Example 5 was extruded into a bath containing 33% hexamethylene diamine in isopropanol. After curing the thread had the following properties

Tensile strength	p.s.i.	6,500
Ultimate elongation	percent	700
300% modulus	p.s.i.	600
Elastic recovery	percent	88

EXAMPLE 14

The polyurethane prepolymer of Example 7 was extruded into a bath containing 4% of ethylene diamine in benzene. After curing the fiber had the following properties

Tensile strength	p.s.i.	10,000
Ultimate elongation	percent	725
300% modulus	p.s.i.	800
Elastic recovery	percent	94

EXAMPLE 15

The polyurethane prepolymer of Example 5 was extruded into a bath containing 5% of piperazine in toluene. After curing the thread had the following properties

Tensile strength	p.s.i.	4,700
Ultimate elongation	percent	325

EXAMPLE 16

The polyurethane prepolymer of Example 8 was extruded into a bath containing 20% of ethylene diamine in isopropanol. After curing the thread had the following properties

Tensile strength	p.s.i.	6400
Ultimate elongation	percent	300

The gauge of the thread is determined by the pump output and the take-up speed. These can be varied over a wide range. As indicated in the examples, the take-up speed was about 200 feet per minute for the production of 100 gauge thread.

Various methods can be employed for curing the prepolymers coagulated in an organic solvent bath of polyamine according to the invention.

Combinations of solvents can also be used in the reaction bath, e.g., a mixture of 60% toluene and 40% isopropanol.

Other additives such as catalysts, surfactants, plasticizers and antioxidants can be incorporated in either the prepolymer or the spinning bath in conventional fashion.

It has been found preferable to form the threads by multifilament spinning. Thus, 12 to 30 filaments can be spun from the spinnerette 8 and the filaments brought together to form a thread as they leave the bath 12. The filaments are normally very fine, i.e., about 50 microns, and are sometimes called worms. The finished threads can be from 44 gauge to 375 gauge. In the following examples threads were formed from a spinnerette having 16 filaments which came together at the surface of the bath. The threads were of 375 gauge, although as indicated, threads of other gauges can also be prepared. In the following examples the temperature of the extruder oven was adjusted to heat the thread to about 175° C. during the stay in the oven of about one minute. As indicated, the exact temperature of this oven is not particularly critical, but the time and temperature in the oven are simply adjusted so that solvent and excess diamine are removed leaving a product with good resistance to hydrolysis. Temperatures up to 220° C. have been used successfully.

EXAMPLE 17

The polyurethane prepolymer prepared in Example 1 was extruded into a bath containing 20% of ethylene diamine in isopropanol. The resulting thread, after passing through the drying oven, was similar to that of Example 9 except the thread of Example 17 had a little better color, a higher 300% modulus, a higher tensile strength, and a little better elastic recovery.

EXAMPLE 18

The polyurethane prepolymer of Example 2 was extruded into a bath containing 4% of ethylene diamine in toluene. The multifilament thread obtained was similar to that of Example 10 but was improved in the same manner as the thread of Example 17.

EXAMPLE 19

The polyurethane prepolymer of Example 3 was extruded into a bath containing 19% of ethylene diamine in acetonitrile. The multifilament thread obtained was similar to that of Example 11 but was improved in the same manner as the thread of Example 17.

EXAMPLE 20

The polyurethane prepolymer of Example 4 was extruded into a bath containing 20% of ehtylene diamine in dimethyl formamide. The multifilament thread obtained was similar to that of Example 12 but was improved in the same manner as the thread of Example 17.

EXAMPLE 21

The polyurethane prepolymer of Example 5 was extruded into a bath containing 33% hexamethylene diamine in isopropanol. The multifilament thread obtained was similar to that of Example 13 but was improved in the same manner as the thread of Example 17.

EXAMPLE 22

The polyurethane prepolymer of Example 7 was extruded into a bath containing 4% of ethylene diamine in benzene. The multifilament thread obtained was similar to that of Example 14 but was improved in the same manner as the thread of Example 17.

EXAMPLE 23

The polyurethane prepolymer of Example 8 was extruded into a bath containing 20% of ethylene diamine in isopropanol. The multifilament thread obtained was similar to that of Example 16 but was improved in the same manner as the thread of Example 17.

EXAMPLE 24

The polyurethane prepolymer of Example 7 was extruded into a bath containing 0.9% of piperazine in toluene. The multifilament thread obtained had the following properties:

Tensile strength	p.s.i.	10,300
Ultimate elongation	percent	675
300% modulus	p.s.i.	1,000
Elastic recovery	percent	98

We claim:

1. A process of preparing an elastic thread comprising the steps of providing a liquid polyurethane prepolymer selected from the group consisting of polyesters and polyethers having terminal groups selected from the group consisting of organic isocyanate groups and chloroformate groups said prepolymer having been prepared from a member of the group consisting of polyesters and polyethers having a functionality of above 2.1, extruding said liquid prepolymer into an organic solvent solution of up to 10 normal of a polyamine selected from the group consisting of primary and secondary aliphatic and heterocyclic amines and thereby forming a filament in said solvent solution, said organic solvent being the sole solvent,

and thereafter removing the solvent and excess polyamine and curing the thread in hot air.

2. A process according to claim 1 wherein the solvent is one which does not form a complex with the polyamine.

3. A process according to claim 1 wherein the solvent is a hydrocarbon.

4. A process of preparing an elastic thread comprising the steps of providing a liquid polyurethane prepolymer which is the reaction product of (1) a polymer selected from the group consisting of polyesters and polyethers having terminal hydroxyl groups with (2) an excess of an organic polyisocyanate, said prepolymer having been prepared from a member of the group consisting of polyesters and polyethers having a functionality of above 2.1, extruding said liquid prepolymer into an organic solvent solution of up to 10 normal of a polyamine selected from the group consisting of primary and secondary aliphatic amines and thereby forming a filament in said solvent solution, said organic solvent being the sole solvent, and thereafter removing the solvent and excess extender and curing the thread in hot air.

5. A process according to claim 4 wherein the polyisocyanate is a diisocyanate.

6. A process according to claim 5 wherein the solvent is a hydrocarbon.

7. A process according to claim 6 wherein the polyamine is used in an amount of 0.1 to 1.5 normal.

8. A process according to claim 7 wherein the amine is ethylene diamine.

9. A process according to claim 1 wherein the prepolymer is spun as a multifilament, the filament is gathered into a thread and the thread is heated for a short period of time at a temperature of at least about 175° C. to remove solvent and excess polyamine and leave a thread which has good resistance to hydrolysis.

10. A process according to claim 9 wherein the solvent is an aromatic hydrocarbon.

11. A process according to claim 1 wherein the polyamine is a diamine.

12. A process according to claim 1 wherein the polyamine is ethylene diamine.

13. A process of preparing an elastic thread comprising the steps of providing a liquid polyurethane prepolymer selected from the group consisting of polyesters and polyethers having terminal isocyanate groups as the sole terminal groups, said prepolymer having been prepared from a member of the group consisting of polyesters and polyethers having a functionality of above 2.1, and extruding said liquid prepolymer into an organic solvent solution of up to 10 normal of a polyamine selected from the group consisting of primary and secondary polyamines and thereby forming a filament in said solvent solution, said organic solvent being the sole solvent, and thereafter removing the solvent and excess polyamine extender and hot air curing the thread.

14. A process according to claim 13 wherein said polyamine is ethylene diamine.

15. A process according to claim 14 wherein the solvent is a hydrocarbon.

16. A process according to claim 1 wherein the organic solvent contains 0.9 to 5% of said amine and the organic solvent consists of aromatic hydrocarbon solvent.

17. A product prepared by the process of claim 1.

References Cited

UNITED STATES PATENTS

3,047,356	7/1962	Polansky	264—184
3,115,384	12/1963	Cacella et al.	260—77.5
Re. 24,689	8/1959	Koller.	
Re. 24,691	8/1959	Steuber.	
3,165,566	1/1965	Murphy et al.	
3,111,369	11/1963	Gregg	264—184
3,121,764	2/1964	Macura	264—184
3,136,830	6/1964	Oertel	264—184
3,198,863	8/1965	Lauer	264—184

FOREIGN PATENTS

847,673	9/1960	Great Britain.
944,015	12/1963	Great Britain.

OTHER REFERENCES

Hill, Rowland (ed): "Fibres from Synthetic Polymers," Elseuier Publishing Co., 1953 (pp. 159–60).

JAMES A. SEIDLECK, *Primary Examiner.*

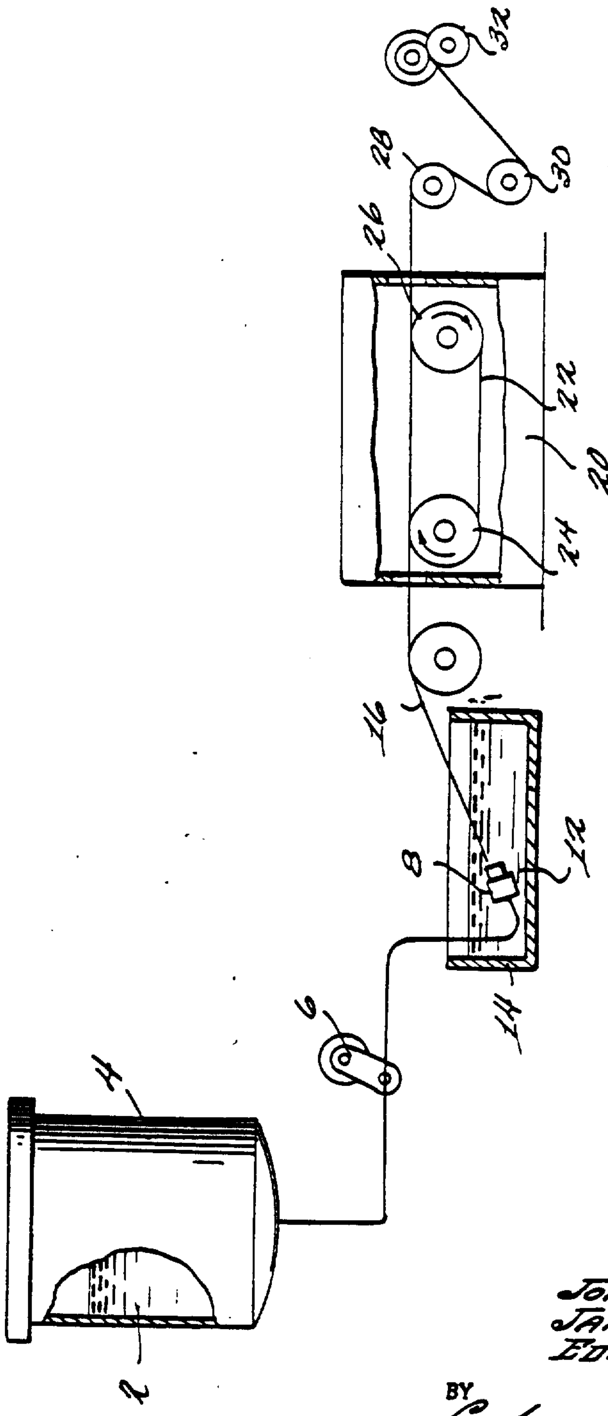
D. J. ARNOLD, ALEXANDER H. BRODMERKEL, *Examiners.*

H. W. LUCKOWER, J. H. WOO, *Assistant Examiners.*

June 4, 1968 J. W. CAHILL ETAL 3,387,071

FIBERS

Filed May 5, 1964



INVENTORS
JOHN W. CAHILL
JAMES I. POWELL
EDWARD A. GARTNER

BY
Cushman, Darby & Cushman
ATTORNEYS

Attachment to docket document A-80-7 II-D-82

DOCKET NO. A-80-7
Subcategory II-D

The following information is located in the confidential files of the Director, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. This information is confidential, pending final determination by the Administrator, and is not available for public inspection.

PACIFIC ENVIRONMENTAL SERVICES, INC. "114 RESPONSE" QUESTIONNAIRE - Correspondence with attached copy of Patent #3,387,071 and Pacific Environmental Services, Inc. (PES) questionnaire received from, R. Legendre, Chief Engineer, Globe Manufacturing Company, 456 Bedford Street, Fall River, Massachusetts 02720, sent to, D. Crumpler, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina 27711, Correspondence dated June 26, 1980.

Confidential material consists of Globe Manufacturing Company responses to PES questionnaire regarding synthetic fiber spandex process and production information.