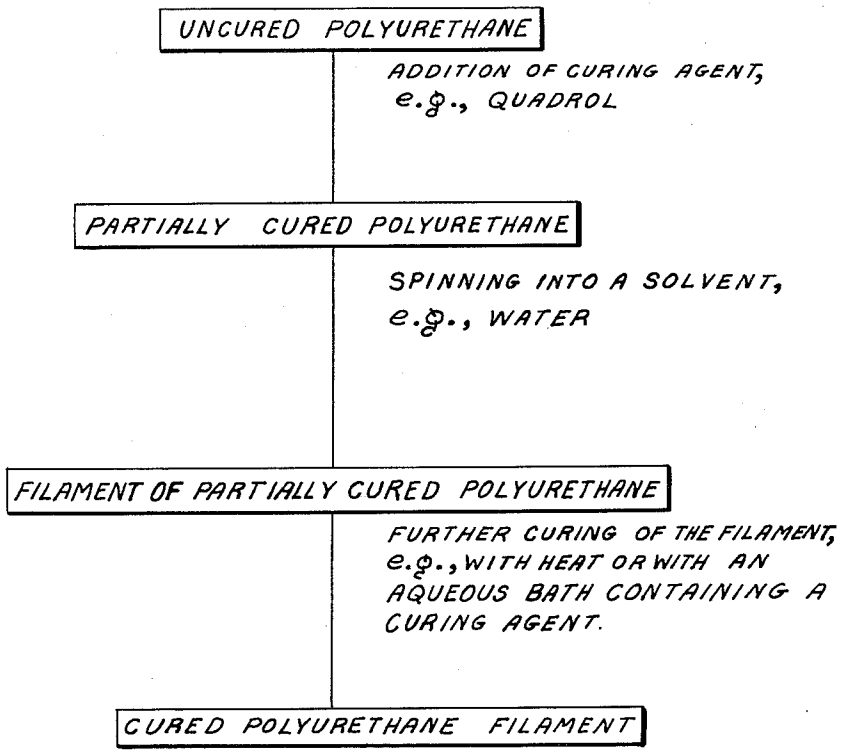
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POLYURETHANES

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POLYURETHANES

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5 Claims. (Cl. 18—54)

The present application is a division of application Serial No. 842,207, filed September 25, 1959.

This invention relates to the spinning of polyurethanes.

One conventional technique for preparing fibers from polyurethanes involves spinning or extruding the filament from the molten polymer. The very precise temperature control required by this procedure impose severe restrictions on its use commercially.

It has also been proposed broadly to dissolve completely cured polyurethanes in an appropriate solvent and thereafter spin the resulting solution. Such a procedure as carried out by the prior art has not been found to be flexible enough and furthermore limits severely the variations which can be made in the physical properties of the products obtained.

Additionally it has been proposed to form filaments from solutions of polymer intermediates by spinning into a liquid which reacts with the spun material. Such procedure also has its disadvantages.

It is an object of the present invention to develop novel procedures for spinning polyurethanes.

Another object is to develop novel spun polyurethane products.

A further object is to develop spinning procedures utilizing polyurethanes prepared from the reaction of diisocyanates with conventional polyesters and polyethers.

An additional object is to eliminate undue tackiness from newly spun polyurethane fibers so that they can readily be processed further.

Yet another object is to prepare a polyurethane spinning solution having an extremely long or infinite pot life.

Still another object is to develop a satisfactory procedure for forming a polyurethane spinning solution having an extremely long or infinite pot life while at the same time avoiding the use of a cured gum.

A still further object is to develop an improved dry spinning process for polyurethanes.

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 through the use of the six spinning procedures described in greater detail below. These procedures are not the equivalent of each other but each has its own advantages as will be more evident hereinafter.

In all of the procedures there is employed a polyurethane which is an isocyanate modified polyester or polyether.

The single FIGURE of the drawing is a flowsheet illustrating the process.

As the isocyanate there can be used hexamethylene diisocyanate, tolylene diisocyanate (65% 2,4 and 35% 2,6), naphthalene diisocyanate, tolylene diisocyanate (80% 2,4 and 20% 2,6); tolylene diisocyanate (100% 2,4), 3,3'-bitolylene-4,4'-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, meta-phenylene diisocyanate, 2,4-tolylene diisocyanate dimer, dianisidine diisocyanate, 4-chloro-m-phenylene diisocyanate.

As the polyether which is reacted with the polyisocyanate to form the urethane there can be used polyethylene glycol, polypropylene glycol and mixed polyethylene glycol-polypropylene glycol, polytetramethylene ether glycol and other polyalkylene oxide polymers. The polyether usually has a molecular weight of 500 to 10,000. A typical example is polytetramethylene ether glycol having an average molecular weight of 960.

As the polyester which is reacted with the polyisocyanate the preferred starting materials are saturated aliphatic products for the most part. As acids there can be used, for example, malonic acid, succinic acid, adipic acid, methyl adipic acid, maleic acid, dihydromuconic acid, thiodipropionic acid, diethyl ether dicarboxylic acid, dimerized linoleic acid (as well as other dimerized unsaturated fatty acids), sebacic acid, suberic acid, etc. Aromatic dicarboxylic acids can be used, e.g. phthalic acid and terephthalic acid. As glycols there may be mentioned ethylene glycol, trimethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,6 hexane diol, methyl hexane-1,6-diol, 1,4-butene diol, diethylene glycol, thiodiglycol, 2,2'-dimethyl-1,3-propylene glycol, etc. Hydroxycarboxylic acids or their lactones can also be used, e.g. caprolactone, to form the polyesters. Mixtures of various dibasic acids and glycols can be used to form mixed polyesters. Other bifunctional reactants can be used which are complementary to the acids and glycols can be used in smaller propertions although their presence is not normally preferred.

Natural polyesters can be used. A preferred example of such a polyester is castor oil. When castor oil is reacted with at least one mole of a diisocyanate for each hydroxyl group, e.g. 1 mol of naphthalene 1,5 diisocyanate or 1 mol of 2,4-tolylene diisocyanate for each hydroxyl group, there is prepared a prepolymer. Typical prepolymers which can be used are shown in Detrick Patent 2,787,601. In place of castor oil there can be used blown drying oils such as blown tung oil, linseed oil and soya oil.

The polyesters used to react with the diisocyanates usually have molecular weights from 400 to 10,000 but the exact weight is not critical.

The prepolymers made by reacting a polyester or polyether with a diisocyanate can have an isocyanate number from just above 0 up to 8 or higher. The isocyanate number is the average number of isocyanate groups present in the polymer molecule.

As curing agents for the prepolymers there can be employed conventional polyurethane curing agents such as triols and tetrols, polyfunctional amines, aminoalcohols, inorganic alkalis, e.g. triisopropanol amine, Quadrol (tetrakis N,N^1-B-hydroxyethyl ethylene diamine), diethylene triamine, tetraethylene pentamine, triethanolamine, ethanolamine, diethanolamine, strong alkalis such as sodium hydroxide and potassium hydroxide, methyl morpholine, triethyl amine (and other trialkyl amines), dimethylaniline, N-coco morpholine) trimethylolpropane, etc.

Spinning is usually done through a spinneret having holes at a diameter of 0.001 to 0.006 inch.

PROCEDURE I

A prepolymer is prepared by reacting a polyisocyanate with a polyester or polyether and cured to the extent that the issuing thread can maintain its own weight instantaneously and is substantially tack free. The polyurethane is still soluble in the solvent which can be any of the conventional polyurethane solvents such as dimethyl acetamide, dimethyl formamide, ethylene carbonate, propylene carbonate, dimethyl sulfoxide, etc. The amount of precure should be just before gelation. This is a readily

recognized condition in between the under cured and the over cured states. If the polyurethane is insufficiently cured, the liquid coming out of the spinning orifice in the subsequent spinning operation will either fall as little spheres or will be too stiff and will therefore break during the "taking up" operation. If cured to gelation the polymer will show insolubility in the solvent.

Partial curing to the proper stage can be accomplished in the usual curing systems, employing glycols, mono and polyalkanolamines and the other curing agents previously set forth, etc.

Immediately after the polyurethane has been partially cured to the desired extent, it is dissolved in a suitable solvent such as dimethyl formamide or any of the other polyurethane solvents previously set forth. The polyurethane is dissolved to form a solution containing about 10 to 60% of the polyurethane by weight. The resulting solution can be held at an elevated temperature for a limited interval of time to permit further curing to occur, in the event the polyurethane employed has not reached the stage of incipient gelation, and then is spun into a liquid bath.

The spinnig bath liquid is preferably water, although any liquid which is a solvent for the polymer dope solvent and a non-solvent for the partially cured polymer may be used, provided it is stable at spinning temperatures which are preferably between 20 and 100° C. The spinning bath liquid, e.g., water can be diluted with up to 60% of dimethyl formamide or other solvent for the polyurethane.

Conventional spinning bath apparatus may be used to take up the resulting filaments on reels, and such apparatus forms no part of the present invention. After spinning, the fibers are heated to complete the cure of the polyurethane.

The physical properties of the fibers formed of course will be modified to some extent according to the choice of polyester, polyether, polyisocyanate and the isocyanate number of the prepolymer obtained from them.

Unless otherwise stated, all parts and percentages in the present specification and claims are by weight.

Example 1

20 parts of a polyester (prepared from adipic acid and ethylene glycol and having a hydroxyl number of 32 and an acid number 2) and 15 parts of tolylene diisocyanate (80% 2,4; 20% 2,6) were mixed and held at 100° C. for 5 minutes. There was then added 0.5 part of tin dibutyl laurate. The melt was held at 100° C. until the viscosity started to increase. It was then dissolved in 20 parts of dimethyl formamide. The dope was advanced to the spinnable state at 40° C. until just short of gelation. At this point it was diluted with 20 parts of dimethyl formamide and spun into a water bath at 100° F. (38° C.). The physical properties of the thread obtained were as follows:

Tensile strength	p.s.i.	8,710
Elongation	percent	600
Permanent set	do	22

Example 2

20 grams of polyglycol P–1200 (polypropylene glycol, M.W. 1200) and 10 g. of tolylene diisocyanate (80% 2,4 and 20% 2,6) were held at 100° C. for 5 minutes. To this was added 1 cc. of 10% solution of triisopropanolamine in methylene chloride. The mixture was partially cured at 100° C. until it became viscous. It was then dissolved in 20 gms. of dimethyl formamide and further matured at 50° C. When it was at the stage of incipient gelation there was added a further 20 gms. of dimethyl formamide and the mixture spun into water at 110° F. (43° C.). After the resulting thread was cured for 3 hours at 100° C., it has a 100% elongation at break.

Example 3

10 gms. of a polyether urethane prepolymer (prepared from polypropylene glycol, mol. wt. 2000, and tolylene diisocyanate (80% 2,4; 20% 2,6) and having an isocyanate number of 7.0), 0.4 cc. butanediol 1,4 and 0.8 cc. of N-coco-morpholine were mixed and held at 100° C. for 10 minutes. The mixture was dissolved in 30 cc. of dimethyl formamide and 0.8 cc. of N-coco-morpholine were added. The solution was held at 80° C. for 15 minutes and then spun into 40° C. water. The fiber was cured at 100° C. for 1 hour at the end of which time it had the folowing physical properties:

Elongation	percent	800
Permanent set	do	171

Example 4

40 gms. of a polyester urethane prepolymer (prepared from the same polyester as Example 1 and tolylene diisocyanate and having an isocyanate number of 2.9) and 0.4 gm. of trimethylolpropane were mixed at 100° C. and held at 100° C. for 30 minutes. The partially cured resin was dissolved in 80 cc. of dimethyl formamide. After cooling to 150° F. (66° C.) 2.0 gms. Caytur DA (a delayed action catalyst manufactured by Du Pont) was added. After 1 hour at 150° F. (66° C.), the dope was spun into water at 150° F. (66° C.). After curing for 2 hours at 200° F. (93° C.) the following physical properties were noted:

Elongation	percent	850
Tensile strength	p.s.i.	4,642
Permanent set	percent	19
Denier		300

Example 5

A mixture was formed consisting of 100 parts of the same polyester prepolymer as Example 1 and having an isocyanate number of 2.96 and 2.0 parts of Quadrol (N,N,N′,N′-tetrakis (2-hydroxypropyl) ethylene diamine) by bringing the two ingredients together and holding the composition at 100° C. for 10 minutes.

This material was then dissolved in 200 parts of dimethyl formamide and an additional 0.1 part of Quadrol was added. Curing to the point of incipient gelation was completed by heating at 80° C. for 2 hours. The partially cured product was spun as a monofilament into water at 50° C. The thread was continuously picked up on a reel and curing was completed on the reel at 120° C. for 1 hour. The fiber product had the following properties:

Tensile strength	p.s.i.	5,000
Elongation	percent	300
100% modulus	p.s.i.	100
500% modulus	p.s.i.	300

Example 6

100 parts of the same polyether prepolymer as Example 3 having an isocyanate number of 7.0, 0.4 part of butanediol-1,4 and 0.4 part N-coco-morpholine were mixed and held at 100° C. for 30 minutes. The mixture was dissolved in 200 parts of dimethylformamide and 0.4 part additional N-coco-morpholine added. The solution was held for 1 hour at 80° C. and then spun into water at 80° C. The fiber had the following physical properties:

Tensile strength	p.s.i.	6,500
Elongation	percent	700
100% modulus	p.s.i.	150
500% modulus	p.s.i.	320

The method described above has numerous advantages in the formation of spun polyurethane threads. Thus the method is more adaptable than the procedure of spinning fully cured polymers. Thus there is a tendency for greater permanent set in the product obtained from

spinning substantially fully cured polyurethanes in contrast to the partially cured polyurethane spun according to the procedure just described. The present spinning procedure has the advantage over melt spinning that it is possible to hold a solution of the partially cured polymer at the optimum spinning stage for longer periods of time than is feasible with most melts. As a consequence, the operating factors are less critical and easier to control.

PROCEDURE II

Procedure I just described, while it has certain advantages over prior methods of spinning polyurethanes, does present several problems. Thus there are some difficulties in completing the operation of making a fiber such as removing the last traces of solvent, drying and curing due to the tackiness of the newly spun fiber. The fiber has a tendency to stick to heated surfaces, e.g., steam drying rolls, oven belts, or even to itself during cures. The present Procedure II overcomes these difficulties by adding a curing agent subsequent to the step of spinning the partially cured polymer and prior to any further heating step. Generally 75% or more of the curing is accomplished during the drying operation.

In Procedure II there are employed the same prepolymers and solvents as in Procedure I. Any of the conventional polyurethane curing agents can be employed. The curing agent is added after the spinning described in Procedure I. Generally the wet fiber is processed over a roll, e.g., a snubby roll or godet wheel and then is passed through a bath containing the curing agent. The concentration of curing agent is not critical. Usually it is added in an amount of 0.005 to 0.5% of the urethane prepolymer. The prepolymer is treated with the curing agent bath for 30 seconds to 15 minutes or longer or is washed by a stream containing the curing agent on an advancing reel, or long bath or pulley. The polyurethane is spun into water and the curing agents, e.g., polyfunctional amines and amino-alcohols are preferably added in aqueous solution. The temperature of the solution containing the curing agent is usually kept between room temperature (20° C.) and 38° C. (100° F.). The fiber is then taken up on a drying mechanism and then cured. The curing can be from room temperature up to 180° C. As a result of following Procedure II there is a quicker cure than in Procedure I, sticking to all hot processing equipment is limited and due to the higher wet tensile strength during processing, fewer breakdowns are encountered throughout the process.

Example 7

100 parts of the same polyester urethane prepolymer as in Example 1 and having an isocyanate number of 2.95 was mixed with 0.56 part of Quadrol and heated at 80° C. for 2 hours. The product was dissolved in 100 parts of dimethyl formamide and heated at 80° C. until just short of gelation. The composition was diluted with another 350 parts of dimethyl formamide. The solution was spun into warm water, the wet thread was continuously taken off a moving roll and fed by means of an advancing reel through a 10% aqueous solution of diethylene triamine. The thread was then dried on another advancing reel and cured at 121° C. (250° F.). The cured thread had the following properties:

Tensile strength	p.s.i.	9,000
Elongation	percent	650
Permanent set	do	15
100% modulus	p.s.i.	300

Example 8

Utilizing the same prepolymer as in Example 7, the catalyst used in the post spinning operation was varied with the results indicated below. The catalyst treatment was for 3 minutes in a 10% aqueous bath at room temperature.

Catalyst (10% Aqueous)	Treated Gel, Wet, p.s.i.	Thread Strength, Dry, p.s.i.
diethylene triamine	2,400	4,500
triethanolamine	2,400	----------
diethanol amine	2,400	----------
ethanol amine	2,400	----------
KOH	2,400	----------

The untreated thread had a gel strength of 600 p.s.i. wet and 600 p.s.i. dry.

Example 9

The procedure of Example 7 was repeated replacing the prepolymer by a polyethylene glycol 400-tolylene diisocyanate prepolymer having a molecular weight of about 1,500 and an isocyanate number of about 3 to obtain a thread having improved wet and dry gel strength after the diethylene triamine post spinning cure.

PROCEDURE III

In the processes described in Procedures I and II, the polyurethanes in the spinning solution continue to cure and eventually the spinning solution is unusable due to gelation. The ability to continue to cure distinguishes from those systems in which the cure is completed prior to solution. When the cure is completed prior to solution there results an elastomer with poorer properties unless certain special conditions are employed as disclosed hereinafter.

It has now been found that it is possible to eliminate the instability of the curable spinning solutions without losing the ability to finish the cure subsequent to spinning.

A polyol, either a hydroxyl terminated polyester, or a polyether or a castor oil derivative as described above is condensed with any of the polyisocyanates described previously to give an isocyanate terminated polymer of any desired weight from double that of the original polyol to several times the original molecular weight. This prepolymer is cured to a hard gum by the addition of cross-linking agents such as those previously set forth e.g. triols, tetrols, triisopropanolamine, Quadrol, etc., in the amount of 0.25 to 3 parts per 100 parts of polymer. The composition is heated until the gum is insolble in solvents such as dimethyl formamide, methylene chloride and diethylene carbonate. Thus the heating can be for 8 to 24 hours at 121° C. (250° F.) although other times and temperatures can be employed. In general the higher the temperature the shorter the time of treatment.

While the gum is insoluble in the above mentioned solvents such as dimethyl formamide, it can be swollen by them at room temperature. Further heating of the swollen mass dissolves the gum by degradation of the polymer forming active hydrogen atoms. The addition of more polyisocyanate, such as those referred to previously in an amount of 0.2 to 2 parts, for example, per 100 parts of the degraded polymer rebuilds the chain length within a period of time dependent upon the amount of toluene diisocyanate (or other polyisocyanate) and temperature to a state suitable for spinning a fiber which has an infiite spinning life. There are enough residual isocyanate linkages available (although below the amount for detection by wet analysis) to cure the polymer after spinning to give a thread having enhanced physical properties.

The high molecular weight, partially cross linked polyurethane solution formed by the degradation and partial rebuilding of the polymer is suitable for spinning fibers by wet spinning processes, e.g. spinning from a solution in dimethyl formamide into water, glycerol, etc. or by dry spinning, e.g. spinning from a volatile solvent such as methylene chloride into air. In either case the polyurethane spinning solution has an indefinite pot life.

Example 10

100 parts of Thiokol ZL–291 (a high molecular weight liquid urethane having an isocyanate number of 2.96 and prepared from toluene diisocyanate and a polyester having free hydroxyl groups and made from adipic acid, phthalic acid, ethylene glycol and propylene glycol) was mixed with 0.5 part of triisopropanol amine. The mixture was heated at 121° C. (250° F.) until viscous, poured onto a flat sheet and baked for 14 hours at 121° C. (250° F.) to form a cured gum. The gum was cut into small pieces and swollen by 4 parts per hundred of dimethyl formamide. The swollen gum was heated at 120° C. until it was dissolved. To hasten solution the mixture was stirred by a high speed shearing type mixer. The solution at this point was not spinnable since the polymer chain was degraded too far. The solution was divided into 3 portions, A, B and C. Tolylene diisocyanate (80% 2,4; 20% 2,6) was added to portion A in an amount of 0.25 part per hundred, to portion B in an amount of 0.5 part per hundred and to portion C in an amount of 1.0 part per hundred. Portions of these compositions were then allowed to stand at room temperature until they could be spun. This took from 2 to 5 hours (solution A taking 5 hours and solution C taking 2 hours). Solutions A, B and C were then spun into water and the threads formed cured by heating at 120° C. for 2 hours. The cured threads had the following properties:

	A	B	C
Tensile strength (p.s.i.)	1,800	2,644	4,500
Elongation (percent)	700	700	750
Permanent set (percent)		22	22

When portions of solutions A, B and C were allowed to stand for 48 hours prior to spinning freshly spun fibers exhibited the following properties:

	A	B	C
Tensile strength (p.s.i.)	2,000	1,200	3,300
Elongation (percent)	750	675	625
Permanent set (percent)		31	50

Example 11

40 grams of Thiokol ZL–291 and 2.0 cc. of triisopropanolamine were heated at 121° C. (250° F.) for 3 hours after gelation. The gum was dissolved in 80 grams of dimethyl formamide at 80–120° C. with agitation by a high speed shearing type agitator. The product formed could not be spun. Then 0.3 cc. of tolylene diisocyanate (80% 2,4; 20% 2,6) were added and the mixture allowed to mature at 54° C. (120° F.) for 3 hours. The solution was spun into warm water and the fiber cured by heating at 120° C. for 2 hours. The spinning operation was repeated using the same spinning solution for 4 consecutive weeks with the following properties for the fibers:

Week	Tensile (p.s.i.)	Elongation (percent)	Permanent set (percent)
1	4,290	900	44
2	10,000	900	16
3	6,000	950	
4	11,500	900	12.5

Example 12

100 parts of a polyethylene glycol 400-tolylene diisocyanate prepolymer having a molecular weight of about 1,500 and an isocyanate number of about 3 was mixed with 1 part of triisopropanolamine and heated at 121° C. for 2 hours after gelation. The gum formed was dissolved at 100° C. in 100 parts of dimethyl formamide. Then 1 part of tolylene diisocyanate (80% 2,4; 20% 2,6) was added and the mixture allowed to mature at 55° C., for 3 hours. The solution was then spun into water at 50° C., and the fiber cured by heating at 120° C. for 4 hours.

PROCEDURE IV

It has also been found that polyurethane prepolymers such as those previously set forth can be spun from solution into air, nitrogen, argon or other gas. This process has the advantages over those previously set forth in that there can be employed solvents which are not necessarily water soluble. Additionally, there is no need to dry the fibers after they are formed.

The partially precured polyurethane prepolymer is dissolved in a volatile solvent and then is advanced as far as possible without the prepolymer being insolubilized in the solvent, i.e. it is advanced to incipient gelation. The solvent employed should have a very high affinity for the partally cured prepolymer and be nonreactive with it. The preferred solvent is methylene chloride but less volatile solvents such as ethylene carbonate, dimethyl formamide, etc., can be employed. When such less volatile solvents are used the atmosphere generally should be heated to close the boiling point of the solvent to insure complete removal thereof from the spun thread.

When the polyurethane has arrived at the proper state of precure the fiber formed has a sufficiently well defined gel structure that after removal of the solvent it can maintain its own weight and be processed on spools, reels, etc.

Example 13

100 parts of a liquid prepolymer (Thiokol ZL–291 having an isocyanate number of 2.96) and 0.38 part of Quadrol were precured at 121° C. (250° F.) for 45 minutes. To this mixture was added 200 parts of methylene chloride and the solution was refluxed for 80 hours, at this time the viscosity had reached the proper point, i.e. incipient gelation, as determined by trial spinning a sample of fiber from the solution into air. The properties of the spun fiber were:

Tensile strength (p.s.i.)	3,000
Elongation (percent)	800
Permanent set (percent)	13.7

Example 14

100 parts of a polyethylene glycol 400-tolylene diisocyanate prepolymer having a molecular weight of about 1,500 and an isocyanate number of about 3 and 0.4 part of Quadrol were precured at 120° C. for 45 minutes and then 200 parts of methylene cloride was added.

The solution was heated at reflux to the point of incipient gelation and then fibers were spun from the solution into air at 40° C.

PROCEDURE V

It has been found advantageous in some instances to spin a polyurethane gel. This can be satisfactorily accomplished by the following procedure. A polyurethane prepolymer e.g. of the polyster or polyether type described previously, is precured with any of the conventional curing agents, such as those previously set forth, for example, to the point of incipient gelation. Ether at this point, or previously, it is dissovled in any of the conventional polyurethane solvents, e.g. dimethyl formamide. Then the mixture is precured further by heating to a stage beyond the point of solution, so that the partially cured polyurethane gells. The gel, however, is so swollen with solvent that it is pourable as such and can be forced by pressure or mechanically stuffed into a spinning feed vessel. The swollen gel usually contains 5 to 60% of solids. The swollen gel is spun into water or an aqueous mixture containing dimethyl formamide or other solvent as previously set forth. The water bath temperature can vary from room temperature (or below) to 82° C. (180° F.) or higher.

Example 15

100 parts of Thiokol ZL–291 was mixed with 0.38 part of Quadrol and precured at 130° C. for 45 minutes. The product was dissolved in dimethyl formamide to 67% solids content and cooled immediately to 40° C. (40° F.). After 24 hours at this temperature, the swollen gel was forced into a feed vessel. To do this the material was cut with a pair of scissors in order to push it into the spinning reservoir since the material was not pourable. The dope was spun into an 18" water bath at 43° C. (110° F.) and the fiber dried on a belt oven for 1 minute. The spooled fiber was cured at 121° C. (250° F.) for 2 hours. The fiber had the following properties:

Tensile strength (p.s.i.)	4,000
Elongation (percent)	650
100% modulus (p.s.i.)	180
Permanent set (percent)	15

Example 16

Example 15 was repeated. In this case the solvated gel was barely pourable. It also was cut with a scissors when the desired amount was poured. The fiber formed had the following properties:

Tensile strength (p.s.i.)	3,800
Elongation (percent)	600
100% modulus (p.s.i.)	210
Permanent set (percent)	12

Example 17

100 parts of a polyethylene glycol 400-tolylene diisocyanate prepolymer having a molecular weight of about 1,500 and an isocyanate number of about 3 was mixed with 0.4 part of Quadrol and precured at 130° C. to the point of incipient gelation as measured in dimethyl formamide. Then the product was dissolved to 60% solids in dimethyl formamide and the product immediately cooled at 5° C. in order to form a swollen gel which was then aged for 24 hours at this temperature and spun into water at 45° C.

It is not necessary to cool the dimethyl formamide solution but instead room temperature can be employed to reach the point of incipient gelation.

PROCEDURE VI

In Procedure III above there is described a method of preparing spinning solutions of infinite pot life. By such a procedure a fully cured gum is degraded by the action of solvents and heat. This is a practical method of putting the polyurethane into a form where it can be spun into fibers. However, the process requires considerable time and labor. It has now been found that the same final end (very long spinnable life and good physical properties) can be attained without the difficulties involved in handling a gum.

A polymeric polyol, e.g. a polyester or polyether such as those previously described, is condensed with an excess of an isocyanate, e.g. any of the diisocyanates previously set forth to form a prepolymer. The latter is then partially cured with conventional diisocyanate curing agents. At a suitable step in the procedure a solvent such as dimethyl formamide, dimethyl sulfoxide, diethylene carbonate or methylene chloride is added. The solution is matured either at room temperature or a slightly elevated temperature until a solvated gel is formed. The gel is then dissolved with agitation at a more elevated temperature. The thus degraded and solubilized polymer cannot be spun at this stage since its molecular weight is not great enough. The polymer chain length and/or cross linking is increased by the addition of more diisocyanate, e.g. 0.05 to 5 parts per 100 parts of prepolymer. The solution increases gradually in viscosity until it is spinnable. After this point there is only a slow increase in viscosity and the polymer solution can be either wet or dry spun for an extended period of time without having the physical properties of the thread impaired.

Example 18

100 parts of Thiokol ZL–391 was mixed with 0.5 part of triisopropanolamine and precured at 100° C. for 7 hours. The product was dissolved to 50% solids in dimethyl formamide and held for 1.5 hours at 50° C. The mixture was diluted with dimethyl formamide to 33% solids and held for 4 hours at room temperature until it gelled. The gel was dissolved at 80° C. in 2 hours. At this point a fiber could not be spun. Regeneration was accomplished by the addition of 0.5 part per hundred of prepolymer of toluene diisocyanate (80% 2,4; 20% 2,6). The resulting solution was spun into water on four different days and the fibers cured at 135° C. (275° F.) for 1 hour to give products with the following properties:

Day	Tensile strength (p.s.i.)	Elongation (percent)	Permanent set (percent)
1	4,000	675	112
5	3,900	550	43
8	4,220	600	59
12	3,750	700	56

The dope was usuable and stable for a period of about 15 days. The spinning results indicate that for best results the dope should be matured for 1 to 3 days prior to spinning.

Example 19

The procedure of Example 18 was repeated except that the solvated gel was dissolved at 120° C. rather than 80° C. The cured fibers prepared by spinning on the several days had the following properties:

Day	Tensile strength (p.s.i.)	Elongation (percent)	Permanent set (percent)
1	4,000	675	137
5	4,250	800	43
8	3,750	725	50
12	4,000	700	75

Example 20

The procedure of Example 18 was repeated replacing the 100 parts of Thiokol ZL–291 with 100 parts of a polyethylene glycol 400-tolylene diisocyanate prepolymer having a molecular weight of about 1,500 and an isocyanate number of about 3.

I claim:

1. A process comprising spinning a curable polyurethane from the state of incipient gelation in a solvent into a liquid in which the polymer is insoluble and the solvent is soluble to form a polyurethane filament and adding a curing agent to said filament and then completing the cure.

2. A process comprising spinning a curable polyurethane from the state of incipient gelation in a solvent into a liquid in which the polymer is insoluble and the solvent is soluble to form a polyurethane filament and passing said filament through a bath containing a curing agent and then curing said filament with the aid of heat.

3. A process comprising partially curing a polyurethane to the point where a thread spun therefrom can maintain its own weight instantaneously and spinning a solution of said partially cured polyurethane in a solvent into a liquid in which the polyurethane is insoluble and the solvent is soluble.

4. A process according to claim 3 including the additional step of heating the thread to further cure the same.

5. A process according to claim 2 wherein the filament is formed by spinning the polyurethane into an aqueous solvent and the bath containing the curing agent is an aqueous bath.

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