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SYNTHETIC FIBERS

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M E M O R A N D U M
SYNTHETIC FIBERS NSPS (ESED PROJECT NO. 80/15)

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FROM: Roy Manley

SUBJECT: Model Plants for Dry and Reaction-Spun Spandex

During the NAPCTAC meeting of September 22, 1981, Mr. J. Bercaw, representing the Man-Made Fiber Producers Association, recommended that EPA develop model plants for all fiber types potentially subject to the recommended standard. This concept had been addressed much earlier in the project during in-house EPA/PES meetings, but perhaps the resolution developed during these meetings was not made sufficiently clear to persons outside EPA through the BID and preamble.

Generally, the industry can be characterized as having a stable commodity fiber-producing portion, and a relatively dynamic portion, into which new fiber types and production methods are almost constantly being introduced. (See the Globe Manufacturing Company patent attached for an illustration of the range of production methods for just one fiber type.) Also, many fiber types are produced in other countries but not currently in the U.S. Still other types are being produced at pilot scale levels, and may or may not expand to full production (solvent-spun rayon, for example). There is an almost infinite variety of fiber types and production methods possible for which model plants could be developed; therefore, in describing the fibers industry, it is impossible to develop a model plant and economic analysis for each possible fiber type. Rather, the industry can be described with a range of model plants that are sufficiently representative of the basic solvent-spun synthetic fiber processes so as to be universally applicable to that segment of the industry. Thus, the BID was written using five model plants and three fiber types. Nevertheless, because of the comments made at the NAPCTAC meeting, a survey was conducted to identify all known solvent-spun synthetic fiber producers and to determine if any fiber types were not adequately described. Only one fiber type was determined to be potentially affected by the standard and not sufficiently characterized in the BID.

This fiber (spandex) is manufactured with two different processes by two companies in the U.S. One process, that used by Globe Manufacturing Company, is a substantially different process than any used for other fiber types by any manufacturer in the U.S. It is the only known reaction-spinning fiber process used in the U.S. Therefore, it was decided (see project team meeting report of October 27, 1981) to

develop a model plant that would describe this fiber type and production process. During the development of the model plant, however, it has not been thus far possible to demonstrate conclusively that emissions (and solvent recovery) could be improved over existing baseline conditions. It appears that there are peculiarities with this process that dictate lower solvent recovery efficiencies, and relatively higher emissions. (This subject is addressed in detail in the November 10, 1981, issue paper from Bob Zerbonia.) Therefore, this type process should not be subject to the recommended standard, since there are no identifiable control options to improve solvent recovery. Alternative means of reducing VOC emissions are being examined, incineration being the most notable, and will likely be too costly to consider as regulatory alternatives.

A second type process used in the manufacture of spandex is the dry-spinning process. In some respects, this process is similar to that used for acetate textile yarn, in that the fiber is dry-spun and immediately wound onto take-up bobbins, then twisted or processed in other ways. Detailed information received from du Pont, the only manufacturer producing spandex using this type process, indicates that the solvent emissions are already below the limit specified in the recommended standard, and no additional control measures are available to further reduce VOC emissions. There are no identifiable control options or regulatory alternatives available, and complete economic analysis need not be conducted. This model plant and related information will not be included in the BID, but will be placed in the public docket for examination. (See the attached discussion of the spandex dry-spinning process.)

Summary - Baseline parameters for the two model plants should be completed and included in the docket for examination. The BID should be revised to include a brief discussion of these two model plants, and a text reference added to the BID to call attention to the docket entries for further information.

3,387,071
FIBERS

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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 develop 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 modulus 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 while 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) poly-

groups 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-butanediol, neopentyl glycol, diethylene glycol, thiodiglycol, etc. The acid usually contains 4 to 20 carbon atoms. Typical examples include succinic acid, maleic acid, dihydromuconic acid, thiodipropionic acid, adipic acid, methyl adipic 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 trimethylolmethane may be included in preparing the glycol-dicarboxylic 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 polyethers. Such polyethers are typically anhydrous chain extended polyethers possessing ether linkage separated 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 (di-propylene 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 Kohn 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 diisocyanate, 4,4'-methylene-bis(cyclohexylisocyanate) and 1,5-tetrahydronaphthalene diisocyanate. Other diisocyanates can be employed including those set forth in Kohn Patent No. 2,953,839, as well as those mentioned in the patents set forth in Kohn. There can be included trisisocyanates or higher isocyanates in order to get added functionality in the coagulating bath. Such isocyanates include PAPI (phenylmethane isocyanate trimer), 2,4,4'-diphenyl ether triisocyanate, 4,4', 4''-trisocyanate triphenylmethane, toluene 2,4,6-trisocyanate.

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 intermediate 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 trimethylpropane 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.	1,300
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 ethylene 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 ter-

minal 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.

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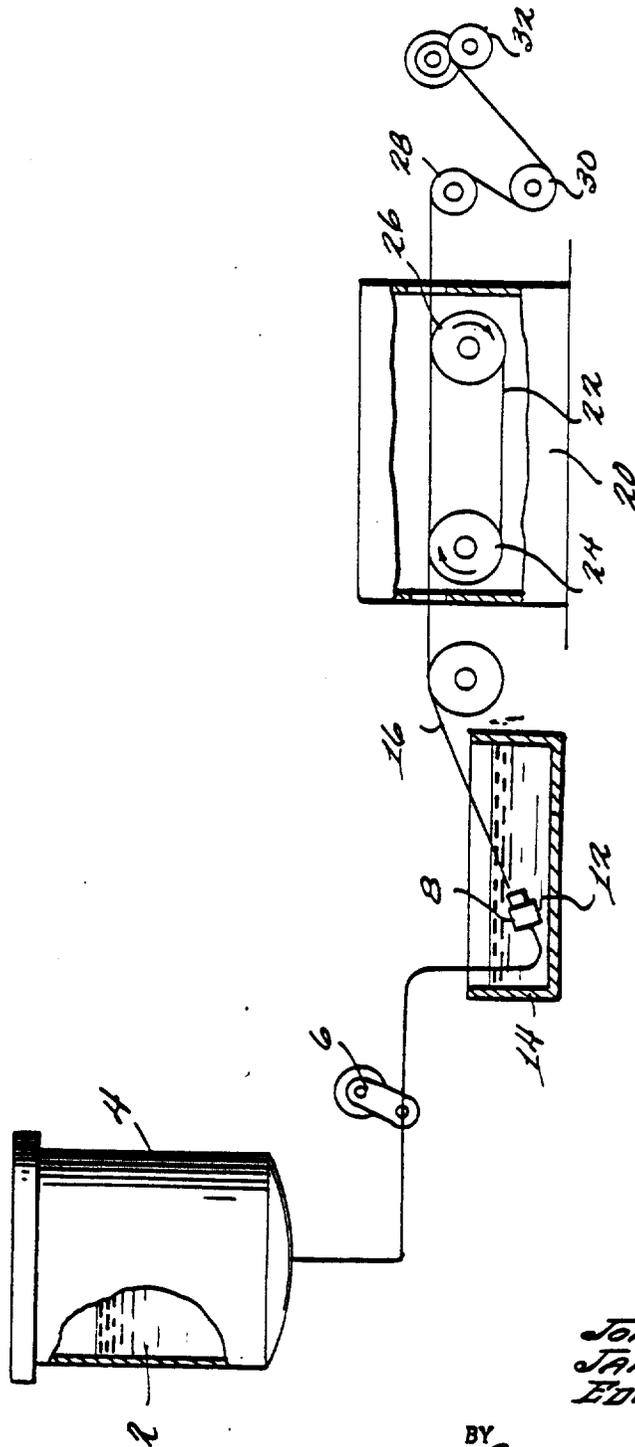
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FIBERS

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Model Plant
For
Spandex Fiber Dry Spinning Process

Spandex fibers are polyurethanes; the Federal Trade Commission defines spandex yarns as "a manufactured fiber in which the fiber-forming substance is a long chain synthetic polymer comprised of at least 85 percent of a segmented polyurethane." In between the urethane groups there are long chains which may be polyglycols, polyesters, or polyamides or copolymers of them. The general type of spandex fibers can be inferred from a study of patent specifications. In U.S. Patent 2,692,873 (1954) du Pont describes elastomers made by co-polymerizing polyethylene glycol and tolylene-2,4-di-isocyanate in the presence of water and a small quantity of an acid chloride.

The spandex synthesis used on production is rather different from the early patented methods. Tetrahydrofuran is the raw material. Its ring is opened and the straight chain compound is polymerized to give a low polymer and this low polymer is treated with an excess of di-isocyanate. The reactant together with any unreacted di-isocyanate is next reacted with some diamine, with monoamine added as a stabilizer. The final polymerization stage is carried out in dimethylformamide solution, and then the spandex is dry-spun from this solution.

The spandex model plant is characterized by use of solution polymerization and dry spinning with an organic solvent. Polymer (or copolymers) is dissolved in solvent, blended with additives, filtered, dry spun, and processed. For the spandex segment of the fibers industry a model plant capacity of 2.5 Gg per year (5 MMPPY) was selected. For this dry spinning capacity, one spinning line, with 10 spinning cells per line is required as well as the appropriate downstream fiber processing and packaging equipment.

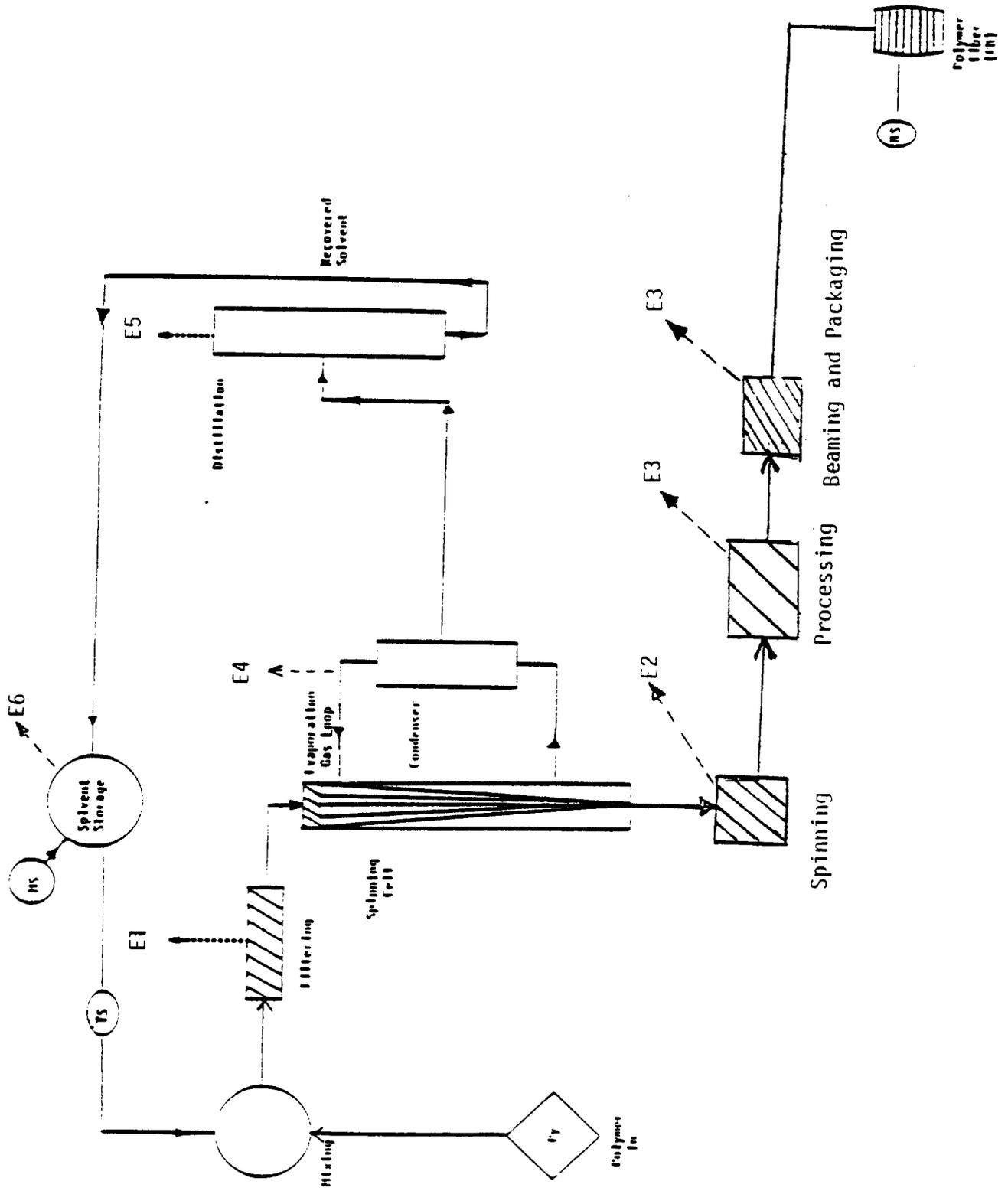


Figure 1. Spandex Fiber Dry Spinning Baseline Control

PARAMETERS FOR SPANDEX FIBER MODEL PLANT
BASELINE CONTROL

<u>General Information</u>	
Type of Plant	Spandex Fiber
Spinning Process	Dry Spinning
Polymerization Medium	Solution
Spinning Solvent	Dimethylformamide (DMF)
Production Capacity	2.5 Gg/year (5 MMPPY)
Capacity Utilization	95 percent
Raw Materials	Polyurethanes, 98 percent Other Materials, 2 percent
Hours of Operation	8,400 hours per year
Pollutant	DMF (as VOC)
<u>Process Variables*</u>	(Relative Quantities*)
Raw Materials In (PY)	1000 kg Polyurethane 20 kg Other Material
Solvent Used (TS)	2000 kg DMF
Make-Up Solvent (MS)	30 kg DMF
Polymer Fiber Out (PS)	1000 kg, Spandex
Residual Solvent in Fiber Product (RS)	4 kg DMF
Miscellaneous Solvent Loss	14 kg DMF
<u>Emission Sources</u>	(Relative Quantities*)
Filtering (E1)	1 kg DMF
Spinning (E2)	8 kg DMF
Processing (E3)	2 kg DMF
Condenser, Column, Tank Vents (E4, E5, E6)	1 kg DMF

*Based on 1000 kg of Polymer

TABLE 1 (CONCLUDED)

Exhaust Gas Characteristics

Filtering (E1)	Intermittent Flow: 1000 ACFM Temperature: 80°F Solvent Concentration: 10 ppm
Spinning (E2)	Flow Rate: 25,000 ACFM Temperature: 80°F Solvent Concentration: 10 ppm
Processing (E3)	Flow Rate: 5,000 ACFM Temperature: 80°F Solvent Concentration: 10 ppm

Immediately after spinning, spandex yarn is wound onto a bobbin as continuous filament yarn. The yarn is later transferred to large spools for shipment or further processing in another part of the plant. As the fibers are initially wound onto bobbins, they may still contain as much as 5 to 10 percent residual solvent. This residual solvent continuously evaporates into room or building air until equilibrium is reached at around 3 to 4 percent (by weight) residual solvent.

Overall emissions from spandex fiber dry spinning are considerably less than other dry spinning processes. It appears that the single most influencing factor that accounts for the lower emissions is that, because of the nature of the polymeric material and/or spinning conditions, the amount of residual solvent in the fiber as it exits the spin cell is considerably lower than other dry spun fibers (e.g., 5 to 10 percent versus 15 to 20 percent). This situation may be due to the lower solvent-to-polymer ratio that is utilized in spandex dry spinning (e.g., 1.5 to 2.0 for spandex versus 2.5 to 3.5 for acrylics and acetates). Thus, the primary solvent recovery system serving the spin cell exhaust gas, although basically the same as in other dry spin processes, is overall more efficient in terms of recovery of total solvent used.

The major emissions from the spandex dry spinning process are volatilized solvent losses which occur at a number of points in the overall production scheme. Solvent emissions occur during filtering of the spin dope, spinning of the fiber, treatment of the fiber after spinning, and during the solvent recovery process. Figure 1 presents a process flow diagram, with emission points shown, for this segment of the spandex fibers industry. Table 1 includes the model plant parameters relevant to the diagram. This production or process sequence is considered as baseline control for this model plant.

Solvent residual in the fiber at the spin cell exit is much lower than that for other fiber types, and the potential for capture and recovery also much lower. This is primarily because the bulk of the volatilized solvent emissions are captured in the spin cell and recovered in the condenser. Enclosures and other capture and control measures employed in other model fiber plants are therefore not attractive means of emission control at dry-spun spandex plants. Beyond the

control measures already described in the baseline parameters, no other methods of emission control have been identified. Therefore, the only Regulatory Alternative recommended is that for baseline controlled plants.

SPANDEX FIRER BASELINE PLANT, 5 MILLION POUNDS
PER YEAR CAPACITY

<u>ITEM INCLUDED IN COST ESTIMATE</u>	<u>COST (MILLION \$)</u>
Tank Farm	0.35
Chemical Storage	0.04
Dope Preparation Area*	1.60
Spinning Equipment	4.25
Processing Equipment	1.06
Solvent Recovery Equipment	1.24
Manufacturing Building	0.70
Warehouse	0.40
<u>QC Lab</u>	<u>0.40</u>
Total	10.04

Not included in the above costs are:

- Polymerization equipment
- Utility Generation
- Waste Treatment
- Streets, Parking Areas, Railroads
- Land Purchase, Preparation, Site Improvement
- Support Facilities (cafeteria, showers, medical, maintenance shops, guard facilities, administrative offices, etc.)
- Raw material unloading

*Does not include polymerization process equipment, buildings, etc.

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