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ELASTIC POLYURETHANE FILAMENTARY MATERIAL
AND METHOD OF MAKING SAME
Filed March 23, 1962

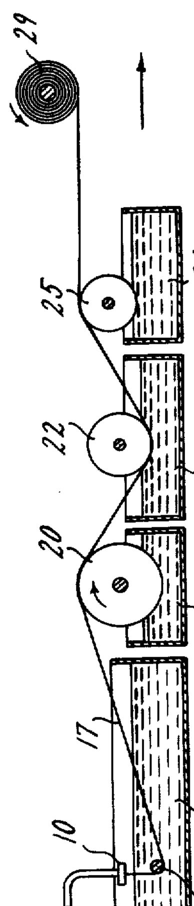

Fig. 1

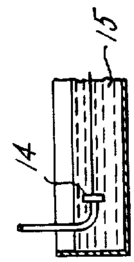

Fig. 2

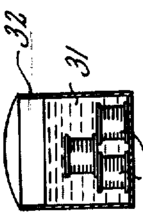

Fig. 3

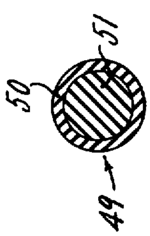

Fig. 4

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ELASTIC POLYURETHANE FILAMENTARY MATERIAL AND METHOD OF MAKING SAME

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10 Claims. (Cl. 18—54)

This invention relates to filamentary material, and more particularly it relates to elastic polyurethane thread or fiber characterized by uniformly of size and shape along its length, as well as to a method of making same.

This application is a continuation-in-part of our commonly assigned copending application Serial No. 123,617, filed July 13, 1961, and now abandoned.

The invention is based upon the discovery that superior coagulation of a polyurethane thread in an aqueous aliphatic diamine bath can be obtained by having an additional organic solvent, selected from the group consisting of monoalcohols, glycols, and mixtures thereof, present in the bath. The thread is subsequently cured by the action of water, preferably with prior washing of the thread immediately upon removal from the coagulating bath.

In one aspect, the invention is an improvement upon the polyurethane thread and method of making same disclosed in U.S. patents of Kohrn et al., 2,953,839, September 27, 1960, and 3,009,762, November 21, 1961. Those patents describe making a polyurethane thread or filament from a polyurethane "prepolymer," which is a reaction product of a hydroxy-terminated polyester or polyether or the like with an organic diisocyanate. Such prepolymer is extruded into an aqueous solution of an aliphatic primary diamine to "coagulate" the thread, that is, to cause a rapid setting or gelling of the surface of the thread. Subsequently, cure of the thread is completed by the action of water. Unfortunately, thread made in this manner trends to be flattened in cross-section rather than round. It also tends to be non-uniform in cross-section, i.e., it may have "thin" spots, and this gives rise to breakage and other undesirable effects in subsequent processing.

The invention will be described with reference to the accompanying drawings wherein:

FIG. 1 is a diagrammatic elevational view representing one method of carrying out the invention;

FIG. 2 is a similar fragmentary view of a modification of the invention;

FIG. 3 is a sectional elevational view representing one step in the invention; and

FIG. 4 is an enlarged cross-sectional view of a thread made in accordance with the invention.

In accordance with the present invention, the aqueous aliphatic primary diamine setting bath additionally contains from 5 to 90% by weight of an organic solvent, selected from the group consisting of monoalcohols, glycols, and mixtures thereof, which causes extremely rapid coagulation, and by careful subsequent handling it is possible to obtain substantially round, essentially regularly shaped thread, by the action of water (in the form of liquid or vapor). The solvents which may be added to the aqueous diamine setting bath for this purpose are monoalcohols, glycols, and mixtures thereof, having up to 10 carbon atoms, which, by physical and/or chemical action, lead to the rapid formation of a much tighter gel structure (i.e., a network of alkylene-diureido linkages) than is possible in a plain water-diamine bath. While it is not desired to limit the invention to any particular theory of operation, it appears possible that the ability to obtain a round thread of uniform cross-section in the present process is directly related to the influence of the added

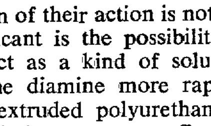
organic solvent in the gelling or setting step. Whether this is a chemical influence, or a physical influence, or a combination of both is not known with certainty, but it may be mentioned that there is an apparent reinforcement of the diamine gelling, whether in the form of a faster gelling or a deeper, more penetrating gelling, or both, as a result of the presence of the solvent. The organic solvents used for this purpose in accordance with the invention are themselves capable of reacting with isocyanate groups, but the extent to which this may be at least a partial explanation of their action is not known. Perhaps at least as significant is the possibility that the solvent apparently can act as a kind of solubilizing agent and serve to carry the diamine more rapidly and/or more deeply into the extruded polyurethane stream, thereby making the coagulation step more effective.

Among the most preferred solvents for addition to the aqueous aliphatic diamine setting bath in accordance with the invention are the alcohols, particularly aliphatic and heterocyclic alcohols, and especially monoalcohols having from 1 to 8 carbon atoms, such as the alkanols. These are especially effective in enhancing the gelling action of the aqueous diamine bath. Preferred alkanols are those having 1–4 carbon atoms, and especially the 3 and 4 carbon atom alkanols. In addition to primary alkanols (e.g., n-propanol, n-butanol), secondary alkanols may be used, such as isopropanol or isobutanol, as well as tertiary alkanols such as tertiary butyl alcohol or tertiary amyl alcohol. Tertiary butyl alcohol is most preferred.

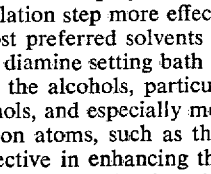
Other monoalcohols that may be used include those containing ether linkages or cyclic structures such as "Ethyl Carbitol" which has the structure

$$HOCH_2CH_2OCH_2CH_2OCH_2CH_3$$

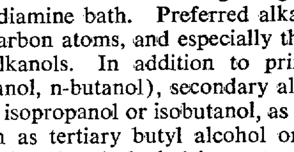
(also "Methyl Carbitol" and "Butyl Carbitol"), "Ethyl Cellosolve" which has the structure $HOCH_2CH_2OCH_2CH_3$ (also "Methyl Cellosolve" and "Butyl Cellosolve"), tetrahydrofuryl alcohol which has the structure



tetrahydropyran-2-methanol which has the structure



4-methoxy-4-methyl pentanol-2 which has the structure



and methoxy triglycol which has the structure

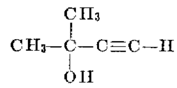
$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

In another preferred form of the invention, monoalcohols such as those described above are used along with glycols (having up to 10 carbon atoms for example), as the organic solvent additive to the aqueous diamine setting bath. Among the suitable glycols may be mentioned the alkylene glycols and alkylene ether glycols, especially those having from 2 to 8 carbon atoms, such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, 2-methyl-2,4-pentanediol

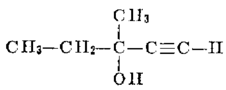
$$[CH_3—CH(OH)—CH_2C(OH)(CH_3)_2]$$

and the like. Although these glycols may be used by themselves as the organic solvent additive to the aqueous diamine setting bath, it is preferred to use them along with one or more of the monoalcohols as described above.

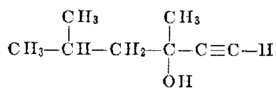
Unsaturated alcohols may be employed, whether ethylenically unsaturated as in the case of allyl alcohol, or acetylenically unsaturated as in the case of methyl butynol:



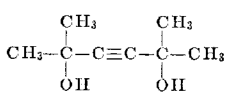
methyl pentynol:



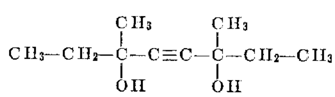
or 3,5-dimethyl-1-hexyn-3-ol:



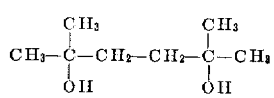
It will be noted that the last three mentioned are tertiary alcohols. Further examples of materials containing tertiary alcoholic groups which may be employed in the invention are pinacol, 2,5-dimethyl-3-hexyne-2,5-diol:



3,6-dimethyl-4-octyne-3,6-diol:



and 2,5-dimethyl-2,5-hexanediol:



It will be noted that unsaturated glycols are included. The last four named materials are solids, but for purposes of the invention they may be regarded as solvents because when dissolved in the bath (with the aid of other more soluble alcohols if necessary), they appear to exert a solubilizing effect, or "carrying" effect on the diamine with respect to the polyurethane prepolymer.

The tertiary glycols, when employed in admixture with primary or secondary alcohols, are of special value in that they appear to aid in reducing any tendency for such primary or secondary alcohols to interfere with, or block, the cure with water.

It will be understood that in the case of those monoalcohols or glycols which are not in themselves readily soluble in water, we typically use them in admixture with the more soluble monoalcohols or glycols, which have a solubilizing action on the less soluble ones.

It will be understood that the described solvent additives employed in the invention are not reactive with the aliphatic diamine in the setting bath, under the conditions of use. Furthermore, they are employed as solutions in setting bath, being either sufficiently water soluble of themselves for this purpose, or sufficiently water soluble in admixture in various combinations.

The organic alcoholic solvent additive, that is, the monoalcohol, the mixture of monoalcohol with glycol, or the glycol, preferably constitutes from 20 to 70% by weight of the setting bath.

With respect to the conventional polyurethane prepoly,-mers that are used in the present invention, reference may be had to U.S. Patent 2,953,839 as disclosing starting polyesters and polyethers, and describing their reaction with polyisocyanates, to make polyurethane prepolymers useful in the invention. Such polyurethane prepolymer is typically a liquid derived from a polymer of molecular weight from 300 to 5000 having terminal hydroxyl groups. Such polymer may be a chain extended polyester 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 from 4 to 20 carbon atoms, and the acid contains from 4 to 20 carbon atoms. An excess of the glycol over the acid is used in preparing the polyester, 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 22 to 225, and preferably 36 to 75, and a low acid value less than 6 and preferably less than 1. The molecular weight of the polyester usually ranges from 500 to 5,000 and preferably from 1500 to 3000. In general the most suitable polyesters are chiefly linear in type with melting point levels of 90° C. or lower.

Other examples of suitable polyesters for use in preparing the prepolymer are polyethylene adipate, polyethylene adipate-phthalate, polyneopentyl sebacate, etc. If desired, small amounts of tri-alcohols such as trimethylolpropane or trimethylolethane may be included in the preparation of the glycol-dicarboxylic acid polyester, and such modified forms of polyester are included within the term polyester as used herein.

As an alternative to the polyesters just described there may be used (for reaction with the polyisocyanate) one or more members of the class of elastomer-yielding polyethers. Such polyethers are typically anhydrous chain-extended polyethers possessing ether linkages (—O—) 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. Usually the polyethers used are chiefly linear in type with melting point levels of 90° C. or lower. The molecular weight may range from 500 to 5,000 (i.e., hydroxyl number of about 225 to 22), but is preferably within the range of 750 to 3,500 (i.e., hydroxyl number of about 150 to 32). Preferred polyethers may be represented by the formula $H(OR)_nOH$ where R is a lower (2-6 carbon atoms) alkylene group and n is an integer such that the molecular weight falls within the range specified. Examples of polyethers used are polyethylene glycol, polypropylene glycol, polypropylene-ethylene glycol, and polytetramethylene glycol. Mixtures of polyesters and polyethers may be used as well as polyesters derived from polyethers [e.g. poly(diethylene glycol adipate), poly(triethylene glycol adipate)].

Further examples of polyesters or polyethers suitable for forming prepolymers useful in the invention are the polyesters and polyethers mentioned in U.S. Patents 2,606,162, Coffey, August 5, 1952; 2,801,990, Seeger, August 6, 1958; 2,801,648, Anderson, August 6, 1957; and 2,814,606, Stilmar, November 26, 1957. It is desired to emphasize that the invention contemplates the use of any and all such known polyethers or polyesters suitable for reaction with an aromatic diisocyanate to yield a polyurethane prepolymer capable of being cured to an elastomeric state by the action of water.

The polyester or polyether is, an indicated, reacted with an aromatic diisocyanate, such as p,p'-diphenylmethane diisocyanate or toluene diisocyanate, using a considerable molar excess, commonly from a 20% to a 250% and preferably from a 50% to a 150% molar excess, of the aromatic diisocyanate over that amount which would be required to react with all of the alcoholic hydroxyl groups furnished by the polyester. In accordance with known practice, the reaction is frequently effected by mixing the polyester and the aromatic diisocyanate under anhydrous conditions either at room temperature, or at a moderately elevated temperature, e.g., 70–150° C., to form a soluble (in methyl ethyl ketone), uncured, liquid prepolymer which is an essentially linear polyurethane having terminal isocyanate groups.

Representative of the aromatic diisocyanates that may be mentioned, by way of non-limiting examples, are such materials as m- and p-phenylene diisocyanate, toluene diisocyanate, p,p'-diphenyl diisocyanate and 1,5-naphthalene diisocyanate, and in this category we include the aromatic-aliphatic diisocyanates such as p,p'-diphenylmethane diisocyanate. Many other aromatic diisocyanates suitable for reaction with polyesters or the like to yield polyurethane prepolymers capable of being cured to the elastomeric state are disclosed in the prior art (such as the patents referred to previously), and it is desired to emphasize that the invention embraces the use of any and all such aromatic diisocyanates.

As indicated previously, the setting bath into which such prepolymer is extruded to form the thread is an aqueous aliphatic diamine bath, modified in accordance with the invention by addition of a monoalcohol, a mixture of monoalcohol with a glycol, or, less preferably, a glycol itself. The solution used as the setting bath may contain, for example, from 0.5 to 20% by weight of the diamine, 5 to 90% by weight of the organic solvent, and 5 to 90% by weight of water, along with small percentages of any desired accessory ingredients, such as wetting agents. It may be employed at ordinary ambient temperatures, or heated to an elevated temperature (e.g., 100° F., up to, for example, 200° F.). Preferably the setting bath is operated at a temperature of from 110° to 160° F., depending on the thickness of the extruded filament. With small filaments of about 150 size (i.e., 150 to the inch), setting bath temperatures of about 110°–120° F. are most suitable. For larger filaments of about 75 size, temperatures of about 140°–160° F. are most suitable.

As indicated in U.S. Patent 2,953,839 the amines most suitable for this purpose are diprimary diamines that may be represented by the general formula $NH_2—A—NH_2$, where A is a divalent organic radical in which the terminal atoms are carbon, and which is preferably devoid of groups reactive with isocyanate, that is, the two primary amino groups are preferably the sole groups in the molecule that will react with the isocyanate groups of the polyester-diisocyanate, to provide the desired curing action. In the preferred diprimary diamines the two primary amino groups are linked by a divalent aliphatic hydrocarbon radical, as in ethylene diamine, hexamethylenediamine, 1,4-diamino-cyclohexane, etc. However, the connecting radical between the two essential primary amino groups need not be purely a hydrocarbon, but may contain other atoms in addition to carbon and hydrogen, as in 3,3'-diaminodipropyl ether, and diamino-dibutyl sulfide. The amine should be at least slightly soluble in water.

In accordance with conventional preferred practice, there is included in the setting bath a small amount (typically about ½%, although the amount is not critical) of a wetting agent. This is frequently found to be useful in insuring complete and uniform setting of the entire surface of the extruded filament. In general, any known wetting agents of the non-ionic or anionic type are suitable for this purpose (such as those disclosed, for example, in Sisley and Wood "Encyclopedia of Surface Active Agents"), and among the more effective wetting agents there may be mentioned the sodium salts of products obtained by sulfation of higher fatty alcohols (e.g., sodium oleyl sulfate).

The improvements realized by further including, in the aqueous diamine setting bath, an organic solvent additive selected from the group consisting of monoalcohols, glycols, and mixtures thereof in accordance with the invention will be brought out in connection with the following detailed description of the forms of the invention represented in the accompanying drawing. Referring to the drawing, and particularly to FIG. 1 thereof, one method of practicing the invention involves forcing a liquid polyurethane prepolymer of the kind described in the form of a round stream from a nozzle **10** suspended just above the surface of a setting bath **11** comprising an aqueous aliphatic diamine containing the organic solvent additive (monoalcohol, glycol, or mixture thereof) in accordance with the invention. (In a modification of the invention, shown in FIG. 2, the nozzle **14** may be immersed below the surface of the setting bath **15**.) The action of the setting bath is such that the round stream of liquid prepolymer is substantially immediately gelled or set upon contacting the bath, forming a round thread or filament **17** (FIG. 1) which is passed under a fixed guide bar **18** located in proximity to the nozzle. The thread passes through the bath for a distance, which may be as little as only about an inch or may be indefinitely longer, usually at a speed of, for example, from 50 to 500 feet per minute and then over the upper portion of a driven spinning roll **20** located just outside of the setting bath. The peripheral speed of the spinning roll exceeds the linear speed of emergence of the prepolymer from the nozzle (usually 2 to 8 times the speed of emergence, preferably 2 to 4 times), with the result that the thread is drawn or stretched out and maintained under slight tension as it passes through the setting bath. The frictional engagement and surface tension forces between the thread and the upper surface of the spinning roll enable the roll to produce a draw or controlled elongation upon the thread. Control of this action is assisted by the guide bar **18** which produces a kind of snubbing action. Since the thread is still quite weak at this point, that is, it is simply set or gelled by the action of the diamine without actually being "cured" to a condition of high tensile strength, care must be taken not to break the thread or to exert so much tension that the soft, round thread would tend to become distorted or flattened out as it passes over the spinning roll. The lower portion of the spinning roll is immersed in a bath of wash water **21**, with the result that the residue of the setting bath carried by the thread is washed away by the action of the continually changing film of wash water carried up from the wash bath on the surface of the spinning roll. To further insure thorough washing, the thread next passes under an additional wash roll **22** partially immersed in a second wash bath **23**. The additional wash roll is driven at the same speed as the spinning roll or at a slightly lower speed. The wash water may of course be changed continuously or intermittently for efficient washing. The turbulence of the wash water on and in contact with the surfaces of the rolls insures effective and rapid washing of traces of the setting bath from the thread. This is an important feature of the invention particularly in connection with those organic solvent additives to the aqueous diamine setting bath which are so reactive with the isocyanate groups of the prepolymer that they can block or interfere with subsequent cure of the thread if they are allowed to remain in the thread for an appreciable time prior to undertaking the final cure. For example, if the setting bath contains n-propanol or the like as the additive and if the thread is not washed thoroughly and appreciable time elapses between setting and final cure, it is found that the thread is not susceptible of final cure by the action of water, presumably because the n-propanol has had sufficient opportunity to react with the free isocyanate groups of the prepolymer, thereby rendering the polymer incapable of further cure.

As indicated, the cure of the thread may be carried out batchwise or continuously, the latter representing a particularly preferred practice of the invention because of its economy, speed, and the uniformly high quality obtainable in the product of the continuous process. For batchwise cure the thread is taken up on reels which are subsequently subjected to the action of water (as a liquid, or in the form of water vapor or steam)—preferably under pressure to forestall any tendency to develop voids in the thread as a result of generation of carbon dioxide which accompanies the water cure of a polyurethane. For continuous cure, the thread is conveyed continuously through a water bath or humid atmosphere, for example on a conveyor belt passing under water in a long tank or passing through a chamber in which a suitable atmosphere is maintained, or the thread may be conveyed by suitable thread advancing reels (partially or completely immersed in the liquid curing bath and/or surrounded by a curing atmosphere containing steam or water vapor and/or subjected to gentle sprays of water) which serve to store and advance the thread while it undergoes cure, typically as a single strand, either at atmospheric or superatmospheric pressure. Such continuous cure may be carried out while passing the thread through one or more baths containing water, or through steam or other humid atmosphere, or through sprays containing water, successively or alternately in any desired order.

It will be understood that the final cure of the thread by the action of water takes place by reaction of water with the remaining free isocyanate groups in the polymer, which reaction leads by cross-linking of the polymer to an insoluble, solid state which has high tensile strength and elasticity.

In the form of the invention shown in FIG. 1, the washed thread passes over a roll **25**, the lower portion of which rotates in a bath **26** of weakly acidic material such as up to 15% aqueous acetic acid or other water soluble fatty acid which serves to neutralize any diamine remaining in the thread (in accordance with U.S. Patent 3,009,765 issued to Slovin on November 21, 1961). The bath **26** also suitably contains a conventional textile lubricant (e.g. 5% of silicone oil textile lubricant whether in emulsion or water-soluble form) and a wetting agent (e.g. ½% of any suitable conventional wetting agent such as a nonionic wetting agent). The purpose of neutralizing the diamine is to prevent too much of the cure of the thread from being accomplished by diamine (i.e., to prevent too many of the available isocyanate groups from being consumed by the diamine, leaving little or no isocyanate groups for subsequent reaction with water), since a predominately diamine-cured polyurethane thread would have inferior physical properties compared to the highly elastomeric, strong (high tensile strength) thread of the invention in which the final cure is effected by reaction with water.

The thread **17** is then wound up into a package on a drum **29**. In order to avoid subjecting the thread to undue tension (with consequent flattening or distortion if not breakage) as it is wound up, the drum **29** is rotated at a speed no greater than or slightly lower than the speed of the spinning roll **20**. For example the peripheral speed of the spinning roll may typically be 1.00 to 1.20 times the take-up speed of the package. Between the last wash roll **25** and the drum **29** the thread is substantially released from tension and slight shrinkage takes place.

The batchwise cure may be effected by immersing a plurality of packages or drums **30** (FIG. 3) bearing the thread under water **31** contained in an autoclave **32** maintained under pressure at an elevated temperature for a suitable period of time. Frequently such batchwise curing may be carried out at temperatures within the range of from 80° F. to 250° F. for a period of time of from ¼ to 24 hours, at pressures ranging from 10 to 250 pounds per square inch gauge. The final cure may if desired be accomplished partly in the autoclave, and then completed in the open atmosphere at ambient temperatures (sufficient moisture being present in the thread and/or available from the atmosphere), or in an oven with a heated and/or humidified atmosphere. Conveniently the continuous cure is carried out at atmospheric pressure, ordinarily at elevated temperature (e.g., 100° F. to 212° F.). The period of hold-up of thread in the curing zone should be sufficient to effect at least partial cure, and for this purpose hold-up times of about one minute to 20 minutes or more are ordinarily employed. The cure water, particularly in the initial stages of the cure, may contain surfactants or catalysts. At the final stages the water may contain lubricants and may serve to flush the thread clean of acid etc., and the cured thread finally may be wound up on a drum. The thread packages thus obtained may be stored at room temperature to advance the cure further if necessary, by the action of residual water in the thread, over a period of time (e.g., 1–2 days). If desired such storage can be shortened to as little as a few minutes or a period of hours by carrying it out in a humid atmosphere at an elevated temperature (e.g. 140° F.).

It should be mentioned that it is desirable to minimize the time between washing of the thread and final cure and for this reason we ordinarily prefer to subject the packages to cure within not more than about two hours of starting to wind the package.

We also desire to emphasize that we have found that it is sometimes advantageous to provide, in the water used to effect the cure, a quantity of weakly acidic material, e.g., about 0.1 to 10% by weight of an organic carboxylic acid, such as benzoic acid, acetic acid or other water-soluble carboxylic acids. We have found that this has a remarkable catalytic effect on the cure, enabling the cure to be carried out more rapidly and thoroughly, to provide a cured product having excellent physical properties, in a short time. For example, the optimum quantity of acetic acid for this purpose is about 4 or 5%, the accelerating effect falling off at lower or higher concentrations. Similarly, other catalysts may be used in the cure water, such as for example 1 to 4% by weight of 1,2-dimethylimidazole or other imidazole, or other tertiary amines such as tetramethyl-1,3-butanediamine; tetramethylethylenediamine; N,N,N',N',N'' - pentamethyldiethylenediamine or 4-methylpyridine.

The cured thread may finally be dried to a predetermined moisture content (usually between ½ and 2%) and rewound if necessary on commercial spools.

The cured thread **49** (FIG. 4) produced as described is remarkable for its uniformity as compared to thread similarly produced by initial setting in a plain water-diamine bath that does not contain the organic solvent additive in accordance with the invention. The present thread shows improved retention of tensile strength in hot alkaline solution as compared to previous thread. It also shows a lower rate of strength loss in hot chlorine bleach solutions. We do not know whether this improvement in resistance to degradation is due to a change in the nature of the surface or merely to greater uniformity of the thread.

The roundness of the thread may be characterized by measuring its "axial ratio" which is defined as the ratio of the maximum cross-sectional diameter to the minimum cross-sectional diameter. Thread having an axial ratio of 1.5 or less is considered as being substantially round.

Since the thread **49** is cured successively with diamine and with water, it may be represented as having an outer shell or skin **50** at the surface wherein much of the combined curative is the diamine and an inner core or center **51** wherein much of the combined curative is water, but it will be understood that there is not necessarily any line of demarcation between these zones, and the respective cures by diamine and water are diffusion-controlled phenomena which probably take place to some extent throughout the whole cross-section of the thread.

The following examples, in which all quantities are expressed by weight unless otherwise specified, will serve to illustrate the practice of the invention in more detail.

EXAMPLE I

A polyester having a molecular weight of 2100 and an acid value of 0.7 was prepared by condensing a 70/30 mixture of ethylene glycol and 1,2-propylene glycol with adipic acid, the glycol being used in slight molar excess to insure hydroxyl terminal groups. Ten percent of titanium dioxide was dispersed into the polyester, for purposes of pigmentation, by paint-milling. 2310 parts (1 mole) of the polyester, containing titanium dioxide, was heated at 55° C. in a glass-lined vessel, provided with a mechanical stirrer, a dry nitrogen inlet-tube, a condenser, and a thermometer. 500 parts by weight (2 moles) of p,p'-diphenylmethane diisocyanate were added to the polyester and the mixture was heated to 120° C. Heating was continued at this temperature for 120 minutes. A blanket of dry nitrogen over the reaction mixture kept out atmospheric moisture. The prepolymer was of white color and had a Brookfield viscosity of 9500 poises at 85° F.

The prepolymer was extruded as described in U.S. Patent 2,953,839 at the rate of 2 cc. per minute into a coagulating bath containing 2 parts of ethylene diamine, 0.5 part of a nonionic wetting agent (e.g., methylphenol-ethylene oxide condensation product, "Triton X-100"), 62.5 parts of water and 35 parts of n-propanol, maintained at 90° F. The diameter of the nozzle opening was 0.02 inch. The surface of the extruded round stream of liquid set to a solid condition immediately as it entered the setting bath. A spinning roll rotating at a peripheral speed of 300 feet per minute, located 10 inches from the nozzle, served to pull the resulting round thread from the gelling bath. The thread was immediately washed thoroughly with water to remove the n-propanol, and then with 10% aqueous acetic acid to neutralize any diamine remaining in the thread, by passing around wash rolls, at a speed of 290 feet per minute. The thread was wound on a drum at a speed of 280 feet per minute and immersed in water at 150° F. under a pressure of 50 p.s.i. for two hours to cure the thread by the action of water on the polymer. The diameter of the thread was 0.0065 inch. Its physical properties were:

Tensile strength	p.s.i.	8000
Elongation	percent	700
Set	do	20
Axial ratio		1.05

The thread was round for all practical purposes, and substantially uniform in thickness and cross-section all along its length. It could be covered with textile material and otherwise processed and fabricated without difficulty and without formation of defects.

The foregoing example was repeated, except that the n-propanol was omitted. The thread did not coagulate nearly as well, and the final thread was flattened and non-uniform in cross-section. It could not be covered or fabricated without difficulties due to the presence of non-uniformities.

The example was repeated except that the n-propanol was not washed off the thread immediately. The thread could not be cured properly with water, presumably because the n-propanol reacted with the available isocyanate groups, thus "blocking" the cure.

The example was repeated with methanol, ethanol and isopropanol, in place of the n-propanol, with substantially equivalent results.

The example was repeated except that the water used in the final curing step contained 5% acetic acid. The cure proceeded with remarkable rapidity. Benzoic acid was particularly effective for this purpose.

EXAMPLE II

Example I was repeated as far as and including the step of washing the thread with dilute acetic acid to neutralize the diamine. The thread was then led continuously onto a moving supporting surface as a single filament and conveyed on such surface without delay through a tank of boiling water. Four minutes were required for the thus-supported thread to traverse the tank, during which time the cure with water became essentially completed. The cross-section of the resulting cured thread was perfectly round (axial ratio, 1.00). It

also showed no trace of linear irregularities. Physical properties were:

Size	150 to the inch.
Tensile strength	9000 p.s.i.
Elongation	720%.
Set	20%.
Massaged modulus*	190 p.s.i.

*Stress at 300% elongation on return cycle after eight repeated strains to 600% elongation.

EXAMPLE III

Example I was repeated, except that the diameter of the nozzle opening was 0.03 inch, the rate of delivery of the prepolymer was 5 cc. per minute, and the speed of the spinning roll was 170 feet per minute. Speed of the wash rolls was 165 feet per minute and speed of the take-up drum was 160 feet per minute. Cure was as in Example I. Thread properties were:

Size	75 to the inch.
Tensile strength	10000 p.s.i.
Elongation	750%.
Set	20%.
Axial ratio	1.10.

EXAMPLE IV

Example III was repeated, except that the thread was cured continuously at the boil as a single filament rather than as a wound package. Thread properties were:

Size	75 to the inch.
Tensile strength	11000 p.s.i.
Elongation	700%.
Set	15%.
Axial ratio	1.00.

EXAMPLE V

In this example the prepolymer was made from a polyether, rather than a polyester. One mole of polypropylene glycol (molecular weight about 2000) was heated 1 hour at 100° C. with about two moles of p,p'-diphenylmethane diisocyanate. Thread was made from this prepolymer as in Example I. Thread properties were:

Size	150 threads to the inch.
Tensile strength	8000 p.s.i.
Elongation	585%.
Set	31%.
300% massaged modulus	250 p.s.i.
Axial ratio	1.05.

EXAMPLE VI

In this example the prepolymer used in Example V was again employed, but the curing procedure of Example IV was employed (i.e. continuous cure of single filament in water at a temperature of 210° F.). Thread properties were:

Size	75 to the inch.
Tensile strength	8400 p.s.i.
Elongation	570%.
Set	34%.
Massaged modulus	230 p.s.i.
Axial ratio	1.00.

EXAMPLE VII

In this example, the prepolymer was based on another polyether, polytetramethylene glycol. Polytetramethylene glycol having a molecular weight of 2146 was paint-milled with ten percent by weight of titanium dioxide. 2361 grams (1 mole) of the polytetramethylene glycol, containing titanium dioxide, was heated to 60° C. in a 3-necked flask, provided with a mechanical stirrer, a dry nitrogen inlet tube, a condenser and a thermometer. 487.5 grams (1.95 moles) of p,p'-diphenylmethane diisocyanate were added and the mixture was heated to 95° C.; the heating was continued for 100 minutes. A blanket of dry nitrogen over the reaction mixture kept out atmospheric moisture. The prepolymer was of a white color and had a Brookfield viscosity of 8250 poises at 100° F. This prepolymer was extruded as in Example I into a setting bath containing 55 parts of n-propanol, 36.5 parts of water, 8 parts of ethylene diamine and 0.5 part of wetting agent. Washing and curing were carried out as in Example I. Thread properties were:

Size	151 to the inch.
Tensile strength	8000 p.s.i.
Elongation	580%.
Set	30%.
Massaged modulus	250 p.s.i.
Axial ratio	1.00.

EXAMPLE VIII

The prepolymer described in Example I was extruded into a variety of organic solvent-aqueous amine solutions in essentially the same manner as in Example I.

Bath was 77 parts of ethylene glycol, 22 parts of water and 1 part of ethylene diamine, maintained at 140° F. Cured thread properties were: Tensile, 1000 p.s.i.; elongation, 670%; set, 9%; axial ratio, 1.28.

Bath was 45 parts of methanol, 54 parts of water and 1 part of ethylene diamine; temperature 130° F. Properties were: Tensile, 8800 p.s.i.; elongation, 745%; cross-section was round.

Bath was 90 parts of isopropanol, 9 parts of water and 1 part of ethylene diamine at 130° F. Tensile, 5500 p.s.i.; round cross-section.

Bath was 90 parts of n-butanol, 9 parts of water and 1 part of ethylene diamine at 110° F. Tensile, 6800 p.s.i.; elongation, 690%; round cross-section.

Bath was 88 parts iso-butanol, 11 parts water, 1 part ethylene diamine at 130° F. Tensile, 5800 p.s.i.; elongation, 690%; round cross-section.

Bath was a 12% solution of ethylene diamine in water at 130° F. Tensile, 6950 p.s.i.; elongation, 665%; flat and irregular cross-section (thus demonstrating the inferior results obtained when the organic solvent additive of the invention is omitted).

Bath was 76 parts methoxy triglycol, 23.5 parts water, 0.5 part ethylene diamine at 130° F. Tensile, 6100 p.s.i.; 675% elongation; round cross-section.

Bath was 40 parts methoxy triglycol, 16 parts n-propanol, 43 parts water with 1 part ethylene diamine at 130° F. Tensile, 5900 p.s.i.; 567% elongation; round cross-section.

Bath was 77 parts diethylene glycol, 22 parts water, 1 part ethylene diamine at 130° F. Tensile, 5800 p.s.i.; elongation, 665%; axial ratio 1.3.

Bath was 41 parts diethylene glycol, 16 parts n-propanol, 42 parts in water, 1 part ethylene diamine at 130° F. Tensile, 7600 p.s.i.; elongation, 685%; axial ratio 1.2.

Bath was 80 parts triethylene glycol, 5 parts n-propanol, 14 parts water, 1 part ethylene diamine at 130° F. Tensile, 5300 p.s.i.; elongation, 670%; round cross-section.

Bath was 20 parts tetrahydropyran-2-methanol, 79.5 parts water, 0.5 part ethylene diamine at 130° F. Tensile, 9000 p.s.i.; elongation, 705%; round cross-section.

Bath was 50 parts "Ethyl Carbitol," 49.5 parts water, 0.5 part ethylene diamine at 130° F. Tensile, 9900 p.s.i.; elongation, 700%; round cross-section.

Bath was 48 parts "Ethyl Cellosolve," 51.5 parts water, 0.5 part ethylene diamine at 130° F. Tensile, 6700 p.s.i.; elongation, 570%; round cross-section.

Bath was 50 parts tetrahydrofurfuryl alcohol, 49.5 parts water, 0.5 part ethylene diamine at 120° F. Tensile, 6500 p.s.i.; elongation, 665%; round cross-section.

EXAMPLE IX

The prepolymer of Example I was extruded into a bath containing 50 parts n-propanol, and 50 parts water at 120° F. in essentially the same manner as Example I. The basic aqueous coagulating agent was varied.

Coagulating agent was 1 part of 1,3-diaminopropane. Tensile, 5900 p.s.i.; elongation, 675%; axial ratio 1.12.

Coagulating agent was 2 parts of 1,6-hexanediamine. Tensile, 6200 p.s.i.; elongation, 690%; round cross-section.

EXAMPLE X

Example I was repeated except that the aqueous coagulating bath contained 35 parts of tertiary butyl alcohol in place of n-propanol, and 1 part of ethylene diamine, maintained at 80° F. The thread had a round cross-section, a tensile strength of 9600 p.s.i. and an elongation of 730%.

The use of tertiary butyl alcohol as the organic solvent additive in the amine setting bath represents a highly preferred practice of the invention.

EXAMPLE XI

Example I was repeated, using various setting baths having the compositions listed in the following table, with excellent results.

Compositions Aqueous Setting Baths (Parts)

Glycol	Tertiary Butyl Alcohol	Water	Ethylene Diamine
16 "Methyl Carbitol"	12	70.5	1½
14 "Butyl Carbitol"	15	69.5	1½
16 methoxytriglycol	12	70.5	1½
14 2-methyl-2,4-pentanc-diol	12	70.5	1½
29 "Butyl Carbitol"		69.5	1½
28 2-methyl-2,4-pentane-diol		70.5	1½

The combinations of glycols with tertiary monoalcohols represent a highly preferred form of the invention.

It is desired to point out that the apparent reinforcing of the coagulating action of the aqueous diamine bath, obtained by including a monoalcohol or glycol therein in accordance with the invention, is particularly unexpected in view of the fact that these monoalcohols, glycols, and mixtures thereof are in themselves incapable of producing initial setting of the liquid polyurethane prepolymer when employed in an aqueous bath that does not contain the diamine setting agent.

It is desired to emphasize that the improved round, uniform thread of the invention is characterized by the ability to be covered with a textile material without undesirable build-up of twist with consequent kinks and similar irregularities. Breaks during the covering and finishing operations are minimized. The thread of the invention feeds evenly through knitting and twisting equipment without requiring excessive lubrication. These improved results are made possible by the use in the aqueous amine setting bath of an organic solvent selected from the group consisting of monoalcohols, glycols, and mixtures thereof as described to build up the initial wet strength of the freshly coagulated thread in round form, so that it can be carried through additional washing and curing steps without distortion of the filament.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. In a method of making a filamentary material comprising the steps of providing a liquid polyurethane prepolymer having terminal isocyanate groups, extruding a stream of said liquid prepolymer into an aqueous aliphatic diprimary diamine bath to effect an initial setting of the extruded material, and thereafter curing the extruded material by the action of water, the improvement comprising providing in the setting bath from 5 to 90% by weight of an organic solvent selected from the group consisting of monoalcohols having from 1 to 8 carbon atoms, glycols having from 2 to 10 carbon atoms, and mixtures thereof.

2. A method as in claim 1, in which the said organic solvent is a monoalcohol having from 3 to 4 carbon atoms.

3. A method as in claim 2, in which the said monoalcohol is tertiary butyl alcohol.

4. A method of making a filamentary material compris-

ing in combination the steps of providing a liquid polyurethane prepolymer having terminal isocyanate groups, extruding a stream of said liquid, passing said extruded stream into a setting solution comprising water, an aliphatic diprimary diamine and a mixture, in amount of from 20 to 70% by weight of the setting solution, of a monoalcohol having from 1 to 8 carbon atoms with a glycol having from 2 to 10 carbon atoms, to effect an initial setting of the extruded stream in the form of a filament, and thereafter curing the filament by the action of water.

5. A method as in claim 4, in which the said monoalcohol is a tertiary alcohol.

6. A method as in claim 5, in which the said glycol is an alkylene glycol having from 2 to 8 carbon atoms and the said monoalcohol has from 3 to 4 carbon atoms.

7. A method as in claim 6, in which the said monoalcohol is tertiary butyl alcohol.

8. A method of making a filamentary material comprising the steps of providing a liquid polyurethane prepolymer having terminal isocyanate groups, extruding a stream of said liquid into a setting bath comprising water, an aliphatic diprimary diamine and an organic additive, in amount of from 20 to 70% by weight of the bath, selected from the group consisting of monoalcohols having from 1 to 8 carbon atoms, glycols having from 2 to 10 carbon atoms, and mixtures thereof, to effect an initial setting of the extruded stream in the form of a filament, passing the filament over a spinning roll rotating at a peripheral speed 2 to 8 times the speed of extrusion of the filament to effect a spinning thereof at a definite spinning speed, immediately washing the filament to remove any residue of the setting bath liquid therefrom, winding the filament up into a package at a definite winding speed, the said spinning speed being 1.00 to 1.2 times the said winding speed, and thereafter curing the filament with water.

9. A method of making a filamentary material comprising the steps of providing a liquid polyurethane prepolymer having terminal isocyanate groups, extruding a stream of said liquid into a setting bath comprising water, an aliphatic diprimary diamine and an organic additive, in amount of from 20 to 70% by weight of the bath, selected from the group consisting of monoalcohols having from 1 to 8 carbon atoms, glycols having from 2 to 10 carbon atoms, and mixtures thereof, to effect an initial setting of the extruded stream in the form of a filament, passing the filament over a spinning roll rotating at a peripheral speed 2 to 8 times the speed of extrusion of the filament to effect a spinning thereof, immediately washing the filament to remove any residue of the setting bath liquid therefrom, and immediately thereafter curing the filament by passing it continuously through a curing zone wherein it is contacted with water.

10. An improved polyurethane thread, characterized by uniformity of size and shape along its length, made by the method of claim 1.

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