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METHOD OF MAKING ELASTIC POLYURETHANE FILAMENTARY MATERIAL USING TERTIARY NITROGEN-CONTAINING CATALYST

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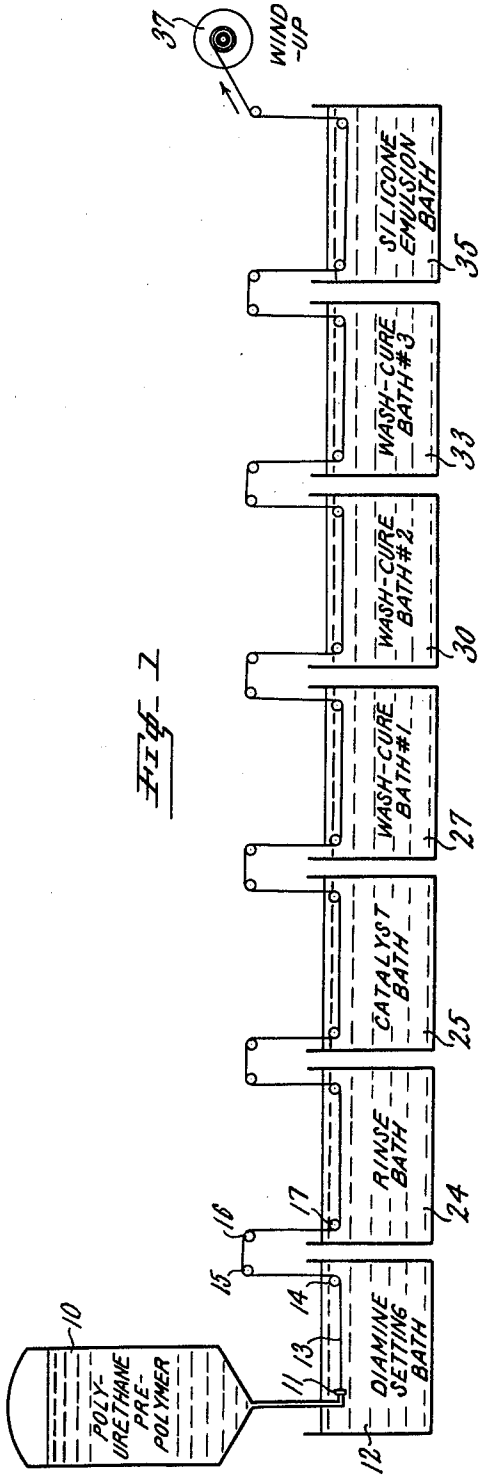


Fig. 1

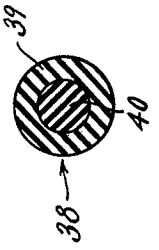


Fig. 2

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METHOD OF MAKING ELASTIC POLYURETHANE FILAMENTARY MATERIAL USING TERTIARY NITROGEN-CONTAINING CATALYST

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This invention relates to a continuous, high-speed method of making filamentary material, and more particularly it relates to a method of making elastic polyurethane thread or fiber, as well as to improved thread made by such method.

The invention is base upon the discovery that usually rapid cure of a polyurethane thread made from a liquid polyurethane prepolymer can be accomplished, in such a manner as to provide a thread of excellent quality, by contacting the thread, subsequent to an initial setting of the thread in a diamine bath but prior to a final cure of the thread in water, with an organic compound containing a tertiary nitrogen atom.

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, and application Serial No. 182,001, filed March 23, 1962, by R. A. Gregg and C. V. Tallman, now U.S. Patent 3,111,-369, November 19, 1963. The patents referred to described making a poly urethane 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 diprimary 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. The copending application referred to deals with the improvement of having a monoalcohol or glycol present in the setting bath to improve the setting action.

Unfortunately, if it is attempted to speed up the water cure of the thread by adding certain catalytic materials to the water in which the thread is conventionally immersed for final cure, there is a tendency for the thread to suffer hydrolytic degradation coincident with cure. This is evidenced by a progressive falling off in the tensile properties of the thread as the catalyst concentration in the cure bath is increased. Also, there is an undesirable tendency for thread cured in water containing a catalyst to exhibit blowing or similar discontinuities occasioned by too rapid formation of carbon dioxide (a normal by-product of the curing reaction of water on polyurethane) in the thread during the cure. Furthermore, the rates of cure achieved when certain catalytic materials are put directly into the final water cure bath are frequently not as high as would be desirable.

We have now found that the foregoing disadvantageous can be overcome, and additional advantages which will be made manifest hereinbelow can be realized, by contacting the thread with am catalyst which is an organic compound containing a tertiary nitrogen atom, subsequent to the initial setting of the thread with a aliphatic diprimary diamine, but prior to the final cure of the thread with water. The most surprising feature of our discovery is that it is peculiarly effective when practiced in conjunction with the use of somewhat acidic solvents, e.g., alcohols, glycols, or water, as carriers for the diamine setting agent in the coagulation step immediately preceding contact of the filament surface with the tertiary

nitrogen-containing organic catalyst. Build-up of modulus in the water cure step when this procedure is followed is several fold that obtained if the tertiary nitrogen-containing catalyst is added in either the coagulation (diamine setting) or the water-cure stages of the process.

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

FIG. 1 is a schematic diagram showing one method of practicing the invention; and,

FIG. 2 is a cross-sectional view, on an enlarged scale, of an elastic thread made in accordance with the invention.

Referring to the drawing, one method of practicing the invention, a liquid polyurethane prepolymer which is contained in a suitable supply tank **10** is extruded in the form of a fine stream through a nozzle **11** having a circular orifice into a bath of coagulating or setting liquid **12**, in the conventional manner. The composition of the polyurethane prepolymer is conventional and requires no detailed exposition here. It may be described as an isocyanate-terminated, uncured polymer which is a reaction product of an hydroxy-terminated polyester or polyether with an excess of an organic diisocyanate. Reference may be had to the aforementioned patents and application, the disclosures of which are hereby incorporated herein by reference, for more detailed description of the prepolymer as well as the setting bath, which is based on an aqueous solution of an aliphatic diprimary diamine. It will be understood that the setting or coagulating bath causes an initial setting or solidification of the cylindrical stream of liquid prepolymer, as it enters the bath, converting it into a thread **13** which can be handled as a solid through subsequent steps of the process. A driven spinning roller **14** controls the rate of advancement of the freshly coagulated or initially set thread **13** away from the extrusion nozzle **11**, and to avoid imposing excessive straining forces on the thread, which is soft and delicate in the initially set and uncured state, a positive conveying device, such as a series of driven rollers **15**, **16**, **17**, etc., guides and advances the thread through subsequent stages of the process to be described below.

As is disclosed in more detail in application Serial No. 182,001, now Patent No. 3,111,369, referred to previously, the setting bath typically includes 5 to 90% (preferably 20 to 70%) by weight of a monoalcohol having 1 to 8 carbon atoms, a glycol having 2 to 10 carbon atoms, or a mixture thereof (e.g. alkanols such as n-propanol, tertiary-butyl alcohol, ethyl Carbitol, butyl Cellosolve, ethylene glycol, hexylene glycol, and the like).

From the coagulating bath the moving filament is passed through a rinse bath **24** of water to remove excess coagulant.

The thread next passes, in accordance with the invention, into a catalyst bath **2** which comprises an organic compound having a tertiary nitrogen atom. Suitable catalytic materials, capable of catalyzing the curing reaction of water with polyurethanes, are tertiary amines or heterocyclic compounds containing at least one ring tertiary nitrogen, and include the following:

(1) Tertiary alkyl amines, for example triethyl amine and N,N,N',N'-tetramethyl-1,3-butanediamine.

(2) Pyridine and substituted pyridines such as alkyl-, halogeno- or amino-pyridines, for example, 2,4-lutidine and 2-chloro-pyridine. Similarly, quinoline and correspondingly substituted quinolines.

(3) 1-alkyl-morpholines, for example, 1-ethylmorpholine and 1,1'-ethylenedimorpholine.

(4) Alkyl-imidazoles, for example, 2-methylimidazole and 1,2-dimethylimidazole.

(5) Alkyl- or amino-piperazines, for example, 1,4-dimethylpiperazine, 1,2,4-trimethylpiperazine and N-(beta-aminoethyl)piperazine.

(6) 1-alkyl-pyrroles and -pyrrolidines, for example, N-methylpyrrole and N-methylpyrrolidine.

(7) Pyrazine and alkyl-pyrazines, for example, 2-methylpyrazine.

Chemicals of the foregoing kinds in which any alkyl groups are lower alkyl groups (e.g., 1–4 carbon atoms) may be mentioned particularly.

Conveniently the foregoing catalytic substances are used in the form of a solution, although with suitable equipment they may be applied from vapor phase. When application is from solution water is usually employed as diluent. However, a wide variety of other water-compatible solvents may be employed in whole or in part such as alcohols, glycols, ethers, ketones, and the like. The only limitations on choice of solvent are that it have only limited reactivity with the polyurethane and that it can be washed off easily once it has fulfilled its roll as catalyst carrier.

The catalyst may be employed singly or in combination. In the latter case, they will sometimes reinforce each other, or one member may improve the solubility of another member. The tertiary-nitrogen-containing catalyst possesses low interfacial tension with both the polyurethane and the water used for cure. The catalyst employed (or combination of catalysts) is soluble both in the prepolymer and in water; if necessary, solvents which promote such solubility may be included in the catalyst bath. The concentration of the catalyst in the catalytic bath is not critical and will vary depending on the particular catalyst employed, the degree of catalytic action desired, and other conditions prevailing in the process. Usually the concentration of catalyst is at least 20% by weight of the bath, ranging up to 80 or 90% or even higher (to 100%), with the more usual concentrations being in the range of 30–80%. The catalyst bath can be employed at room temperature but it is preferably heated slightly to a range of 90–130° F. for example. The contact of the thread with the catalytic bath is very brief. In many cases a contact time as little as one second is more than sufficient to sensitize the thread appreciably to the action of the subsequent water cure. Somewhat longer contact times are more usual, say 2 to 8 seconds, but in any event it is not necessary to contact the thread with the catalyst for appreciably longer periods than 10–20 seconds. As a result of such contact with the catalytic bath containing a tertiary-nitrogen organic compound, a small but effective amount of the catalytic material diffuses into or is dissolved in the uncured thread and is carried along with the thread as the latter leaves the catalyst bath **25**.

In accordance with an important feature of the present invention, the thread is removed from the catalyst bath for completion of the cure by the action of water after the excess catalyst has been washed off the thread. By arranging the water cure so that the thread is exposed to a succession of conditions such that the temperature and purity (i.e., freedom from catalyst) of the water are increased as the cure progresses, rapid build-up of cure and thorough wash-out of catalyst are accomplished concurrently. Thus, after leaving the catalyst bath **25**, the thread may pass into a first washing and curing bath **27** of water heated to a relatively moderate temperature of, for example, 140–160° F. to remove the bulk of the excess catalyst from the surface of the thread and to start the water-curing of the thread. The thread next passes into a subsequent washing and curing bath **30** of water which is somewhat hotter, say 160°–180° F., than the first bath **27**, and in which the cure is advanced in water that is even purer than the water of the first bath (because the bulk of the excess catalyst was washed off in the first bath). The process thus proceeds in as many stages as desired to a final washing and curing bath **33** of water which may be the hottest of the series (e.g., almost boiling) and in which the wash water is essentially pure (i.e., catalyst-free) because virtually all of the water-extractable catalyst has by this time been removed. The treatment is thus counter-current in the sense that the thread progresses in the direction of increasing temperature and increasing purity of the washing and curing water. In this last bath the water-cure of the thread becomes so far advanced that the thread, after running through a bath **35** of textile lubricant (silicone emulsion) and being wound up in a package **37**, is, after standing 24 hours or so, virtually completely cured, although there is usually no definite end-point to the cure and changes in physical properties may in some cases continue for a period of days, particularly by virtue of the action of moisture remaining in the thread and/or moisture absorbed from the air. It will be understood that, if the conditions in the successive washing and curing baths (particularly with respect to temperatures employed and duration of exposures to the baths) are not such as to bring the cure to a substantially completed stage, the package of thread may if desired be immersed in hot water (suitably in an autoclave) to complete the cure.

As mentioned previously, carbon dioxide gas is normally evolved as a result of the reaction of water with polyurethane. In conventional practice this gives rise to difficulties because the evolved gas tends to produce voids or other discontinuities in the thread. Such difficulties are particularly likely to occur if it is attempted to carry out the cure rapidly, by previously known methods. However, it is an important feature of the present invention that the tertiary-nitrogen-containing catalyst which is present within the thread when it enters the first stage of cure acts to hold the carbon dioxide in the dissolved state. This dissolved carbon dioxide, along with remaining traces of catalyst, is removed as contact with progressively hotter and cleaner water is made. When the cure is effected with the individual filament surrounded by the water bath as described, the gas has time to diffuse out of the filament into the surrounding water in which it is soluble. By this sequence bubble formation, as well as hydrolytic degradation of the polyurethane by the catalyst, are avoided to a remarkable degree, and a given level of cure (as evidenced by development of elastic properties and insolubility) is achieved much more expeditiously than by prior practice.

The final cured thread is accordingly a product which has initially been set or solidified (cross-linked) on its surface by the action of a diamine, and in which the cure (cross-linking) has been completed by the action of water. Thus the product **38** may be represented as in FIG. 2 as having concentric zones **39** and **40**, the outer zone **39** being such that a substantial part of the cross-linking has been accomplished by diamine and the inner zone **40** being such that the cross-linking has been accomplished predominantly by water. However, it will be understand that there is no definite demarcation between the diamine-cured surface and the water-cured interior, and the entire thread is probably in some measure cured partly by both cross-linking agents, diamine and water, because diffusion of both of the agents probably takes each of them to all parts of the thread.

In place of carrying out the curing process on a running filament as described, the thread may instead be wound up into a package at an appropriate stage—for example, after washing away the catalyst composition—and the thread may thereafter be cured batchwise—for example, by immersing the package in water under pressure at elevated temperature. Any combination of such procedures may be used if desired; for example, cure of the catalyst-treated thread may be started by running the thread through warm water (which also serves to wash out the catalyst), the thread may then be wound up into a package, and such package immersed in water in an

autoclave. It will be understood that the contact of the thread with the final cure water need not be by actual immersion in all cases, but may be accomplished, for example, by spraying it with water, or even by subjecting it to steam, particularly in the last stages of the cure when the thread is sufficiently washed, strong and non-thermoplastic.

We desire to emphasize that it is an important aspect of the invention that the substantially uncured polyurethane thread is sensitized by contact with catalyst subsequent to the initial setting or coagulation of the liquid prepolymer by diamine but prior to substantial advancing of the water-cure. Contact with the catalyst is relatively brief and transitory in comparison with the length of the water curing period. No detectable cure takes place in the catalyst bath when judged by the fact that no increase in gel strength occurs during this step.

By the process of the invention, in which the initially set thread is sensitized by brief contact with a catalyst comprising an organic compound having a tertiary nitrogen atom, and is then washed and cured, attainment of a given level of cure can be accomplished in approximately one-fourth the time, with less risk of bubble formation or hydrolysis, that is required if the catalyst is incorporated in the actual cure water. It is indeed remarkable that a faster, improved cure is achieved by pretreatment of the set thread with catalyst, as opposed to curing the thread in water containing the catalyst. Especially is this true where the aqueous diamine setting bath contains the preferred alcohol and/or glycol additive.

The following examples will serve to illustrate the invention in more detail.

Example I

A polyester having a molecular weight of 2100 and an acid value of 0.7 is prepared by condensing a 70/30 mixture of ethylene glycol and 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 is dispersed into the polyester, for purposes of pigmentation, by paint-milling. 2310 parts (1 mole) of the polyester, containing titanium dioxide, is 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 is added to the polyester and the mixture is heated to 120° C. Heating is continued at this temperature for 120 minutes. A blanket of dry nitrogen over the reaction mixture keeps out atmospheric moisture. The prepolymer is of white color and has a Brookfield viscosity of 9500 poises at 85° F.

The prepolymer is extruded at the rate of 3 cc. per minute into a coagulating bath containing 2 parts of ethylene diamine, 1.0 part of a nonionic wetting agent (e.g., methylphenol ethylene oxide condensation product, "Triton X–100"), 62 parts of water and 35 parts of n-propanol, maintained at 90° F. The diameter of the nozzle opening is 0.02 inch. The surface of the extruded round stream of liquid sets to a solid condition immediately as it enters the setting bath. A spinning roll rotating at a peripheral speed of 100 feet per minute, located 10 inches from the nozzle, serves to pull the resulting round thread from the nozzle. The thread is immediately rinsed with water to remove the n-propanol, dipped in a pre-sensitizing catalyst bath consisting of 100% N-ethylmorpholine maintained at a temperature of 90° F., laid on a conveyor to allow the catalyst 3 seconds to penetrate, and then carried immediately into a bath of water to be washed and cured. Conditions in the water bath are regulated so that clean water enters at the far end and passes counter-current to the thread. Temperature of feed water is near the boil and of discharge water near 150° F. Temperature is highest and water cleanest at the termination of the cure. Dwell time in the cure is approximately 30 seconds. Washing occurs throughout the cure.

The cured thread is run through a lubricating solution of silicone emulsion and wound into a package. Tensile strength at this time is typically 2000 p.s.i. and rises to near 5000 p.s.i. in a few minutes at ambient room conditions. After 24 hours, properties of the thread are: tensile strength—10,800 p.s.i.; elongation at break—740%; 300% massaged modulus—210 p.s.i.; set—11%.

Example II

The same prepolymer as in Example I is extruded at the rate of 5 cc. per minute into a coagulating bath containing 2 parts ethylene diamine, 2 parts of nonionic wetting agent, 56 parts water and 40 parts hexylene glycol maintained at 130° F. The diameter of the nozzle is .024 inch and the spinning roll rotates at a peripheral speed of 75 feet per minute. The pre-sensitizing catalyst bath consists of 4 seconds dwell in 55% N-ethylmorpholine, 20%, 1,4-dimethylpiperazine, and 25% water, maintained at 110° F. Dwell time in the first cure under the same conditions as in Example I is approximately 15 seconds after which the thread is lubricated with silicone, and a thin layer of thread is laid on a curing cylinder under substantially no tension. Tensile strength at this stage is typically 200 p.s.i. and lower layers build to near 2000 p.s.i. prior to doff. When between 8 and 16 ounces have been laid on the cylinder, the package is doffed and immersed in water at 120° F. under 50 p.s.i. pressure for an additional 30 minutes. This treatment gives a final wash and results in thread with a uniform tensile of around 10,000 p.s.i.

Example III

Example I was repeated except that rate of feed was 2.5 cc. per minute, peripheral speed of the spinning roll was 240 feet per minute, dwell time in the catalyst was 2 seconds, and dwell time in the cure was 20 seconds. Tensile strength when wound up was 3000 p.s.i. and of final thread was 10,000 p.s.i.

Example IV

Example I was repeated using in turn each of the following catalysts to get the listed tensile at take-up:

	P.s.i.
2,4-lutidine (80% in water)	3000
N,N,N',N'-tetramethylbutanediamine (70% in water)	1000

Example V

In this example, the prepolymer is based on a polyether, polytetramethylene glycol, rather than a polyester. Polytetramethylene glycol having a molecular weight of 2146 is paint-milled with ten percent by weight of titanium dioxide. 2361 grams (1 mole) of the polytetramethylene glycol, containing titanium dioxide, is 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 is added and the mixture is heated to 95° C.; the heating is continued for 100 minutes. A blanket of dry nitrogen over the reaction mixture keeps out atmospheric moisture. The prepolymer is of a white color and has a Brookfield viscosity of 8250 poises at 100° F. This prepolymer is converted into thread as in Example I. Representative properties are:

Tensile strength at windup—1600 p.s.i.; after final cure, tensile—6000 p.s.i.; elongation—580%; set—30%; 300% massaged modulus—250 p.s.i.

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 fine stream of said liquid prepolymer into an aqueous aliphatic diprimary diamine setting bath to effect an initial setting of the extruded material in the form of a thread, and thereafter curing the thread by the action of water, the improvement comprising sensitizing said thread, subse-

quent to said initial setting but prior to said water cure, by contacting the thread with a catalytic material that is soluble in water and soluble in the said prepolymer, and washing the catalyst out of the thread prior to completion of said cure, the said catalytic material comprising an organic compound containing a tertiary nitrogen atom selected from the group consisting of alkyl tertiary amines, pyridine, alkyl-pyridines, halogeno-pyridines, amino-pyridines, quinoline, alkyl-morpholines, alkyl-imidazoles, alkyl-pyrroles, alkyl-pyrrolidines, pyrazine, and alkyl-pyrazines, the said alkyl groups being lower alkyl groups.

2. A method as in claim 1 in which the said setting bath contains 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.

3. A method as in claim 2 in which at least a first portion of the water cure is carried out by conveying the thread through successive stages of progressively hotter water, whereby the amount of catalyst remaining in the thread becomes progressively less as the cure advances.

4. A method as in claim 3 in which the catalyst comprises N-ethylmorpholine.

5. A method as in claim 3 in which the catalyst comprises 1,4-dimethylpiperazine.

6. A method as in claim 3 in which the catalyst comprises 2,4-lutidine.

7. A method as in claim 3 in which the catalyst comprises N,N,N',N'-tetramethylbutanediamine.

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