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[54] IMPROVED ELASTOMERIC FIBERS

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[58] Field of Search 260/858, 77.5 SP; 264/205, 264/235, 290, 342, 346, 210

[56]

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2,962,470	11/1960	Jung.....	260/858
3,357,954	12/1967	Kirkaldy.....	260/75

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[57]

ABSTRACT

Improved elastomeric fibers are disclosed and claimed which are comprised of alternating hard and soft segments, i.e., polyesterurethane copolymers, wherein the fibers are improved in properties, particularly permanent set. The fibers of this invention have utility in conventional textile uses.

2 Claims, No Drawings

IMPROVED ELASTOMERIC FIBERS

This application is a divisional application of Ser. No. 370,371, filed May 26, 1964, matured as U.S. Pat. No. 3,536,803, issued on Oct. 27, 1970.

Our invention relates to a process for producing an improved elastomeric fiber and more particularly relates to a process for producing such an improved fiber by stretching, relaxing and heat treating the fiber.

We have found that an improved elastomeric fiber can be obtained by stretching a fiber of a segmented elastomeric copolymer at least about 150 percent of its initial length, then relaxing the stretched fiber so that it returns to a length less than its stretched length and finally heating the stretched and relaxed fiber at constant length at a temperature above about 75° C. and below the softening point of the fiber. In practicing the process of our invention it is essential that all three steps of the process be employed, since neither the stretching and relaxing steps alone without the heat treating nor the heat treating without the prior stretching and relaxing will produce a fiber with all the desirable characteristics attained in accordance with our invention. Moreover, any desirable characteristics which might possibly be obtained as a result of employing one of the steps separately are not necessarily permanent. For example, certain desirable characteristics can be imparted to the fiber by stretching, but such characteristics are not stable when the fiber is subjected to exposure to boiling water as is encountered in conventional textile operations, such as scouring and/or dyeing.

In the stretching step of our process, a stretch of at least about 150 percent and usually in the range of from 200 percent to 500 percent over the initial length of the fiber, i.e., the length of the fiber in its unstretched state prior to any treatment in accordance with our invention, is operable to impart desirable characteristics to the fiber when employed in conjunction with the remainder of our process. This initial length can be the length of a somewhat elongated fiber resulting from draw down or draft coincident with spinning. Preferably, however, the amount of stretch employed is from about 250 percent to about 400 percent. The period of time during which the fiber is maintained in the state of stretch is not critical to the advantageous employment of our process and can vary from periods of less than a second up to periods of several minutes. The fiber, however, must be maintained at a temperature below its softening point. Normally, the stretching can be conducted at about room temperature.

The relaxing step of our invention can be conducted at about the same temperature as the stretching step and generally is conducted at about room temperature. The period of time during which the fiber is maintained in the relaxed state is not critical.

In the heating step of our process, a temperature above about 75° C. has been found to be effective, and generally, any temperature up to the softening point of the fiber is effective. Once the softening point of the fiber has been attained there is a tendency for some of the desirable characteristics which have been imparted to be lost. A temperature in the range from about 100° to about 150° C. is adequate to develop desirable characteristics in elastomeric fibers produced from segmented elastomeric copolymers, with particularly advantageous results being obtained with temperatures ranging from about 100° - 120° C. The length of time a fiber is subjected to heating in accordance with our invention can vary from a few minutes up to several hours. Usually, the general rule of employing a longer time at a lower temperature and a shorter time at a higher temperature is applicable.

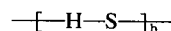
The term "segmented elastomeric copolymer" as used throughout this specification and in the claims is meant to describe elastomeric copolymers comprised of two principle types of segments which are chemically connected and alternate in the chemical chain. One segment, preferably essentially amorphous, is derived from low melting soft polymers such as, for example, an aliphatic ester polymer, an ether polymer, a hydrocarbon polymer, and the like. These soft polymers are characterized by weak interchain attractive

forces. The other segment, derived from a hard high melting polymer such as, for example, a urea polymer, a urethane polymer, amide polymer, and the like.

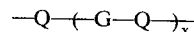
In particular, the soft segments of these elastomers are derived from low melting polymers having a melting point below about 60° C., having a molecular weight of from about 250 to about 5,000 and containing terminal radicals possessing active hydrogen atoms. The hard, high melting segments are derived from linear hard polymers having a melting point above about 200° C. in their fiber forming molecular weight range, i.e. above about 5,000. The soft segments, as present in the elastomer appear as radicals of the initial polymer from which the terminal active hydrogens have been removed. Generally, the hard segments comprise from about 10 percent to about 40 percent by weight of the segmented copolymer and may be defined as comprising at least one repeating unit of the linear crystalline polymer from which they are derived.

The preparation of these segmented elastomeric copolymers is well known in the art and is described, for instance, in U.S. Pat. Nos. 2,625,535; 2,813,776; 2,871,218; 2,953,839; 2,957,852; 2,962,470 and Re 24,691.

The polymeric structure of some of these elastomers can be represented by the formula:



wherein H and S denote the hard and soft segments, respectively; and wherein ---H--- is further represented by



wherein Q is a divalent radical derived by reaction of an organic diisocyanate with active-hydrogen-containing functional groups; G is the residue resulting from the removal of active hydrogen from the terminal functional groups of a low molecular weight bifunctional molecule having a molecular weight less than 500; x is an integer or zero; b is an integer greater than zero; S is the residue resulting from the removal of the active hydrogen from the terminal functional groups of a polymer melting below 60° C., having a molecular weight of from about 250 to about 5,000. Terminal functional groups possessing active hydrogen can be, for example, ---OH , ---NH_2 , ---SH , ---COOH , ---CONH_2 , ---NH , ---CSNH_2 , $\text{---SO}_2\text{NH}_2$, and $\text{---SO}_2\text{OH}$. The hard segment in a repeating unit of a linear polymer may be further defined as having a melting point above about 200° C. in its fiber forming molecular weight range.

Generally, these synthetic elastomers are copolymer formulations based on low molecular weight aliphatic polyesters or polyethers having terminal hydroxyl groups which are capable of further reaction with diisocyanates. This latter reaction can be used to couple the lower molecular weight polyester or polyether via urethane links or the diisocyanate can be used in excess so that it becomes a terminal group. In this latter case, the macro diisocyanates formed can be coupled by means of other reagents such as water, diols, amino alcohols and diamines with the subsequent formation of the high polymer. These elastomeric products are also known as block copolymers.

A variety of organic diisocyanates may be used to prepare the elastomeric copolymers suitable for employment in our invention. Illustrative examples of these diisocyanates are: trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, cyclopentylene-1,3-diisocyanate, 1,4-diisocyanato cyclohexane, p-phenylene diisocyanate, m-phenylene diisocyanate, the tolylene diisocyanates, the naphthalene diisocyanates, 4,4'-diphenyl propane diisocyanate, 4,4'-diphenylmethane diisocyanate.

Illustrative of the types of elastomeric copolymers suitable for employment in our invention are isocyanate modified polyesters such as those described in U.S. Pat. No. 2,755,266 wherein linear polyesters prepared from polycarboxylic acids

and polyhydric alcohols are reacted with an excess of a diisocyanate over the terminal hydroxyl groups of the polyester to form diisocyanate modified polyesters containing terminal isocyanate groups which are then further reacted with a bifunctional cross-linking agent. Polyesterurethane copolymers which are substantially free of cross-links, such as those described in U.S. Pat. No. 2,871,218 wherein a critical ratio of an essentially linear hydroxyl terminated polyester prepared from a saturated aliphatic glycol having terminal hydroxyl groups and a dicarboxylic acid or its anhydride, and a diphenyl diisocyanate are reacted in the presence of a saturated aliphatic free glycol having terminal hydroxyl groups so that no unreacted isocyanate and hydroxyl groups remain, can also be employed. Broadly such a copolymer is obtained by reacting one mole of polyester with from 1.1 to 3.1 moles of a diphenyl diisocyanate in the presence of from about 0.1 to 2.1 moles of free glycol. Another type of elastomeric copolymer which can be used in our invention is the type described in U.S. Pat. No. 2,957,852. An elastomer of this type can be prepared by providing polyether glycol with isocyanate ends by reaction with a diisocyanate. This "capped" prepolymer can then be reacted with a chain-extending agent such as a hydrazine which provides a final polymer having repeating units containing hydrazine resins linked through carbonyl groups.

In another aspect, our invention comprises further adjusting such characteristics and properties of an elastomeric fiber as elongation, tenacity, and permanent set by a judicious blending of varying proportions of a comparatively flexible and a comparatively stiff segmented, elastomeric copolymer. The flexibility or stiffness of two elastomeric copolymers is determined by the ratio of the amount of polyurethane to polyester or polyether in the block copolymer with, of course, the more flexible copolymers being that which has a greater proportion of the soft polymer.

In this aspect of our invention, both the stiff and the flexible copolymers are of the type described above. For example, both the stiff and the flexible copolymers can be synthesized from substantially the same starting material or at least starting materials of the same type. Thus a soft or flexible copolymer of the type described in U.S. Pat. No. 2,871,218 can be produced by employing as starting materials larger proportions of the linear polyester and the aliphatic glycol thereby producing a segmented copolymer having a greater number of amorphous or soft blocks. Similarly, a higher molecular weight amorphous polymer employed as a starting material will provide a copolymer having longer soft blocks. To obtain a comparatively stiff copolymer a larger proportion of the diisocyanate, the linear crystalline component, can be employed thereby producing a segmented copolymer having a larger number of rigid blocks or a copolymer having longer rigid blocks depending upon the relative proportions of the other ingredients or upon the molecular weight of the polyester. Thus, it will be seen that the stiffness or flexibility of the resulting copolymer can be affected by only very small variations in the molar ratios of the ingredients and/or employing a polyester of a higher or lower molecular weight.

The advantageous results obtained through this aspect of our invention are extremely surprising and unexpected inasmuch as blends including up to 50 percent of flexible or soft copolymers, which alone cannot withstand the severity of the steps of our process, particularly the heating, can be employed to yield extremely desirable fibers. Usually, the flexible copolymers alone are unstable as fibers at temperatures above about 75° C. and have even disintegrated on the bobbin at temperatures of about 100° C. The stiff copolymers alone are generally stable as fibers up to temperatures of at least 200° C.

Furthermore, the characteristics possessed by a fiber spun from a blend are superior to those of a fiber spun from a single copolymer of comparable chemical composition. More specifically, a blend of a stiff copolymer obtained by reacting given quantities of certain reactants and a flexible copolymer obtained by reacting other given quantities of certain reac-

tants in the manner described above yields a fiber having more desirable characteristics than a fiber produced from a single copolymer obtained by reacting together the same quantities of all of the reactants employed to produce the stiff and the flexible copolymers.

In order to illustrate further our invention, reference is made to the following examples. In each of these examples permanent set was determined by the same method unless otherwise indicated. Briefly, all samples were conditioned for 24 hours at 23° C. and 65 percent relative humidity prior to testing. Each sample was then marked, while in a taut (not stretched) state, to delineate a 3.00 inch test length. The sample was then clamped between jaws set 5 inches apart so that the 3.00 inch test length was midway between the jaws. The jaws were then moved apart so that the sample was extended until the distance between the marks (3.00 inches before extension) was 12.00 inches for a 300 percent extension. After maintaining the sample in its extended state for 2 hours, the sample was released and allowed to recover unrestrained for 30 minutes. The sample was then made taut (not stretched) and the length between the marks was measured. The increase in the length between the marks over the original 3.00 inches expressed as a percent of the original 3.00 inch length is the permanent set.

EXAMPLE I

A comparatively soft or flexible polyesterurethane copolymer of the type described in U.S. Pat. No. 2,871,218 and obtained by reacting hydroxyl poly (tetramethylene adipate) (molecular weight about 850, hydroxyl number - 130.4, acid number - 0.89) butanediol-1,4 and diphenyl methane-p,p'-diisocyanate in a molar ratio of about 1.0:0.3:1.3, respectively, was employed in this example. A 30 percent solution of this copolymer in acetone solvent was employed to dry spin an elastomeric fiber.

The apparatus used was of the type traditionally employed in the art and essentially included a spinnerette at the upper end of a spinning column and a godet roll at the bottom of the column. The filaments were passed through the column where the solvent was substantially evaporated therefrom by contact with hot air introduced at a temperature of 150° C. and was then passed about the godet roll moving at a velocity of 20 meters/minute.

After leaving the godet roll, the fiber was subjected to a drawing operation at room temperature, in which the first draw roll was travelling at a speed of 20 meters per minute and the second draw roll was travelling at a speed of about 100 meters per minute thereby effecting a stretch of 400 percent. After being stretched by means of the drawing operation, the fiber, at room temperature, was relaxed by removal of all but a minimum amount of tension necessary to handling. The fiber was then wound on a bobbin. Physical testing of the fiber as spun indicated a tenacity of 0.64 grams per denier, elongation of 450 percent and a permanent set of 3.0 percent (4 hours at 300 percent strain). Subsequently, the fiber, no longer on the bobbin, was subjected to boil off treatment in steam at 100° C. for one-half an hour. This resulted in a boil-off shrinkage of 35 percent and an increase in permanent set from the original 3.0 percent up to 80 percent. Thus, it can be seen that desirable characteristics, particularly the permanent set of the stretched fiber, in the absence of heat treating were completely destroyed by the steam boil off.

EXAMPLE II

In this example a comparatively stiff polyesterurethane copolymer of the type described in U.S. Pat. No. 2,871,218 was employed. The copolymer was obtained by reacting hydroxyl poly (tetramethylene adipate) (molecular weight about 1010, hydroxyl No.=106.1), butanediol-1,4 and diphenyl methane-p,p'-diisocyanate in a molar ratio of about 1:1:2, respectively. A 30 percent solution of this copolymer in a 90 percent methylene chloride-10 percent methanol solvent mix-

ture was employed to dry spin an elastomeric fiber. The apparatus employed was the same as that used in Example I. A portion of the fiber was taken-up directly from the spinning column without stretching and wound on bobbins. A second portion of the fiber was subjected to a drawing operation at room temperature after leaving the spinning column to obtain a stretch of 350 percent (4.5X). After being stretched by means of the drawing operation, the fiber, at room temperature, was relaxed by removal of all but a minimum amount of tension necessary to handling and was then wound on bobbins. Each of these portions of the fiber, the unstretched, and the stretched and relaxed, was again divided into two portions, one portion of each of the unstretched, and the stretched and relaxed fiber, was subjected to boil-off treatment in 100° C. steam for half an hour. Samples of each of the four portions of the fiber were subjected to physical testing. The results are indicated below in Table I.

TABLE I
Properties of Stretched and Unstretched Fibers

Orientation Stretch	as spun	None boiled-off	350% as spun	boiled-off
Denier	231	307	215	454
Tenacity, g/d	0.59	0.54	1.62	0.67
Elongation, %	453	508	283	523
Stress at 300%				
Extension, g/d	0.21	0.14	—	0.13
Permanent Set, %	53	56	—	56

A comparison of the characteristics of the "as spun" unstretched and the stretched and relaxed fibers demonstrates that the stretching increases the strength of the fiber as indicated by the increased tenacity of the stretched fiber. The gain in strength, however, was lost when the stretched fiber was subjected to boil-off as shown by the decrease in tenacity from 1.62 to 0.67. Furthermore, subjecting the stretched fiber to boil-off also produces an undesirably high permanent set, i.e., 56 percent.

EXAMPLE III

In this example the same copolymer as used in Example II was employed. A 25 percent solution of the copolymer in 91/9 mixture of methylene chloride/methanol solvent was spun to produce an elastomeric fiber. In order to produce a complete basis of comparison, portion of the fiber was taken-up without being subjected to either stretching or heat treatment. Another portion of the fiber was subjected to a drawing operation at room temperature after leaving the spinning column in which the fiber was stretched 300 percent. After stretching, the fiber was relaxed at room temperature by removal of all but a minimum amount of tension necessary to handling. The fiber was maintained in this relaxed state while it returned to a length intermediate between initial and stretched length. A sample of both the stretched and unstretched fiber wound on a bobbin and maintained at constant length was subjected to heat treatment. Samples of both the stretched and unstretched fibers which were not heat treated were subjected to boil-off treatment in 100° C. steam for half an hour as were the heat-treated stretched and unstretched fibers. Samples of each of the variously treated fibers were then subjected to physical testing. The results are given below in Table II.

TABLE II
Improvement of Fiber Properties on Heat Setting

	as spun 300	as spun boiled-off 300		heat set boiled-off 300
Stretch %			0	0
Heat	None	None	None	1 hr. 1 Hr.

Treatment	1.5	0.65	0.60	at 145°C. 0.60	at 145°C. 0.70
Tenacity g/d					
Elong.	295	525	425	540	450
Stress at 300%					
Elong., g/d	—	0.14	0.18	0.16	0.28
Permanent Set, %	—	55	53	30-35	17-20

These data demonstrate the extremely advantageous characteristics possessed by fibers produced in accordance with our invention. A comparison of the characteristics of the stretched and relaxed fiber as spun with the characteristics of the stretched and relaxed fiber which have been subjected to boil-off demonstrates the loss of desirable characteristics resulting from boil-off. In fact, the stretched, relaxed and boiled-off fiber possesses characteristics not greatly, if at all, superior to the unstretched fiber which have been subjected to boil-off. Examination of the characteristics of the unstretched fiber which has been heat treated demonstrates that heat treating alone does not, of itself, produce a fiber having extremely desirable characteristics. Thus, for example, the heat-set, unstretched fiber possesses characteristics in many instances quite similar or only slightly improved over the stretched and unstretched fiber after boil-off. Thus, while heat treatment alone may improve permanent set to a certain degree, the permanent set is still not at a desirable level. A comparison of the physical characteristics attained by a fiber which has been subjected to stretching, relaxing and heat treatment and then boil-off with the characteristics of all the other fibers shown in Table II demonstrates the permanence of the desirable characteristics, particularly tenacity, stress at 300 percent elongation and permanent set.

EXAMPLE IV

In this example fibers were dry spun from solutions of the copolymer employed in Example II and a blend of the copolymers of Examples I and II, and a comparison was made of the physical characteristics of the fibers obtained both before and after heat treating. It will be noticed in the data shown below that a satisfactory fiber is obtained from the blend of copolymers. This is particularly unexpected, first, due to the tremendous increase in permanent set obtained during boil-off of the copolymer of Example I, and second, due to the fact that previous attempts to heat treat the copolymers of Example I were completely ineffective since this copolymer has a tendency to decompose even under the mildest heat treating and actually disintegrates on the bobbin at a temperature of about 100° C. The proportions of copolymer blends employed, along with the composition of the spinning solution and the operating conditions are listed below in Table III. All of the stretched fibers were relaxed at room temperature by removal of all but a minimum of tension necessary to handling and the heat treating consisted of maintaining the fibers on a bobbin in a circulating air oven maintained at 110° C. for a period of 2 hours.

TABLE III

Composition, Ex. I/Ex. II	0/100	25/75
Polymer I.V.*	1.10	0.90/1.10
Pigment, (percent) TiO ₂	5	5
Dope solids, wt. (percent)	25	26
Top cabinet temp., °C. (air)	75-80	75-80
Bottom cabinet temp., °C. (air)	195-200	195-200
After stretch (percent)	350	350
Final spinning speed, m./min.	60	150

	Boiled—	Boiled—
	As Spun Off	As Spun Off
Properties before heat treating:		
Denier	180	100
Tenacity, g/d	1.6	1.8

Elongation (percent).....	280	550	250	590
Boiling water shrinkage, (percent).....	50		60	
Stress at 200% strain, g/d.....	0.75		1.1	
Stress at 300% strain, g/d.....		0.14		0.11
Permanent set (percent).....		26		21
Properties after heat treating:				
Denier	180	200	100	110
Tenacity, g/d	0.8	0.8		0.8
Elongation (percent).....	410	440		480
Boiling water shrinkage (percent).....	10		10	
Stress at 300% strain, g/d.....	0.34	0.28		
Permanent set (percent).....		18		13

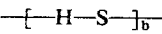
*I.V. — Intrinsic viscosity.

The data of Table III not only demonstrate an additional example of the stretching, relaxing and heat treating of our invention, but also illustrate another aspect of our invention, and the fact that the physical properties, including permanent set values, are stable to boiling water, i.e., blending a relatively soft or flexible copolymer with a relatively stiff copolymer to provide a satisfactory fiber. It will be noted that the addition of the copolymer from Example I to the copolymer from Example II results in slight alterations of the fibers characteristics, i.e., a higher elongation with a lower modulus (stress at 300 percent strain) and a lower permanent set.

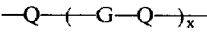
Any departure from the above description which conforms to the present invention is intended to be included within the scope of the invention as defined by the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An elastomer fiber having a permanent set value stable to boiling water prepared by a process which comprises treating a segmented, elastomeric copolymer represented by the formula:



wherein H denotes the hard segment and S denotes the soft segment; and wherein H has a melting point above about 200° C. in its fiber-forming molecular weight range and is further represented by



wherein Q is a divalent radical derived by reaction of an organic diisocyanate with active-hydrogen containing functional groups; G is the residue resulting from the removal of active hydrogen with the terminal functional groups of a low molecular weight bifunctional molecule having a molecular weight less than 500; x is an integer from 0 to 1; b is an integer greater than zero; and, wherein S is the residue resulting from the removal of the active hydrogen from the terminal functional groups of a polymer melting below 60° C. having a molecular weight of from about 250 to about 5,000, said treatment comprising

1. dry spinning said polymer;
 2. stretching said fiber at least about 150 percent of its initial length at below its softening point;
 3. relaxing the stretched fiber to return it to a length less than the stretched length of the fiber; and,
 4. heating the stretched and relaxed fiber at a constant length at a temperature above about 75° C. and below the softening point of the fiber.
2. The elastomer fiber of claim 1 wherein said permanent set value is less than about 20 percent.

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