

1

3,560,137

WHOLLY AROMATIC POLYAMIDES OF INCREASED HYDROLYTIC DURABILITY AND SOLVENT RESISTANCE

Walter Leopold Hahn, Waynesboro, Va., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.
No Drawing. Filed Aug. 15, 1967, Ser. No. 660,602

Int. Cl. D06m 9/00

U.S. Cl. 8—115.5

6 Claims

ABSTRACT OF THE DISCLOSURE

Heating crimped synthetic, linear, wholly aromatic polyamide and polyimide fibers to a temperature in the range of 275° C. to 400° C. for 1 to 10 minutes increases their hydrolytic durability and solvent resistance.

BACKGROUND OF THE INVENTION

In the process for manufacture of synthetic aromatic polyamide and polyimide fibers or conversion of such fibers to useful articles, the fiber is subjected to a variety of mechanical actions, some of which are potentially damaging. These are exemplified by winding, twisting, knitting, weaving and crimping. It has been found that, in addition to the more obvious damage such as ends-down or broken individual filaments, more subtle damage may be present. Specifically, the fine structure of the filament may be altered by certain mechanical manipulations in a manner as yet incompletely understood such that the polymer of which the fiber is composed becomes substantially more susceptible to degradation by hydrolytic action. Effectively, this reduces the strength of the fiber and shortens its useful life where exposed to hydrolytic action, alone or in combination with abrasion. A method for overcoming this limitation upon the broad utility of aromatic polyamide and polyimide fibers would be highly desirable.

The unusual resistance of aromatic polyamide and polyimide fibers to high-temperatures and chemical attack has led to uses in a variety of severe industrial applications. Further advantages accrue in some applications to a fiber which is resistant to attack by a few extremely powerful solvents, e.g., concentrated sulfuric acid.

SUMMARY OF THE INVENTION

The specification describes a novel method for treating crimped, linear, synthetic, wholly aromatic polyamide and polyimide fibers to increase their resistance to hydrolytic action and solvent attack comprising heating the fibers to a temperature in the range of 275° C. to 400° C. for a period of time ranging from about 1 to about 10 minutes.

DEFINITIONS AND STANDARDS

The term inherent viscosity has the generally accepted meaning. In these examples, it is determined in dimethyl acetamide containing 4% lithium chloride, using a concentration of 0.5 gram polymer per 100 ml. of solution,

2

measurements being made at 25° C. The fibers of this invention comprise aromatic polyamides of at least 0.2 inherent viscosity.

Hydrolytic durability is determined by either of two methods, the choice being indicated in the individual examples:

Method A.—Yarn, staple or fabric samples are boiled in 10% sulfuric acid for one or more periods of time. After each period of exposure, either twenty-five or more filaments are tested for toughness, or fabric samples are tested for breaking strength (see below). The average of each determination is compared with the values obtained on similar samples without exposure to boiling acid. Results are expressed as percent of toughness retained or actual breaking strength retained.

Method B.—A fabric sample is ironed with a steam iron of the type sold for home use. The iron is equipped for continuous addition of a measured flow of water and set to maintain a mean temperature of 260° C. The iron is moved by mechanical means through a stroke of 12 inches at the rate of 18 strokes per minute until a well defined hole is developed in the fabric. The time-to-failure is reported as "percent of untreated sample"; i.e., percent of the time-to-failure observed for a fabric which has not had the heat treatment of this invention.

Toughness is calculated as the ratio of the area under the stress-strain curve to the denier of the filament being tested. Results are reported, unless otherwise specified, as "percent of original," i.e., percent of the toughness of the non-heat-treated sample before being subjected to the hydrolytic conditions of Method A for determining hydrolytic durability.

Breaking strength is the load, expressed in grams, required to break a 5" x 0.25" (about 12.7 cm. x 0.67 cm.) fabric specimen.

EXAMPLES

The following examples are included as illustrative of the invention and are not to be construed as delimitative.

EXAMPLE I

Filaments are dry-spun from a solution of poly(metaphenylene isophthalamide) in dimethyl acetamide containing calcium chloride substantially as taught in U.S. Pat. 3,287,324. After extraction of the solvent and salt in boiling water while simultaneously drawing the fibers to 440% of their as-spun length, they are dried by passage over hot rolls and stabilized by passage over two rolls heated, respectively, to 290° C. and 370° C. Exposure on each stabilizing roll amounts to 0.125 second. These drawn filaments are accumulated to a tow of convenient size, crimped in a stuffing box crimper and cut to 1.5 inch staple which has a denier per filament of 2.

The staple is spun to 24 singles cc. yarns and woven in a 2 x 2 twill herringbone (broken on 8 ends). Strips of this fabric measuring about 5 x 0.25 inches are heated for five minutes to a range of temperatures and subjected, along with unheated comparison strips, to the action of boiling 10% sulfuric acid. Table 1 summarizes the breaking strength of the fabric strips as a function of tempera-

ture of heat treatment and time of exposure to hydrolytic durability Method A.

have not been heated. Table 3 summarizes the results obtained.

TABLE 1

[Breaking strength (in gms.) of samples heated 5 minutes at various temperatures (° C.) before the indicated exposure to boiling 10% sulfuric acid]

Exposure time (hours)	No heat	275	300	310	320	350	360
160.....	3,500	4,000	*5,000+	5,000+	5,000+	5,000+	5,000+
138.....	3,200	2,700	3,800	5,000+	5,000+	5,000+	5,000+
159.....	2,300	3,000	4,000	4,000	4,200	4,050	4,800
180.....	1,350	3,400	4,500	5,000	4,500	4,850	5,000
248.....	TWTT	1,750	2,600	2,500	2,500	2,650	2,550
272.....		1,300	2,250	2,300	2,900	3,000	3,000
296.....		800	1,400	2,000	1,990	2,700	2,900
318.....		550	1,400	1,500	1,500	1,850	2,350
339.....		150	500	1,100	1,400	1,150	1,500
406.....	TWTT	TWTT		150	150	300	350
430.....			TWTT	TWTT		150	310

*Too strong, no break obtained with test method, (strength over 5000 gm.).
NOTE.—TWTT—Too weak to test.

Example II

This example illustrates the criticality in selection of temperature and duration of the heat treatment in the development of optimum properties in fiber which has been mechanically crimped.

A staple fiber such as employed in making the fabric of Example I is subjected to boiling 10% sulfuric acid for 7 hours after various heat treatments and none. The toughness of each lot of fiber is determined by measuring the tensile properties of 25 individual filaments on an Instron, integration of the area under the stress-strain curve, dividing by the filament denier and averaging. The average value, having dimensions of gm.-cm./den., is reported as a percentage of the original fiber toughness (i.e., fiber which has had no heat treatment and no treatment in sulfuric acid). Table 2 summarizes the results of these tests.

TABLE 2
[Toughness retained]

Time of heating (min.)	None percent	250° C., percent	275° C., percent	300° C., percent	325° C., percent	350° C., percent
0.0	27					
0.1						27
0.4						32
0.5						64
1		30	41	68	68	69
2					69	70
3					69	71
5		41	48		69	66
7				69.5		63
10		50	53	69.5	69.5	56
15				69.5	69.5	

It is seen that at temperatures substantially above 325° C. the advantage gained in toughness by a short treatment is lost to an appreciable degree by more prolonged treatment. Also, treatments at lower than 275° C. are substantially less effectual in restoring hydrolytic durability lost as a result of mechanical crimping.

Example III

This example illustrates determination of hydrolytic durability of woven fabrics by Method B.

A flat-woven fabric of 40 x 40 construction is made from 16/2 cc. yarns comprising 2.0 d.p.f. staple which is equivalent to that of Example II. Such fabric finds utility in ironing board covers and industrial uses where exposure to steam is involved. The fabric is laid over a household ironing board pad, and the assembly is stretched lightly over a padded perforated metal table top. A steam or dry iron of a generally available type is adjusted to control at a temperature of 260° C. and provided with a metered supply of water. By means of a reciprocating hydraulic drive, the iron is moved in 12 inch straight line strokes over the fabric rate of 18 strokes per minute until a well defined hole is developed. The average time for failure of 2 samples is reported as a percent of the average time for failure of the comparison samples which

TABLE 3

[Hydrolytic durability (expressed in percent of unheated, comparison sample)]

	250° C.	275° C.	300° C.	325° C.	350° C.
25 Heating time (min.):					
1.....	106	113	122	116	95
2.....			170		
3.....	112	122	165	137	86
4.....			141		
5.....	114	120	117	125	81

In an additional comparison between a fabric heated at 300° C. for two minutes and an unheated comparison fabric, samples are tested for durability with and without steam in the procedure of this example. It is found that the removal of steam increased the life of the heat-treated and non-heat-treated samples about equally (169% and 167%, respectively). A durability increase to 170% for the heat-treated sample over the non-heat-treated sample, when subjected to steam ironing, is reflected in Table 3. It is also found that abrasion resistance is improved by the process of this invention as evidenced by an increase to 173% in dry-ironing durability.

Example IV

A solution consisting of anhydrous bis(4-aminophenyl)ether (3.4 parts) in 27.8 parts of anhydrous dimethylacetamide is prepared in a glass-lined reaction vessel under a nitrogen atmosphere. The temperature of this solution is kept within 15–18° C. by external cooling and continuous stirring during dissolution of the diamine. Anhydrous pyromellitic dianhydride (3.5 parts) is added, in portions, to the well-stirred diamine solution during an interval of about 100 minutes, during which period the solution is kept at a temperature within 18–28° C. by external cooling. When the ingredients have completely reacted, the solution is transferred, under nitrogen, to a second reaction vessel equipped with an efficient stirring apparatus. An additional 0.08 part of dry pyromellitic dianhydride is then added to the nitrogen-blanketed, well-stirred solution which is maintained below 35° C. This polymer solution is brought to the desired spinning viscosity of 1,960 poises (inherent viscosity is 1.3) at 30° C. by the incremental addition, under nitrogen, of about 0.8 part of a 10% slurry of pyromellitic anhydride in dimethylacetamide during a 100 minute period. This spinning solution is stored under nitrogen at a temperature below 0° C. When needed for spinning, it is pumped to another vessel wherein it is kept at 17° C., under nitrogen, prior to being pumped through a pancake filter to the head of the spinning cell. At the latter point the solution is maintained at 62° C. The polymer solution is extruded at the rate of about 45.5 ml./min. through a spinneret having 60 holes of 0.006-inch diameter into a drying column whose walls are kept at a temperature of 202° C. The column is swept with a co-current stream of dry nitrogen gas which enters the column at 265° C.

The emerging yarn, of approximately 400 denier, is wound up on a bobbin at the rate of 180 yd./min., after applying about 150 ml./min. of water to the threadline as it emerges from the spinning cell. About 8% of the polyamide linkages present in the polymer prior to spinning are converted to polyimide linkages in preparing this yarn, as determined by infrared analysis. The wet as-spun yarn, containing about 38% dimethylacetamide and about 95% water by weight (based on the dry weight of the yarn) is stored at room temperature in polyethylene bags prior to being drawn. (Yarn stored in this manner is preferably drawn not more than 2 days after spinning.) The yarn is then removed from the bobbin at the rate of 75 yd./min. and is led through a three-foot-long bath of distilled water at 75° C., wherein the yarn is drawn 1.5×. The yarn is subsequently dried by passing it over drying rolls heated to 140° C. (yarn contact time is about 1.0 sec.), after which it is wound onto cardboard tubes by a traversing friction drive roll. The yarn has a dimethylacetamide content of about 18% at this point.

From the tubes the yarn is made into skeins which are suspended from racks and exposed in an oven for 30 minutes at 100° C. and 275° C. for 15 minutes. This thermal treatment converts the drawn, as-spun yarn to the polyimide composition. The converted yarn is again transferred to a bobbin from whence it is led, at a rate of 55 yd./min., into contact with a heated plate maintained at 550° C. On the plate the yarn is further drawn 1.5× to provide 220-denier polyimide yarn having *T/E/M* values of 3.5/11.7/50 and loop *T/E* values of 3.1/12.0.

The filaments are accumulated to a tow and crimped in a stuffing box crimper. This treatment reduces the toughness of the fiber to 69% of that of the uncrimped fiber.

The uncrimped fiber, after testing for hydrolytic durability by Method A is found to have retained 68% of the toughness of the original.

When the crimped fiber is tested for hydrolytic durability by Method A, it is found to have retained only 11% of the toughness of the original.

The crimped fiber is heated at 400° C. for five minutes and tested for hydrolytic durability by Method A. It is found to have retained 67% of the toughness of the original.

GENERAL DESCRIPTION

The heat treatment of this invention can be applied to the fiber while taut or relaxed, although it will be recognized by one skilled in the art that, if tension on the fiber is sufficient to draw it to any substantially degree during heating, the resulting fiber will have increased shrinkability, but the crimp necessary for best textile processibility to fabric will be removed. The increase in shrinkability can be overcome where textile processibility is not of serious concern by suitable further heat treatment under relaxed conditions (which permits shrinkage to take place), or the fiber may be taut-annealed without further stretching (which eliminates shrinkage with less loss of length). In any event, the total extent of heat treatment optimally should be within the limits outlined above.

The heat treatment may be applied at any convenient stage of manufacture or conversion of the fiber to useful articles subsequent to damaging mechanical action. Tow which has been mechanically crimped may be laid on a perforated belt and guided through a suitable hot zone, or it may be cut to staple and processed as a loose bed of fiber through a treating oven. Alternatively, the tow may be carried over internally heated rolls or conveyed by rolls through a heated space. The heat treatment may also be applied to fabric, as for example by processing through a high-temperature tenter, in which case any loss in hydrolytic durability resulting from textile processing steps such as twisting, quilling, weaving or knitting operations will be corrected. It is also within the scope of this invention to apply heat treatment at two or more stages of manufacture and/or processing into useful structures.

It has been found that the fiber heat treatment of this invention also has an effect on the molecular weight of the polymer it comprises, as indicated by change in inherent viscosity. The effect of temperatures up to 300° C. is a slight increase in inherent viscosity (e.g., from 1.60 to the range of 1.62–1.65 after five minutes exposure). At temperatures of 325° C. and higher, cross-linking of the polymer begins to take place as evidenced by the development of a completely insoluble fraction in the polymer. After treatment at 350° C. for five minutes, very little of the fiber is soluble. Such molecular modifications have an effect on fiber properties, but such extreme treatments are advantageous for certain applications in which even greater resistance to solvent attack is desirable.

Although this invention, for convenience, has been exemplified only with fiber of poly(metaphenylene isophthalamide) it is equally applicable to fibers of the other aromatic polyamides and polyimides known to the art.

Among the diamines suitable for preparation of aromatic polyamides and polyimides useful for preparing the shaped structures used in the present invention are metaphenylene diamine, para-phenylene diamine, benzidine, 4,4'-diaminodiphenyl methane, N,N'-m-phenylene bis(m-aminobenzamide), N,N'-p-phenylene bis(m-aminobenzamide), N,N'-m-phenylene bis(p-aminobenzamide), N,N'-p-phenylene bis(p-aminobenzamide), 2,2 - bis(4-aminophenyl)-propane, bis(4-aminophenyl)sulfide, bis(4-aminophenyl)sulfone, 2,6-diamino-p-xylene, 4,4'-diaminobenzophenone, 4,4'-di-aminodiphenyldisulfide, diazodiphenyl 4,4'-diamine, and the like, and mixtures thereof, it being understood that the meta and para orientations are both suitable in those cases where only one orientation is listed.

Among the diacyl halides suitable for reacting with the above diamines in the preparation of aromatic polyamides are iso- and terephthaloyl; 4,4'-bibenzoyl; 1,2-bis(4-carbonylphenyl)ethane; bis(4 - carbonylphenyl)methane; bis(3-carbonylphenyl)methane; 2,2-bis(4-carbonylphenyl)propane; bis(4 - carbonylphenyl)ether; bis(4-carbonylphenoxy)ethane; bis(4-carbonylphenyl)sulfone; bis(4-carbonylphenyl)sulfide (or disulfide); bis(4-carbonyl)benzophenone, and the like and mixtures thereof, it being understood that the meta and para orientations are suitable in those cases where only one orientation is listed. The tetracarboxylic acids taught in U.S. Pat. 3,179,614 are among those useful in preparation of polyimide-acids, which are precursors to polyimides benefitted by this invention.

In addition to those listed in the previous paragraphs, such starting materials having one or more non-amide-forming substituents on at least one aromatic ring are suitable. By non-amide-forming is meant those which do not react with the reactive groups of either starting material to form an amide group under the conditions of polymerization. Such substituents as chloro, bromo, cyano, sulfo, nitro, lower alkyl, lower alkoxy, and lower carbalkoxy are exemplary.

Aromatic polyamides derived from AB-type monomers also are benefitted by this invention. This type of monomer is characterized by presence of both the acyl halide and amino moieties on the same molecules, and is exemplified by meta (or para) amino benzoylchloride-hydrochloride.

The class of ordered polyamides disclosed in the Preston U.S. Pat. 3,240,760 is exemplary of fiber-forming polymers which can be benefitted by this invention.

This invention is especially useful in the preparation of fiber for, or in the conversion of such fiber to fabrics which will be subjected to high-temperatures and more especially those which, additionally, will be subjected to hydrolytic attack. Such uses include filter bags for chemical processing and carbon black production, ironing board covers, press cloths and pads, steam hoses, fire hoses, brake and clutch facings, sewing threads, protective clothing, gas filters for a variety of high-temperature processes, conveyor belts, tents, life rafts and textile process uses such as Palmer blankets, Sanforizing belts, leader tapes

and cloths, and press flannels. Such hydrolytically stable fibers also find utility in a wide range of gasket and valve packing, muffler packing and the like. Military uses include parachutes and ropes associated therewith for personnel and deceleration, airship envelopes, fuel cells, radome covers, radiation shields, etc.

Although the preferred embodiments of this invention have been illustrated as lending superior hydrolytic stability to a mechanically damaged fiber, in many instances an increase in hydrolytic durability may be obtained by heating an uncrimped fiber as disclosed herein. Many alternatives to the specific embodiments which are within the spirit and scope of this invention will be apparent to those skilled in the art. The invention is limited only by the claims which follow.

What is claimed is:

1. A method for treating polymetaphenylene isophthalamine fibers to increase their resistance to hydrolytic action after the fibers have been heat stabilized and then mechanically damaged by crimping, said method comprising heating the fibers to a temperature in the range of 300° C. to 400° C. for a period of time ranging from about one minute to ten minutes.

2. The method of claim 1 wherein the temperature range is 300° C. to 325° C.

3. A method for treating polymetaphenylene isophthalamide fibers to increase their resistance to hydrolytic ac-

tion after the fibers have been heat stabilized and then mechanically damaged by crimping, or more processing steps, selected from the group consisting of winding, twisting, knitting, weaving and crimping, the said method comprising heating the fibers to a temperature in the range of 300° C. to 400° C. for a period of time ranging from one-half minute to about five minutes.

4. A fabric prepared from fibers treated by the method of claim 1.

5. A fabric prepared from fibers treated by the method of claim 3.

6. A fiber treated by the method of claim 1.

References Cited

UNITED STATES PATENTS

3,354,125	11/1967	Smith et al.	260—78
3,232,910	2/1966	Preston	260—78
3,179,634	4/1965	Edwards	260—78

GEORGE F. LESMES, Primary Examiner

B. BETTIS, Assistant Examiner

U.S. Cl. X.R.

117—138.8; 260—78

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,560,137 Dated February 2, 1971

Inventor(s) Walter Leopold Hahn

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 18 (in line 2 of claim 1), the term "amin" should read -- amide --.

Column 8, lines 2-4 (lines 4-6 of claim 3), cancel the w
"or more processing steps, selected from the g
consisting of winding, twisting, knitting, we
and crimping, the".

Signed and sealed this 6th day of July 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents