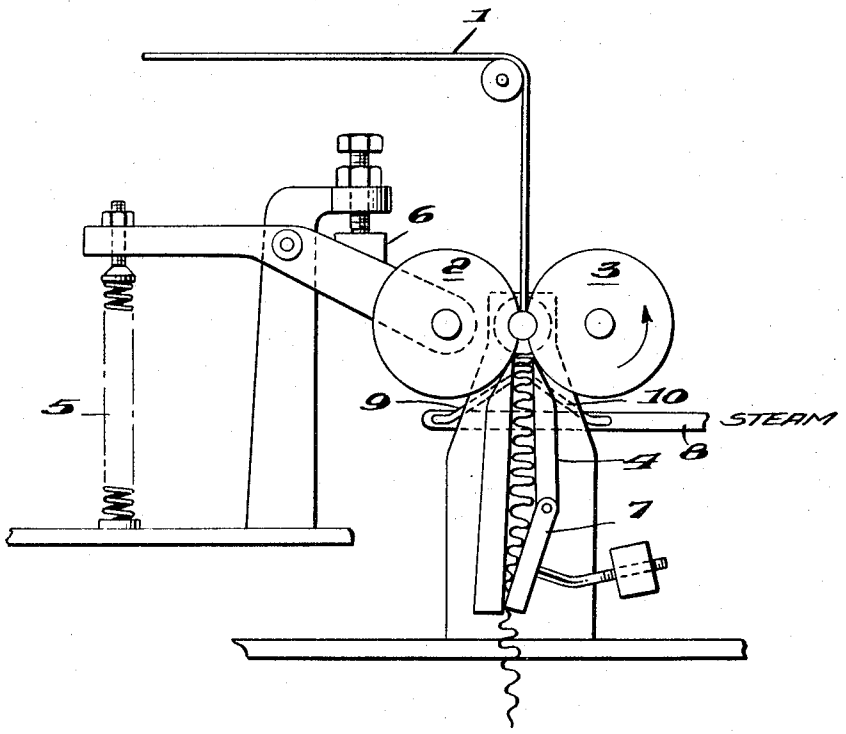
Feb. 28, 1967 E. P. H. MEIBOHM 3,305,897

CRIMPING PROCESS

Filed Oct. 28, 1964



INVENTOR

EDGAR P.H.MEIBOHM,

BY Gordon R. Coons

AGENT

United States Patent Office 3,305,897 Patented Feb. 28, 1967

3,305,897

CRIMPING PROCESS

Edgar P. H. Meibohm, Kinston, N.C., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Filed Oct. 28, 1964, Ser. No. 407,130
10 Claims. (Cl. 19—66)

This invention relates to spontaneously extensible structures of synthetic linear polyesters and more particularly to a novel process for producing synthetic polyester tow and staple having the property of undergoing a spontaneous and irreversible extension in length when heated.

Polyester fibers having the ability to undergo spontaneous and irreversible extension in length, and methods for their preparation, have been disclosed in U.S. Patents 2,931,068 and 2,952,879. The basic requirements for preparing such fibers are that (1) the fiber be oriented while maintaining its crystallinity less than about 35%, following which (2) it is caused to undergo a shrinkage of about 20% to 70% by heat, with (3) heating being discontinued before maximum crystallinity is achieved. In the preparation of spontaneously extensible tow and staple on a commercial scale, the initial orientation may be carried out by the general process described in U.S. Patent 2,918,346 wherein tow, carried on a suitable system of rollers, is preheated in an aqueous bath at a relatively low temperature and then drawn in a second bath at a higher temperature, e.g., about 70° C. to 80° C. Subsequent to this orientation the tow is passed through an additional heating zone at a temperature above 65° C., and preferably above 95° C., while it is allowed to relax or shrink 20% to 70% of its original drawn length.

Since tow and staple are normally sold in a crimped condition, shrinking step (2) would normally be followed by a crimping step in which the tow is subjected to some form of crimping operation, e.g., run through a stuffing box crimper of the type described in U.S. Patent 2,311,-174. However, tow prepared in this manner has been found to be of relatively low quality, showing uneven thickness, excessive splitting, neps, strings, and the like.

Accordingly, an object of this invention is to provide a method for preparing good quality crimped polyester tow and staple having the property of spontaneous and irreversible extensibility upon further heating. Other objects will appear hereinafter.

The objects of this invention are accomplished by a process in which an oriented synthetic linear condensation polyester tow having a birefringence of at least 0.15 and a crystallinity of less than about 35% is passed through a stuffing box crimper while at the same time being treated with hot fluid at a temperature in the range of from about 85° C. to about 250° C., the exposure time to the hot fluid being no greater than 2.0 seconds. Preferably, the tow is heated with steam at a temperature in the range of from about 100° C. to about 150° C. If desired, the crimped tow may then be passed through a low temperature drying oven, e.g., 60° C. to 100° C., for removal of residual moisture without significant loss of its spontaneous extensibility properties.

The accompanying drawing illustrates a diagrammatic sketch of a stuffing box crimper which can be used in the novel process of this invention.

Referring to the drawing, tow **1** is forwarded into contact with crimping rolls **2** and **3** and into stuffing box **4**. Crimping roll **3** is driven by means not shown and crimping roll **2** is an idler, urged into contact with the tow by means schematically represented by spring **5**. The approach of crimper roll **2** toward crimper roll **3** may be limited by adjustable stop **6**. Clapper **7** restricts egress of the crimped tow from stuffer box **4**. Hot fluid line **8**, from a fluid source not shown, introduces the required hot fluid into stuffing box crimper **4** through lines **9** and **10**.

The tow produced by the process of this invention is found to be composed of fibers which, when immersed for five minutes in water at 100° C., show spontaneous and irreversible extensibility values in the range of 1% to 20%, depending upon the exact conditions of processing. The tow is of excellent quality, being essentially free of neps, tow splits, and areas of non-uniform thickness. The higher levels of spontaneous extensibility would appear to be obtained by using steam temperatures in the lower end of the indicated range, and by using short exposure times in the crimper. Exposure times greater than about 2.0 seconds do not produce the desirable results of this invention and times less than 1.0 second are preferred.

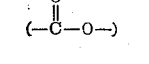
The term "tow," as used herein, refers to a large number of continuous, substantially parallel, synthetic filaments without definite twist collected in a loose, rope-like form. Generally speaking, the minimum number of filaments to which the term "tow" is considered applicable is of the order of about 10^3 and, while there is no fixed maximum number, tows containing on the order of 10^6 filaments, or even considerably more, are encountered. In general, the size of the filaments is in the range of 1 to 10 denier per filament.

The term "spontaneous and irreversible extensibility" refers to the property whereby a fiber or filament increases permanently in length without tension being applied to the ends of the fiber or filament, i.e., the fiber or filament does not retract to its original length when cooled and dried. The numerical value is calculated as percentage boil-off length increase based on the initial length of the fiber. In accordance with the present invention, the amount of spontaneous and irreversible extensibility exhibited by the fibers in the tow or staple may be as low as about 1%, but is usually more. In some case, filaments having an extensibility of up to about 30% are known.

Percentage crystallinity may be determined by X-ray diffraction measurements as described in U.S. Patent 2,952,879 (i.e., column 3) and the effect of crystallinity upon the production of spontaneously extensible fibers is also fully described.

Birefringence, which is a measure of the orientation of polymer molecules along the longitudinal axis of a filament, may be measured as described in *Fibers From Synthetic Polymers* by R. Hill (Elsevier Publishing Co., New York, 1953) pages 266 to 268.

By "synthetic linear condensation polyester" is meant a linear polymer comprised of recurring structural units containing, as an integral part of the polymer chain, recurring units containing, as an integral part of the polymer chain recurring carbonyloxy groups



and having a relative viscosity of at least about 8 in a solution of 10.75 grams of the polymer in 100 ml. of a mixed solvent composed of ten parts by weight of phenol and 7 parts by weight of trichlorophenol. Preferably, at least about 75% of the recurring structural units of the polyester are derived from a glycol containing 2 to 12 carbon atoms and a dicarboxylic acid selected from the group consisting of terephthalic acid and the naphthalenedicarboxylic acids. The polyesters may be prepared by reacting the dicarboxylic acid or an ester-forming derivative thereof with an excess of a glycol, $G(OH)_2$, where —G— is a divalent organic radical containing from 2

to 12 carbon atoms and attached to the adjacent oxygen atoms by saturated carbon atoms or an ester-forming derivative of the glycol. Following the preparation of the monomeric ester, polycondensation is carried out at elevated temperature and reduced pressure with elimination of excess glycol. Examples of suitable glycols include ethylene glycol, diethylene glycol, butylene glycol, decamethylene glycol, and cis- or trans-hexahydro-p-xylylene glycol. Mixtures of such glycols may suitably be used to form copolyesters, or small amounts, e.g., up to about 25 mol percent, of a higher glycol may be used, such as a polyethylene glycol. The acid component of the polyester preferably consists of at least 75 mol percent terephthalic acid or a naphthalenedicarboxylic acid, especially 2,6-naphthalenedicarboxylic acid or 2,7-naphthalenedicarboxylic acid. Similarly, copolyesters may be formed by replacing up to about 25 mol percent of the terephthalic or naphthalenedicarboxylic acid or derivative thereof with another dicarboxylic acid or ester-forming derivative thereof, such as adipic acid, sebasic acid, isophthalic acid, bibenzoic acid and hexahydroterephthalic acid. Up to 10 mol percent of the acid component may be of a type having ionic substituents, such as sodium 2,5-dicarboxybenzene sulfonate. The copolyester may also be formed by replacing part of the terephthalic or naphthalenedicarboxylic acid or derivative thereof with a hydroxy acid or derivative thereof, such as p-(2-hydroxyethyl) benzoic acid or methyl p-(2-hydroxyethoxy) benzoate.

In general the advantages of the fiber produced by the present invention are realized most fully in mixed staple yarns also containing shrinkable fibers where the yarns are heated to bulk them only after they have been woven or knitted into fabric. However, in some cases, it may be desirable to impart to the staple yarns a certain amount of bulkiness prior to weaving or knitting. For example, it may be desired to dye the staple yarns prior to making the fabric in order to achieve certain patterns effects in the fabric. In such cases, due to the ease of dyeing of the spontaneously and irreversibly extensible fiber, the yarn may be dyed under mild conditions to minimize bulking, after which it may be processed into fabric and a further heating treatment may be given to provide additional fabric bulkiness.

The following examples will serve to illustrate the invention, although they are not intended to be limitative. The examples are specifically directed to fibers prepared from polyethylene terephthalate, this being the best known commercial polyester fiber. However, it should be obvious that other polyesters, as defined above, may be substiuted in the examples with substantially equivalent results. Polyethylene terephthalate is prepared in accordance with the general procedure described in U.S. Patent 2,465,319 to Whinfield and Dickson, in which dimethyl terephthalate and ethylene glycol are heated together in the presence of a catalyst until the evolution of methanol ceases, following which the mixture is heated at an elevated temperature and reduced pressure with evolution of excess glycol until a polymer of the desired molecular weight is attained.

Example 1

Polyethylene terephthalate having a relative viscosity of 27 is melt-spun at 290° C. through a 320-hole spinneret at a spinning speed of 1,500 yards (1370 meters) per minute. The filament bundles from several spinnerets are combined into a "rope" and deposited in the form of a loose coil in a circular container by the method of U.S. Patent 2,971,683. The "rope" is composed of filaments having an undrawn denier of about 5.7, a birefringence of 0.005 to 0.006, and a crystallinity level of about 0%.

The contents of several containers are further combined to give a tow having a total undrawn denier of about 1,480,000 which is fed to a drawing machine of the type described by U.S. Patent 2,918,346. The tow is pre-heated in an aqueous bath at 30° C. and then drawn 3.13× in a spray-draw zone in which an aqueous liquid having a temperature of 72° C. is sprayed on the tow. The tow then passes over a set of draw rolls maintained at about 40° C. and rotating at the speed indicated in Table I, at which point the filaments are oriented but still possess a low level of crystallinity.

The drawn tow is passed directly to a stuffing box crimper which has been modified by the connection of a steam line to the crimper chamber so that saturated steam at a controllable pressure is introduced into the chamber along with the tow. The steam pressure (gauge) is indicated in Table I for each sample prepared. The exit gate of the stuffing-box crimper is loaded with a pressure of 39 pounds per square inch (2.74 kg./cm.^{2}) for one sample, and loaded with substantially zero pressure for three samples. The samples are identified in the table. Net shrinkage (Table I) is calculated from denier change in the crimper.

Proceeding from the crimper, the tow is deposited in a relaxed condition on a moving conveyor belt which carries the tow through a drying oven maintained at a temperature of about 80° C., following which the dried tow is deposited in a loose coil in a paper carton.

Selected physical properties of each of the samples are presented in Table II. The indicated value for spontaneous elongation (percent S.E.) is determined using a sample which has a total denier of about 2,000 and a length of about 30 cm. The sample length is accurately measured before and after the sample is subjected to 3 minutes exposure to boiling water under zero tension. Length measurements are made with the sample under a tension of 0.1 gm./denier, which straightens the filaments without stretching them. The numerical value is calculated from the formula:

$$\text{Percent S.E.} = \frac{\text{length increase}}{\text{original length}} \times 100$$

A control sample prepared in similar fashion but without injection of steam into the crimper is found to undergo shrinkage instead of spontaneous elongation when exposed to boiling water for three minutes.

Samples 1*c* and 1*d* are carefully examined and found to be essentially free of splits, fold-overs, twists, tangles, and other indications of low-quality tow.

Each of the samples showing spontaneous elongation in boiling water is found to undergo further spontaneous elongation when heated in dry air at a temperature of 170° C.

TABLE I.—COMBINED CRIMPING AND RELAXATION CONDITIONS

Sample Number	Draw Speed		Total Tow Denier	Steam Pressure		Steam Temp., ° C.	Crimper Gate Pressure		Shrinkage in Crimper, Percent	Exposure time in Crimper (Seconds)
	(y.p.m.)	(m.p.m.)		(p.s.i.)	(atm.)		(p.s.i.)	(kg./cm.^{2})		
1a	325	(296)	660,000	20	(1.36)	126	0	(0)	28	0.74
1b	325	(296)	675,000	25	(1.70)	130	0	(0)	30	0.74
1c	325	(296)	788,000	40	(2.71)	142	0	(0)	40	0.74
1d	390	(356)	661,000	40	(2.71)	142	39	(2.74)	29	0.62

TABLE II.—FIBER PROPERTIES

Sample No.	Crimps		Denier (d.p.f.)	Tenacity (g.p.d.)	Percent S.E.
	(c.p.i.)	(cr./cm.)			
1a	6.7	(2.6)	2.54	4.8	1
1b	8.9	(3.5)	2.60	4.4	1
1c	9.9	(3.9)	3.04	3.6	5
1d	7.6	(3.0)	2.56	4.0	1

Example II

Each of the samples described in Example I is processed into sliver using a Pacific Converter (described in U.S. Patent 2,438,469) adjusted to give a variable cut staple having a nominal length of 3½ inches. The sliver obtained is then spun into yarn using conventional equipment and procedures for pin-drafting, roving, and spinning. Fabric samples are woven from the yarns and are found to have the good handle, superior bulk, and excellent dyeability characteristics of fabrics prepared from spontaneously extensible polyester fibers.

Example IIII

The general procedure of Example I is repeated using a copolymer of polyethylene terephthalate containing in the polymer molecule 2 mol percent sodium 3,5-dicarboxybenzenesulfonate for improved dyeability with basic dyes. Substantially equivalent results are obtained.

Example IV

This example illustrates the use of the present invention in the preparation of spontaneously extensible fibers from low molecular weight polyester to give fibers suitable for the preparation of non-pilling fabrics.

Polyethylene terephthalate having a relative viscosity of 14.3 is melt-spun and drawn according to the general procedure of Example I using the specific conditions set forth in Table III below. Crimping and relaxing are carried out in steam in a stuffing box crimper in accordance with the general principles illustrated in Example I. Three samples are prepared and all three are found to possess the property of spontaneous extensibility when exposed to boiling water for 3 minutes under zero tension as indicated in the table.

TABLE III

Sample Number	Supply Tow Denier	Draw Ratio	Draw Zone Temp., degrees	Draw Speed, y.p.m.	Crimper Steam Pressure		Grimper Gate Pressure		Shrinkage in Crimper, percent	Denier (d.p.f.)	Tenacity (g.p.d.)	Percent S.E.
					(p.s.i.)	(atm.)	(p.s.i.)	(kg./cm.²)				
IVa	1,090,000	3.53	69	340	25	(1.7)	12.5	(0.88)	28	2.65	2.65	1
IVb	1,090,000	3.46	66	340	25	(1.7)	9	(0.63)	35	3.00	2.25	3
IVc	1,090,000	3.46	69	340	31	(2.1)	14	(0.99)	29	2.76	2.47	2

The present invention provides a simple process whereby polyester fiber manufacturers with only the simple modification of the introduction of a hot fluid into the chamber of a conventional stuffing box crimper, can produce tow and staple possessing the property of spontaneous and irreversible extensibility.

With respect to the crimper, it should be obvious that any suitable crimper apparatus could be advantageously utilized as long as the hot fluid temperature and exposure time can be maintained within the limits hereinbefore described. When using a stuffing box crimper, it should be readily appreciated that the degree of crimp is dependent upon total resistance of tow passage through the chamber, which in turn depends upon exit gate pressure and wall friction. When a hot fluid is also present, the pressure that should be put on the exit gate will depend upon the specific design. Although it is preferred to have the hot fluid be water or steam, it should be obvious that any inert fluid could be advantageously utilized.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

What is claimed is:

1. The process of preparing crimped structures while simultaneously providing the capability of spontaneously and irreversibly extending in length which comprises passing a synthetic linear condensation polyester tow having a birefringence of at least 0.15 and a crystallinity of less than about 35% through a stuffing box crimper while at the same time heat shrinking said synthetic linear condensation polyester tow in said stuffing box crimper with a hot fluid at a temperature in the range of from about 85° C. to about 250° C., the exposure time of said synthetic linear condensation polyester tow to said hot fluid being less than about 2.0 seconds.

2. The process of preparing crimped structures while simultaneously providing the capability of spontaneously and irreversibly extending in length which comprises passing a synthetic linear condensation polyester tow having a birefringence of at least 0.15 and a crystallinity of less than about 35% through a stuffing box crimper while at the same time heat shrinking said synthetic linear condensation polyester tow in said stuffing box crimper with a hot fluid at a temperature in the range of from about 85° C. to about 250° C., the exposure time of said synthetic linear condensation polyester tow to said hot fluid being less than about 2.0 seconds and thereafter drying said synthetic linear condensation polyester tow at a temperature in the range of from about 60° C. to about 100° C.

3. The process of claim **1** wherein said synthetic linear condensation polyester is polyethylene terephthalate.

4. The process of claim **2** wherein said synthetic linear condensation polyester is polyethylene terephthalate.

5. The process of claim **1** wherein said synthetic linear condensation polyester tow is a copolymer of polyethylene terephthalate with the acid component of the polyester comprising from about 1 to about 10 mol percent of sodium 3,5-dicarboxybenzene sulfonate based upon the total number of mols of the acid component.

6. The process of claim **2** wherein said synthetic linear condensation polyester tow is a copolymer of polyethylene terephthalate with the acid component of the polyester comprising from about 1 to about 10 mol percent of sodium 3,5-dicarboxybenzene sulfonate based upon the total number of mols of the acid component.

7. The process of claim **1** wherein said exposure time is less than 1.0 second.

8. The process of claim **2** wherein said exposure time is less than 1.0 second.

9. The process of claim **1** wherein said hot fluid is steam at a temperature of from about 100° C. to about 150° C.

10. The process of claim **2** wherein said hot fluid is steam at a temperature of from about 100° C. to about 150° C.

(References on following page)

References Cited by the Examiner

UNITED STATES PATENTS

2,575,781	11/1951	Barael	28—72
2,575,839	11/1951	Rainard	28—72
2,734,228	2/1956	Hay	28—72
2,747,233	5/1956	Hitt	28—72
2,854,701	10/1958	Rainard	28—1
2,952,879	9/1960	Kitson et al.	264—290
2,979,883	4/1961	Waltz	264—345 X
3,099,064	7/1963	Haynes	28—1
3,160,941	12/1964	Williamson	28—1

MERVIN STEIN, *Primary Examiner.*

L. RIMRODT, *Assistant Examiner.*