

[54] **PRODUCT AND PROCESS**

[75] Inventors: **Gail Crolley Guinn**, Gastonia, N.C.;
Joseph W. Jenny, Jr., Camden, S.C.

[73] Assignee: **E. I. du Pont de Nemours and Company**, Wilmington, Del.

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[63] Continuation-in-part of Ser. No. 89,918, Nov. 16, 1970, abandoned.

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[58] Field of Search..... **260/79.3 R, 79.3 MU; 264/182**

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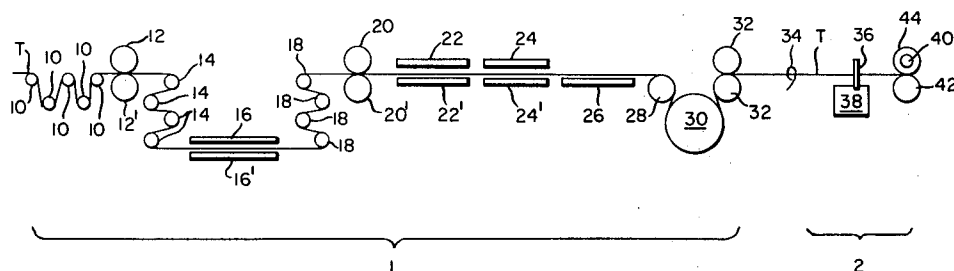
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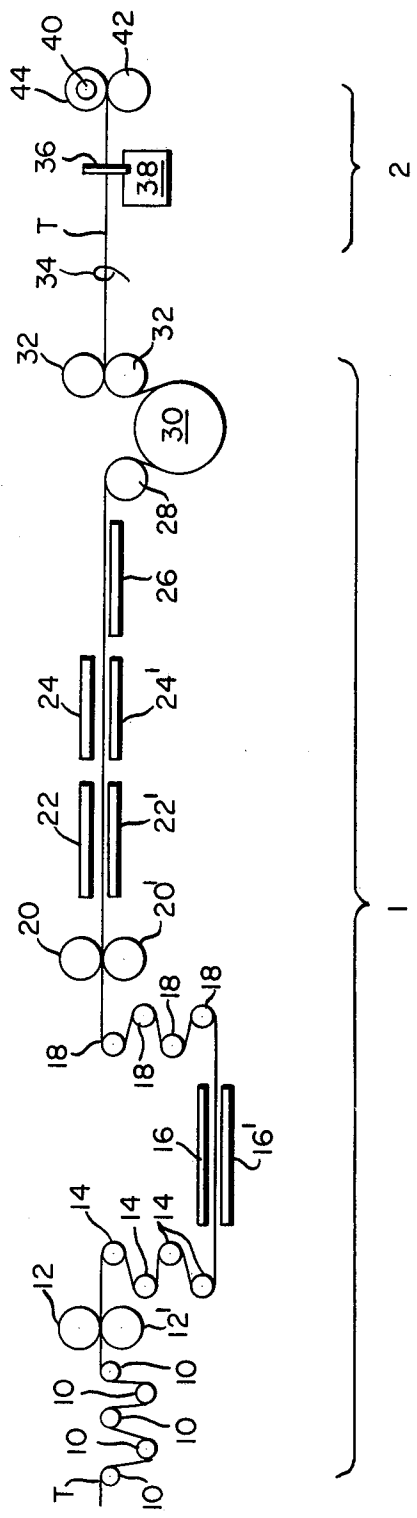
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[57] **ABSTRACT**

This application discloses acrylic fibers having high tenacity, a break elongation of 8–18% and a shrinkage in boiling water of 13–26% in combination with an X-ray porosity index less than about 1.5 in the void size range of each of 45–90A and 90–140A and a molecular orientation of at least about 66.5, the particular fiber having the chemical composition of 93–95% acrylonitrile, 5–7% methylacrylate and up to 0.5% sodium styrene sulfonate. The fibers are prepared by specific drawing, drying and redrawing steps.

3 Claims, 1 Drawing Figure





PRODUCT AND PROCESS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 89,918, filed Nov. 16, 1970, and now abandoned.

The present invention relates to a tow of a new acrylic homofiber (single component) fiber useful in knitwear.

Acrylic staple fiber yarns are used in many forms of knitwear. In this use it is desirable for the fiber to have a shrinkage in boiling water of at least 13% and most preferably 13 to 26%.

Conventionally such acrylic staple fibers may be formed on a Turbo Stapler, a conventional device wherein a tow of acrylic fibers is drawn and immediately broken. The drawing step in the Turbo Stapler should give the fiber the desired break elongation to process properly (break) in the second step breaking of the filaments into staple over breaker bars, and also imparts stresses in the filament to yield the desired shrinkage in the staple. The product of the Turbo Stapler is a sliver of fibers resulting from the drawing and stretch breaking of the tow of filaments fed to it.

An acrylic tow which can be directly broken into staple without employing the Turbo Stapler is provided by the present invention. The filaments in such tow consist essentially of 93-95% acrylonitrile, 5-7% methylacrylate and up to 0.5% sodium styrene sulfonate. The filaments have an X-ray porosity index of less than about 1.5 in the void size range of each 45-90A and 90-140A, a molecular orientation of greater than about 66.5%, a break elongation of 8 to 18%, a shrinkage in boiling water of 13 to 26% and a tenacity of above about 3.6 gpd. Preferably the sodium styrene sulfonate will be present in an amount between about 0.1% and 0.5%. Preferably also the tow is in the form of a ball warp having a density of filaments of 35 to 55 lbs./ft.³. Alternatively, the tow can be packaged in a carton to the same density.

The present invention also comprehends a process for stretching acrylic filaments under conditions which will increase their tenacity and reduce their X-ray porosity index. This process involves spinning acrylic filaments from solution, i.e., dry or wet spinning, washing said filaments, drawing said filaments in a first draw step between about 4 and 5X in an aqueous bath, drying said filaments in a heated gas under relaxed conditions at a temperature of 135°-145°C. to yield filaments having less than 2% moisture, and subsequently drawing said filaments in a second draw step at least 1.4X in a zone at a temperature of at least 121°C. for at least 1.7 seconds and cooling the filaments. In the preferred embodiment, the filament consists essentially of 93-95% acrylonitrile, 5-7% methylacrylate and up to 0.5% sodium styrene sulfonate.

THE INVENTION IN MORE DETAIL

The critical aspects of the instant process arise after the fibers have been spun, wash-drawn, and dried in the relaxed state. The dried fiber in accordance with this invention is then drawn at least 1.4X in a hot zone for a period of at least 1.7 seconds.

The degree of draw should be at least 1.4X. The upper limit of draw is governed by the number of broken filaments found acceptable in processing.

The temperature in the hot draw zone will normally be at least 121°C., but it is to be understood that the maximum suitable temperature will be related to the residence time of the filament in the hot draw zone.

Preferably, the temperature of the hot draw zone will be between 133°-190°C.

The residence time of the filaments in the draw zone should be at least 1.7 seconds. Residence time, of course, will be related to the temperature of the hot draw zone as stated above and will be such that excessive degradation and discoloration of the polymer is avoided.

For the preferred composition — 93-95% acrylonitrile, 5-7% methylacrylate and up to 0.5% sodium styrene sulfonate — the filaments are drawn 1.4-2.0X and preferably 1.5-7X at a temperature in the hot draw zone of between 135°C. and 190°C.

Before the tow is packaged it must be cooled to below about 70°C. to avoid shrinkage problems involving shrinkage of the filaments in the package on further cooling. Until this temperature is reached the filaments are held under tension sufficient to prevent relaxation.

The tow of this invention need not be crimped, thus avoiding a process step typically present in providing tow for breaking into staple.

THE DRAWING

The preferred apparatus for carrying out the drawing step of the process after the filament has been spun, wash-drawn and dried in the relaxed state is shown in the attached schematic drawing. It is basically a drawing zone such as found in Turbo Tow Processor, 1, coupled to a ball warper 2 modified to provide a uniform traverse of the tow on the package. The apparatus is shown with a tow, T, threaded therethrough. The tow first extends around a group of guide bars 10 followed by the first set of nip rolls, commonly called the input rolls, 12, 12'. The tow then passes around the first set of cascade rolls 14 and thence between the first set of heater plates 16 and to the second set of cascade rolls 18. Tow is pulled to this point by means of a second set of nip rolls, commonly called intermediate rolls, 20, 20' and is stretched the desired amount by means of a pre-selected speed differential between this second set of nip rolls and the first set 12, 12'. Two more sets of heater plates 22, 22' and 24, 24' are followed by a cooling plate 26, a guide roll 28, a cooling drum 30 and the third set of nip rolls 32, 32'. Tow is advanced by differential speed between roll set 32, 32' and set 20, 20'. Heating and subsequent partial cooling are possible in this region. The tow then extends through stationary guide 34 and thence to traverse guide 36 which is driven by traverse guide drive mechanism 38. Tow then is wound on a core 40 by means of drive roll 42 thus forming the ball warp package 44. Alternatively, the very high density package of this invention may be prepared in a closed free standing container by substituting for the ball warper the type of container and apparatus conventionally used in such packaging.

The filaments of the tow of this invention have a tenacity at least 3.6 and a porosity index of less than 1.5 in each of the void size ranges of 45-90A and 90-140A which is believed related to improved uniformity of dye due to slower initial dye uptake. In addition these fibers have a break elongation of between 8-18% and a shrinkage in boiling water of 13-26%.

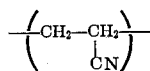
The shrinkage range is desirable for staple fiber in knitwear. The break elongation is desirable for direct cold breaking of the tow into staple. As shown in Table I, when this elongation is exceeded the directly cold-broken sliver is of poor quality.

The denier of the tow processed in accord with the invention is not critical. It may range between 100,000 and 1,000,000 or more in denier. The filaments may have a denier of between 1 to 10.

DEFINITIONS

"Acrylic" filaments refers to filaments consisting essentially of polymer containing at least 85% by weight of acrylonitrile.

Acrylic filaments as used herein, included filaments of any long chain synthetic polymer composed of acrylonitrile units of the formula



in the polymer chain. As is well understood, the term includes the homopolymer of acrylonitrile (i.e., polyacrylonitrile) and copolymers of acrylonitrile and one or more suitable monoethylenically unsaturated monomers copolymerizable with acrylonitrile. Among the typical addition monomers as exemplary of those which are copolymerizable with polyacrylonitrile are methyl acrylate, methyl methacrylate, vinyl acetate, styrene, methacrylamide, methacrylonitrile, vinyl chloride, vinylidene chloride, methyl vinyl ketone and the like as well as any of the available vinyl pyridines. The preferred compounds include methyl acrylate, vinyl acetate, styrene and the vinyl pyridines.

Among the copolymerizable sulfonates are the sulfonated styrenes, vinyl sulfonate, allyl sulfonate, methallyl sulfonate and their alkali-metal or alkaline-earth-metal salts, and the like, it being necessary only that the compound chosen from this class be copolymerizable with acrylonitrile to the desired extent. The preferred compounds are the sulfonated styrenes.

"Molecular orientation" and "X-ray porosity" refer to structural features of the filaments comprising the tow as measured by tests as follows:

Molecular orientation and porosity indices were obtained from X-ray diffraction measurements made in a conventional manner. [For example, generally as described by Statton in A.S.T.M. Spec. Tech. Bull. No. 247 (1958)].

Yarn test samples of about ½ gm. were uniformly wound on a stainless steel card (1¼ × 1¼ × 1/32 inch) with a ¾ inch diameter aperture. The thus arranged specimen was mounted in the spinning or stepped rotation holder of the diffractometer. Thus, wide angle, crystalline, diffraction pattern was used for measuring orientation and the small angle scattering for porosity. Commercial Philips Electronic Instruments Co. instrumentation was used to provide and make the required intensity measurements on the X-ray diffraction patterns. The X-ray source comprised a copper target with a 40KV, 20 ma power supply. The monochromator employed ¼° divergence and receiving slits along with a 1° pre-slit.

Measurements of diffracted radiation intensity were made by means of a scintillation counter with pulse height analyzer. Determinations of intensity were made in terms of the reciprocal of the time required for a

specified number (usually 500) of counts for each angular position. For determining the porosity indices, intensity was determined at discrete diffraction angle (2θ) steps of ¼° from a value of 2θ of ¾° to 1° for the 90-140A index and 1° to 2° for the 45-90A index. These measurements were extended to a 2θ value of 36° for normalization computations. For orientation measurements, intensity was determined at azimuthal (ψ) angle intervals of 2° extending from 0° through 180° for a constant, preselected, 2θ value equal to 16.8°.

Raw intensity values were corrected by subtracting air and electronic noise background. The raw air background values were first corrected by multiplying by sample transparency values before then subtracting. In addition normalized corrected intensity values were computed in order to correct for small variations in the amount of sample in the beam. This was accomplished by multiplying by a factor found necessary to achieve a value of 1 for the integrated area under the corrected intensity versus 2θ curve from 2θ equal to 6° to 36°. Sample transparency, the zero (2θ) angle intensity reduction was determined by using nine Ni filters each 0.007 inch thick and measuring beam intensity with and without the sample for 500 sec. as I and I₀ respectively. Transparency values were then computed as the ratio I/I₀.

Molecular orientation was computed from the azimuthal intensity variations curve according to the equation: Orientation (%) = 100 (90 - dψ_{A/2}/90). The value of dψ_{A/2} is obtained from the corrected intensity vs. ψ curve by first determining the total area, A, under the curve, computing the value A/2, and then finding that width, dψ_{A/2} in degrees, of the intensity peak selected, symmetrically around the peak, so that the area under the peak confined by this width is equal to A/2.

The two porosity indices were computed from the normalized corrected intensity vs. diffraction angle data according to the following expressions:

$$P(45-90A) = 100 \times \text{Area } (2\theta = 1^\circ \text{ to } 2^\circ)$$

$$P(90-140A) = 100 \times \text{Area } (2\theta = 3/4^\circ \text{ to } 1^\circ)$$

Thus these indices are indicative of the relative number of pores (inhomogeneities) which contribute to the X-ray scattering over a certain range of the intensity vs. 2θ curve.

"Elongation" and "tenacity" are measured by the Instron tester in accord with ASTM D-540-64 after the filaments have been conditioned as per ASTM D-1776.

"Shrinkage" refers to the reduction in length of the fiber after immersion in boiling water for 30 minutes as determined by tests hereinafter described. Percent shrinkage is calculated as

$$L_0 - L_b / L_0 \times 100$$

wherein L₀ is the length of fiber before immersion in boiling water and L_b is the length of fiber after 30 minutes immersion in boiling water.

In the following examples all parts are by weight unless otherwise indicated.

EXAMPLE 1

Acrylic filaments of the following composition, 93.9% of acrylonitrile, 6% methylacrylate and 0.1% sodium styrene sulfonate was spun from dimethylformamide solution in conventional manner, wash-drawn 4.5X at 96°C. in an aqueous bath and dried in a relaxed

state in hot air at a temperature between 135°–145°C.

A tow of these filaments of denier, 470,000 total of 6 dpf. fiber was then processed as set forth in Table I in a tow stage draw. The tow was then cooled over a cooling plate and drum to reduce the temperature of the tow to approximately 135°F. before each sample was wound under tension on a core of a ball warp. The ball warp was permitted to cool to room temperature.

Specimens of fibers from the tow in each ball warp sample were removed at random, conditioned at normal textile testing conditions of 65% R.H., 70°F. (21°C.), and then tested for tensile properties and loop properties by means of well known Instron (Product of the Instron Engineering Co., Canton, Mass.) tensile tester by the tests set forth above. Similar specimens were tested for shrinkage in boiling water by the test set forth above.

Processing conditions and product properties for the different samples of this example and controls are shown in Table I below. The ultimate acceptability of each sample was judged on the basis of its processability into staple sliver on a Turbo Stapler. This latter machine was operated according to accepted standard practice except that the heater plates were held open and not heated and no significant stretch (about 1.15X) was imposed on the tow in the initial sections merely to attenuate kinks in the tow. All of the samples prepared by the process of the present invention processed well into sliver. The control samples processed poorly.

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i	4.30
j	6.45
k	4.62
l	2.31
m	6.93
n	4.62

EXAMPLE 2

To demonstrate the very high package density of filaments of this invention, a sample of the tow was first spun, wash-drawn and dried as described in Example 1 and was given a "second draw" as follows at 60 yards/min. as measured at rolls 20, 21 in the Figure on the apparatus above described. The heater plate temperatures were as follows:

Heater plate temperatures:

1st heater: 180°C. (16, 16' in the Figure)

2nd heater: 180°C. (22, 22' in the Figure)

3rd heater: 180°C. (24, 24' in the Figure)

Draw Ratios:

1st stage draw: 1.309X (at heater plates 16, 16')

2nd stage draw: 1.260X (at heater plates 22, 22', 24, 24')

Residence time in the draw zone is calculated on the same basis as Example 1, to be 2.15 seconds.

The ball warp thus produced was weighed and dimensions measured. The ball weighed 656 lbs. Cylindrical dimensions of this package were: length 40 in.,

TABLE I

Process Conditions				Product Properties					Stretch break Processing to Silver Evalua- tion of Sliver Produced
Item	T.P. Speed ⁽¹⁾	Draw Ratio	Heater plate Temp.°C. ⁽²⁾	Fiber					
				Ten. (g/d)	Elong. (%)	Mod. (g/d)	Loop Work	Shrinkage (%)	
							to Break (g.cm) (den.-cm.)		
a	4	1.31/1.26	190	4.5	14.2	98.9	0.01	14.2	Good
b	1	1.31/1.26	190	4.1	16.6	83.8	0.01	16.6	do.
c	4	1.31/1.26	180	4.2	15.5	90.4	0.01	20.5	do.
d	4	1.31/1.26	170	4.2	14.1	94.2	0.01	22.9	do.
e	4	1.12/1.12	190	3.5	24.5	76.5	0.06	16.4	Poor
f	2	1.55/1.26	190	4.8	11.7	97	0.01	17.5	Good
g	1	1.55/1.26	180	4.8	12.7	103.8	0.01	15.2	do.
h	2	1.55/1.26	180	4.7	11.1	107.2	0.01	18.1	do.
i	2	1.31/1.26	180	3.5	12.8	83.6	0.01	19.0	do.
j	1	1.31/1.26	170	4.0	14.3	90.9	0.01	18.2	do.
k	2	1.12/1.12	170	3.5	24.2	77.4	0.06	15.2	Poor
l	4	1.12/1.12	180	3.1	24.3	73.0	0.07	16.0	do.
m	1	1.12/1.12	180	3.2	25.7	73.2	0.07	11.8	do.
n	2	1.12/1.12	190	3.1	26.7	73.9	0.09	13.1	do.

⁽¹⁾ - Speed 1 = 20 yd./min., 2 = 30 yd./min., 4 = 60 yd./min. at intermediate rolls, 20, 21 in the Figure.

⁽²⁾ - Temperature of heater plates, 16, 16', 22, 22', 24, 24' in the Figure.

Residence time in seconds in the draw zone is calculated from the take-up speeds in each zone assuming that is the velocity of the fiber throughout that zone and is as follows for the runs in Example 1.

a	2.15
b	6.45
c	2.15
d	2.15
e	2.31
f	4.30
g	6.45
h	4.30

outer dimensions 27 in. and inner diameter 5 in. The computed package density was, therefore, 51.4 lb./cu. ft.

In an identical run, tow temperature readings were taken by means of an infrared thermometer. Results were:

210°F. (99°C.) at exit of heater plate 16, 16' in the Figure

260°F. (127°C.) at exit of heater plate 24, 24' in the Figure

240°F. (116°C.) at entrance to cooling drum 30 in the Figure

165°F. (75°C.) at exit from machine to wind up at 32, 32' in the Figure.

Fiber characterization for this run showed tenacity = 3.7 gm./den., elongation = 14%, modulus = 86 gm./den. and shrinkage = 21.5%.

EXAMPLE 3

A. A sample of tow was first spun, wash-drawn and relaxed as described in Example 1 and was dry stretched on the apparatus above described between heater plates at 60 ypm. as measured at rolls 20, 20' of the Figure. The tow was drawn in two stages. The first stage draw occurred between heater plates 16, 16' and the second stage between heater plates 22, 22' and 24, 24'. The first stage draw was 1.309X and the second stage draw was 1.230X. Each set of heater plates is at 149°C. Residence time in the draw zone is calculated to be, on the same basis as Example 1, 2.18 seconds for item A and 6.54 seconds for item B. The tow was packaged as a ball warp of a density about 45 lbs./cu. ft. Fiber specimens were taken from the tow before dry relaxing and from the ball warped tow.

B. Experiment A was repeated but drawing speed measured at rolls 20, 20' of the Figure was 20 yds./min.

The specimens were characterized by the above described X-ray scattering techniques to give first an index of porosity of the internal structure and secondly a measure of molecular orientation.

Table II records the values of porosity index and orientation for these samples and also fiber properties. Table II records the values of porosity index and orientation for a control sample (the sample of tow before the additional stretching).

The product has been shown to have important utility in its direct processability into sliver in the second stage of the Turbo Stapler machine (breaking).

TABLE II

	Control	Test A	Test B
5 Porosity Index			
45-90A	2.97	1.47	1.27
90-140A	3.87	1.35	1.18
Orientation	58.8	68.9	73.8
Tenacity (gpd)		4.0	4.0
Elongation (%)		14.6	15.2
10 Modulus (gpd)		92.1	95.0
Shrinkage		16.6	14.7

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

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

1. A tow of acrylic filaments, said acrylic filaments consisting essentially of 93.9% acrylonitrile, 6% methylacrylate and 0.1% sodium styrene sulfonate, the filaments have an X-ray porosity index of 1.27-1.47 in the void size range of 45-90A and 1.18-1.35 in the void size range of 90-140A, a molecular orientation of 68.9-73.8%, a brake elongation of 14.6-15.2%, a shrinkage in boiling water of 14.7-16.6% and a break tenacity of about 4.0 gpd.

2. The tow of claim 1 in the form of a ball warp having a density of filaments of 45 lbs./ft.³.

3. A carton of the tow of claim 1, said tow having a density of filaments of 45 lbs./ft.³.

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