

June 14, 1966

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FIBERS

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Filed May 5, 1961

FIG. 1

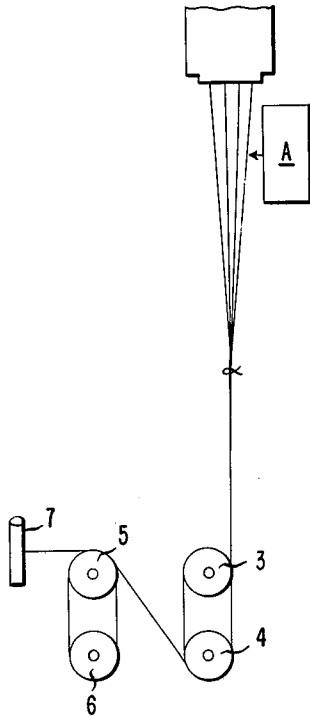


FIG. 2

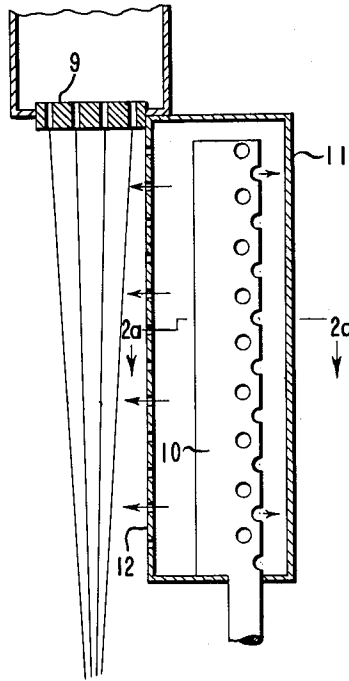
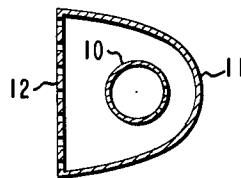


FIG. 2a



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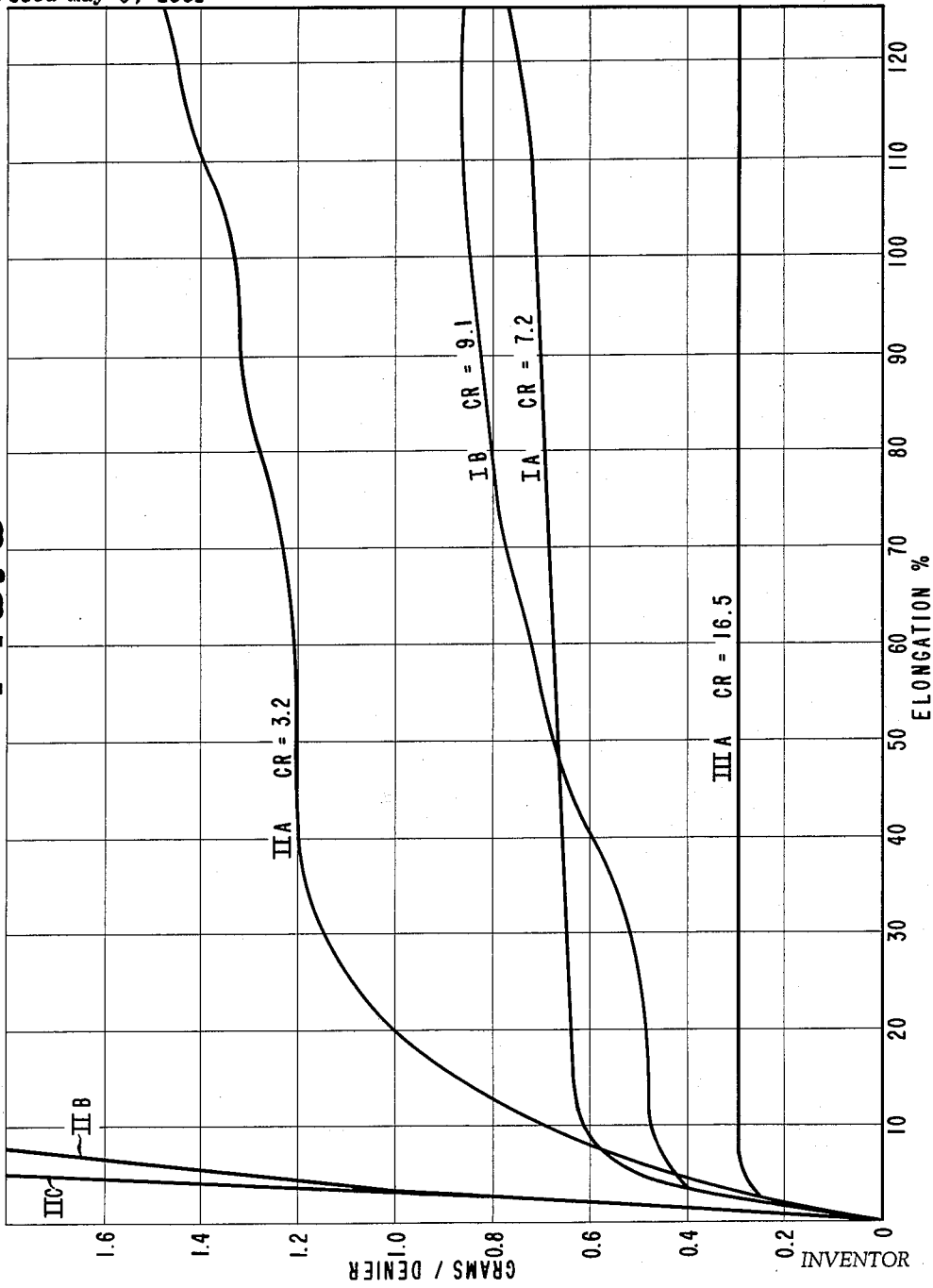
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FIG. 3



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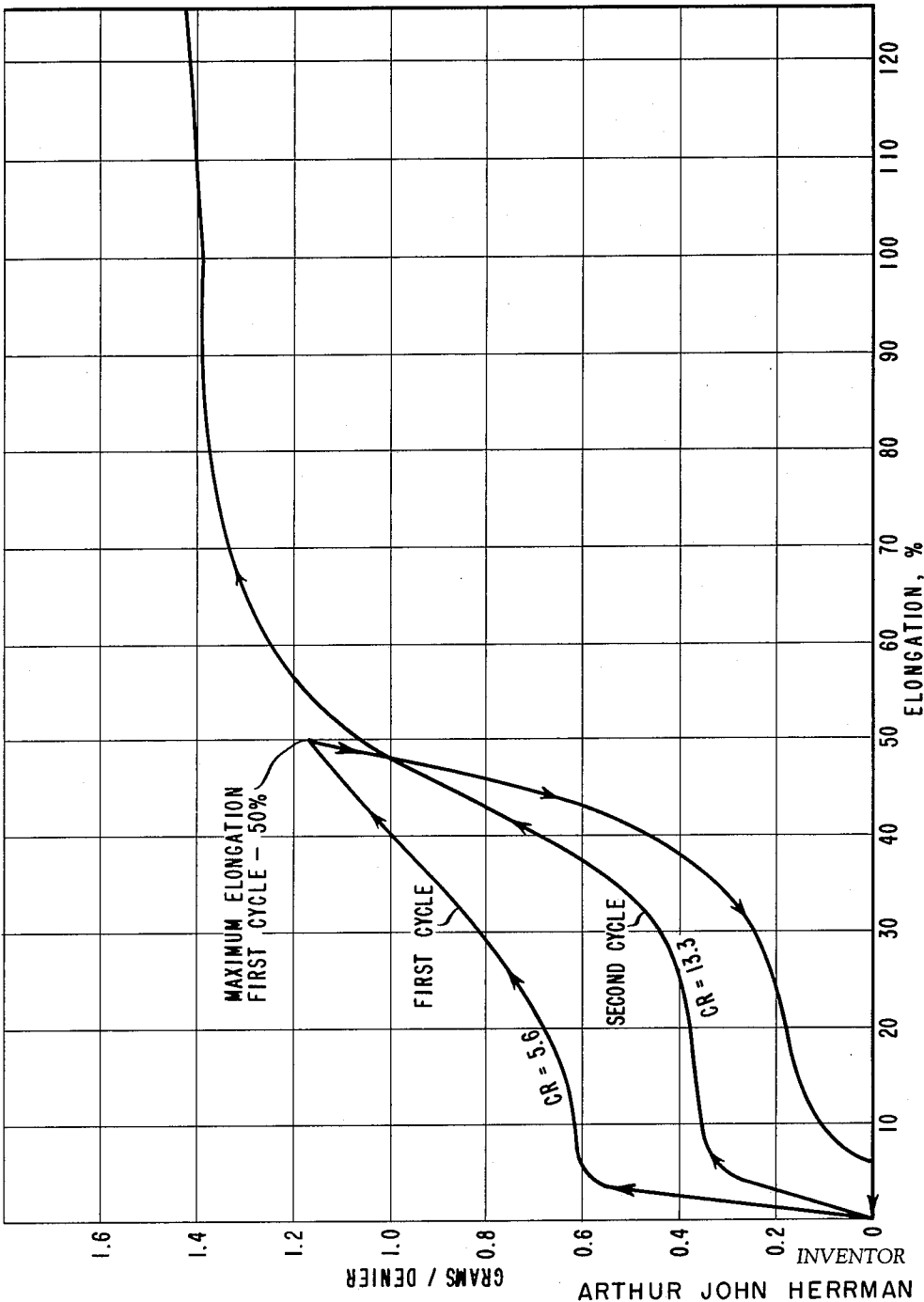
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FIG. 4



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FIG. 5

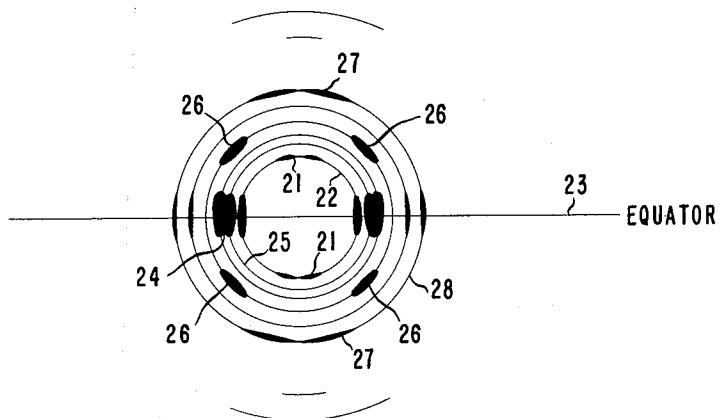
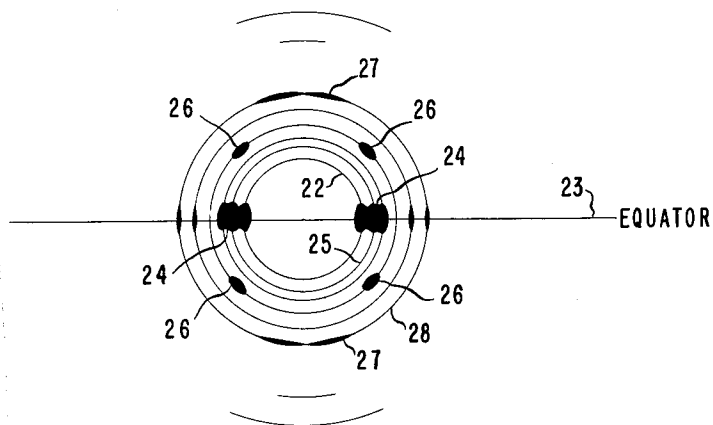


FIG. 6



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FIBERS

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4 Claims. (Cl. 260—93.7)

This invention relates to fibers and, more particularly, to elastomeric fibers of polypropylene.

Much effort has been expended heretofore in attempting to make fibers from synthetic polymers having many of the desirable attributes of fibers made from natural rubber without the disadvantages of natural rubber fibers. Results have been varied but, on the whole, these attempts have not been too successful. Usually, fibers have had extremely low moduli of elasticity in the regions of the elongation used in most applications of fibers. That is, the fibers were characterized by a very low stress at useful elongations and, hence, required heavy denier fibers to provide suitable resistance to elongation. The problem of getting a fiber with, in layman's language, some elasticity but not a ruinous amount, persisted.

Not only have the heretofore proposed polymers been lacking in desired degree of elasticity when formed into fibers but the solutions proposed have involved polymers whose production was quite expensive and difficult to control.

Fibers from highly crystalline, high molecular weight polypropylene are well known. Although some of these fibers have been described as "highly elastic," useful elastic fibers of propylene have nevertheless not been forthcoming and, in general, the problem of producing useful elastic polypropylene fibers and the like has been just as difficult as when using other synthetic polymers.

An object of this invention is to provide new fibers of polypropylene. A further object is to provide such fibers having a suitable balance between elasticity, i.e., recovery from elongation, and a useful degree of resistance to elongation. A more particular object is to provide fibers of polypropylene adapted for a wide variety of uses in which some degree of elasticity is highly desirable, such as auto seat covers, covers for lawn chairs, carpets, and hose. Other objects will be apparent from the description of this invention given hereafter.

The above objects are accomplished according to the present invention by forming fibers of polypropylene whose physical structure is characterized by gamma orientation and a heat-stable orientation angle of 10° to 30°. In a preferred form, the invention comprises a fiber of polypropylene having a gamma intensity ratio of at least 1.0 and a heat-stable orientation angle of 10° to 21°.

It has been found that fibers of polypropylene whose physical structure is characterized by gamma orientation and a heat-stable orientation angle of 10° to 30° possess a highly favorable combination of properties, including good recovery from elongation. Such fibers have the following properties: a tenacity of at least 0.8 grams per denier, an elongation at break of from 100% to 700%, a tensile recovery on the second and the succeeding cycles from a 25% elongation of at least 82%, a compliance ratio (5% to 30% elongation) of from 2 to 15, a stress at 5% elongation of between 0.1 and 0.8 grams per denier, and an initial modulus of 5 to about 25 grams per denier.

In the preferred form of this invention wherein the fiber of polypropylene has gamma orientation, a gamma intensity ratio of at least 1.0, and a heat-stable orientation angle of 10° to 21°, the fiber has a tensile recovery on the second and succeeding cycles from a 25% elongation of at least 85% and, as shown in the examples, may be above 90%.

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For purposes of clarity and definiteness, certain terms used in describing the invention are defined below. They are used throughout the specification and claims as defined.

"Orientation angle" is a parameter which represents the alignment of molecular axes of the material forming a fiber with respect to the fiber axis. The orientation angle is indicated by the azimuthal extent of the intensity of the (040) X-ray diffraction arc at $2\theta=16.7^\circ$. These indices are used according to G. Natta et al., *Atti accad. nazl. Lincei, Rend. Classe si. fis. mat. e nat.* [8] 21, 365 (1956). The orientation angles are measured according to the technique by H. G. Ingersol, *Journal of Applied Physics*, 17, 924 (1946), on the instrument described by J. E. Owens and W. O. Statton, *Acta Crystallographica*, 10, 560 (1957). This angle using the (040) arc is a measure of crystallite orientation with respect to the fiber axis (C axis).

"Gamma" orientation is the unusual orientation or condition of material in an object which is detected by X-ray diffraction techniques by a diffraction pattern in which the (110) diffraction arc at $2\theta=14.0^\circ$ exhibits intensity maxima at an azimuthal angle greater than 50° from the equator. The intensity maxima has a ratio greater than 0.6 when compared to the intensity maxima of the (022, $1\bar{2}2$) X-ray diffraction arc at $2\theta=28.6^\circ$. This ratio (I_γ/I_α), is determined from a radial photometer trace obtained 10° from the meridian on the Leeds and Northrup Knorr-Alber model 6700-P-1 microphotometer with 0.01 mm. slit width and 1.5 mm. slit length. The peak intensities of the maxima are determined above the background scattering in the following manner: For the peak at $2\theta=14.0^\circ$ a straight line is drawn on the photometer trace connecting the intensity values at $2\theta=9.3^\circ$ and $2\theta=11.3^\circ$; this sloping straight line is extended under the peak and the intensity value of this line at the peak 2θ position is used as the background value and subtracted from the peak value to give a quantity, I_γ . For the peak at $2\theta=28.6^\circ$ a sloping straight line is drawn connecting the intensity values at $2\theta=26.0^\circ$ and 31.2° ; the value on this line at the peak position is subtracted from the peak value to give a quantity, I_α .

Oriented fibers having a gamma intensity ratio (I_γ/I_α) of less than 0.6 are designated as having "normal" orientation hereinafter. Oriented fibers having a gamma intensity ratio greater than 1.0 are preferred.

By the term "potential gamma orientation" is meant a structure that will show gamma orientation upon drawing to 1 to 2.5× and heating 10 minutes at 135° C.

By the term "heat-stable," used in connection with polypropylene in the "gamma" condition, is meant that the orientation angle does not change more than 8% upon heating at a temperature of 135° C. for 10 minutes.

By the term "tensile recovery" which is hereafter designated TR, is meant the percent of the elongation a fiber recovers after an elongation (stated as a subscript to the TR designation) at a rate of 100% per minute, being held at the maximum elongation for 1 minute and then being permitted to recover at the rate of 100% elongation per minute. Unless otherwise designated, the TR's used herein to describe the invention are obtained from the second cycle on a tester 1 minute following the recovery from the first test after reclamping the fibers.

By "compliance ratio," hereafter designated "CR," is meant—(compliance at 30% elongation—compliance at 5% elongation)/5 which may be expressed as

$$CR = \left(\frac{L_{30}}{L_5} - \frac{5}{1} \right) \frac{1}{5}$$

where L_{30} and L_5 are the stress in grams per denier at the respective elongations. It will be noted that a high com-

pliance ratio tends to indicate a fiber relatively easy to elongate 30% but requiring almost as much effort to elongate 5%—a rubber band would be an extreme illustration. On the other hand, a low compliance ratio tends to indicate a fiber relatively difficult to elongate 30% but substantially easier to elongate 5%.

Initial modulus, hereafter designated "*M_i*," is obtained by a straight line extrapolation of the initial portion of the stress strain curve from 0 elongation to 100% elongation. It is expressed in grams per denier, hereafter designated "g.p.d." Tenacities and elongations at the break are expressed in the usual units of g.p.d. and percent, respectively, and are measured on dry samples of yarns.

Polypropylene adapted for use in making the fibers of this invention, is highly crystalline as shown by sharp and distinct X-ray diffraction patterns and should preferably show a stiffness of greater than 120,000 pounds per square inch when prepared in test bars according to ASTM test D-747. The polypropylene can be of any high molecular weight polymer characterized by a melt index (ASTM standards, 1958 D-1238-57T, part 9, page 38) of 0.1 to 200, preferably 0.5 to 30. The preferred range affords products with significantly superior elastic properties.

The term "inherent viscosity" as used in the examples is defined as: $\ln(n)_r/c$ wherein c is the concentration in grams (0.10) of the polymer in 100 ml. of the solvent (decahydronaphthalene), $(n)_r$ is the relative viscosity which is the ratio of the flow times in a viscosimeter of polymer solution and of the solvent, both at 130° C. An antioxidant (0.2%) is normally added to both the polymer solution and the solvent.

The present invention resides in fibers of polypropylene as herein characterized and not in any particular method of preparing such fibers. However, preparation of the fibers does, in general, involve consideration of three critical areas which are discussed below specifically in terms of fibers for purposes of simplicity and clarity.

1. *Spinning conditions.*—The extrusion of the fibers should be under such conditions so as to afford gamma orientation or potential gamma orientation. The spinning variables are adjusted to regulate the viscosity of the polymer melt as extruded through the spinneret hole, and the viscosity of the fiber as it changes from the molten to the solid state in the threadline. Under any one set of conditions of polymer type, spinneret orifice dimensions, the number of orifices and polymer throughput, gamma or potential gamma orientation is achieved through temperature regulation and windup speed. The temperature will be a function of the temperature of the molten polymer before being extruded, the rate of extrusion, the geometry of the spinneret, the extent of cooling or heating on the spinneret by outside heat or quenching air. A cooling air quench may be used as the fibers form to assist with the proper temperature control.

2. *Orientation.*—The fiber should be oriented to an extent giving an orientation angle of 10° to 55° by suitable selection of spin stretching under suitable quenching conditions (i.e., windup speed/calculated speed of polymer leaving the orifice) and/or suitable drawing of the solidified fiber. The drawing can be done under any suitable conditions but the draw ratio must not exceed 2.5×. Preferred products are made without drawing.

3. *Heat treatment.*—This step is essential to the development of useful recoveries from tensional deformations in polypropylene. With fibers prepared under optimum spinning conditions (so that no separate drawing step is needed) a temperature of 105° to 160° C. can be used for useful products. For the best products, a temperature of from 130 to 140° C. should be used.

This treatment on fibers having gamma orientation produces a heat-stable orientation angle of 10° to 30°, providing the fiber has an orientation angle between 10° and 55° before the heat treatment.

The fiber preferably is in a free-to-shrink condition dur-

ing the treatment, the amount of relaxation (shrinkage) by the treatment usually varying from 1 to 50%.

The time of treatment is not critical and can range from 0.6 second to 24 hours. The heating can be done as a distinct separate process as in an oven or an autoclave or it can be conducted continuously.

The following examples illustrate specific embodiments of the invention. Reference is made to the accompanying drawings wherein:

FIG. 1 is a schematic showing of a fiber spinning and treating apparatus suitable for producing the fibers of this invention;

FIG. 2 is an enlarged side elevation of a spinneret and quenching apparatus suitable for producing the fibers of this invention, shown partly in vertical section for purposes of illustration;

FIG. 2a is a section on the line 2a—2a of FIG. 2;

FIG. 3 illustrates stress-strain curves for various fibers of Examples I, II and III;

FIG. 4 illustrates two stress-strain curves showing the difference in behavior of a fiber in the first and second cycles on a tensile recovery tester;

FIG. 5 is a graphic representation of an X-ray diffraction photograph illustrating gamma-type orientation which characterizes the polypropylene of which the shaped articles of this invention are composed;

FIG. 6 is a graphic representation of an X-ray diffraction photograph illustrating the "normal" orientation characteristic of the polypropylene in heretofore known shaped articles.

EXAMPLE I

Crystalline polypropylene of melt index 0.7 (inherent viscosity of 2.75) (Profax made by the Hercules Powder Co., Wilmington, Delaware) is extruded as a melt at 289° C. through a spinneret 9 at 238° C. (spinneret temperature measured at the surface) using the apparatus of FIG. 1 wherein the solidified yarn is advanced over the feed rolls 3 and 4 rotating at 45 yards per minute (y.p.m.), then over the draw rolls 5 and 6 rotating at the same speed, and is finally wound up on a package 7. The spinneret 9 contains 34 orifices of 0.015 inch in diameter arranged in a rectangle one inch by $\frac{3}{16}$ inch in a staggered disposition. As indicated generally by A in FIG. 1 and shown in detail in FIGS. 2 and 2a, a quenching apparatus is disposed perpendicularly to the face of the spinneret 9. The quenching apparatus comprises a $\frac{3}{4}$ inch outside diameter tube 10 containing a plurality of $\frac{1}{16}$ inch diameter holes adapted to direct air against the walls of cylindrical chamber 11 in which it is mounted, except the wall facing the threadline. On the wall facing the threadline, the chamber 11 is provided with a 200-mesh screen 12. Air forced through the tube 10 strikes the solid walls of chamber 11 and is deflected therefrom through the screen wall 12 facing the threadline against the threadline. Air is supplied to the tube 10 at 1.8 cubic feet per minute. The as-spun yarn wound up on the package 7 has a total denier of 1409, an orientation angle of 22°, gamma orientation, and a gamma intensity ratio of 1.5.

Physical properties of a sample of this as-spun yarn without further treatment are measured and set forth as item IA, Table I. The yarn has not been given a heat treatment and, as a consequence, the angle of orientation is not heat-stable. A second sample of this yarn is skeined and treated in an air oven for 10 minutes at 135° C. After this "hot relaxation" step the fibers have a heat-stable orientation angle of 20°, gamma orientation and a gamma intensity ratio of 3.1. This is an example of the preferred form of this invention and its physical properties are reported as item IB, Table I. The initial modulus (*M_i*), tenacity, and elongation are all given for one stress-strain test from zero elongation to the break for each sample. FIG. 3 of the drawings shows the stress-strain curves for samples IA and IB. Sample IA had a CR of 7.2 while IB had a CR of 9.1.

Items IA and IB are identical except that IB was heat relaxed. Table I shows that both samples have quite similar properties except for tensile recovery. IB has an excellent TR_{25} of 92% while IA has a very poor TR_{25} of 57%. It is surprising that the heat relaxation step applied to this yarn could so drastically alter the tensile recovery property.

The same polymer as above is extruded through a spinneret having 3 orifices of 0.020 inch diameter, quenched as above with 1 cubic foot per minute of air, wound up at 525 y.p.m. and then hot relaxed as above. The yarn had gamma orientation, a heat-stable orientation angle of 14°, and physical properties as shown in item IC of Table I. This is a preferred specific embodiment of the invention and possess excellent (94%) tensile recovery after 25% elongation, second cycle.

In this Example I, none of the fibers has been drawn, the spinning conditions effecting the orientation. Item IA vividly illustrates that merely having an orientation angle within the defined limits will not give the fiber of this invention; it must be heat-stable to get the high tensile recovery combined with the other high level physical properties which characterize these fibers.

A peculiar characteristic of the behavior of the elastic polypropylenes of this invention is illustrated in FIG. 4 showing two stress-strain curves. The sample used to obtain these curves was prepared as item IB above and was substantially identical with it. The sample was elongated in the first cycle to 50% elongation and then allowed to recover under standard conditions. It was then reclamped in the testing apparatus for the second cycle and elongated out to the break. As FIG. 4 shows, on the first cycle the fiber showed a CR of 5.6 as against the appreciably higher CR of 13.3 for the second cycle. On the third and subsequent cycles the fiber behaved as in the second cycle. On boiling in a relaxed condition in water, the fiber reverts to a form which gives the first cycle behavior for the first time and thereafter goes to the second cycle type of behavior. This behavior is characteristic to a greater or lesser degree of the polypropylenes of this invention and is the reason for giving TR values based on the second cycle. Other polypropylenes outside of this invention may behave similarly.

EXAMPLE II

This example illustrates the effect of drawing the fiber. So far as favorable elastic behavior in the preferred range of 85% tensile recovery and up is concerned, it is preferred not to draw the fiber at all. However, some drawing is permissible but with too high a draw ratio, fibers having gamma orientation and the exceptional tensile recovery of the fibers of this invention are not obtained. A draw ratio up to $2.5 \times$ can be tolerated but is not preferred. The procedure of Example I is repeated with the yarn being forwarded by the feed rolls at 45 y.p.m. and the draw rolls run at higher speeds to give the various draw ratios mentioned below.

Referring to Table I, item IIA is a fiber drawn $2 \times$ in room temperature air; item IIB is a fiber drawn $4 \times$ over a metal pin (not shown in FIG. 1) 1 inch in diameter at 100° C. (one 360° wrap) placed between the feed rolls 3 and 4 and the draw rolls 5 and 6; and item IIC is a fiber drawn $5 \times$ over a metal pin at 60° C. Each fiber is "hot relaxed" by heating at 135° C. for 10 minutes in a tensionless condition and the physical properties are then determined.

Item IIA is a fiber within the present invention but it represents a non-preferred embodiment and, as shown in Table I, has a TR_{25} of 82%, the lower limit on tensile recovery for fibers of this invention. But as the draw ratio is increased, without change in other essential conditions, the fiber does not have gamma orientation and the TR_{25} drops well below the minimum 82%; note items IIB and IIC in Table I. Thus, the conventional practice of drawing to increase tenacity and M_i , must be carefully restricted to get the fibers of this invention.

In FIG. 3 is shown a portion of the stress-strain curves for items IIA, IIB and IIC. IIA has a CR of 3.2 while the curves for the other two indicate very low CR's for both. The contrast of the curves for items IIB and IIC as compared to IIA is very marked.

FIG. 6 is a graphic representation of an X-ray diffraction photograph of a substantial duplicate of fiber IIB. It shows no apparent gamma orientation and has a gamma intensity ratio of only 0.02. On the other hand,

Table I

Item	Total Draw Ratio	Hot Relaxation	Orientation		Physical Properties				
			Angle	Type	TR_{25} , Percent	Tenacity g.p.d.	Elongation at break, Percent	M_i , g.p.d.	D.p.f.
IA	1 $\times$	No	22°	Gamma	57	1.3	650	10.	41
IB	1 $\times$	Yes	20°	do	92	1.1	620	8.4	43
IC	1 $\times$	Yes	14°	do	94	1.9	455	10.3	15
IIA	2 $\times$	Yes	25°	do	82	2.5	215	10.5	21
IIB	4 $\times$	Yes	13°	Normal	78	4.9	45	23.3	13
IIC	5 $\times$	Yes	12°	do	63	5.5	27	56.9	9
IIIA	1 $\times$	Yes	180°	None	38	-----	-----	-----	-----
IIIB	2 $\times$	Yes	14°	Gamma	86	-----	-----	-----	-----
IIIC	3 $\times$	Yes	13°	Normal	76	-----	-----	-----	-----
IIID	4 $\times$	Yes	11°	do	66	-----	-----	-----	-----
IIIE	5 $\times$	Yes	14°	do	60	-----	-----	-----	-----
IIIF	6 $\times$	Yes	14°	do	57	-----	-----	-----	-----

For example, Table I gives TR_{25} values of 57% and 92% for items IA and IB, respectively; these are based on second cycle measurements. However, based on first cycle measurements, items IA and IB show TR_{25} values of 50% and 90%, respectively. Third and following cycle measurements conform with the second cycle measurements.

FIG. 5 is a graphic representation of an X-ray diffraction photograph of the fiber whose stress-strain curves are shown in FIG. 4. This clearly shows gamma orientation and is typical of the polypropylenes of which the fibers of the present invention are composed.

fiber IIA shows gamma orientation and a gamma intensity ratio of 1.6.

EXAMPLE III

The procedure of Example I is followed with the substitution of a spinneret containing one 0.030 inch diameter orifice, a quench intensity of 1.9 cubic feet per minute, and the use of the same speeds on all four rolls to give a windup speed of the as-spun yarn of 216 y.p.m. The as-spun monofilament (item IIIA, Table I) has a denier per filament of 108 and an as-spun orientation angle of about 180° (indicating an almost completely

unoriented structure). However, it has potential gamma orientation.

A portion of the stress-strain curve of the above yarn is shown in FIG. 3 as item IIIA. It has a compliance ratio of 16.5, outside the range for fibers of this invention.

After the above as-spun yarn is obtained, the draw rolls are adjusted to give a 2 × draw in air and the yarn designated item IIIB, Table I, is collected. Portions of this yarn are then drawn in air additionally to give total draws of 3 ×, 4 ×, 5 × and 6 × to yield items IIIC, IIID, IIIE, and IIIF, respectively. X-ray diffraction photographs of items IIIC to IIIF show no gamma orientation. A microphotometer trace of items IIIC and IIID gives gamma intensity ratios of only 0.20 and 0.12, respectively.

None of these samples, items IIIB to IIIF, as drawn, shows a TR₂₅ as much as 50%. A portion of each sample is skeined and heat relaxed at 135° C. for 10 minutes to give the TR₂₅ values reported in Table III. IIIB is a fiber within this invention and shows a fairly good TR₂₅ of 86%. None of the items IIIC to IIIF are within the invention although heat relaxation does effect noticeable improvement in their tensile recovery as Table I shows. However, even item IIIC has a TR₂₅ well below the minimum limit of 82%. Actually, item IIIC takes a permanent set on 25% elongation of over 72% greater than the IIIB fiber, a striking illustration of the loss of elastic behavior by drawing the filament 3 × as against 2 ×.

Item IIIB fiber has a compliance ratio between the limits 2 and 15 and a stress at 5% elongation between the limit 0.1 and 0.8 g.p.d.

EXAMPLE V

This example illustrates the preparation of five fibers, items V-A to V-E, Table III, all exemplifying preferred embodiments of this invention. These fibers have excellent tensile recoveries of at least 85%, gamma orientation, and heat stable orientation angles from 10° to 21°. The fibers of this example are not drawn.

Various polypropylenes are spun using the apparatus of Example I with the feed and draw rolls adjusted so that no drawing is performed and an undrawn yarn is obtained. All preparations are made with a spinneret having 34 holes of 0.012 inch in diameter similar to the spinneret of Example I except item V-C for which is used a spinneret containing 30 holes of 0.014 inch in diameter placed on a 1 inch diameter circle.

The polymer of Example I is used for items V-A and V-B. For item V-C a polypropylene of melt index 15 is made by heating the polymer of Example I in a screw extruder at 230° C. in the presence of t-butyl hydroperoxide and then adding 0.1% of 4,4'-butylidene bis(6-t-butyl m-cresol) as a stabilizer.

The polymer of Example I is repeatedly extracted with boiling commercial grade n-heptane until approximately 8% of its weight had been extracted. The residue is used to prepare item V-D.

A crystalline polypropylene of melt index 0.18 "Escon," made by Enjay Co., Inc. of 15 W. 51st St., New York, N.Y., is used to prepare item V-E.

Physical properties of the as-spun fibers after hot-relaxing at 135° C. for 10 minutes are given in Table III.

Table III

Item	Spinning Conditions					Physical Properties				
	Spinneret Temp., ° C.	Quench, c.f.m.	Windup, y.p.m.	Orientation		TR ₂₅ , percent	Tenacity, g.p.d.	Elongation at break, percent	Mi, g.p.d.	D.p.f.
				Angle	Type					
V-A*	290	3.6	100	16°	Gamma	93	1.6	480	10	12
V-B*	290	6.7	100	10-21°	do	95	1.7	396	7.5	13.6
V-C*	270	6.7	180	14°	do	87	1.3	147	10	4.4
V-D*	290	3.6	90	15°	do	93	1.7	342	12.3	12.5
V-E*	290	2.6	90	11°	do	85	1.9	190	11.3	8.2
VI-F	295	1.6	100	43°	Normal	74	1.2	497	10.0	16.6
VI-G*	295	3.6	100	10-21°	Gamma	89	1.6	520	9.7	18.5
VI-H*	295	6.0	100	18°	do	93	1.6	414	10.3	18.0
VI-I	290	2.0	100	-----	Normal	77	1.2	477	9.3	13.3
VI-J	290	6.0	100	10-30°	Gamma	84	1.6	469	9.3	13.0
VI-K*	260	6.0	100	10-21°	do	92	1.6	417	11.3	10.7
VI-L*	250	3.6	137	10-21°	do	90	1.8	312	12.7	4.1
VI-M*	250	3.6	300	10-21°	do	85	2.0	243	13.0	3.8
VI-N*	280	4.4	245	10-21°	do	90	-----	-----	-----	-----
VI-O	300	3.2	123	-----	Normal	55	1.0	509	4.7	7.4

*These fibers all have compliance ratios between 2 and 15 and show stresses at 5% elongation of between 0.1 and 0.8 gpd.

EXAMPLE IV

This example illustrates not only that heat relaxation is required to obtain the fibers of this invention but it must be appreciable to get a heat-stable orientation angle and a TR₂₅ within the range of this invention. Further, too drastic a heat relaxation (150° C. in Table II) can also be harmful.

Skeins of item IIIB of Example III (the drawn fiber before any heat treatment) are heated for ten minutes in an air oven in a tensionless state at various temperatures. The tensile recoveries from 25% elongation (TR₂₅) on the second cycle are given below in Table II.

Table II

Temperature of treatment °C.:	TR ₂₅
100	42
110	58.2
120	76.0
130	84.2
140	87.9
150	75.1

EXAMPLE VI

This example illustrates the preparation of ten fibers, items VI-F to VI-O, Table III, using different spinning variables to show the effect on the properties of the fibers produced. In all instances, the polypropylene of Example I is extruded as a melt at 289° C. using the apparatus of FIG. 1 with the feed and draw rolls adjusted so that no drawing is performed and an undrawn yarn is obtained. The resulting fibers are all subjected to identical heat relaxation, i.e., 10 minutes in a 135° C. oven in a tensionless condition.

Fibers VI-F, VI-G and VI-H are all prepared identically except that a supply of 21° C. air is fed to the quench chamber at the rates of 1.6, 3.6, and 6.0 cubic feet per minute, respectively. The spinneret contains 25 holes 0.009 inch in diameter arranged in a rectangular pattern. By reference to Table III, the marked increase in tensile recovery by increasing the rapidity of cooling of the extruded fiber, other conditions remaining constant, will be apparent. Fiber VI-F clearly is outside this invention.

Fibers VI-I, VI-J and VI-K are all prepared as above except the spinneret has 40 holes of 0.009 inch diameter in a pattern similar to that of the spinneret used in Example I and the top of the quenching chamber 11 (FIG. 2) is located one inch below the level of the face of the spinneret 9. However, the air supply and spinneret temperatures are varied as shown in Table III. The location of the quenching chamber delays the cooling of the fiber to a certain extent and fiber VI-I falls well outside this invention. Even using the same rate of air supply (6.0 cubic feet per minute) that gave the optimum VI-H fiber, only a fiber (VI-J) in the non-preferred area of this invention is obtained. It was necessary to lower the spinneret temperature to 260° C. in order to get a fiber (VI-K) approaching fiber VI-H in desirable elasticity.

The effect of windup speed alone is illustrated by fibers VI-L and VI-M spun from a spinneret having 34 holes (0.012 inch in diameter) arranged in in-line rows with the quenching chamber used as shown in FIG. 1. The faster windup speed used in spinning fiber VI-M cools the threadline too rapidly and, as a result, the TR₂₅ drops to 85% from the 90% of fiber VI-L. Both fibers, however, are well within this invention.

Fibers VI-N and VI-O illustrate the effect of a combination of spinning variables. They are spun in the same manner as fiber VI-L except for the spinning conditions set forth in Table III. Whereas fiber VI-N is a preferred specific embodiment of the invention, fiber VI-O which uses a higher spinneret temperature, a lower quench intensity, and a lower spinning speed, all conditions tending to increase the cooling time, is far outside the invention with a TR₂₅ of only 55%. It does not have gamma orientation.

EXAMPLE VII

Using a spinneret having 3 holes (0.030 inch in diameter), yarn is spun according to the procedure of Example I but using an air feed rate of 0.9 cubic feet per minute in the quench and with the feed rolls 3 and 4 running at a speed of 189 y.p.m. and the draw rolls 5 and 6 at a speed of 264 y.p.m. The three drawn filaments thus produced are separated and wound on to separate packages. One of these packages of yarn is used in this example. It is heated for 30 minutes at 130° C., the yarn being under tension since it was in package form. This effects the so-called "heat relaxation" although it is usually preferred to heat the yarn in a tensionless condition and let it shrink as much as it will. However, in the present example, it was desirable to leave some shrinkage in the yarn.

The yarn is then coned by conventional means and knitted into hose on a 400-needle single feed seamless knitting machine using 44 courses per inch. Commercial 66 nylon yarn is used for welt, heel and toe sections. Normal 66 nylon knitting conditions are used except for a lower feed tension of 0.5 gram. The knit hose is boarded on a conventional metal form for 15 minutes in 150° C. air with a resulting 14% shrinkage. After boarding, the hose are scoured at 90° C., rinsed and dried.

The hose thus formed have a good appearance and are notably superior in stretchability, indicated by high tongue stretch values, to both hose knitted from normal polypropylene yarn or 66 nylon yarn. They resist bagging as well as 66 nylon hose and are much more resistant than normal polypropylene hose.

In the following Table IV, yarn samples are removed from the hose to determine tenacity and elongation while the tongue stretch is determined on the hose as explained below.

Table IV

	Tenacity, g.p.d.	Elonga- tion, percent	Tongue Stretch, percent
1. Hose made as above.....	2.03	241	43
2. Hose made from 66 nylon yarn.....	4.84	59	22
3. Hose made from polypropylene yarn having normal orienta- tion.....	3.67	56	20

The polypropylene yarn removed from the finished hose made as above has gamma orientation, a heat-stable orientation angle of 10-30°, and a TR₂₅ of 82%. Thus it is a fiber within the present invention.

The tongue stretch values given in Table IV are determined by measuring the inside diameter of the hose at the knee shape section under no stress (D₀), under a stress of 7 grams (D₇) and under a stress of 101 grams (D₁₀₁). The stress is applied on the inside of the hose by 1 inch square plates pivotally mounted on the ends of 2 rods which rods are pivotally connected near their mid points.

$$\text{Tongue stretch} = \frac{D_{101} - D_7}{D_0} \times 100$$

It will be understood that the above examples are merely illustrative and the present invention broadly comprises a fiber of polypropylene having gamma orientation and a heat-stable orientation angle of 10° to 30°.

The preparation and description of numerous fibers not falling within the invention have been given in the examples, the purpose being to illustrate the effect of changing various process conditions. These fibers not falling within the invention are not necessarily prior art fibers. So far as known, the single closest prior art is believed to be Australian application 36,834, Example 2. This Example 2 draws the polypropylene yarn 3.5 ×, too great to obtain the fiber of this invention even if other conditions were set in the light of the teaching herein. Actually, this Example 2 is so lacking in specificity of conditions that fibers of all sorts of properties could be obtained by varying conditions not specified. The example states the yarn produced is "very bulky" which is certainly not true of the yarns whose production is described in the examples herein. It would require further process changes to make the fibers of the instant examples bulky.

As previously noted, FIG. 5 is a graphic representation of an X-ray diffraction photograph of polypropylene fiber having gamma orientation and being within the present invention; FIG. 6 is a similar representation of a polypropylene fiber which is outside of the invention and has normal rather than gamma orientation.

The diffractions 21 located on the circle 22 (2θ=14.0°) at an azimuthal angle greater than 50° from the equator 23 in FIG. 5 are characteristic of gamma orientation. No such diffraction is observed on the circle 22 of FIG. 6. The portion of the diffraction 24 that is centered on circle 25 (2θ=16.7°) determines the orientation angle of the fiber. The higher crystallite orientation angle of FIG. 5 (16°) as compared to FIG. 6 (13°) is apparent. The diffractions 26 are typical of all oriented polypropylene fiber but are not pertinent here. The diffractions 27 are located on a circle 28 (2θ=28.6°) and are used in the determination of gamma intensity ratio. It should be noted that the pattern is symmetrically divided by the equator. The meridian is located at right angles to the equator through the center of the pattern.

To those skilled in the art, the difference in the diffraction patterns of FIGS. 5 and 6 is striking and significant. The diffractions 21 of FIG. 5 are unusual and immediately reflect the unique crystalline structure of the polypropylene fibers of the present invention.

The elastomeric fibers of the present invention have an extremely favorable combination of properties, featured

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by an elasticity heretofore unknown in polypropylene fibers. Example VII shows the use of fibers of the invention in hosiery. These fibers are quite advantageous for use in such applications as automobile upholstery, seatcovers, and the like because such fabrics and material possess unusually good form recovery. The use of fibers of this invention in non-woven fabric is likewise advantageous because they impart such good form recovery.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The invention claimed is:

1. An elastomeric fiber of highly crystalline polypropylene characterized by melt index of from 0.1 to 200, said fiber having an elongation at break of from 100% to 700%, gamma orientation, a heat stable orientation angle of 10° to 30°, and a tensile recovery on the second and succeeding stretch cycles from a 25% elongation of at least 82%, said tensile recovery having been achieved by a separate heat treatment of the fiber, after it has

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been spun, at an elevated temperature of from 105° C. to 160° C.

2. The fiber of claim 1 having a gamma intensity of at least 1.0 and a heat-stable orientation angle of 10° to 21°.

3. The fiber of claim 1 having a tensile recovery on the second and succeeding stretch cycles from a 25% elongation of at least 90%.

4. The fibers of claim 1 in the form of a non-woven fabric.

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