Aug. 4, 1942. M. M. BRUBAKER 2,291,873

SYNTHETIC FILAMENT

Filed July 14, 1939

Fig. 1.

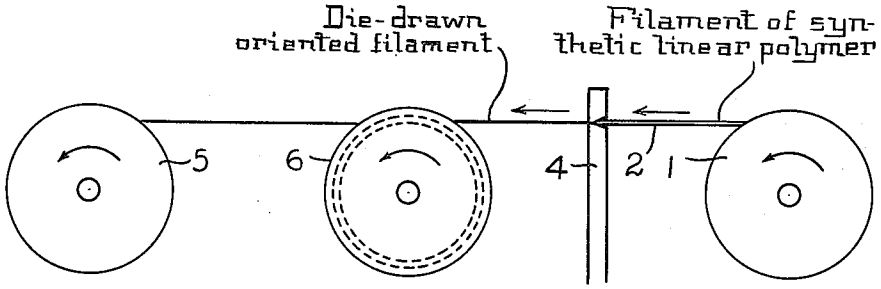


Fig. 2.

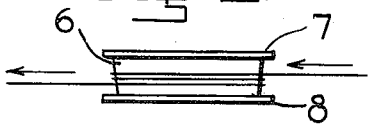


Fig. 3.

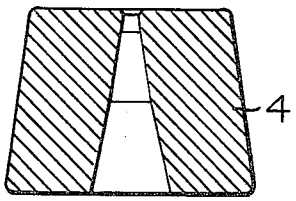


Fig. 4.

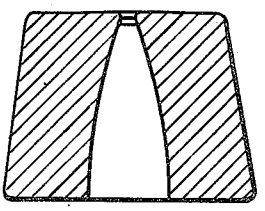
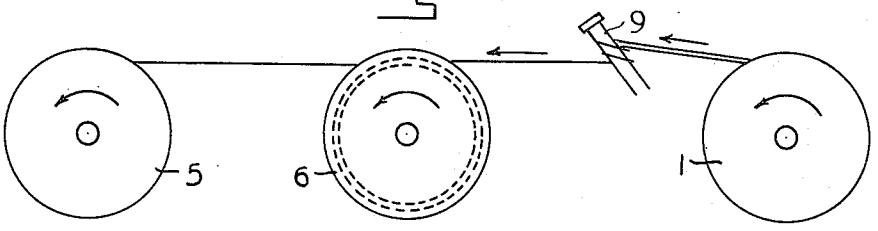


Fig. 5.



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UNITED STATES PATENT OFFICE

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SYNTHETIC FILAMENT

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Application July 14, 1939, Serial No. 284,556

2 Claims. (Cl. 18—54)

This invention relates to synthetic filaments and more particularly to the production of oriented filaments from synthetic linear polymers.

Synthetic linear polymers which are readily oriented by the process of the present invention are those described in Patent 2,071,250. Although in general applicable to these linear polymers and to other polymers capable of being oriented by drawing, this invention is particularly applicable to the synthetic linear polyamides described in Patents 2,071,253 and 2,130,948. These polyamides are of two types, namely, those obtainable from polymerizable monoaminomonocarboxylic acids and their amide-forming derivatives (ester, halide, anhydride, lactam or amide) and those obtainable from the reaction of suitable diamines with suitable dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids. On hydrolysis with strong mineral acids the polyamides revert to amino acids or diamines and dibasic carboxylic acids depending upon the reactants from which they were derived.

As indicated in the above mentioned patents, the high molecular weight, synthetic linear polyamides may be formed into useful filaments which upon application of tensile stress are permanently stretched or "cold drawn," that is, drawn in the solid state, into pliable filaments of increased strength which show by characteristic X-ray diffraction patterns that they are microcrystalline in structure and are oriented along their fiber axes. Orientation may also be effected by the application of compressive stress such as that which takes place in the process of cold rolling. The orientation of the filaments by cold drawing under tension usually takes place by a necking down process, which causes one or more portions of the filament to be completely drawn while the remainder has undergone only slight deformation. The shoulders, or points at which drawing takes place, can be seen to progress longitudinally until the whole is drawn. But in the case of larger filaments, which are more subject to breakage by this process, nodes are sometimes left at the points where two of these shoulders come together from opposite directions.

This invention has as an object new and improved methods and apparatus for drawing filaments capable of undergoing permanent elongation. A further object is the manufacture of synthetic linear polyamide filaments which have a high degree of toughness, resiliency, transparency and uniformity and which have a cross section of predetermined shape. A further object is to prepare large oriented filaments by a process which results in little or no breakage during orientation. Other objects will appear hereinafter.

These objects are accomplished by cold drawing filaments capable of being elongated at least 150% of their original length, particularly synthetic linear polymer filaments, by a method wherein the filament is gripped or held by suitable means over a small area which restricts the position of the portion of the filament at which drawing takes place (the necking or draw point) to the zone of the mentioned holding means.

In a preferred embodiment of my invention, which is particularly adapted to the production of large oriented filaments, the filament to be oriented is drawn through a die having an opening of suitable size and shape.

I have discovered that filaments of synthetic linear polymers can be successfully oriented by drawing through a die, and that this method results in decreased breakage in the case of large filaments and possesses other advantages hereinafter mentioned over the orientation of the filaments by the usual tension drawing process.

The manufacture of wire from a metal bar by drawing the bar through a tapered hole is well known. The effects and results obtained in the die drawing of the synthetic linear polymers differ widely in many respects from those accompanying the die drawing of metals into wire. In the first place the linear polymer filaments can be, and usually are, drawn to the final diameter desired in one drawing through the die, whereas in wire drawing the reduction obtained per draft varies from 5 to 40% depending upon the hardness and ductility of the metal. It is therefore necessary to pass the wire through a series of successively smaller dies to obtain a product of the desired diameter, and in some instances annealing is necessary between passages. Furthermore, the resulting wire has essentially the same diameter as the die orifice. On the other hand, the diameter of the drawn polyamide filament is normally substantially less than that of the die even though the point of drawing is within the die. The polymers have a well defined limit to the extent of possible cold drawing. In the case of the polyamides, polyhexamethylene adipamide, polyhexamethylene sebacamide, and polydecamethylene sebacamide, for example, the cold drawn filament usually has a length of three

and one-half to five times that of the undrawn filament. It is, however, possible to effect some die drawing, as much as 25 to 50% in some cases, of a filament which has been tension drawn. In the die drawing of wire there is no definite limit to the amount of elongation that may be produced in a given rod of starting material, especially if the reduction is carried out stepwise with annealing between steps.

In the manufacture of the present die-drawn oriented filaments, a die having a round opening for the production of circular cross-section filaments is used. It is possible, however, by suitable selection of the shape of the die to obtain oriented filaments of various cross-sectional shape which have increased utility for certain purposes.

In order to "thread" the die a short section of the filament is usually tension drawn, by hand, in order to reduce the diameter sufficiently to permit it to pass through the die. Another method is to trim the end of the filament to smaller diameter with a sharp knife.

An apparatus for carrying out my invention is shown on the accompanying drawing in which

Fig. 1 is a diagramamtic view in elevation illustrating the die and mechanism for drawing the filament therethrough;

Fig. 2 is a plan view of the pulley;

Fig. 3 is a cross-sectional view of the die shown in Fig. 1;

Fig. 4 shows a further form of die; and

Fig. 5 is a diagrammatic view of an apparatus which may be used in a further method involving the principle of my invention.

In the drawing, the numeral 1 indicates a bobbin from which is unwound a filament 2 of synthetic linear polyamide. The filament is drawn from the bobbin and then through the orifice of a die 4 by wind-up bobbin 5. Before passing to the wind-up bobbin 5 the filament 2, in order to localize the drawing force, is wound several times around the pulley 6 provided with flanges 7 and 8. The peripheral speed of the pulley is greater than that of the unwinding bobbin 1 in order to effect the necessary drawing. It is usually desirable to have a certain amount of cant on the flanged pulley, i. e., the diameter at one side should be slightly greater than that at the other, in order that the drawn filament may slide across its surface and not wind on itself and become tangled. The speed of the wind-up bobbin 5 is so regulated that the filament is wound up as fast as it leaves the pulleys. In Fig. 5 the draw point is prevented from shifting beyond a narrow fixed zone along the length of the filament by passing the filament around a fixed smooth pin 9 of not more than one-half inch diameter which serves to localize the draw point. By this means the draw point is maintained within a zone not more than one-half inch along the length of the filament, this distance being about the maximum permitted in accomplishing the objects of this invention. The wind-up roll, pulley, and wind-up roll correspond to those in Fig. 1.

The filament is passed around the snubber pin 9 several turns so that the tension developed by the pin will preferably be at least one-half of the tension required in the drawing operation. The pin is of smooth material, such as stainless steel, and is preferably mounted with a tilt so that successive turns of the filament about the pin will remain separated. This method of accomplishing the objects of this invention is not specifically claimed herein since it is claimed in the copending application of Dale Friend Babcock, S. N. 284,569, assigned to the assignee hereof and filed of even date herewith.

In the usual tension drawing process it is frequently advantageous to cold draw the filament between rolls with closely spaced centers. This is particularly advantageous in the drawing of tapered bristles since the difference in diameter of the bristles along its length leads to frequent breakage if the rolls are part apart. Similarly, in the die drawing process it is frequently desirable to place the pulley (Fig. 1) or a snub roll very close to the die. For example, a tapered bristle can be drawn through a V-shaped die with the aid of a snub roll so placed in order that only a very short section of the bristle (only small taper over short section) is under high tension at any one instant.

The following examples are illustrative of the practice of the present invention:

Example I

A filament of oval cross-section having extreme diameters of 105 and 125 mils was prepared from polyhexamethylene sebacamide by extruding the molten polymer through a spinneret into a bath of cold water. The solid, non-gelatinous and non-tacky filament thus prepared was drawn through a die having a round opening 56 mils in diameter at its smallest point. A continuous filament was obtained having an almost round cross-section, the largest and smallest diameters being 53 and 55 mils. When the filament initially used in the above example was tension drawn by the ordinary method, trouble was encountered due to repeated breakage and the portion successfully drawn still had an oval cross-section, the diameters of which were 44 and 60 mils.

Example II

The procedure of Example I was repeated with the exception that the filament was initially practically round, the largest and smallest diameters being 102 and 103 mils. When die drawn, a round filament having principal diameters of 57 and 58 mils was obtained.

In contrast to the results of the above examples, tension drawings even of round filaments will not always yield round filaments. Thus cold drawing of a filament like that used in Example II resulted in a filament of oval cross-section the diameters of which were 43 and 62 mils.

Example III

An undrawn filament of polymeric hexamethylene adipamide having a diameter of 25 mils was soaked in hot water and cold drawn by passing it through a die which was substantially smaller than the diameter of the undrawn filament and practically the same size as the fully drawn filament. The filament obtained was uniformly smooth and had a circular cross-section.

Example IV

A filament having extreme diameters of 102 and 109 mils obtained from a composition comprising 75 parts by weight of polyhexamethylene adipamide and 25 parts by weight of a mixture of N-ethyl-o and p-toluenesulfonamides as plasticizer was cold drawn three times through round dies having successively smaller diameters. The resulting filament was a round fiber 55 mils in diameter.

Example V

A polydecamethylene sebacamide filament 22 mils in diameter was passed through water and drawn through a slit to give a flat filament or ribbon 6 mils thick and 22 mils wide.

Example VI

A polyamide prepared by the polymerization of caprolactam was extruded to form a filament 41 mils in diameter. Upon drawing through a round die the diameter of this filament was reduced to 20 mils.

Typical examples of other polyamides which can be die drawn are polydecamethylene adipamide, polydecamethylene phenylenediacetamide, the interpolyamide obtainable from hexamethylene diamine, decamethylene diamine, adipic acid and sebacic acid, and the interpolymer obtainable from 6-aminocaproic acid, hexamethylene diamine and adipic acid.

Example VII

A polymer prepared by the interpolymerization of adipic acid, ethylene glycol and hexamethylenediammonium adipate (the latter ingredient being 15% of the whole) was extruded in the form of a round filament 92 mils in diameter. Upon die drawing a tough, elastic, transparent filament 50 mils in diameter was formed.

Example VIII

A filament of the interpolyamide prepared from 30 parts of hexamethylenediammonium adipate and 70 parts of hexamethylenediammonium sebacate was tension drawn from an original diameter of 110 mils to an average diameter of 58.5 mils. This tension drawn filament was then further drawn to a diameter of 55 mils by pulling it through a die.

Filaments prepared as in Example I by extrusion from the molten polymer followed by rapid cooling or quenching in cold water have improved toughness and pliability which further diminishes the possibility of breakage in the case of large filaments. Examples III and V are illustrative of the fact that the die drawing process is generally facilitated by the presence of absorbed water or certain other liquids, particularly hydroxylated compounds, which have a temporary plasticizing action on the polyamides. Filaments prepared from some polymers become less ductile upon aging and consequently it is frequently desirable to draw them immediately after spinning since a greater reduction in diameter can thus be obtained and the resulting filaments have greater strength and, in some cases, lower elongation.

Conditioning treatments applied after drawing the filament, particularly in the case of polyamides, are an important factor in determining its properties. Conditioning usually involves a heat treatment in the presence of water, steam, or other non-solvent swelling agents, e. g., methanol, ethanol, butanol, or aniline. Such treatments have a "setting" effect on the filament, i. e., they set the filament in a shape to which it tends to recover after deformation. During conditioning the filament tends to shrink, internal stresses are relieved, the crystal structure becomes more perfect, as evidenced by the X-ray diffraction patterns, and the elongation at break tends to increase. In too severe a conditioning treatment, especially at prolonged periods at above 70 pounds per square inch steam pressure, these benefits are at least partially counteracted by the deleterious hydrolyzing action of the steam on the polymer. This will of course depend on the composition of the polymer being conditioned. The shrinkage during conditioning (in the relaxed state) and the elongation at break for a sample of die drawn polyhexamethylene sebacamide filament are shown in the following table:

Polyhexamethylene sebacamide conditioned 30 minutes in saturated steam

Pressure (pounds per square inch)	Temperature	Shrinkage	Elongation at break*
	°C.	*Per cent*	*Per cent*
10	115.2	8.1	29
20	126.0	8.2	31
30	134.5	9.1	33
40	141.5	9.7	40
50	147.6	10.0	50
60	153.0	11.2	55
70	157.8	11.5	57
Unconditioned			25

*After standing a week in air at 50% relative humidity and 25° C.

Unconditioned filaments tend to shrink slowly upon aging. During the conditioning treatment this effect is greatly accelerated.

The polyamides referred to herein include not only the simple polyamides and interpolyamides but also interpolymers obtained by including with the poyamide-forming reactants from which the polymer is made other bifunctional reactants such as glycols and hydroxy acids. As examples of such modified polyamides may be mentioned those derived from diamines, dibasic acids and glycols (Example VII); those derived from diamides, dibasic acids and hydroxy acids; those derived from amino acids, dibasic acids and glycols; and those derived from amino acids and hydroxy acids. Like the simple polyamides these modified polyamides do not in general exhibit fiber-forming properties until their intrinsic viscosity is at least 0.4. The filaments may be conditioned either in the relaxed state, so as to allow free shrinkage to take place, or they may be held under tension. In the latter case it is advantageous to use a bobbin or holder so designed that the filaments will not be distorted in places by lateral tension or pressure since at high conditioning temperatures, in the presence of water or other swelling agents, plastic flow and/or permanent strains might be induced. In my preferred process the filament is conditioned in such a manner that free shrinkage occurs.

Filaments of from 1 to 200 mils (the term mil as used herein refers to one thousandth of an inch) diameter can be die drawn with greatest success. In the case of the small filaments a V-shaped die is sometimes useful. Die drawing is not generally applied to filaments of small diameter since these can be tension drawn satisfactorily by the prior practice. The use of a die is especially advantageous in the preparation of filaments having drawn diameters above 20 mils. The upper limit in diameter of filaments which can be satisfactorily die drawn depends upon the composition and history of the polymer; however, it frequently occurs that filaments which break upon the application of tensile stress alone can be die drawn satisfactorily.

As previously indicated, this invention is applicable to any filament capable of being permanently elongated. In most cases this will mean that the filament is composed of a crystalline material. As additional examples of such fila-

ments might be mentioned those prepared from polyesters, polyethers, polyacetals, polyurethanes, polythioamides, and solid ethylene polymer such as that described in U. S. Patent 2,153,553. The filaments may contain modifying agents, e. g., plasticizers, resins, pigments, dyes, or cellulose derivatives, such as cellulose acetate, ethyl cellulose, or cellulose nitrate. The use of a die lubricant is advantageous at times although it is usually not necessary to use a lubricant when the filament is soaked in water or other hydroxylated non-solvent swelling agent immediately prior to drawing.

The heat liberated during the drawing process is usually dissipated by radiation and by the evaporation of the wetting liquids which may be used; however, in some cases it is desirable to control the temperature and improve the lubrication by keeping the die within a liquid bath or spray.

For some uses it is desirable to modify further the cold drawn filaments by dipping them into solutions or emulsions containing waxes or oils. In the case of bristles, for example, this treatment considerably reduces the scroop or rustle of the bristles as they are crushed together, improving their handle or feel. Effective materials for this purpose are dilute solutions of montan or paraffin wax in benzene, hydrogenated peanut oil in chloroform and an aqueous emulsion of a sulfonated oil known to the trade as Stanapol 109. Other materials which may be used include an aqueous emulsion of polymeric butyl methacrylate, teaseed oil, hydrogenated castor oil in benzene, carnauba wax in chloroform and a product known to the trade as warp size 818.

The application of my invention by either of the methods described above by restricting movement of the draw point makes possible the production of filaments of uniform properties not obtainable by the prior practice. In the case of large filaments, however, the method of die drawing presents several additional advantages. Filaments which do not tension draw satisfactorily due to repeated breakage can frequently be die drawn without breakage. Filaments which give cold drawn filaments having oval cross-sections by tension drawing can, by the use of a die, be drawn into practically round filaments which in some cases have an improved degree of transparency. Die drawn filaments tend to be more uniform both in cross-sectional area and in shape than tension drawn filaments. In tensile strengths the die drawn filaments are frequently somewhat higher than that of tension drawn filaments and the elongations somewhat lower.

The present invention through the selection of different shape openings in the die makes possible the production of filaments of various forms, for example, filaments which approach being triangular, square, rectangular, oval, star, etc. Thus the filaments may be made straw-like for the use of hats or cane-like for use in the manufacture of wicker-work or furniture. Bristles having a star shaped cross-section have better stiffness than those having the same cross-sectional area in the form of a circle. Although the amount of distortion that may be produced in a filament in the drawing step is limited, the configuration of the cross-section of the drawn filament tends to conform to that of the die annd may be distinctly different from that of the tension-drawn filament as illustrated in Examples I, II and V. This indicates that die drawing involves compressive forces as well as tension forces. The fact that die drawn products are more transparent than tension drawn products is further evidence that compressive forces are involved, for cold rolling (application of compressive force) brings about an improvement in clarity.

The large filaments described above are particularly useful as strings for badminton, squash and tennis rackets and for musical instruments. They are also useful where continuous monofils of high strength are required, and in such uses as fishline leaders where the high degree of moisture resistance and toughness are of advantage.

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 I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for drawing in the solid state filaments of synthetic linear polymer into oriented filaments having a uniform diameter with decreased tendency of breakage of the filaments in the drawing operation, said process comprising unwinding a filament of synthetic linear polymer in an essentially non-gelatinous, nontacky state and capable of at least 150% permanent elongation in the solid state from an unwinding supply roll to a roll moving at greater speed to provide a drawing force, and restricting the movement of the draw point to a small fixed distance not exceeding one-half inch along the length of the filament by holding the filament in its travel between said rolls in tension-developing contact with a rigid surface corresponding to said distance, the tension developed in the filament on said rigid surface being at least one-half that required to draw the filament.

2. A process for drawing in the solid state filaments of synthetic linear polymer into oriented filaments having a uniform diameter above 20 mils with decreased tendency of breakage of the filaments in the drawing operation, said process comprising unwinding a filament of synthetic linear polymer in an essentially non-gelatinous, non-tacky state and capable of at least 150% elongation in the solid state from an unwinding supply roll to a roll moving at greater speed to provide a drawing force, and restricting the movement of the draw point to a small fixed distance not exceeding one-half inch along the length of the filament by passing the filament in its travel between said rolls through a rigid die having an orifice of substantially smaller cross-sectional area than that of said filament from said first mentioned roll.

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