

March 19, 1963

H. BLADES ET AL
FIBRILLATED STRAND

3,081,519

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3 Sheets-Sheet 1

FIG. 1

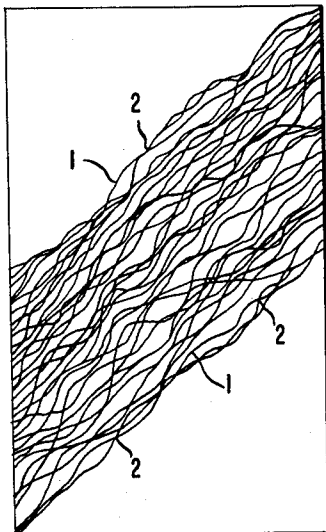


FIG. 2

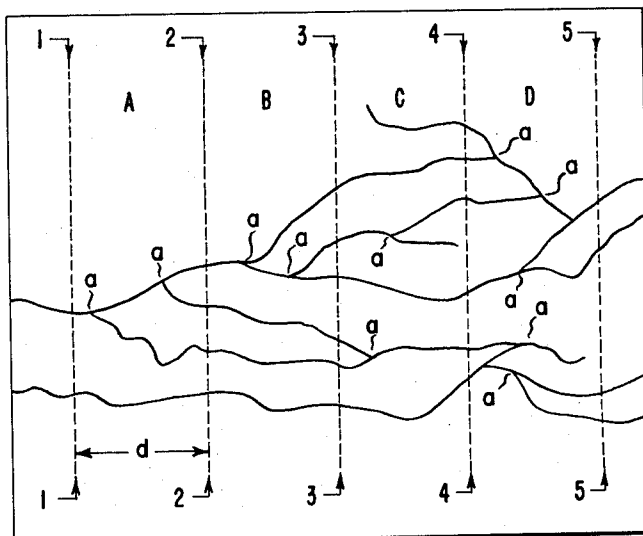


FIG. 3

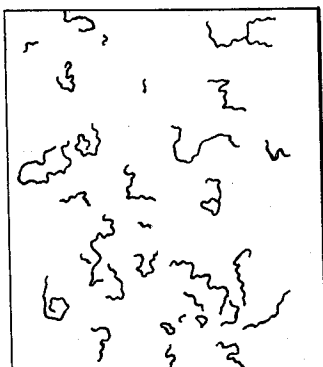


FIG. 4a

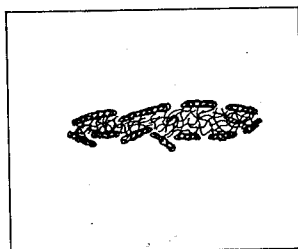


FIG. 5

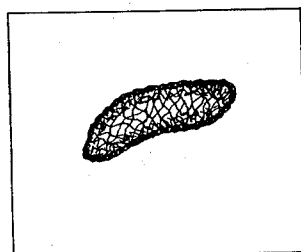
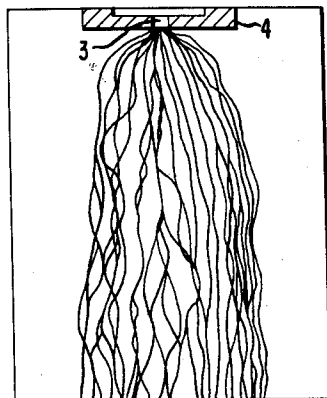


FIG. 4b

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FIG. 6

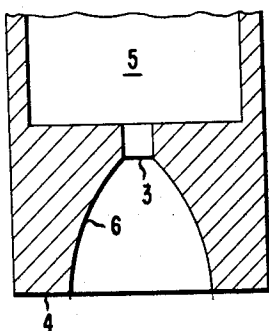


FIG. 7

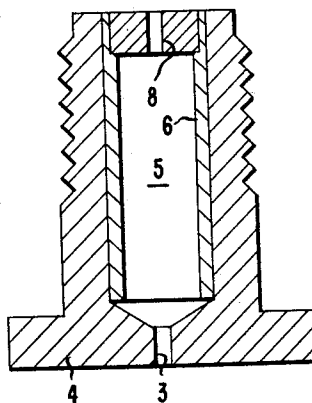


FIG. 8

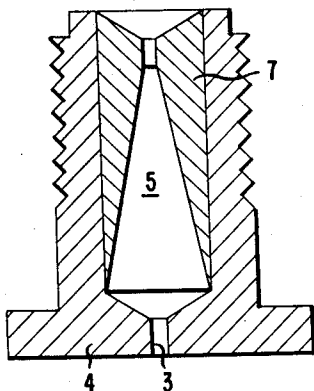


FIG. 9

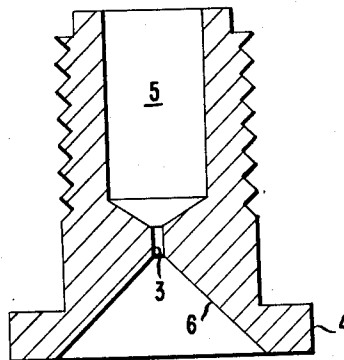


FIG. 10

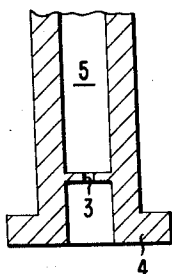
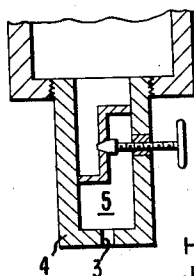


FIG. 11



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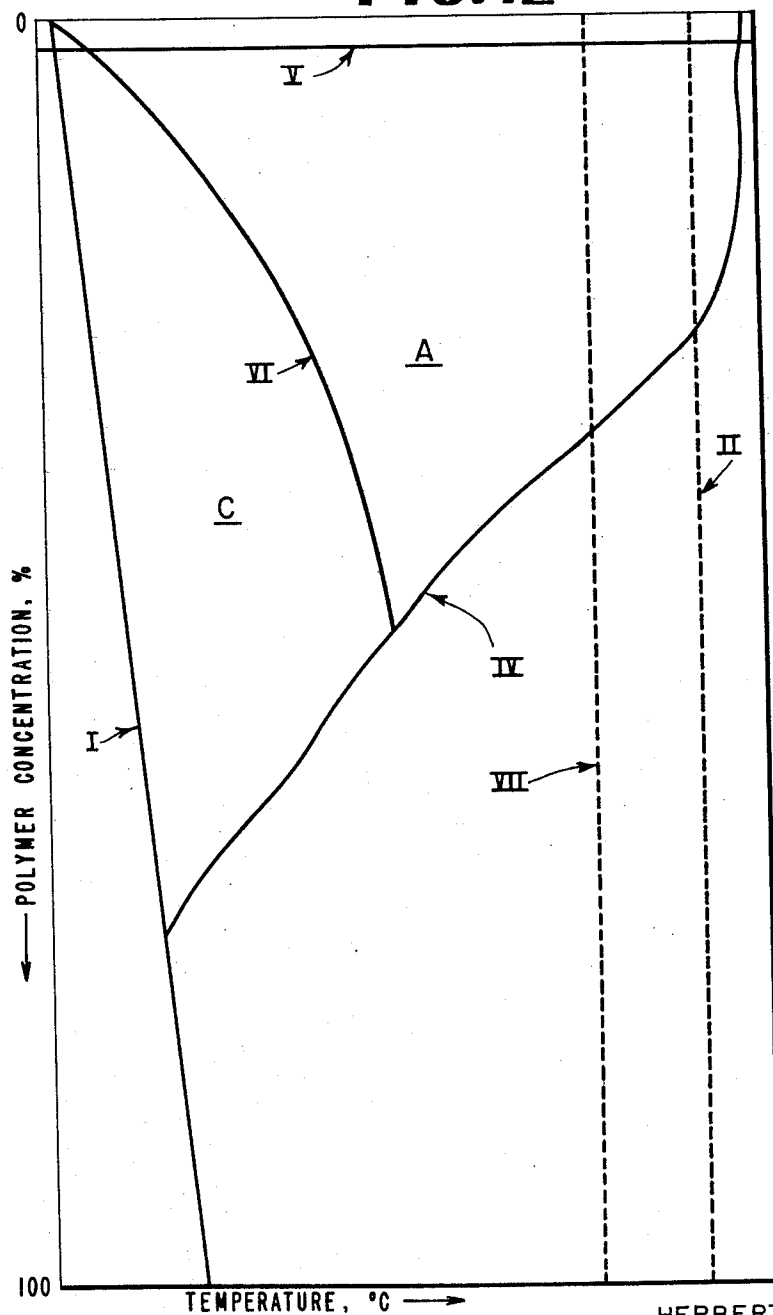
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FIG. 12



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FIBRILLATED STRAND

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Filed Jan. 31, 1962, Ser. No. 170,182

21 Claims. (Cl. 28—81)

This invention relates to a new process for shaping fiber-forming polymers and the novel multi-fibrous strands thereby produced.

Synthetic polymers in fluid form can be directly converted into solid fibrous products by various procedures. Exemplary of such methods are the conventional extrusion through multi-hole spinnerets of polymer solutions, polymer melts, plasticized polymer compositions, and reactive polymer precursors; spray gun methods wherein air jets or electrical fields are made to attenuate a stream of fluid polymer; shear precipitation methods; and others.

In general, those procedures which can directly produce multi-filament, yarn-like strands of adequate uniformity and texture for textiles usually require critical process control and afford relatively low productivity. Thus, for example, conventional spinning through multi-hole spinnerets requires that the fluid polymer be carefully filtered to prevent clogging of the minute orifices. In addition the polymer viscosity must be low enough to permit extrusion at practical pressures, and yet high enough so that re-solidification of the polymer in fibrous form will occur with reasonable ease. Polymers of high molecular weight, which generally impart desirable physical properties to fibers such as increased strength and flexibility, often cannot be spun from conventional spinnerets since melt or solution viscosities are often too high for extrusion at reasonable pressures. Multi-filament strands produced by multi-hole spinnerets have, because of their fineness and consequent high surface area, greater bulk and covering power and better texture than a monofilament strand of equal denier. However, further improvements in these properties cannot be obtained by reduction of filament denier since individual filament diameters less than about 4 microns are not ordinarily obtainable. Furthermore, production is limited by the fact that each filament, regardless of size, requires a separate orifice in the spinneret.

Multi-filament strands consisting of a bundle of parallel filaments are often difficult to handle in textile operations because the individual filaments tend to stray from the main bundle and become entangled with adjacent strands. Contact with surfaces during backwinding or other operations interferes with yarn handling. This problem is generally more serious, the finer the individual filament deniers. Thus, it is often necessary to improve the integrity of these strands by twisting or the application of a size.

Spray gun, shear precipitation and similar methods form short fine random length fibers of irregular configuration at higher productivities and with fewer critical process limitations. Such fibrous products are suitable for textile use. However, these methods do not without further processing produce textile strands of adequate strength and uniformity for use in acceptable quality fabrics.

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It is an object of the present invention to provide a novel process for spinning synthetic polymers. It is another object to provide a process for the production of integral, multi-fibrous, bulky strands directly from fluid polymer. Another object is to provide a high productivity process for making multi-fibrous strands of high strength and uniformity. Still another object is the production of such products which are processable by conventional textile machines and methods into acceptable quality fabrics. Another object is to provide an integral multi-fibrous yarn-like strand of high surface area wherein the fibrous elements are film-like materials defined in greater detail below and which have a film thickness on the average under about 4 microns. A further object is to provide a high productivity spinning process for the production of a multi-fibrous strand by extrusion of a fluid polymer from a single orifice wide enough to obviate fine filtering of the fluid polymer and to accommodate high viscosity solutions of high molecular weight polymers. Other objects and advantages will be apparent from the following specifications and the appended claims.

In accordance with the present invention a novel and useful multi-fibrous, yarn-like strand is formed by extruding a homogeneous solution of a fiber-forming polymer in a liquid which is a non-solvent for the polymer below its normal boiling point, at a temperature above the normal boiling point of the liquid, and at autogenous pressures or greater into a medium of lower temperature and substantially lower pressure. The vaporizing liquid within the extrudate forms bubbles, breaks through confining walls, and cools the extrudate, causing solid polymer to form therefrom. The resulting multi-fibrous yarn-like strand has an internal fine structure or morphology which may be characterized as a three-dimensional integral plexus consisting of a multitude of essentially longitudinally extended interconnecting random length fibrous elements, hereafter referred to as film-fibrils, which have the form of thin ribbons of a thickness less than 4 microns. The film-fibril elements, often found as aggregates, intermittently unite and separate at irregular intervals called "tie points" in various places throughout the width, length and thickness of the strand to form an integral three-dimensional plexus. The film-fibrils are often rolled or folded about the principal film-fibril axis, giving the appearance of a fibrous material when examined without magnification. The strand comprising a three-dimensional network of film-fibril elements is hereafter referred to as a plexifilament. The plexifilaments are unitary or integral in nature, meaning the strands are one piece of polymer, are continuous in nature, and the elements which constitute the strand are cohesively interconnected. Minor physical treatments of the continuous strand such as shaking, washing, or textile processing will not cause appreciable amounts of the film-like elements to separate from the strand.

Two classes of the plexifilamentary strands are described in detail in subsequent paragraphs. They are (1) a fibrillated strand which is very fibrous in nature and is an open network of narrow ribbon-like elements or film-fibrils generally coextensively aligned with the longitudinal axis of the strand; and (2) a partially condensed strand having the structure of the fibrillated strand and containing densified sections of film-fibril layers.

The latter class encompasses plexifilamentary strands in any of several forms termed monotubular, split tubular and ribbon or highly split tubular all described in greater detail below.

A better understanding of the invention may be obtained by reference to the figures:

FIGURE 1 is a schematic drawing of a longitudinal microscopic view at about four power magnification ($4\times$) of a plexifilament consisting predominantly of film-fibrils 1 having tie points 2 throughout the strand.

FIGURE 2 is a schematic drawing of longitudinal microscopic view (at about $250\times$) of a spread out fibrillated strand.

FIGURE 3 is a drawing of a cross-sectional microscopic view of a portion of the fibrillated structure of FIGURE 1 (about $420\times$). The film-like nature of the film-fibrils in the fibrillated species is indicated in the cross-sectional view of FIGURE 3.

FIGURE 4(a) is a schematic drawing of a cross-sectional view (at about $4\times$) of a ribbon strand.

FIGURE 4(b) is a schematic drawing of a cross-sectional view (at about $4\times$) of a monotubular strand.

FIGURE 5 is a drawing showing a fibrillated plexifilament being spun.

FIGURES 6, 7, 8, 9, 10, and 11 are drawings showing cross-sectional views of spinnerets suitable for use in the practice of the present invention.

FIGURE 12 is a graphical representation showing the effect on strand morphology of initial spinning solution concentration and temperature.

For the purpose of simplifying the visualization of the fibrillated plexifilament strands, one may suppose that all the morphological elements of the plexifilament are derived from bubbles in the viscous solution which form rapidly as the pressure is reduced during the initial stage of conversion of fluid polymer to strand. The bubbles then grow and rupture in various ways to form the multi-fibrous network. The extreme thinness of the pellicular material imparts desirable aesthetic properties such as softness and suppleness to plexifilaments and enables them to be easily discernible from multi-fibrous strands or coarsely porous fibers of the prior art.

The strands of this invention are continuous in nature and can be produced in essentially endless lengths. They can be wound on bobbins, or other packages or can be cut into short staple lengths like other textile strands. The whole strands can have deniers as low as 15 or as high as 100,000 or even higher. Preferably, they have deniers between 100 and 10,000. They can exist in a condensed moderately fibrillated form or can exist in a highly fibrillated form. The latter form in heavy deniers has the appearance of silver or tow from extremely fine fibers. The film-fibrils of the present invention, however, are connected in a network, there being few if any unconnected fibril ends.

The strands of this invention have tenacities of at least 1.0 g.p.d. and when drawn give tenacities as high as 23.0 g.p.d. They were twisted 8 t.p.i. before measurement.

All of the strands of this invention are characterized morphologically by a three-dimensional network of film-fibril elements. These networks may exist in various forms, but in all cases the film-fibrils are extremely thin. On the average the film-fibril thickness determined as described below is less than 4 microns thick. In the preferred products the film-fibrils are less than two microns thick and may indeed have a thickness of less than 1 micron. The film-fibril elements are at least five times as wide as they are thick, the actual width being between about 1 micron and about 1000 microns.

The thickness of the film-fibril elements may be determined by use of the interferometer microscope. Samples are prepared by pressing a strip of cellophane adhesive tape ("Scotch Tape") against the plexifilament. (In the case of the monotubular type, the material is cut open first to expose the film fibrils.) The adhesive

tape is then pulled away from the strand and then has film-fibrils adhering to it. It is dropped into chloroform which dissolves the adhesive material and frees the film-fibril elements for observing on a microscope slide.

The film-fibril elements in plexifilaments are found in the form of fibril composites which are laminates, aggregates or bundles within the gross strand. Because these fibril composites continuously divide and parts of them join other bundles, it is difficult to count individual film-fibrils in the strand. However, for convenience, the average number of fibril composites in a 0.1 mm. thick cross-sectional cut of the strand is used as a measure of degree of fibrillation. The number of these fibril composites per 1,000 denier in a 0.1 mm. length of strand is hereafter referred to as the free fibril count. It is recognized that the number of additional film-fibrils which can be pulled away from the fibril composites with slight tension will be many times the number found already free, but film-fibrils which adhere to each other are not counted as separate fibrils in the standard test.

For the purposes of this invention, the free fibril count is determined by immersing a sample of the strand in water containing a small amount of wetting agent such as "Triton" X-100, a product of Rohm and Haas. The wet sample is frozen using a bath of liquid nitrogen and is then transferred to a freezing microtome where cross sections are cut 0.1 mm. thick. After cutting, each section is dispersed in a drop of water on a microscope slide. After the water has evaporated, the number of fragments in each section is counted under a microscope at about $50\times$ magnification. The average number of fragments per section is used as a quantitative measure for the degree of fibrillation. The test is run on three sections separated from each other along the length of the strand and the results are averaged. The denier of the strand is determined by weighing a few centimeters of strand. Then the data are reported as free fibrils/1000 denier/0.1 mm. length.

FIGURE 2 is an enlarged longitudinal view of a portion of the strand of FIGURE 1 to show the network structure of plexifilaments. It is planar projection of the three-dimensional network. The points *a* represent tie points in the structure. The lines 1-1, 2-2, 3-3, 4-4, and 5-5 represent the location of cross-sectional cuts taken in a plane perpendicular to the paper and to the strand axis. The distance *d* is the thickness of the cross-sectional cut. In the specified free fibril count for this invention the distance *d* is 0.1 mm. In this particular example cross-sections A, B, C, and D, will have free fibril counts of 2, 4, 6, and 2, respectively, if the fibrils are not welded together by the cutting process. Welding is avoided by freezing the strand before cutting. Preferably more than half of the fibrils have lengths under 1.5 cm. (i.e., between points of attachment). The tie points being spatially arranged in various planes along the width, length and depth of the strand are responsible for the three-dimensional structure which results.

The predominantly longitudinal orientation of the film-fibrils of all plexifilament strands is readily apparent from the fact that all such strands are much more resistant to tearing or breaking transversely than to splitting lengthwise. The general coextensive alignment of the fibrous elements in the direction parallel to the strand axis is easily discernible to the naked eye for most plexifilamentary species.

The plexifilamentary strands of the invention are made of crystalline polymer. It has been found, quite unexpectedly, that the pellicular material in the as-spun strand when consisting of a crystalline polymer is substantially oriented as measured by electron diffraction, i.e., it has electron diffraction orientation angles smaller than 90° . It is believed that the high strength of the plexifilamentary strand as spun is closely related to the crystalline orientation within the film-like ribbon and in the structural arrangement of the fibrils themselves in the strand. In the

preferred crystalline oriented products of the invention, the film fibrils have electron diffraction angles of less than 55° . The orientation of the crystallites in the film-fibrils is in the general direction of the film-fibril axis.

X-ray diffraction patterns which are obtained using the whole strand instead of just film-fibrils show a substantial amount of orientation in the strand as spun. The X-ray diffraction orientation angles are less than 55° in the preferred embodiments of the invention. The substantial orientation which is exhibited by the gross strands indicate that not only are crystallites oriented along the fibrils, but the fibrils are themselves oriented in the general direction of the strand.

Plexifilament strands have a surface area greater than $2 \text{ m}^2/\text{g}$, as measured by nitrogen adsorption methods. Due to the extremely high polymer/air interfacial area the strands have marked light scattering ability and high covering power. The surface area of the plexifilamentary strand is determined using essentially the procedure and apparatus described in Faeth, P. A., Willingham, C. B., "Technical Bulletin on the Assembly, Calibration, and Operation of a Gas Adsorption Apparatus for the Measurement of Surface Area, Pore Volume Distribution, and Density of Finely Divided Solids," Mellon Institute of Industrial Research, September 1955. In this procedure, the surface area is calculated from the amount of nitrogen adsorbed by the sample at liquid nitrogen temperature by means of the Brunauer-Emmett-Teller equation using a value of 16.2 square angstroms for the cross-sectional area of the adsorbed nitrogen molecule.

An important characteristic of the strands of this invention is the fibrillar texture of the gross strand as observed with the polarizing microscope.

In order to observe fibrillar texture, a specimen is prepared as follows: a short length of strand is frozen in liquid nitrogen and a segment which is 1-5 millimeters long is cut from the frozen strand. The segment is placed on its side in immersion oil on a microscopic slide, and the slide is placed in a vacuum chamber and pumped down to remove trapped air. After removing the slide from the vacuum chamber, the specimen is observed in a polarizing microscope using about $45\times$ magnification. A cover glass is used over the immersed sample. The view which is seen in the microscope is of a longitudinal segment of the whole strand. A first order red plate is used in the microscope and the Nicols prisms are crossed at 90° to one another.

A striking color view of the sample is seen in the polarizing microscope. In the strands of this invention long streaks of uniform color run parallel to the strand axis. Although there are variety of colors, each color extends for long periods along the length of the strand. An interpretation of the polarized light patterns may be found in Fiber Microscopy, by A. N. J. Heyn, Interscience Publishers, 1954, pp. 288-352. Monochromatic streaks in color photomicrographs taken with polarized light are derived from areas of equal optical path difference and in general will be due to equal orientation and equal thickness in the strand. These photos demonstrate therefore that the strands have a high degree of organization, and the highly organized areas extend for considerable distances along the length of the strand. The strands are characterized as fibrillar if at least half of the material making up the strand appears as monochromatic streaks when observed in the polarizing microscope. The monochromatic streaks are oriented in the direction of the strand axis and have an actual (unmagnified) length of at least 0.2 mm. The monochromatic areas are considered as streaks when they have a length at least 10 times the width.

While all of the species of this invention have the strand and film-fibril characteristics described in the preceding paragraphs, certain species can be singled out and described in more detail. The most distinctive of

these are the fibrillated strand, the monotubular strand, the split tubular strand and the ribbon strand.

A fibrillated strand is illustrated in FIGURE 1 which is a longitudinal photomicrograph of the strand at about four-fold magnification. This strand consists of a three-dimensional integral plexus of film-fibrils which are separated from each other laterally, and extend generally in a longitudinal direction along the length of the strand. The film-fibrils are interconnected at random intervals in both longitudinal and transverse directions to provide a three-dimensional network or lattice in which all elements are integral with each other. In some instances, it is possible to detect minor amounts of polymeric material present which is not in the form of film-fibrils but rather as small polymer masses and other forms. The quantity of this material is however insignificant and exerts no deleterious effects on the properties of the strand.

The fibrillated plexifilament is a soft, supple strand having the outward appearance of a bulky, staple spun yarn. When examined at $400\times$ magnification, the film fibrils have the appearance of ribbons of extremely thin pellicular material, folded or rolled approximately about the film-fibril axis. For this reason they appear to be fibrous when examined without magnification.

In the most preferred form, the fibrillated strands can be spread transversely to many times their original width without breaking any appreciable number of film-fibril elements. In general, the film-fibrils separate when the strand is stretched transversely instead of breaking. The thickness of pellicular material in the cross-section averages less than 4 microns.

The free fibril count for the fibrillated species is at least 50 free fibrils/1,000 denier/0.1 mm. length and counts of 1,000 or higher are obtained with strands of this species. The strands will however, have a minimum of 25 free fibrils per 0.1 mm. length regardless of denier.

The fibrillated species of this invention is especially preferred for preparing fabrics with high optical cover and exceptional softness. For cigarette filters the predominantly fibrillated species is preferred because of its very high adsorptive capacity at a filter pressure differential of about 3 inches of water. The high surface area also provides these plexifilament strands with high reactivity toward chemical treatments and remarkable adsorption efficiencies in applications such as in packing material for gas chromatography columns. These advantages of fibrillated plexifilament strands, attributable to high interfacial surface area, i.e., a large area of polymer contacting the atmosphere, are not achieved by conventional fine denier yarns, closed-cell foam yarns or strands having a coarsely porous morphology.

The monotubular embodiment of this invention comprises a tubular strand having a film-like outer wall and a fibrous interior. The outer wall which is not necessarily cylindrical is a fibrous skin comprising a dense laminate of film-fibrils. The fibrous nature of the outer wall can ordinarily be demonstrated by examination under a microscope, by working or by pressing a strip of cellophane adhesive tape against the plexifilament as mentioned above. Within the tube is a more open film-fibril network structure whose outer portion, i.e., that part closest to the tube wall, appears to be partially embedded in, connected to or a continuation of the plexifilament structure at the inside of the tube wall. Near the film wall on the inside of the tube, the film-fibrils are layered together in close association, but near the center of the strand, the film-fibrils are in a fairly open configuration. In some cases the film-fibrils on the inside of the tube criss-cross one another to form a diamond pattern, which is readily visible when the tube is cut open longitudinally. Often the center of the tube is open enough to allow free passage of air through a substantial length of the strand whenever one applies air pressure as by blowing through the strand. In other instances the material cannot be expanded by applying air pressure.

A probe or dissecting needle simply punctures one of the walls when an attempt is made to separate the walls.

Despite the embedded nature of the film-fibrils in the monotubular species, the structure is nevertheless three-dimensional in nature and has the other characteristics of an integral film fibril plexus. For example, this species has a surface greater than 2 m.²/g. and a film thickness less than 4 microns. The three-dimensional nature of the film-fibril network is obvious in longitudinal views of the fibrous interior. In addition, it is obvious when film-fibril elements are pulled from the inside wall of the structure that the elements are arranged in a three-dimensional network. A cross-sectional view of the monotubular embodiment is shown in FIGURE 4(b). The tube collapses during spinning. The view presents a partially inflated embodiment.

Strands of extremely high strength can be obtained by drawing some monotubular yarns. These may be knit or woven into fabrics of high strength. In addition, these strands may be beaten or chopped to produce fibrils as defined in Morgan U.S. Patent 2,999,788 with high strength in the wet-laid form.

The split tubular and highly split tubular or ribbon strands of this invention are closely analogous species. Whereas the monotubular strand appears to have a continuous skin or casing, the split tubular strand has one or more slits in the dense skin running in the machine direction of the strand, thus exposing portions of inner less dense network material. It is postulated that under spinning conditions more extreme than those employed with the monotubular strand, the solvent vapor escapes at such great velocity as to split the outer skin which forms. The split tubular strand has its wall essentially intact. The ribbon strand, a name descriptive of its shape, presents an outward appearance of wall fragments of indefinite width and length interspersed with coarsely fibrillated material when examined under the microscope. It is believed to be formed by the complete rupture of a monotubular strand during spinning. Both of these species can be drawn to obtain strands of very high tenacity or can be beaten in an aqueous system to obtain fibrils suitable for use in making synthetic papers.

The continuous strands of this invention are satisfactory for processing on standard textile equipment. Furthermore, these plexifilament strands can be drawn from 2× to 13× to achieve extremely high tenacities. For example, plexifilaments of linear polyethylene drawn about 11.5×, having achieved tenacities of about 23 grams/denier; whereas conventionally produced fibers of the same polymer do not exceed 13 grams/denier. This strength level surpasses all other synthetic polymer fibers and clearly points out the novelty and remarkable attributes of the present invention. Drawing a plexifilament changes its appearance also; it becomes a lustrous, compact, low bulk structure which has the appearance of a conventional untextured continuous filament yarn. From this status it can be worked into a fluffy, high bulk material again, if desired, by blowing air through it or by any other conventional method.

Drawing can be accomplished with the usual means, e.g., hot plate, hot pin, liquid bath, drawing rolls, air jets, etc.

The plexifilaments of this invention may be prepared from synthetic filament-forming polymers or polymer mixtures which are capable of having appreciable crystallinity and a high rate of crystallization. A preferred class of polymers is the crystalline, non-polar group consisting mainly of crystalline polyhydrocarbons. Common textile additives such as dyes, pigments, antioxidants, delusterants, antistatic agents, reinforcing particles, adhesion promoters, removable particles, ion exchange materials, and U.V. stabilizers may be mixed with the polymer solution prior to extrusion.

Suitable liquids for use in forming the high temperature, high pressure polymer solutions required for forming

the plexifilaments of the invention should preferably have the following characteristics: (a) a boiling point at least 25° C. below the melting point of the polymer used; (b) it should be substantially unreactive with the polymer during extrusion; (c) it should be a solvent for the polymer under the temperature and pressure conditions suitable in this invention as set forth below; (d) it should dissolve less than 1% of the high polymeric material at or below its normal boiling point; and (e) the liquid should form a solution which will undergo rapid phase separation (i.e., in less than .01 second) upon extrusion forming a non-gel polymer phase, i.e., a polymer phase containing insufficient residual solvent to plasticize the structure. In these requirements, the process of the present invention differs radically from conventional solution spinning techniques, wherein the spinning solvent is invariably a solvent for the polymer below the normal boiling point and generally is a solvent at a room temperatures.

Among those liquids which may be utilized in the spinning process, depending upon the particular polymer used, are aromatic hydrocarbons such as benzene, toluene, etc.; aliphatic hydrocarbons such as butane, pentane, hexane, heptane, octane, and their isomers and homologs; alicyclic hydrocarbons such as cyclohexane; unsaturated hydrocarbons; halogenated hydrocarbons such as methylene chloride, carbon tetrachloride, chloroform, ethyl chloride, methyl chloride; alcohols; esters; ethers; ketones; nitriles; amides; fluorocarbons; sulfur dioxide; carbon disulfide; nitromethane; water; and mixtures of the above liquids.

Flashing off of solvent during the spinning process of this invention is similar in some respects to the flash evaporation of solvent in flash distillation procedures. The rapid and substantial reduction in pressure upon the confined polymer solution when the valve is opened results in the production of bubbles within the still fluid polymer followed by expansion of the bubbles and evaporative cooling of the polymer to form pellicular material which ruptures and deforms with resultant production of the integral plexus of this invention. The initial heat content of the spinning solution will affect the final morphology. If the initial heat content is too small, a closed cell morphology will result and if too high, a sintered product will be produced. It is surprising that despite the violent nature of the process, indefinitely continuous strands may be obtained.

Certain principals which are helpful in establishing the optimum conditions for preparing products of this invention may be demonstrated by reference to FIGURE 12. This figure is a generalized diagram, descriptive of a large number of polymer/solvent systems, showing the effect of changes in spinning solution temperature and polymer concentration on the product morphology. The ordinate of the diagram indicates the initial polymer concentration in weight percent for the solution, the low polymer concentrations being at the top of the diagram and the high concentrations at the bottom. The abscissa indicates the initial temperature of the solution in degrees centigrade, the highest temperatures being toward the right of the diagram. The various areas of the figure indicate the type of strand morphology obtained from certain combinations of temperature and polymer concentration.

Curve I represents the freezing points of a given polymer solvent system at various concentrations.

Curve II represents the critical temperature, T_c , of the solvent (° C.). The fibrillated species is in general obtained at temperatures above $T_c - 45^\circ$ indicated by dotted line VII and may be obtained at temperatures even above the critical temperature. If nucleating agents are present, the temperatures which may be employed can be even lower than $T_c - 45^\circ$.

Curve V is a boundary representing a concentration of 2% polymer in solution. At concentrations lower than

2% continuous strands are generally not obtained. The product obtained from concentrations below 2% is usually a discontinuous fibrous mass or a solvent-laden material.

Curve IV represents a series of borderline conditions. Combinations of temperature and concentration below curve IV give sintered products, either sintered foams or coarse sintered fibrillar material. Conditions of concentration and temperature above curve IV give either cellular products (area C) or products comprising film-fibrils (area A).

Curve VI is a boundary line separating the conditions for making cellular products and making film-fibril products. In general lower temperatures and higher polymer concentrations favor the formation of cellular products. All temperatures on the graph are higher than the normal boiling point of the solvent.

Area A of FIGURE 12 bounded by lines IV, V, and VI defines the initial conditions of spinning solution temperature and concentration which, in conjunction with other herein described process factors, will produce the plexifilamentary strands of the present invention. The selection of specific temperatures and concentrations for spinning a particular polymer-solvent combination to produce the product of the invention would be well within the skill of the art in view of the aforementioned teachings.

It is preferred to use conditions of temperature above the normal melting point of the 100% pure polymer, and polymer concentrations below 30%. For the fibrillated species, it is especially preferred to operate at temperatures within 45° C. of the solvent critical temperature. It has been found that a linear polyethylene-methylene chloride system yields the product of the invention when the polymer concentration on a weight percent basis is between 2 and 20% and the temperature is above ($T_c - 45^\circ \text{C.}$) or 193° C.

The solution may also contain dissolved therein, a gas, i.e., a substance which is normally gaseous under the conditions of temperature and pressure prevailing on the downstream side of the spinning orifice. Thus, gases such as N_2 , CO_2 , He, H_2 , methane, propane, butane, ethylene, propylene, butene, etc., may be employed. The presence of a dissolved gas is generally conducive to the production of the highly fibrillated morphology. In this connection, the less soluble gases are generally preferred, i.e., gases which dissolve in the polymer solution under spinning conditions to the extent of less than 7% at saturation based on the weight of the solution.

It is preferred to operate the extrusion process at velocities which produce more than about 3,000 yards of plexifilament per minute. At these velocities, an internal orientation force is exerted on the polymer solution during the brief formative interval in which the polymer solution undergoes transition first to a system containing vapor bubbles and polymer solution, and thence to a shaped solid; during which time critical transient viscosity and velocity gradients exist. The orientative force facilitates the general longitudinal orientation of the fibrils which characterizes plexifilaments.

Plexifilamentary strands can be produced at velocities as high as about 17,000 y.p.m. and higher. The extrusion velocity appears to be generally dependent upon the pressure gradient across the orifice, the orifice length and cross-sectional area, solution viscosity, and the geometry of the low pressure side of the orifice. The pressure within the extrusion vessel may be increased by using higher temperatures to obtain higher autogenous pressures, or using pumps, pistons, or inert gases under high pressure. Also, the pressure may be reduced in the region of lower temperature and pressure into which the solution is extruded.

In general, the fibrillated strands with free fibril count greater than 50 fibrils/1000 denier/0.1 mm. are produced using spinning conditions of low polymer concen-

tration and/or higher temperatures, or conditions producing high rates of bubble nucleation before the solution leaves the orifice. High rates of bubble nucleation may be obtained in the following ways: (1) A dissolved gas, especially a very slightly soluble one, may be dissolved in the solution prior to extrusion. (2) A preflashing chamber may be employed, as described in the discussion below of FIGURE 7, wherein a pressure slightly less than the pressure in the heated pressure vessel prevails. (3) Solution temperatures within 45° C. of the critical temperature of the liquid may be employed, since at these temperatures the liquid becomes self-nucleating with respect to bubble production. (4) Finely divided inert particles may be dispersed in the spinning solution to act as sites of bubble nucleation.

Monotubular plexifilament strands may be obtained in general by spinning from spinnerets similar to FIGURES 6 and 10 which have a shroud or tunnel following the spinneret orifice and which do not have two orifices in tandem. In general the temperatures should be lower and the concentration should be higher than for producing fibrillated strands.

The ribbon strands are produced by extruding at lower temperatures or pressures or by using higher polymer concentration than with fibrillated strands.

The design of the orifice and neighboring structural elements affect the nature of the product obtained. For example, the spinneret device of FIGURE 7 provides a chamber 5 having an intermediate pressure between the extrusion orifice 8 of the vessel and the actual spinning orifice 3, thereby nucleating or inducing bubble formation. Nucleation gives rise to a high bubble count with subsequent production of highly fibrillated structures of relatively low strand deniers. The spinneret assembly in FIGURE 8 contains a venturi insert 7 and is a useful alternate for the spinneret of FIGURE 7. The orifice diameter is generally from 4 to several hundred mils. The spinneret of FIGURE 9 having a taper of about 120° leading toward the internal end of the orifice and a flare 6 of roughly 90° extending about 500 mils outwards from the orifice, is useful for spinning from methylene chloride at temperatures over about 195° C. for producing high strength strands. The spinnerets of FIGURES 6 and 10, having a downstream shroud or tunnel chamber following the orifice, are conducive to the production of continuous strands having a monotubular configuration. Other spinneret and orifice designs may be employed such as multi-hole spinnerets, spray jets wherein the immediately extruded stream impinges on a surface which redistributes the stream, swirl jets, slot orifices, annular orifices, and the like. The spinneret of FIGURE 11 has the orifice located in a flat downstream surface.

The orifice cross section may be of any simple shape but it is preferred that the smallest cross-wise dimension be at least about 4 mils, otherwise, unusually high static may be generated during spinning.

The valve in FIGURE 11 is a part of the spinneret assembly and, if non-constrictive, does not affect the nature of the product.

The process of the present invention can be carried out batchwise or continuously. In the case of continuous operation, a solution of polymer in a suitable solvent is heated to the temperature which provides optimum conditions for the ejection of a plexifilament of the desired structure. This solution may be supplied to an orifice by a metering pump, thus maintaining a uniform pressure and adequate polymer solution supply at the orifice. In such an arrangement, several pressurized containers may be used to make up the solution. Solutions are alternately taken from each of the pressure tanks and discharged through the orifice. Alternatively, polymer and solvents may be mixed continuously at any suitable temperature, passed through a heat exchanger, if necessary, to attain the desired spinning temperature and then continuously discharged through the spinning orifice. Of

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course, the polymer can be prepared, i.e., polymerized, in the spinning solvent to produce a slurry which, at elevated temperatures will yield solution of the right composition or concentration. This is desirable since it simplifies the over-all manufacturing process and thereby affords a considerable economic advantage.

While the plexifilamentary strands of the present invention have been described as three-dimensional network structures, it is possible to obtain webs having only a two-dimensional appearance by a flattening procedure. This results, for example, when in the process of preparing a fibrillated strand, a baffle is interposed in the issuing stream a short distance from the orifice. The web which can be several times wider than the issuing strand contains the film-fibrils and tie points as before in a three-dimensional plexus.

Among the numerous utilities for the plexifilaments of this invention, it is especially noteworthy that strong, commercially desirable papers can be prepared therefrom. Few shaped structures of synthetic, hydrophobic polymer can be converted on a regular paper-pulping machine into a slurry which will form satisfactory paper products. The most serious shortcoming of beaten hydrophobic fibrous polymeric material of the prior art has been that the waterleaf formed from the beaten slurry does not possess enough strength to support its own weight; and this much strength is necessary to permit the waterleaf to be removed from the initial water-leaf forming filter screen for subsequent operations. It is generally felt that the wet water-leaf, after pressing (or couching) on the filter screen should have a tenacity of at least about .002 gram/denier to support its own weight during removal from the screen. Plexifilaments converted into pulp on commercial paper-pulping machinery in standard treatment times, produce slurries which will form water-leaves having more than the necessary 0.002 gram/denier wet, couched tenacity.

The following examples illustrate specific embodiments of the invention. All parts and percentages are by weight unless otherwise indicated.

In the following examples the pressures which are indicated may be either autogenous pressures, i.e., the pressure generated by the solvent, or may be higher because of the addition of inert gases or because of mechanical pressure exerted by a piston or pump. The melt index of the polymer is the flow in g./10 min., as determined by ASTM Method D1238-57T, condition E, and is inversely related to molecular weight. By linear polyethylene is meant polyethylene having a density of 0.94 to 0.98 g./cm.³, but preferably has a density of 0.95 to 0.97 g./cm.³. The polymers are of at least film-forming molecular weight.

EXAMPLE I

Linear polyethylene (LPE) of melt index 0.50 is mixed with methylene chloride to produce a mixture containing 7% by weight LPE. The mixture is heated with agitation in a pressure vessel to 210° C. to produce a homogeneous solution with an autogenous pressure of about 630 p.s.i. The pressure vessel is connected via a valved transfer line to a spinneret which has a single round orifice with a diameter of 75 mils and a length of 75 mils. Upon suddenly opening the above-mentioned valve, the solution is ejected and forms a continuous plexifilament strand at a rate of about 5000 y.p.m. The strand as spun has a denier of 370, a tenacity of 1.1 g.p.d., an elongation of 63% and a modulus of 2.1 g.p.d. The strand is fibrillated and has a fibrillation count of 303 free fibrils/1000-denier/0.1 mm. The fibrils varied in width from 1-50 microns.

EXAMPLE II

A solution containing 13% linear polyethylene in methylene chloride at 195° C. is extruded under 625 p.s.i.

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through a round orifice of 49 mils in length and 40 mils in diameter without any construction ahead of the orifice. Immediately downstream from the orifice is a section flared out at the total angle of 90° extending for a distance of 0.5 inch. The yarn, obtained at a velocity of about 9,000 y.p.m., is a split tube strand comprising an integral, three-dimensional, interconnected assembly of film-fibrils partially embedded in a thin ribbon-like matrix and of high as-spun tenacity. The yarn properties after various subsequent operations are given in Table I.

Table I

Yarn treatment	Denier	Tenacity T (g.p.d.)	Elongation E (percent)	Modulus M (g.p.d.)
None, as spun.....	406	2.7	75	2.1
Coned.....	341	3.2	37	13
Twisted 10 t.p.i.....	404	3.6	100	3.8
Coned and drawn.....	112	14.8	7.7	205
Coned, twisted 10 t.p.i. and drawn.....	96	15.6	7.5	233

EXAMPLE III

A 13% solution of linear polyethylene in methylene chloride, contained in a ten gallon autoclave heated to 196° C. by an external heating block, and pressured with nitrogen gas, is spun from a spinneret similar to that shown in FIGURE 7 wherein the upper orifice 8 is 125 mils long and 60 mils in diameter, the preflashing chamber 5 is .36 inch internal diameter and two inches long, and terminates in an exit orifice 3, 40 mils in diameter and 45 mils long. The spinneret differs however from that of FIGURE 7 in having a 90° flare, 500 mils long following the exit orifice, and in having a flat, non-tapered face on the upstream side of the exit orifice. Several strands are spun using different autoclave pressures. The temperature in the preflashing chamber and the yarn properties for each sample as spun are shown in Table II. The undrawn strands are coarsely fibrillated.

Table II

Sample	Pressure	Temp., ° C.	Denier	Tenacity (g.p.d.)	Elongation (percent)	Modulus (g.p.d.)
A.....	610	192	250	2.9	83	3.7
B.....	620	194	270	3.0	82	4.9
C.....	780	196	260	3.5	80	4.0

Sample A is drawn 6.7 times in an ethylene glycol bath at 132° C. at a windup speed of 140 y.p.m. to produce a drawn yarn of 42 denier having a tenacity of 19.8 g.p.d., an elongation of 5.9% and a modulus of 429 g.p.d. The drawn strand is lustrous and ribbon-like in form after drawing, but dissection reveals a three-dimensional film-fibril network in the interior of the strand.

EXAMPLE IV

Linear copolymers of ethylene and an alpha-olefin were spun from 13% solutions in methylene chloride at 200° C. and at about 700 p.s.i. using the spinneret of FIGURE 10 having an orifice 60 mils long and 60 mils in diameter followed by a cylinder 500 mils by 500 mils. The ribbon strands were drawn 3.5× in hot ethylene glycol and tested for creep resistance. The data of Table III indicate that strands prepared from copolymers wherein the comonomer is a 4-10 carbon alpha-olefin have better creep resistance than the linear polyethylene homopolymer. The creep resistance is also seen to improve with decreasing copolymer melt index (increasing molecular weight). In general, the comonomer may have from 3-12 carbon atoms in the molecule.

Table III

Comonomer		Polymer density g./cm. ³	Melt index	Time for 3 gram/denier load to break strand, hours
Type	Weight percent			
1-butene.....	2	0.942	0.68	280
Do.....	3	0.938	1.16	101
1-octene.....	1.5	0.944	0.63	>218
1-decene.....	1.2	0.946	0.054	5,200
Do.....	5.5	0.929	0.09	>6,200
1-dodecene.....	5.0	0.931	1.18	63
Linear polyethylene homo-polymer.....	0	0.954	1.7	30

EXAMPLE V

As-spun, undrawn plexifilament strands prepared from linear polyethylene using methylene chloride and conditions indicated in Table IV were tested for X-ray diffraction orientation angle by the procedure of H. G. Ingersoll, "Fine Structure of Viscose Rayon," Journal of Applied Physics (1946), 17, 924. Additionally, for each strand, samples of pellicular material having an as-spun thickness of about 1/2 micron were carefully removed and submitted to electron diffraction orientation angle determination using a Philips 100-A electron microscope, a 100 kilovolt electron beam, and a procedure essentially the same as that used for the X-ray procedure described above. In the following table, the first three products have the tubular morphology, the fourth and fifth have the split tube morphology and the last three are fibrillated.

Table IV

DEGREE OF ORIENTATION OF VARIOUS LINEAR POLYETHYLENE PLEXIFILAMENT STRANDS

Spinneret type	Poly. melt index	Spin temp., ° C.	Spin press., p.s.i.g.	Poly. conc., percent	X-ray orientation angle, deg.	Electron diffraction	
						Average orientation angle, deg.	Number of determinations
A.....	1.66	207	900	21	45	28	12
A.....	1.60	197	700	16	36	38	14
A.....	1.52	207	900	20	40	48	10
A.....	0.55	206	800	12	42	48	9
A.....	1.41	207	900	8	51	51	24
B.....	1.25	212	720	8	39	24	9
B.....	1.60	190	600	13	37	44	10
B.....	1.50	216	930	12	32	32	11

Spinneret A is the spinneret of FIGURE 10, wherein the orifice is 50 mils long and 50 mils in diameter, and the cylindrical shroud is 500 mils long and 375 mils in internal diameter. Spinneret B is the spinneret of FIGURE 7, wherein the upper orifice is 125 mils long and 75 mils in diameter, the downstream or spinning orifice is 200 mils long and 86 mils in diameter, and the preflash chamber 5 is 2 inches long and 364 mils in internal diameter. As Table IV indicates, both the X-ray and electron diffraction orientation angles are less than 55°. All the strands tested were soft, strong and well suited for the production of high quality woven or knitted fabrics.

EXAMPLE VI

A 13% solution of linear polyethylene in methylene chloride at 200° C. is saturated with CO₂ at a total equilibrium pressure in the vessel of 1000 p.s.i. The amount of CO₂ dissolved in the solution is 3.7%. Before spinning a pressure of 1060 p.s.i. of nitrogen is impressed on the solution, but the solution is not equilibrated with this gas, i.e., the nitrogen does not dissolve to saturation in the solution. The solution is then extruded through a simple "knife-edge" orifice whose diameter is 67 mils. A well fibrillated plexifilament strand is obtained at about 12,000 y.p.m. The strand has a denier of 1120, a tenacity of 3.9 g.p.d., an elongation of 78%, a surface area of 8.5 m.²/g. and an X-ray diffraction orientation angle of about 24°. The pellicular material averages less than 2 microns in

thickness and has an electron diffraction orientation angle of 30°. This yarn is eminently suited for the production of high quality fabrics. Fibril widths ranged from about 1-25 microns.

EXAMPLE VII

A 13% solution of linear polyethylene in methylene chloride at 200° C. is saturated with nitrogen gas at 1915 p.s.i. total pressure. Before spinning, a pressure of 1950 p.s.i. is impressed on the solution but equilibrium is not established at that pressure. About 2% of nitrogen exists dissolved in the solution. The solution is then extruded through a two-orifice spinneret as shown in FIGURE 7, the first orifice having a diameter of 70 mils with a length of 70 mils and the second orifice being a knife-edge type 67 mils in diameter. The pressure between the two orifices is 1490 p.s.i. A monofilament strand or yarn is produced at a rate of about 8500 y.p.m.

The yarn produced has unusually high bulk and is formed of relatively short and numerous film-fibrils. The free fibril count of this yarn is 463/1000-denier/0.1 mm. The yarn is equal in many aesthetic qualities to high quality spun staple yarns or texturized continuous filament yarns. The tenacity is about 1 g./denier and the surface area is about 9.0 m.²/gm.

EXAMPLE VIII

A 20% solution of a linear polyethylene (1.5 melt index) in methylene chloride is prepared by stirring at a temperature of 205° C. in a pressure vessel. Stirring is stopped and additional pressure is provided by introducing nitrogen under pressure to the atmosphere above the liquid in the pressure vessel. The total pressure is 800 p.s.i. A spinneret similar to that shown in FIGURE 10 is used. The spinneret has a spin orifice of 50-mil diameter with a 50-mil length. The terminal shroud has a diameter of .375 inch and a length of .500 inch. The as-spun product is a monotubular plexifilament strand comprising a highly-fluted essentially continuous outer wall with an attached inner filling comprising an integral, three-dimensional, interconnecting assembly of film-fibrils, the film-fibrils having essentially no unattached ends. In cross section the outer wall of the tubular strand is deeply crenulated due to partial collapse of the tubular form subsequent to spinning. The tubular strand can, however, be re-inflated by blowing a gas into a cut end thus indicating that there is considerable free space between many of the film-fibrils which form the plexifilamentary interior of the strand. This plexifilamentary yarn form is ideally suited to an after-stretching treatment to produce very strong, lustrous yarn such as was made in Example III.

EXAMPLE IX

A 16% solution of a linear polyethylene (1.4 melt index) in methylene chloride is prepared and spun as in Example VIII except that a spin pressure of 700 p.s.i. is used. A plexifilament strand of outward tubular form similar to that obtained in Example VIII is obtained; however, in the present case, the tubular form is even less completely filled. The inner lining of the tubular strand comprises an interconnecting, three-dimensional assembly of film-fibrils, the film-fibrils being arranged in a unique cross-hatched array in interconnecting layers. A probe can be inserted into a cut end of the partly hollow tubular strand along its principal axis without causing cohesive tearing of the film-fibril plexus which forms an integral lining within the outer wall of the tubular strand. The as-spun plexifilament strand has a tenacity of 2.6 g.p.d. and an elongation of 56%. A wet-process paper made from the product yarn has a tensile strength of 15.4 lbs./in./oz./yd.², an elongation of 56% and an Elmendorf tear value of 1 lb./oz./yd.².

EXAMPLE X

A 16% solution of a linear polyethylene (0.43 melt index) in methylene chloride is prepared and spun by

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the method of Example VIII except that the spin temperature is increased to 215° C. The as-spun product comprises a plexifilament strand of intact tubular form similar to that obtained in Example IV except that the film-fibrils constituting the lining of the tubular yarn are substantially parallel to the principal axis of the strand. Also, many of the film-fibrils or composites, continue for inches and even feet before terminating in strong cross-tie connections with other film-fibrils of the plexifilamentary, integral lining of the tubular strand. The product form of this example is eminently suited to production of strong sheets via the wet-paper process route.

EXAMPLE XI

A 10% solution of a linear polyethylene (0.58 melt index) in methylene chloride is prepared and spun according to the method of Example IX except that the spin temperature is 197° C. A plexifilament strand is obtained similar to that of Example X except that the tubular form is split open in a direction more or less parallel to the principal axis of the strand. The highly folded ribbon-like vestigial "outer wall" comprises a plexifilamentary assembly of essentially parallel film-fibrils embedded in a thin filmy matrix. The as-spun strand has a tenacity of 4.3 g.p.d. and an elongation of 61%. The essentially fibrillar character of this ribbon strand is readily demonstrated by subsection of the strand to an air-jet texturizing treatment which will impart a highly-fibrillated, open, high-bulk form to the yarn strand. The opened strand comprises a three-dimensional network of film-fibrils.

EXAMPLE XII

A 15% solution of a linear polyethylene (1.3 melt index) in methylene chloride is prepared with a temperature of 223° C. and a superautogenous pressure of 910 p.s.i. The spinneret used is similar to that shown in FIGURE 7 except that it comprises a series of three orifices in tandem with the following diameter/length dimensions (mils) for the three orifices, going from the inside of the pressure vessel to the outside: 86/125, 105/125, and 100/200. Two different sets of spinning conditions (a) and (b) are used:

Part (a).—A spin pressure of 910 p.s.i. is used. A fibrillated plexifilament strand of 790 denier which has a tenacity of 1.2 g.p.d. and a break elongation of 35% is spun out at about 12,300 y.p.m. It has a fibrillation count of over 200 free fibrils/1000 denier/0.1 mm.

Part (b).—The spin pressure is increased to 1125 p.s.i. and the temperature is increased to 225° C. A fibrillated strand is spun out at about 17,000 y.p.m. The continuous plexifilament strand possesses a superfine fibrillation (about five times the fibrillation count of part (a)) is obtained. This soft, pliant high bulk yarn has an enormous specific surface (12.4 m.²/gram) and a very uniform texture and is very useful in cigarette filters. The plexifilament yarn has a denier of 690, a tenacity of 1.2 g.p.d. and an elongation of 31%.

EXAMPLE XIII

A 15% solution of a linear polyethylene (1.4 melt index) in methylene chloride is prepared with a temperature of 218° C. and a total pressure of 880 p.s.i. A two-orifice spinneret is used similar to the spinneret shown in FIGURE 7 with an attached terminal shroud such as is shown in FIGURE 10. The first orifice of the spinneret has a 75-mil diameter and a 125-mil length, the second orifice has a 100-mil diameter and a 200-mil length and the shroud has a 0.4375 inch diameter and a 0.875 inch length. A fibrillated plexifilament strand is obtained with a tenacity of 2.7 g.p.d. and an elongation of 46%.

EXAMPLE XIV

A 14% solution of a linear polyethylene (0.55 melt index) in methylene chloride is prepared and spun by

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the method of Example XI. The as-spun product is a plexifilament strand in a split tubular form. The yarn has a tenacity of 2.4 g.p.d. and an elongation of 53%. Converted to a sheet via the wet-process paper route, the resulting product has a tensile strength of 36.6 lbs./in./oz./yd.², an elongation of 70% and an Elmen-dorf tear value of 1.22 lbs./oz./yd.².

EXAMPLE XV

A 5.1% solution of a linear polyethylene (1.6 melt index) in methylene chloride is prepared and heated to a temperature of 217° C. and a total pressure of 900 p.s.i. A spinneret of the type shown in FIG. 8 without insert 7 having an orifice diameter of 125 mils and a length of 100 mils is used. A fibrillated, high bulk plexifilament strand is obtained. A portion of the yarn was tested as a cigarette filter along with a commercial filter of 6 d.p.f. cellulose acetate continuous filament. The data which are recorded in Table V show the superior tar-removing ability of the plexifilamentary filter when the pressure drop is approximately equivalent to that of the acetate filament filter. The excellent filtering ability of the plexifilament strand is accomplished with only one fourth as much filter medium as is used in the acetate fiber filter.

Table V

RESULTS OF COMPETITIVE CIGARETTE FILTER TESTING¹

	Cigarette filter from plexifilament strand (CH ₂ Cl ₂)	Acetate fiber filter
Filter weight, mg.-----	41	167
Pressure drop across filter, inches H ₂ O-----	3.7	3.3
Tar passed, mg.-----	5.6	12.7

¹ Snell method.

EXAMPLE XVI

A 12% solution of a linear polyethylene (1.3 melt index) in "Freon-11" (trichlorofluoromethane) is prepared and heated to a temperature of 179° C. The pressure vessel is charged with nitrogen under pressure, the dissolved nitrogen content being about 1% and the total pressure being 900 p.s.i. A spinneret with an orifice of 50 mil diameter and 50-mil length of the type used in Example XV and following the spinneret orifice is a trumpet-like shroud with an entry diameter of 0.625 inch, and an exit diameter of 4 inches and with an over-all length of 24 inches. The product obtained is a fibrillated, high bulk plexifilament strand whose component superfine film-fibrils exhibit a high degree of crimping or folding along their main axes as a consequence of the retarding action of the trumpet-shroud. A portion of the product yarn was tested in cigarette filter form and compared with a continuous filament (6 d.p.f.) cellulose acetate filter as shown in Table VI.

Table VI

RESULTS OF COMPETITIVE CIGARETTE FILTER TESTING¹

	Cigarette filter from plexifilament yarn (CFCl ₃)	Acetate fiber filter
Filter weight, mg.-----	14	90
Pressure drop across filter, inches H ₂ O-----	3.3	3.2
Tar passed, mg.-----	20.0	27.7

¹ Cambridge method, reference, Wartman, W. B., Jr., et al., Analytical Chemistry, 31 N. 10 1705-9 (1959).

EXAMPLE XVII

A 12% solution of a linear polyethylene (0.56 melt index) in "Freon-11" (trichlorofluoromethane) is prepared with a temperature of 166° C., about 2% of dis-

solved nitrogen and a total pressure (at spinning) of 1190 p.s.i. The spinneret used is similar to the one shown in FIGURE 10 with a spin orifice of .25-inch diameter and 100-mil length followed by a shroud of .250-inch diameter and .500-inch length. A very strong, predominantly fibrillated plexifilament strand is obtained. In the as-spun form it has a denier of 205, a tenacity of 4.3 g.p.d. and an elongation of 18%. After imparting to the yarn a twist of 8 turns per inch, the yarn has a tenacity of 6 g.p.d. and an elongation of 33%.

EXAMPLE XVIII

A 12.4% solution in "Freon-11" of copolymer made from 95% ethylene and 5% octene (0.9 melt index, density 0.94 g./cm.³) is prepared at a temperature of 165° C. and a total pressure of 1275 p.s.i. (About 0.5% of N₂ is dissolved in the solution during its preparation.) The spinneret used is similar to that of FIGURE 10 with the spin orifice having a diameter of 50 mils and a length of 50 mils and with the terminal shroud having a diameter of .375 inch with a length of .500 inch. A plexifilament strand is obtained in a folded ribbon-like form which can be unfolded to give a ribbon of twice the original width. The product is a ribbon strand. Closer examination of the strand with a microscope at a 50-fold to 100-fold magnification shows the strand to consist of an integral, three-dimensional, interconnecting assembly of film fibrils, some partially embedded and others almost completely embedded in a film-like matrix, which is a composite or laminar structure of film-fibril material.

EXAMPLE XIX

The procedure of Example I is carried out using a 13.5% by weight linear polyethylene and 86.5% by weight of a solvent which is a mixture of 95% methylene chloride and 5% butane by volume. A spinneret with an orifice of 75 mils and a length of 75 mils is used. Spinning of the solution at a temperature of 200° C. and a pressure of 545 p.s.i. yields a continuous plexifilament strand which is well fibrillated with a fibrillation count of 443 free fibrils/1000 denier/0.1 mm. The as spun yarn has a denier of 393.

EXAMPLE XX

A 10% solution of polypropylene (0.17 melt index, density 0.906) in methylene chloride is prepared and heated to a temperature of 223° C., and a pressure of 720 p.s.i. is applied. A spinneret such as shown in FIGURE 10 is used. The spin orifice has a diameter of 50 mils and a length of 50 mils and the spinneret orifice is followed by a shroud (as shown in FIGURE 10) which has a diameter of 0.375 inch and a length of 0.500 inch. A fibrillated plexifilament strand is obtained.

EXAMPLE XXI

Various physical mixtures of linear polyethylene with another polymer are used to prepare spinning solutions by dissolving them in methylene chloride at suitable temperatures and by spinning them as plexifilament strands with certain improved characteristics as shown in Table VII.

This application is a continuation-in-part of U.S. application, Serial No. 858,725, filed December 10, 1959, and now abandoned, and Serial No. 736,337, filed May 19, 1958, which are in turn continuations-in-part of application, Serial No. 665,099, filed June 11, 1957, and now abandoned.

What is claimed is:

1. A yarn-like strand having a surface area greater than 2 m.²/g., comprising a three-dimensional integral plexus of synthetic organic, crystalline polymeric, fibrous elements, said elements being coextensively aligned with the strand axis and having the structural configuration of oriented film-fibrils, an average film thickness of less than 4 microns and an average electron diffraction orientation angle of less than 90°.
2. The product of claim 1 wherein the surface area is greater than 5 m.²/g.
3. A tobacco smoke filter comprising the product of claim 1.
4. The product of claim 1 wherein the polymeric material is polyethylene.
5. The product of claim 1 wherein the crystalline polymer is a copolymer of ethylene and a 3-12 carbon alpha olefin.
6. The strand in accordance with claim 1 said strand having an average X-ray diffraction orientation angle of less than 55°.
7. The product of claim 1 wherein the fibrous elements have essentially no unattached ends.
8. The strand of claim 1 drawn from 2-13×
9. The strand of claim 4 which has been drawn and has a tenacity greater than 13 grams/denier.
10. The product of claim 1 having an undrawn, twisted tenacity than 1 gram/denier.
11. A fibrillated strand consisting essentially of a three-dimensional integral plexus of synthetic organic, crystalline polymeric film-fibrils, said film-fibrils being coextensively aligned with the strand axis and having an average film thickness of less than 4 microns, and an average electron diffraction axial orientation angle of less than 90°, said strand having a surface area of at least 2m.²/g. and a free fibril count greater than 50 fibrils/1000 denier/0.1 mm. and at least about 25 free fibrils per 0.1 mm. length.
12. The strand of claim 11 wherein the film-fibrils have a width to thickness ratio greater than five.
13. A fibrillated strand consisting essentially of a three-dimensional integral plexus of crystalline polyhydrocarbon film-fibrils, said film-fibrils being coextensively aligned with the strand axis and having an average film thickness of less than 4 microns and an average electron diffraction axial orientation angle of less than 90°, said strand having a surface area of at least 2 m.²/g. and a free fibril count of at least 50 fibrils/1000 denier/0.1 mm., and at least 25 free fibrils per 0.1 mm. length.
14. The strand of claim 13 wherein the crystalline hydrocarbon is linear polyethylene.
15. A partially condensed strand of synthetic organic, crystalline polymer, said strand having a surface area of at least 2 m.²/g. and said strand consisting essentially of a three-dimensional integral plexus of film-fibrils which

Table VII

PLEXIFILAMENT STRANDS MADE FROM POLYMER BLENDS

Polymer blend	Percent polymer in solution	Spin temp., °C./spin press., p.s.i.g.	Product description
Polyethylene, 90%; polystyrene, 10%-----	10, plus 0.2% dissolved N ₂	220/1,050	Predominantly fibrillated strand, bulkier and more resilient than that from polyethylene alone.
Polyethylene, 85%; basic dyeable polyester, 15%-----	16-----	207/700	Split tubular yarn of excellent dyeability.
Polyethylene, 50%; polyoxymethylene, 50%-----	12-----	217/1,050	Predominantly fibrillated tough yarn.
Linear polyethylene, 50%; branched polyethylene, 50%-----	12-----	210/1,050	Highly fibrillated, resilient yarn with microcrimp in film-fibrils.

¹ The condensation product of ethylene glycol with a 98/2 molar mixture of terephthalic/5-(sodium sulfo)-isophthalic acid.

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are coextensively aligned with the strand axis and having an average film thickness of less than 4 microns, and an average electron diffraction axial orientation angle of less than 90° and densified sections of film-fibril layers.

16. The strand of claim 15 wherein the polymer is a crystalline polyhydrocarbon.

17. The strand of claim 15 wherein the polymer is linear polyethylene.

18. The strand of claim 15 wherein the densified regions are in the form of tubular outer wall.

19. The strand of claim 15 wherein the densified regions are in the form of a split tubular outer wall.

20. The strand of claim 15 wherein the densified regions are in the form of wall fragments.

21. A strand comprising a three-dimensional integral plexus of synthetic organic crystalline polymeric film-

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fibril elements which are coextensively aligned with the strand axis, said film-fibril elements having a thickness less than 4 microns and an average electron diffraction orientation angle of less than 90°, said strand having fibrillar texture and a surface area greater than 2 m.²/g.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,081,519

March 19, 1963

Herbert Blades et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, line 57, for "7%" read -- 10% --.

Signed and sealed this 16th day of June 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents