FIG. 1

FIG. 2
ABSTRACT OF THE DISCLOSURE

The process of extruding a spinning dope from an orifice through a layer of fluid into a coagulating bath, said dope comprising a polyamide in a solvent consisting essentially of sulfuric acid of at least 98% concentration, chlorosulfuric acid or fluorosulfuric acid or mixtures thereof at a concentration (C) of at least 30 grams of said polyamide per 100 ml of solvent, the said polyamide having an inherent viscosity of at least 2.0 but no less than (2.8—0.05 (C—30)) and consisting essentially of recurring units selected from the group:

(I) \[ \text{O} - \text{C-R-N'-N} \]

and

(II) \[ \text{H} - \text{H} \]

and

(III) \[ \text{O} - \text{H} - \text{C-R''-N} \]

wherein units I and II, if present in the polyamide, are present in substantially equimolar amounts, R, R', and R'' which may be the same or different, are divalent radicals, n may be zero or the integer one, and at least about 95 mol percent of the total R, R', and R'' radicals in the polyamide consist of single rigid radicals with extended bonds or a series of such rigid radicals which are linked together directly by extended bonds with the proviso that rigid ring radicals may be linked by azo or azoxy groups.

This application is a continuation-in-part of my application Ser. No. 239,377, filed Mar. 29, 1972, and now abandoned, and my application Ser. No. 172,515, filed Aug. 17, 1971, and now abandoned, which is a continuation-in-part of my application Ser. No. 138,210, filed Apr. 28, 1971, and now abandoned.

Application Ser. No. 268,057, filed June 30, 1972 relates to a product which may be prepared by the present process.

This invention relates to an improved process for the preparation of fibers from certain polynomials and to novel spinning dopes. The resulting fibers are useful in tire cords and for other applications.

BACKGROUND OF THE INVENTION

The prior art U.S. Pat. 3,414,645 to Morgan teaches a dry-jet wet spinning process of extruding a solution of wholly aromatic polyamides through a gaseous medium into a coagulating bath, followed by stretching in a wash liquid, washing, drying and hot drawing to produce filaments.

German Offen. 1,810,426 to Kwolek teaches the use of certain optically anisotropic dopes of carbocyclic aromatic polyamides in wet spinning processes to afford fibers of good strength as-spun, i.e., without a drawing process. A heat treatment with tension raises the strength to higher values. It is a desirable objective to prepare aromatic polyamide fibers of higher as-spun strength.

SUMMARY OF THE INVENTION

The invention involves the process of extruding a dope of a hereinafter described nature from an orifice through a layer of an inert non-coagulating fluid into a coagulating bath to form fibers or films. The dope comprises a polyamide as specified below in a solvent consisting essentially of sulfuric acid of at least 98% concentration, chlorosulfuric acid or fluorosulfuric acid and mixtures of these acids at a concentration of at least 30 grams and preferably at least 40 grams of such polyamide per 100 ml of solvent.

The processes of this invention can provide as-spun fibers having a filament tenacity of at least 15 grams per denier and a modulus of at least 300 grams per denier. Preferred conditions afford as-spun filaments of at least 20 grams per denier.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a schematic view of one type of apparatus for carrying out the process of this invention.

FIG. 2 shows a schematic view of another embodiment of apparatus for carrying out a process of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Detailed description of the drawing

In FIG. 1, the spin dope is pumped through transfer line 1 through a spinning block 2, through the orifices of spinneret 3 through the layer of gas 5 and into the coagulating liquid 6 where the filaments 4 are conducted under guides 7 and 8 and strong as-spun yarn 15 is wound up on a rotating bobbin 9.

FIG. 2 shows a modification whereby the extruded filaments 4 are forwarded through the coagulating liquid 6 that is flowing from container 11 through spin tube 10 to container 12 from whence the liquid is returned by pump 13 and tube 14 to container 11. The filaments are conducted under guide 7 and strong as-spun yarn 15 is wound on rotating bobbin 9.

Suitable polyamides

The linear condensation polymers employed in the present invention consist essentially of recurring units selected from the group:

(I) \[ \text{O} - \text{C-R-N'-N} \]

and

(II) \[ \text{H} - \text{H} \]

and

(III) \[ \text{O} - \text{R} - \text{C-R''-N} \]

wherein units I and II, if present in the polymer, are present in substantially equimolar amounts, R, R', and R'' which may be the same or different are divalent radicals, n may be zero or the integer one, and at least about 95 mol percent of the total R, R', and R'' radicals in the polymer consist of single rigid radicals with extended bonds or a series of such rigid radicals which are linked together directly by extended bonds. In addition, azo \(-\text{N=N=}\) and azoxy \(-\text{N=N=}\) radicals can serve to link two rigid ring radicals. Thus, the essential portion of the polymer consists of polyamide units (including polyoxamide units when n is zero), which provide stiff chains.
By the expression "rigid radicals" is meant (a) the ring radicals: single ring or fused multi-ring aromatic carbocyclic or heterocyclic radicals, trans-1,4-cyclohexylene

\[
\begin{align*}
\text{and 1,4(2,2,2)-bicyclo-octylene and (b) the linear unsaturated radicals: vinylene} \\
\text{C=C} \\
\text{and ethylene} -\text{C}-\text{C-}. \text{ It will be understood that monomers containing amino groups directly attached to linear unsaturated radicals are not stable and hence vinylene or ethylene cannot serve as R' or that portion of a R'' radical attached to} \\
\text{H} \\
\text{N} \\
\text{By the expression "extended bonds" is meant chain-extending bonds of the radical (as determined by the true bond angles) which are essentially coaxial} \\
\text{(as in p-phenylene,} \\
\text{and trans-1,4-cyclohexylene)} \\
\text{or parallel} \\
\text{and oppositely directed. These polymer structures additionally have the characteristic of forming anisotropic or liquid crystalline phases when mixed with certain strong protonic acid solvents, as will be discussed in greater detail in a later section.} \\
\text{Preferred radicals with extended bonds suitable for} \\
\text{R, R' and R'' are trans-1,4-cyclohexylene, 1,4-phenylene, 1,5-naphthylene,} \\
\text{2,6-naphthylene} \\
\text{and 1,4-phenylene groups linked by trans-vinylene, ethylene, azo or azoxy. In addition, R may be trans-vinylene, ethylene,} \\
\text{trans, trans-1,4-butenylene} \\
\text{or} \\
\text{trans, trans-1,4-cyclohexylene} \\
\text{The latter may also serve as R''.} \\
\text{R, R' and R'' are intended to include substituted and/or unsubstituted radicals. The substituents, if any, should preferably be nonreactive (e.g., thermally). Such reactivity may be undesirable in that it may cause branching and cross-linking of the polymer and may adversely affect the dope and/or fiber properties. Among the preferred nonreactive substituents may be named halogens (e.g.,} \\
\text{chloro, bromo and fluoro), lower alkyl (e.g., methyl, ethyl and isopropyl), methoxy, cyano, and nitro. Other suitable substituents will be evident to those skilled in the art and are contemplated herein. Generally, it is preferred that no more than two (and more preferably no more than one) suitable substituents be present per single radical. Preferably no more than 20 mol percent of the total} \\
\text{R, R' and R'' radicals in the polymer should be substituted R''.} \\
\text{A preferred class of the polymers of the group described above are those polyamides (n being the integer one) wherein at least 50 mol percent of the total of R,} \\
\text{R' and R'' radicals are wholly aromatic. A more preferred class of these polymers are those polyamides wherein R and} \\
\text{R' are selected from the group 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthylene, 2,5-pyridylene, trans-vinylene and trans-1,4-cyclohexylene and R'' is 1,4-phenylene with the proviso that at least 50 mol percent of either} \\
\text{R or R' radicals are 1,4-phenylene.} \\
\text{The chains of the linear condensation polymers of the group described above may include up to about 5% (mol basis) of radicals not conforming to the above cited description, e.g., not having extended bonds or non-rigid.} \\
\text{It is to be understood that these non-conforming radicals differ in their effect on the properties of the spun fibers. Thus, rigid radicals such as m-phenylene, whose chain extending bonds are neither coaxial nor parallel and oppositely directed, and highly flexible radicals such as hexamethylene and decamethylene will ordinarily be used in small proportions, whereas radicals such as 4,4'-biphenylene may be used in larger amounts, even exceeding 5% while still obtaining substantial benefit from practice of the invention. While it is not preferred, a small proportion of the amide units in the linear condensation polymer chain may be replaced, if desired, by other stable nonamide-forming units, e.g., ester-forming units or urea or sulfonamide-forming units. In general, such products are more difficult to prepare and are more restricted in their utility.} \\
\text{The polymer to be spun may be a homopolymer, random copolymer, ordered copolymer or blend of homopolymers and/or copolymers of the above description, and may contain additives such as dyes, delustrants, antioxidants, etc.} \\
\text{Among the suitable polyamides may be named:} \\
poly(p-phenylene terephthalamide) (hereafter PPD-T); 
\text{poly(p-phenylene p,p'-biphenyldicarboxamide);} 
\text{poly(p-phenylene 1,5-naphthalenedicarboxamide);} 
\text{poly(trans, trans-4,4'-dodecaldihydrobiphenylene terephthalamide);} 
\text{poly(trans, 1,4-cinnamamide);} 
\text{poly(1,4(2,2,2)-bicyclo-octylene terephthalamide);} 
\text{poly(p-phenylene 4,4'-azoxybenzene dicarboxamide/} 
\text{terethalamide);} 
\text{poly(p-phenylene 4,4'-trans-stilbenedicarboxamide) and} 
\text{poly(p-phenylene acetylenedicarboxamide).} \\
\text{Preparation of polyamides} \\
\text{The polymers for use in this process are conveniently made by reacting suitable monomers in the presence of an amide type solvent by low temperature techniques as taught in U.S. Pat. 3,063,966 to Kwolek et al. In order to obtain high molecular weight polymers the monomers and solvent should contain a minimum of impurities and the water content of the total reaction mixture should be less than 0.03% by weight.} \\
\text{Poly(p-phenylene terephthalamide) is conveniently made by dissolving 1728 parts of} 
\text{phenylenediamine in a mixture of 15,200 parts of hexamethylenediamine and 30,400 parts of} 
\text{N-methylpyrrolidone, cooling to 15° C. in a polymer kettle blanketed with nitrogen and then adding 3245 parts of powdered terephthahloic} 
\text{chloride with rapid stirring. The solution gels and turns into a dry crumb-like material in 3 to 4 minutes. The product is} 
\text{continued for 1.5 hours when possible with cooling to keep} 
\text{the product temperature at about 25° C. The polymeriza-}
tion is essentially quantitative and the final reaction mixture contains 7.5% polymer of about 5.5 inherent viscosity (hereinafter I.V.). The I.V. of the polymer from this system can be controlled by the ratio of monomer to solvent. Reduction of the amount of monomer from 9.83% above to 8.64% gives a reaction mixture containing 6.5% polymer of 6.0 I.V. The use of about 11.7% of monomers gives a reaction mixture of 9.0% polymer of 2.5 I.V.

The crumb-like acidic product is vigorously stirred or ground with water in a Waring Blender or a colloid mill and the resulting polymer slurry filtered. The wet polymer is further washed by reslurrying with soft water to remove soluble monomers. The polymer is then dried at 120-140° C. Polymerizations can also be carried out by the continuous mixing of the monomers.

Suitable dope solvents

Suitable solvents consist essentially of sulfuric acid of a least 98% concentration, chlorosulfonic acid, fluorosulfonic acid, or combinations of these acids. The sulfuric acid may be of greater than 100% concentration, i.e., fuming surface acid. Sulfuric acid at a concentration of about 99.8% is preferred. Higher concentrations may be used, however, the presence of excess sulfur trioxide tends to degrade the polymer causing a reduction in the inherent viscosity. This could cause loss of filament tenacity. This degradation is time and temperature dependent so that if fuming sulfuric is used, the exposure time at elevated temperatures should be kept to a minimum. This definition of suitable solvents is not intended to preclude the presence of certain additives. Thus, hydrochloric acid, halogenated alkylsulfonic acids, halogenated aromatic sulfonic acids, halogenated acetic acids, halogenated lower alkyl alcohols, and halogenated ketones or aldehydes can optionally be present in an amount up to about 30% of the total weight of the solvent and additive. The exact amount of additive that may be present will, of course, depend upon the particular solvent-polymer combination that is employed. The use of fluorosulfonic (rather than sulfuric) acid, or lower polymer concentrations permits the use of a greater amount of additive. In general, the greater the percent of halogen present in the additive, the greater the amount of additive that can be used up to the limit of phase separation. Trifluorothiolanesulfonic acid can ordinarily be present in an amount equal to the weight of that above hydrochloric acid. Additionally sulfones, chlorinated phenols and nitrobenzene can be used as a solvent additive in lesser amounts than the halogenated additives described above.

Preparation of dopes

The water content of the dope should be carefully controlled to be less than 2%. Excessive water can interfere with the formation of dopes suitable for spinning and also to excessive degradation of the polymer. The relatively dry polymer (preferably less than 1% water) should be mixed with a "dry" solvent under conditions minimizing exposure to atmospheric moisture and the dope exposed to a dry atmosphere.

The dopes should be mixed and held during the spinning process at as low a temperature as is practical to keep them liquid in order to reduce degradation of the polymer resulting in lower I.V. values. Exposures to temperatures over about 90° C should be minimized. A particularly useful method is to continuously prepare the dope and feed directly to the spinnerets, thus minimizing the holding time. If batch processes are used and dopes are to be stored for later use, they may be frozen to a solid form, preferably under a blanket of dry nitro-
gen. Such solidified dope can be crushed to granules or powder and subsequently used to feed a screw melting device leading to a spinneret.

The concentration (C) of the dope is defined herein as grams of polyamide (specified above) per 100 ml of solvent at 25° C. By "solvent" is meant the actual sulfuric acid plus any solvent-additive present. At least 30 grams of polymer per 100 ml of solvent should be employed. Preferred dopes for the instant spinning process employ between 40 and 56 grams of poly(p-phenylene teraphthalimide) having an I.V. of at least 3.0 per 100 ml of acid. This amounts to between about 18 and 23.4 weight percent of polymer in the previously mentioned acid dopes.

Since the tenacity and moduli of the fibers made by the process of this invention are so high, the polyamides (specified above) can be diluted by blending with another polymer not meeting the requirements of the invention and fibers of high tenacity prepared. Such a blend can contain as much as 30% by weight of the dilluent polymer which should be compatible with the other polymer in the acid solvent and reasonably stable.

It should be understood that the defined concentration (C) of the dope to be extruded as mentioned herein and in the claims is based on the content of polyamide meeting the requirements of the invention and polyamide consisting essentially of units I, II and/or III as previously described. The concentration (C) does not include the content of dilluent polymer (one that does not consist essentially of I, II and/or III) which may be present in the dope that is spun.

It may be noted that the useful solvents all have high density (H₂SO₄), 1.83, HSO₃Cl, 1.79, HSO₃F, 1.74 g./ml.). Use of such high density solvents leads to a much higher volume fraction of polymer than obtained when alkylamides like hexamethylenetramine and dimethylacetamide (densities about 0.9 to 1.0 g./ml.) are used. High volume fraction is also provided by the high concentrations of polymer in the dopes.

In the present invention it is useful to use as high dope concentration as possible. It has been found in general that the tenacity of the fibers produced increases with the concentration of the dope from which they were spun. Dopes of useful concentrations are solid at room temperature and melt to spinnable liquids when the temperature is raised. Increasing temperature causes polymer degradation as shown by loss in I.V.

It is desirable that the extrusion of a dope result in a fiber with an I.V. of at least 2.0, preferably at least 3.0. A given fiber I.V. can be obtained by starting with a polymer of a moderate I.V. and processing to keep degradation to a minimum or by starting with a higher I.V. and processing for more severe degradation. For purposes of the present invention, the I.V. of the polymer in the as spun fiber (assuming appropriate washing and drying to prevent undue degradation) is taken as the I.V. of the polymer in the dope as it is extruded. Thus, the I.V. of the dope as it is extruded should be at least 2.0 and should be no less than [2.8-0.05 (C-30)] where (C) is as defined above.

The spin dopes of the present invention possess unexpected stability. It appears that the "acidity" of the sulfuric acid is reduced by the presence of high concentrations of the stiff chain polyamides. Dopes are made of PPD-T polymer of 4.88 I.V. in sulfuric acid (100%) at concentrations of 46, 21.8 and 3.7 g./100 ml. The dopes are heated for 3 hours at 100° C. Polymer isolated from the heated solutions has an I.V. of 4.2, 2.8 and 1.9 respectively. Further evidence for reduced "acidity" of the concentrated dopes is the fact that PPD-T dopes of 46 g./100 ml are substantially non-reactive with aluminum metal at 70-80° C whereas dopes of 25 g./100 ml concentration react vigorously.

It has been found advantageous in some instances to deaerate the liquid dope at reduced pressure prior to spinning.
The dopes or polymer-solvent system used in this process behave much like polymer melts. A typical dope of 46 grams of PPD-T per 100 mL of sulfuric acid represent the highest concentration that can be handled in the conventional mixers, transfer lines and spinning equipment due to the extremely high bulk viscosity of the mixes. When the usual technique of lowering the viscosity by raising the temperature is used, excessive degradation of the polymer occurs. The use of more effective mixers in combination with more efficient cooling in the mixer will permit the use of higher concentrations. The viscosities at these higher concentrations are a function of the polymer-solvent system used. Example IV shows the extrusion of a dope having 56 g. of a polymer per 100 mL of solvent (23.4 weight percent).

In general, dopes can be extruded at any temperatures from the lowest at which they are sufficiently fluid to be handled up to about 120° C. Since the amount of degradation is dependent upon the time and temperature, temperatures as low as practical should be used, preferably below 90° C. If higher temperatures are desired for any reason, the equipment should be designed so that the exposure time of the dope to the elevated temperature is kept at a minimum.

The spinning dopes of this invention are unusual. At room temperatures most are solid. As the temperature is raised, they melt, becoming less viscous and translucent to transparent. They are optically anisotropic, i.e., microscopic regions of a given dope are birefringent; a bulk dope sample depolarizes plane polarized light because the light transmission properties of the microscopic areas of the dope vary with direction. This characteristic is associated with the existence of at least part of the dope in the liquid crystalline or mesomorphic state. These dopes exhibit anisotropy while in the relaxed state.

For a well mixed dope of given composition and concentration, the temperature at which melting occurs is fairly reproducible and reversible. This melting behavior is accompanied by an absorption of heat as indicated by differential thermal analysis. The melting temperature of solidified dopes can also be determined by measuring the intensity of polarized light passing through a thin sample and a 90° crossed analyzer as the temperature is raised. The melting temperature is that temperature at which the transmitted light intensity increases rapidly. In general, the melting temperature increases as the concentration increases. For example, PPD-T/sulfuric acid dopes of 32, 40 and 46 g./100 mL acid show melting temperatures of 40–50° C., 63–65° C. and 72–82° C., respectively. A dope that is incompletely mixed and has a distribution of phases of different concentration will have a broadened melting range.

As the temperature of a molten, anisotropic dope is increased, a point is reached at which the amount of anisotropic phase begins to decrease. This temperature (Tm) can be determined by a measurement of the change in the scattering of polarized light at small angles (e.g., 1°) on passing through a thin layer of dope. Tm increases with the concentration of the polymer, e.g., for PPD-T/H2SO4 dopes of 32, 40 and 46 g./100 mL concentration Tm values are found to be about 80–100° C., 82–135° C. and 110 to 122° C., respectively. Even above these temperatures the dopes are largely anisotropic and give good results in the present process, but highest tenacity fibers will be obtained by the spinning of dopes at temperatures above the melting point and below Tm.

Extrusion conditions

These conditions are discussed in terms of spinning conditions for fibers in the following section. It will be understood that the comments can apply to the extrusion of films.

Spinnernet: Spinnernet and all other apparatus parts should be constructed of materials resistant to the strong acids used.

The diameters of the holes (orifices) and the ratio of the length of the capillary/diameter of the hole (L/D) in the spinneter are not critical. Strong fibers have been obtained with round orifices ranging from 1.0 to 10 mils (0.025 to 0.25 mm.) diameter and having a L/D ratio of from 1.0 to 8.3. The process is also operable with non-round holes of various shapes including narrow slits: .02 x .05 mm. or .02 x .25 mm. or .175 x .75 mm. for example.

The spacing of the holes is not critical and would be dictated by construction materials and by the threadline stability produced in spinning.

Jet velocity: The jet velocity (designated “IV”) is the average velocity of the dope in the spinneter capillary as calculated from the volume of dope passing through an orifice per unit time and from the cross-sectional area of the orifice. It may range from 17 feet/minute (f.p.m.) (5.1 meters/min.) or lower to 1150 f.p.m. (350 meters/min.) or higher. The minimum value for a given dope and orifice is determined by the ability to form a filament of relatively uniform denier and the desired physical properties. The maximum useful spin stretch factor is limited by filament breakage in the process. In general, increasing the spin stretch factor from a low value at a given jet velocity awards fibers with higher tenacities and moduli and lower elongations and denier. One skilled in spinning will readily adjust orifice diameter, thickness of the gas layer, jet velocity and spin stretch factor for a given spinning dope and apparatus to obtain a fiber of the desired denier and physical properties.

Fluid layer: It is essential that the spinneter face be separated from the coagulating bath by a fluid layer of gas or a non-coagulating liquid such as toluene, heptane, etc. The thickness of the fluid layer can vary from 0.1 to 10 cm., or more and preferably is from about 0.5 to 2 cm. thick. Use of larger thicknesses increases the opportunity for adjacent filaments to fuse together.

Spin tube and guides: The configuration of the spin tube 10 and the character of the guide 7 in FIG. 2 can affect the elongation and modulus in the a-spun yarn. At the same jet velocity and windup speeds, a straight tube generally produces higher yarn elongation and lower modulus than a tube constricted at its lower end. Similarly, a roller guide generally produces higher yarn elongation than a snubbing pin. Useful spin tube dimensions will vary with spinning speeds and yarn denier.

Coagulating bath: A variety of baths may be used to coagulate the fiber. Satisfactory results have been obtained with both aqueous and non-aqueous systems. Useful aqueous systems have ranged from pure water to systems containing high concentrations of sulfuric acid (70%), ammonium hydroxide, or salts such as calcium chloride, potassium carbonate or sodium chloride. Aqueous baths containing water miscible organic solvents such as methanol, and ethylene glycol are also useful. Examples of non-aqueous coagulation baths include 100%
methanol and methylene chloride solutions containing 5 to 50% of methanol, N,N'-dimethylformamide or N,N' -dimethylacetamide. Bath temperatures ranging from -25° C. to 28° C. have been satisfactory. It is considered that a wide variety of coagulants can be used at temperatures from -zer0 to 50° C. or more. Preferably the temperature of the bath is kept below 10° C. (more preferably below 5° C.) in order to obtain the highest tenacity in the filaments.

Washing: Due to the degrading effects of even small amounts of acid in the yarn, complete removal of the acid is very important in obtaining high tenacity fibers. Water alone or combinations of alkaline solutions and water may be used for its removal.

A convenient method is to spray the thread line as it leaves the coagulating bath with an aqueous alkaline solution (e.g. saturated NaHCO₃ or 0.05 N NaOH), remove surface liquid from the thread line with a wiping device (e.g. a sponge) or a jet, wash with water (ca. 75° C.) to reduce the acid content to about 1% (on a dry fiber basis) and wind up on bobbins. Such bobbins can be stored for short periods (up to about 24 hours) in water or dilute alkaline solution before the final wash. Preferably the final wash (e.g. with 75° C. water) should reduce the acid or base content below 0.01% (on a dry basis).

While small amounts of yarn can be washed and neutralized on the bobbin, it is preferred that the yarn be washed as in such thin layers in flumes, on rolls with overhead sprays, on screens, belts or the like. In a continuous process the thread line can be washed and neutralized continuously at the same speed as the thread line at any point between spinning and wind up.

Drying: The thoroughly washed fibers can be dried on the bobbin with air at up to 150° C. The fibers can conveniently be dried on heated rolls (e.g. 160° C.). If the fibers are dried while under a tension of less than about 0.3 g.p.d., which is a preferred method, the properties are not significantly changed. The use of tensions above 0.3 g.p.d. reduces the elongation and increases the modulus from that obtained by tensionless drying.

Heat treatment: The properties of the as-spun yarn can be altered by a heat treatment. Heating a yarn under tension, preferably in an inert atmosphere, at temperatures of 150° C. to 550° C. increases the yarn modulus from about 15 to 100% and reduces the yarn elongation by about 50%. The modulus increase is greater with increasing tension and temperature. Typical tensions and times of exposure used at 150° C. are about 2 to 12 g.p.d. for 1.5 to 6 seconds and at 550° C. are 0.5 to 2 g.p.d. for 1 to 6 seconds. At low and intermediate temperatures, the yarn tenacity is not significantly changed, but it may be reduced after treatment at 450° C. or more.

Yarns to be heat-treated are usually dry beforehand but the heat treatment effects can be produced on wet yarns direct from washing or on rewet dried yarns by slightly lengthening the time of heating.

Test procedures

Inherent viscosity: Inherent viscosity (I.V.) is defined by the equation:

\[ \text{I.V.} = \frac{\ln (\eta_{sp})}{c} \]

where \( c \) is the concentration (0.5 gram of polymer or fiber in 100 ml of solvent) of the polymer solution and \( \eta_{sp} \) (relative viscosity) is the ratio between the flow times of the polymer solution and the solvent as measured at 30° C. in a capillary viscometer. The inherent viscosity values reported and specified herein are determined using concentrated sulfuric acid (95-98% \( \text{H}_2\text{SO}_4 \)) unless otherwise specified.

Fiber tensile properties: Filament properties are measured on fibers that have been conditioned at 21° C. and 65% relative humidity (R.H.) for at least 16 hours unless otherwise specified. Yarn properties are measured on yarn that has been conditioned at 24° C. and 55% R.H. for at least 16 hours. All measurements are made in the fiber conditioning environment.

Tenacity (breaking tenacity) (Ten.), elongation (breaking elongation) (E), initial modulus (MI), and toughness (breaking toughness) (Tou.) are obtained from breaking a single filament or a multifilament yarn on an Instron tester (Instron Engineering Corp., Canton, Mass.).

Single filaments are broken with a gage length (distance between jaws) of 1.0 inch (2.54 cm.). The results on 3 filaments are averaged. Yarns are given 3 turns per inch (2.54 cm.) twist (under 0.1 g.p.d. tension) and broken with a 10 inch (25.4 cm.) gage length. All samples are elongated at a constant rate of extension (10% elongation/minute for fibers having an E of under 8%, and 50% elongation/minute for fibers with E of 8 to 100%) until the sample breaks.

The denier of a single filament (d.p.f.) is calculated from its functional resonant frequency, determined by vibrating at 7 to 9 cm. length of fiber under tension with changing frequency. (A.S.T.M. D1577-66, part 25, 1968).

This filament is then used for 1 break.

The denier of yarn is determined by weighing a known length (at 0.1 g.p.d. tension); 90 cm. length is convenient.

The tenacity (grams/denier, g.p.d.), elongation (percent), initial modulus (g.p.d.) and toughness (gram-centimeters per denier centimeter or simply g.p.d.) as defined in A.S.T.M. D2101, part 25, 19693 are obtained from the load-elongation curve and the measured denier. In actual practice, the measured denier of the sample, test conditions and sample identification are fed to a computer before the start of a test; the computer records the load-elongation curve of the fiber as it is broken and then calculates the fiber properties.

It should be noted that different values are obtained from single filaments (filament properties) and from multifilament strands (yarn properties) of the same sample. Filament tenacities are higher than yarn tenacities—typically about 1.21, filament elongations are higher than yarn elongation and filament moduli are lower than the yarn values. Unless specified otherwise all properties given herein are filament properties.

Bulk viscosities: Bulk viscosities are measured by a Brookfield Viscometer with a No. 7 spindle at 10 r.p.m.

Of course it will be understood that use of process conditions other than optimum can affect the resultant fiber tenacity adversely.

**EXAMPLE I**

(A) PPD-T of 4.4 I.V. is mixed in a beaker with sulfuric acid (100.2% \( \text{H}_2\text{SO}_4 \)) in the ratio of 46 grams of polymer per 100 ml. of acid (20% by weight). The crude mixture of dough-like consistency is transferred to a mixing device consisting of two open top cylinders (each of about 250 ml. capacity) connected by a base block. Each cylinder has a hole in its base above a filter pack (3-30 mesh screens/1-325 mesh screen/3-50 mesh screens, mesh/inch (mesh/2.54 cm.)) in the base block which leads to a passage in the block to the other filter pack and cylinder. The mixing device is fitted to a pair of pistons which closely fit each cylinder. A small hole in each piston is opened for the initial fitting by each piston to insure the removal of air and then closed. A water bath at about 95° C. is placed around the mixing device. After about 1 to 2 hours the polymer-solvent mixture is pushed by the pistons from 1 cylinder to the other for a total of about 15 cycles. With all of the mixture (now a dope) in 1 cylinder (and the connecting passage), the mixing device is connected through a hole (previously plugged) in the base block leading to the connecting passage by a length of copper tubing in the shape of a goose.
neck to an electrically heated spinning block having a polypropylene felt filter and a 0.5 in. diameter spinneret with 20 holes of 2 mil (0.05 mm.) diameter. The 95° C. water bath is replaced around the mixing device and the copper tubing. The short length of the tubing between the water bath and the spinning block (100° C.) is insulated with glass wool.

The spinning block is positioned (FIG. 1) so that the face of the spinneret is inclined at about 45° to the surface of a coagulating bath of 15° C. water with the lower edge of the spinneret being about 2 cm. above the surface of the water.

The dope is extruded from the spinneret at a jet velocity of 240 feet/minute (f.p.m.) (73 meters/minute, m.p.m.), through air into the coagulating bath, under a pin near the bottom of a bath and then under a second pin and out of the bath to a windup bobbin to give a SSP of 2.17.

The fibers are washed free of acid with water, and air dried. The filaments of 3.8 d.p.f. have a tenacity of 15 g.p.d., an elongation of 3.9%, an initial modulus of 520 g.p.d. and an I.V. of 4.1.

(B) The above mixing procedure is repeated to make a solution of 46 grams of PPD-T of 5.4 I.V. per 100 ml. of sulfuric acid (99.7% H₂SO₄) (20% by weight). The dope is pumped from the mixing device at 95° C. through the tubing (steam jacketed outside of the bath), through the spinning block at 100° C. containing stainless steel felt (Dynafoy X5 made by Fluid Dynamics, Inc., Morristown, N.J.) as a filter and extruded through a spinneret containing 50 two mil (0.051 mm.) diameter holes at 210 f.p.m. (64 m.p.m.) jet velocity through a 1 cm. layer of air vertically into water at 4° C. using a spinning tube and windup similar to that shown in FIG. 2 and at a speed to give a SSP of 6.9.

The filaments after thorough washing and air drying have an I.V. of 4.8 and a d.p.f. of 0.92.

A portion of the dried yarn is plied to a total denier of 183 and passed through a 10 feet long (3.05 meters) tube containing nitrogen at 525° C. under a tension of 1.4 g.p.d. at a speed to give a residence time of about 2 seconds (1000 f.p.m.). The yarn is only drawn about 1,005 times its original length.

Properties of the as-spun and heat treated fibers are given below.

### EXAMPLE II

(A) PPD-T of 6.0 I.V. is added to sulfuric acid (99.7% H₂SO₄) at 40° C. in a water-jacketed commercial planetary mixer through a top entrance over about 2 minutes to give a ratio of 46 grams of polymer/100 ml. of acid. The mixer is sealed and placed under 68.5 to 76 cm. of Hg vacuum. The temperature of the water jacket is increased to 85° C. and the planetary mixing blades started at a slow speed. After about 12 minutes the jacket temperature is reduced to 77° C. which affords a temperature in the solution of between 79-82° C. Mixing is continued for about 2 hours. The solution then has a bulk viscosity of 2300 poises.

The dope is transferred to a glass-lined, water-jacketed (90° C.) kettle. A vacuum of about 69-76 cm. of Hg is applied for about 30 minutes to remove any air or bubbles caused by the transfer. The dope is pumped from the kettle through a transfer line closely wrapped with a waterline (90° C.) to an electrically heated (80° C.) spinning bath and attached gear pump. The gear pump meters the dope back through another passage in the block to a water-jacketed (80° C.) spinneret pack containing a backing screen, stainless steel felt and a 0.5 inch (12.7 mm.) diameter spinneret containing 100 holes of 2 mil (0.051 mm.) diameter. The dope is extruded from the spinneret at a jet velocity of about 207 f.p.m. (63 m.p.m.) vertically through a 0.5 cm. layer of air into 1° C. water in a spinning tube similar to that shown in FIG. 2. Items (a) and (b) are made using a freely revolving roller under the spin tube to direct the threadline to the windup while item (c) uses a ceramic rod. The yarn is wound up at different speeds on a bobbin under a water (50° C.) spray. The bobbins of yarn are stored in a tank of water. The bobbins are then submerged in 0.1 N NaHCO₃ and further extracted with water (70° C.) on an advancing reel extracting device of the type shown in U.S. Pat. 2,659,225. The extracted yarn is wound up and dried on the bobbins at 70° C. Properties of the dried yarn of 5.2 I.V. are given below.

<table>
<thead>
<tr>
<th>Item</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin stretch factor</td>
<td>1.45</td>
<td>1.38</td>
<td>4.55</td>
</tr>
<tr>
<td>Filament, denier</td>
<td>3.7</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Yarn, Ten.</td>
<td>21.6</td>
<td>22.8</td>
<td>28.8</td>
</tr>
<tr>
<td>Yarn, Ef.</td>
<td>28.9</td>
<td>28.6</td>
<td>28.9</td>
</tr>
<tr>
<td>Yarn, Mi.</td>
<td>947</td>
<td>727</td>
<td>948</td>
</tr>
<tr>
<td>Yarn, Toti</td>
<td>0.39</td>
<td>0.36</td>
<td>0.36</td>
</tr>
</tbody>
</table>

(B) The above mixing procedure is repeated using distilled (4 days at 75° C. under vacuum) PPD-T polymer of 5.9 I.V. to give a dope with a ratio of 45.8 grams of polymer/100 ml. of sulfuric acid (100% H₂SO₄) (20% by weight). The dope is extruded using the equipment and conditions of part A with the exception of (1) a kettle temperature of 87° C. with all other dope temperatures at 85° C. (2) a jet velocity of 96 f.p.m. (29.2 m.p.m.) and a SSP of 5.2. A roller is used between the spin tube and windup.

The windup bobbin is sprayed with a saturated aqueous solution of NaHCO₃ (25° C.) as the yarn is wound up. The bobbins are stored in water for 12 hours and then further extracted with water (70° C.) by passing a plied yarn from 6 bobbins submerged in a tank of saturated aqueous solution of NaHCO₃ to the extractor device at the same conditions as used in part A. The extract is then wound up and dried on the bobbin at 40° C. The dried yarn of 5.2 I.V. has yarn properties as follows: tenacity 24 g.p.d., elongation 3.9%, initial modulus 530 g.p.d., toughness 0.43 g.p.d. and a total denier of 719 for the 600 filaments.

(C) A dope containing 46 grams of PPD-T per 100 ml. of sulfuric acid (above 99% H₂SO₄) is made by mixing the polymer of 4.8 I.V. with the acid and stirring at 80 to 90° C. for about 0.5 hour and then at 95° C. for 1.5 hours. The dope is transferred to a kettle where it is maintained at about 100-110° C. Spinning is started about 3.5 hours after the transfer to the kettle. The dope is extruded through a spinneret with one hundred-3 mil (.076 mm.) diameter holes—using the general procedure of part A above. Fibers obtained 5.0 and 3.5 hours after the start of spinning have an I.V. of 2.9 and 2.0 respectively. The latter fiber has filament properties (Ten./E/Mi/d.p.f.) of 15/3.5/402/1.5.

(D) A dope containing 46 grams of PPD-T (I.V. 5.9) per 100 ml. of sulfuric acid (above 99% H₂SO₄) is mixed and extruded from a slot 2.5 mil x 0.35 inch (0.63 x 8.9 mm.) at a jet velocity of about 64 feet (19.3 m.) per minute through a 2 mm. jet. As-spun material is winded through a vertical flume of 7° C. water and the film passed under a ceramic rod and wound up on a bobbin at SSP.
of about 2.3. The bobbin is sprayed with dilute aqueous NaHCO₃ solution. After neutralizing, washing, and drying the film of 871 denier has a Ten./E/M 18/5.7/358 when broken using a 2" (5 cm.) gage length at 100% elongation per minute. Conditioning testing is done in the environment used for yarns.

EXAMPLE III

This example shows the use of other solvents.

Dopeds from PPDI-T of 5.4 l.v. (4.6 for items (f), (k), (m) and (n)) are left after hand mixing following by 15 to 120 minutes of mixing in the mixing device of Example I. The dopeds are extruded with apparatus similar to Example IB through a spinneret with twenty 3 mil (0.076 mm.) diameter holes through a 1 cm. layer of air into 1°-3° C. water, wound up, thoroughly washed in water and air dried on the bobbin.

Specific conditions and results are given below. Solvents used are HSO₃Cl, HSO₃F, HSO₃F/H₂SO₄ mixture (49/51 by weight) and H₂SO₄ (100%) for items (a), (b), (c), and (d) respectively. The solvent for item (e) is a mixture of FSO₃H and hydrofluoric acid and for items (f)–(n) a mixture of an additive and H₂SO₄ (100%) is used. Windup speeds used range from 608 (item (f)) to 2000 (item (g)) feet/minute (185 to 610 m.p.m.). The concentration of the spinning dopes ranges from 34 (item (a)) to 47 (item (f)) grams of polymer/100 ml. of solvent and additive. Other specific conditions and fiber properties are given in Table I.

It is observed that the use of the sulfonic acids as additives in items (f) and (g) affords a lower viscosity dope than with sulfonic acid alone.

The dope of item (e) containing hydrofluoric acid has a melting point that is about 30° C. lower than the melting point of a dope with fluorosulfonic acid as the solvent (e.g., item (b)) and can be spun at a lower temperature.

The fiber from item (g) has an unusually high high-as spun yarn modulus. Similar high values have been obtained from dopings containing trifluoromesanesulfonic acid as an additive.

The amount of additive that can be tolerated, under normal spinning conditions, by the dope is limited. The use of a 60/40 additive/solvent ratio for item (f) yields only a paste that cannot be extruded. The use of a 20/80 additive/solvent ratio for item (m) and 20% polymer gives a very viscous mixture that cannot be extruded. The use of a 40/60 additive/solvent ratio for item (j) gives only a dry crumb.

### TABLE I

| Item | Solvent Additive | Solvent-additive | Percent polymer | Spins tear block tenacity | S.S.F. | Filament properties
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>None</td>
<td>100/0</td>
<td>18</td>
<td>60</td>
<td>4.0</td>
<td>21</td>
</tr>
<tr>
<td>(b)</td>
<td>do</td>
<td>100/0</td>
<td>20</td>
<td>60</td>
<td>4.1</td>
<td>25</td>
</tr>
<tr>
<td>(c)</td>
<td>do</td>
<td>100/0</td>
<td>20</td>
<td>60</td>
<td>4.4</td>
<td>27</td>
</tr>
<tr>
<td>(d)</td>
<td>Hydrofluoric acid</td>
<td>80/20</td>
<td>16</td>
<td>50</td>
<td>4.3</td>
<td>27</td>
</tr>
<tr>
<td>(e)</td>
<td>Trifluoromesanesulfonic acid</td>
<td>80/20</td>
<td>20</td>
<td>80</td>
<td>7.7</td>
<td>27</td>
</tr>
<tr>
<td>(f)</td>
<td>1,1,2-trifluoroethanesulfonic acid</td>
<td>80/20</td>
<td>20</td>
<td>108</td>
<td>12.5</td>
<td>21</td>
</tr>
<tr>
<td>(g)</td>
<td>p-Chloromesanesulfonic acid</td>
<td>80/20</td>
<td>20</td>
<td>80</td>
<td>11.5</td>
<td>19</td>
</tr>
<tr>
<td>(h)</td>
<td>Trifluorectonic acid</td>
<td>80/20</td>
<td>17</td>
<td>77</td>
<td>4.7</td>
<td>25</td>
</tr>
<tr>
<td>(i)</td>
<td>Dichloroacetic acid</td>
<td>80/20</td>
<td>20</td>
<td>90</td>
<td>4.4</td>
<td>17</td>
</tr>
<tr>
<td>(j)</td>
<td>Ethanolsulfonic acid</td>
<td>80/20</td>
<td>17</td>
<td>110</td>
<td>4.4</td>
<td>18</td>
</tr>
<tr>
<td>(k)</td>
<td>2,3,5-trifluoropropion-1</td>
<td>80/20</td>
<td>17</td>
<td>80</td>
<td>5.0</td>
<td>15</td>
</tr>
<tr>
<td>(l)</td>
<td>Nitrobenzene</td>
<td>88/12</td>
<td>18</td>
<td>80</td>
<td>5.0</td>
<td>15</td>
</tr>
</tbody>
</table>

This example shows the use of various polymides made from diamines and dicarboxylic acid halides. The polymides are made by dissolving the amine in the solvent, cooling the amine solution to about 5 to 10° C., then rapidly adding the dicarboxylic acid with stirring and continuing the stirring, when possible, for at least about 1 hour. The polymer is recovered from the crumbs or gel by pulverizing it in water in a Waring Blender type-mixer, collecting on a filter and repeated washings with water and then drying. The usual precautions in forming high molecular weight polymides are observed.

Monomers used and the polymers formed are shown in Table II where the abbreviations "PPDI" and "TCl" are used for p-phenylene and terphenylaloyl chloride respectively. Some specific details of the polymerization are given in Table III. When 2 monomers of the same type are used for copolymer the molar ratio of the monomers is given.

Mixtures of 2 solvents, hexamethylenediamine (A) and N-methylpyrrolidone (B) are used for all items except item (a), where 100% N,N-dimethylacetamide (DMAc) was used and item (i), where equal volumes of B and DMAc were employed. The weight ratio of the 2 solvents is given in the table as is the weight ratio of the solvent to the total monomers.

Dopings are prepared using sulfuric acid (99.7 to 100.0% H₂SO₄) (a mixture of equal weights of sulfuric and fluorosulfonic acids for items (j), (l) and (n)) to give 46 grams of polymer/100 ml. of acid (20 weight percent). In some cases the polymer used is a blend of several polymerizations.

The dopings are extruded at temperatures (spinnerr block) between 51 and 100° C. (except item (j), 35° C.) using the apparatus and technique of Example IB from spinners containing 2 or 3 mil (0.051 or 0.076 mm.) diameter holes through a layer of air (0.5 to 1.9 cm.) into water (0 to 4° C.) and the filaments wound up at speeds ranging from 230 f.p.m. (71 m.p.m.) for item (j) to 1430 f.p.m. (438 m.p.m.) for item (p) The fibers are thoroughly washed in water and dried on the bobbins.

S.S.F. and filament properties are given in Table III. The I.V. on item (c) is measured at a concentration of 0.1%.

Doping containing 56 g. of polymer per 100 ml. of sulfuric acid (23.4 weight percent) is made from poly-(chloro-p-phenylene terephthalaldehyde) of 4.1 l.v. (item(s)) and satisfactorily spun by the above procedure into fibers with filament tenacity of 17 g.p.d.
A 20/80 copolymer of item (q) (Table II) of 3.3 I.V. is spun by the above procedure into fibers.

### TABLE II

<table>
<thead>
<tr>
<th>Item</th>
<th>Diamine, diacid chloride</th>
<th>Polymer</th>
<th>Polymer code</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Chloro-p-phenylene diamide (6-TCl)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>CIPPD-T</td>
</tr>
<tr>
<td>(b)</td>
<td>Chloro-p-phenylene diamine (FIP-D)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>CIIPPD-D</td>
</tr>
<tr>
<td>(c)</td>
<td>1,4-diphenyl-5-phenyl diamine (FIP-TCl)</td>
<td>Poly(1,4-bis(p-phenylene amide) terephthalalamide)</td>
<td>DIPPD-T</td>
</tr>
<tr>
<td>(d)</td>
<td>4,4'-dimethyl benzenetricarboxylic acid (FIP-TCl)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>DMIPP-T</td>
</tr>
<tr>
<td>(e)</td>
<td>4,4'-bipyridyl chloride (FIP-TCl)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>FIP-PD-T</td>
</tr>
<tr>
<td>(f)</td>
<td>2,5-diphenyl enamide (FIP-D)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>FIP-DD-T</td>
</tr>
<tr>
<td>(g)</td>
<td>4,4'-diamino diphenyl ether (FIP-D)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>FIP-D</td>
</tr>
<tr>
<td>(h)</td>
<td>2,5-diamino diphenyl ether (FIP-D)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>FIP-D</td>
</tr>
<tr>
<td>(i)</td>
<td>4,4'-diamino diphenyl ether (FIP-D)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>FIP-D</td>
</tr>
<tr>
<td>(j)</td>
<td>2,5-diamino diphenyl ether (FIP-D)</td>
<td>Poly(chloro-p-phenylene terephthalalamide)</td>
<td>FIP-D</td>
</tr>
</tbody>
</table>

### EXAMPLE V

This example shows polyamides made from A-B monomers. An ordered copolymer (item (a)) is made by dissolving 4,4'-diaminobenzanilide in hexamethylphosphoramide, cooling the solution to about 6°C, and rapidly adding a molar equivalent of terephthaloyl chloride with stirring and continuing the stirring (for about 1 min). The polymer is recovered from the gel by pulverizing it in water with a Waring Blender type mixer, collecting on a filter, repeating the washing and filtering and drying. The ratio of monomers to the amide solvent is 5.7.

A random copolymer (item (b)) (p-benzamide/p-phenylene terephthalalamide 25/75) is made by adding p-aminobenzoyl chloride hydrochloride to a cooled (about 6°C) solution of p-phenylene-diamine in a mixture of 10.4 parts by weight of hexamethylphosphoramide and 10 parts by weight of p-nitroaniline. After about 5 minutes and with continued cooling to about 6°C, the terephthaloyl chloride is rapidly added with stirring. Stirring is continued for about 3 minutes. The polymer is recovered as above. The mole ratio of the three monomers used is 1:3:3 respectively.

A homopolymer (item (d)) [poly(p-benzamide)] is made by cooling N,N-dimethylacetamide to 10°C and rapidly adding 4-(p-aminoazobenzene) benzoyl chloride hydrochloride (solvent/monomer weight ratio=0.6-5) with stirring. After 2.75 hours of stirring, the mixture is neutralized with lithium carbonate and stirring is continued another 1.5 hours. The polymer is recovered as above.

The polymer I.V. range from 4.0 (item (c)) to 5.9 (item (b)). Dopes are prepared using sulfuric acid (99% to 100% H2SO4) to give about 46 grams of polymer/100 ml of acid (20 weight percent) for all items except (d) (40 g./100 ml. or 18 weight percent). The dopes are extruded at temperatures between 37°C (item (c)) and 68°C. (item (d)) using the apparatus and technique of Example 1B from spinners containing 2 or 3 mill (0.051 or 0.076 mm) diameter holes into a layer of air (0.5 to 1.2 cm.) into water (1 to 3°C) and the filaments wound up at speeds ranging from 600 f.p.m. (184 m.p.m.) for item (c) to 1208 f.p.m. (370 m.p.m.) for item (a). The fibers are thoroughly washed in water and dried on the bobbins.

### TABLE III

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>CI PFP-D</td>
<td>11.3 8.2 9.3 18 6.5 370 3.9 0.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>CI PFP-D T-25/75</td>
<td>6.0 3.1 3.1</td>
<td>18 6.5 369 3.9 0.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>DPFP-D T-25/75</td>
<td>6.0 3.8 3.4</td>
<td>17 6.9 373 3.8 0.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>DPFP-D T-25/75</td>
<td>5.7 3.8 3.4</td>
<td>17 6.9 373 3.8 0.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>DPFP-D T-25/75</td>
<td>5.7 3.8 3.4</td>
<td>17 6.9 373 3.8 0.61</td>
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</table>

### TABLE IV

<table>
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</thead>
<tbody>
<tr>
<td>(a)</td>
<td>4.3 17</td>
<td>3.9</td>
<td>630 1.6 0.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>4.7 22</td>
<td>8.5</td>
<td>680 1.6 0.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>2.0 19</td>
<td>4.0</td>
<td>670 1.0 0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Properties are given in Table IV.
EXAMPLE VI

This example shows some variables in the spinning process. Dopes of PPD-T in sulfuric acid (99.7-100% H2SO4) are made and spun using the apparatus and general techniques of Example IB. Some specific conditions and results are given in Table V. All dopes contain 46 g. polymer/100 ml. solvent (20 weight percent) except item (e) which uses 38 g./100 ml. (17 weight percent).

All dopes are extruded at about 95°C. (spinnneret blank except items (e), (f) and (g)) 73(85 and 80°C. respectively) from a spinneret with 2 mil (0.051 mm.) diameter holes except items (c), (d), and (f) [10, 8 and 3 mil (0.25, 0.20 and 0.076 mm.) diameter respectively] through a layer of air of from 0.5 to 1.5 cm. thick into a coagulating bath.

The coagulating bath is water for all items except (f), (g) and (h) which use 47.5, 54 and 70% H2SO4 respectively. For the latter 3 items the yarn coming from the coagulating tube is passed under a rod and into a second bath (water 15°C.), under a rod and thence to the windup. Windup speeds of from 650 to 1450 f.p.m. (198 to 440 m.p.m.) are used.

All fibers are thoroughly washed and dried on the bobbin. Filament tenacities are given in Table V. All items have filament (a) elongation of 3.5 to 4.8%, (b) moduli of 420 (item (e)) to 850 g.p.d. (item (f)), (c) deniers per filament of 1.1 to 2.7 except items (c) and (d) (12.4 and 10.5 respectively) and all have toughness values of 0.22 to 0.69 g.p.d.

When the processing of item (e) is changed by placing the face of the spinneret under the surface of the water the maximum windup speed that can be used is only 90 f.p.m. (27 m.p.m.) at a spin stretch factor of 0.6 to give 9.2 d.p.f. filaments with a tenacity of 37 g.p.d.

Using the processing of item (a) with a SSF of 3, filaments with tenacities of 23, 22 and 21 g.p.d. are obtained when spinning tube lengths of 8.5, 4 and 0.5 inches (21.6, 10, and 1.27 cm.) are used. The variation in spinning tube length varies the velocity of the water and hence the tension on the threadline.

The spinning conditions of item (a) are modified by extruding the dope at about 90°C. (from 4.6 I.V. polymer) through a 1 cm. layer of air vertically into a bath of 4°C. water, under a guide and out of the bath to a windup at 480 f.p.m. (147 m.p.m.) with a SSF of 3.0. The washed and dried fibers have a filament tenacity of 17 g.p.d. This process was essentially repeated with the layer of air replaced by a 1 cm. layer of toluene so that the spinneret face is immersed in toluene.

EXAMPLE VII

This example shows the effect of extrusion temperature on the process. A dope containing 46 g. polymer/100 ml. of sulfuric acid (99.4-100% H2SO4) made from PPD-T of 5.2 I.V. is extruded—using the general procedure of Example II—from a spinneret having 100 holes of 0.05 mm. diameter, through about a 4.8 mm. layer of air into 5°C. water. The fiber was wound up at about 500 f.p.m. (153 m.p.m.) with a SSF of about 4.7 to 5.5. The dope in the kettle is kept at about 85°C. The temperatures of the transfer line, spinning block and spinneret are adjusted to about the extrusion temperature for each spin. The estimated temperature of the dope—as extruded, the I.V. of the fiber and the filament properties are given below.

```
<table>
<thead>
<tr>
<th>Item</th>
<th>Inherent viscosity</th>
<th>Extrusion temp., °C</th>
<th>Coagulation bath temp., °C</th>
<th>Spin stretch factor</th>
<th>Filament tenacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>4.7/4.2</td>
<td>ca. 95</td>
<td>5.5</td>
<td>3.9</td>
<td>28</td>
</tr>
<tr>
<td>(b)</td>
<td>4.7/4.5</td>
<td>ca. 95</td>
<td>4</td>
<td>12.1</td>
<td>17</td>
</tr>
<tr>
<td>(c)</td>
<td>4.7/4.5</td>
<td>ca. 95</td>
<td>4</td>
<td>10.6</td>
<td>17</td>
</tr>
<tr>
<td>(d)</td>
<td>5.7/5.7</td>
<td>ca. 95</td>
<td>10</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>(e)</td>
<td>5.6/5.7</td>
<td>ca. 95</td>
<td>8</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>(f)</td>
<td>5.6/6.0</td>
<td>ca. 95</td>
<td>7</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>(g)</td>
<td>5.6/6.5</td>
<td>ca. 95</td>
<td>7</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>(h)</td>
<td>6.9/6.0</td>
<td>ca. 95</td>
<td>8</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>(i)</td>
<td>6.9/6.5</td>
<td>ca. 95</td>
<td>8</td>
<td>16</td>
<td>10</td>
</tr>
</tbody>
</table>
```

What is claimed is:

1. A method comprising extruding a spinning dope from an orifice through a layer of inert non-coagulating fluid into a coagulating bath, said dope comprising a polyamide and a solvent consisting essentially of sulfuric acid of at least 98% concentration, chlorosulfonic acid or fluorosulfonic acid and mixtures thereof at a concentration (C) of at least 20 grams of said polyamide per 100 ml. of solvent, said polyamide having an inherent viscosity of at least 1.5.
least 2.0 but no less than \([2.8-0.05 \text{ (C-30)}]\) and consisting essentially of recurring units selected from the group:

\[
\begin{align*}
\text{(I)} & \quad \text{O} \quad \text{O} \\
\text{(II)} & \quad \text{H} \quad \text{H} \\
\text{(III)} & \quad \text{O} \quad \text{H} \\
\quad \text{C} \quad \text{R}_n \quad \text{C} \\
\quad \text{N} \quad \text{R}^{\prime} \quad \text{N} \\
\end{align*}
\]

wherein units I and II, if present in the polyamide, are present in substantially equimolar amounts, \(R, R', \) and \(R''\) which may be the same or different, are divalent radicals, \(n\) may be zero or the integer one, and at least about 95 mol percent of the total \(R, R',\) and \(R''\) radicals in the polyamide consist of single rigid radicals with extended bonds or a series of such rigid radicals which are linked together directly by extended bonds with the proviso that rigid ring radicals may be linked by azo or azoxy groups.

2. The method of claim 1 wherein the acid is sulfuric acid of at least 98\% concentration.

3. The method of claim 2 wherein the polyamide has an inherent viscosity of at least 3.0 and is present at a concentration of at least 40 grams per 100 ml. of solvent.

4. The method of claim 2 wherein the polyamide is poly-(p-phenylene terephthalamide).

5. The method of claim 1 wherein the layer of fluid is between 0.1 and 10 cm. thick.

6. The method of claim 1 wherein the layer of fluid is a gas.

7. The method of claim 1 wherein the coagulating bath is at a temperature of under 50\% C.

8. The method of claim 7 wherein the fluid layer is air and the coagulating bath is aqueous and at a temperature of 28\% C. or lower.

9. The method of claim 1 wherein the rigid radicals are single ring or fused multi-ring aromatic carbocyclic or heterocyclic radicals, trans-1,4-cyclohexylene, 1,4-[2,2,2]-bicyclo-ctylene, vinylene or ethynylene.

10. A method comprising extruding a spinning dope from an orifice through a layer of inert non-coagulating fluid into a coagulating bath, said dope comprising a polyamde and a solvent consisting essentially of sulfuric acid of at least 98\% concentration, chlorosulfuric acid or fluorosulfuric acid and mixtures thereof at a concentration (C) of at least 30 grams of said polyamide per 100 ml. of solvent, said polyamide having an inherent viscosity of at least 2.0 but no less than \([2.8-0.05 \text{ (C-30)}]\) and consisting essentially of recurring units selected from the group:

\[
\begin{align*}
\text{(I)} & \quad \text{O} \quad \text{O} \\
\text{(II)} & \quad \text{H} \quad \text{H} \\
\text{(III)} & \quad \text{O} \quad \text{H} \\
\quad \text{C} \quad \text{R}_n \quad \text{C} \\
\quad \text{N} \quad \text{R}^{\prime} \quad \text{N} \\
\end{align*}
\]

wherein units I and II, if present in the polyamide, are present in substantially equimolar amounts, \(R, R', \) and \(R''\) may be the same or different divalent radicals, \(n\) may be zero or the integer one, and at least about 95 mol percent of the total \(R, R',\) and \(R''\) radicals in the polyamide are selected from the group of trans-1,4-cyclohexylene, 1,4-phenylene, 1,5-naphthalene, 2,6-naphthalene, 2,5-pyridylene, 4,4'-biphenylene, trans-trans-4,4'-bicyclohexylene radicals and 1,4-phenylene groups linked by trans-vinylenes, ethynyl, azo or azoxy with the proviso that \(R\) may also be selected from trans-vinylene, ethynylene, trans, trans-1,4-butenylene and 2,4'-trans-vinylene-naphthalenicene.

11. The process of claim 10 wherein at least 95 mole percent of the total \(R, R',\) and \(R''\) radicals are 1,4-phenylene radicals.

12. The method of claim 10 wherein the spinning dope passes from the orifice through a layer of gas and into an aqueous bath at a temperature of under 50\% C. and wherein the polyamide has an inherent viscosity of at least 3.0 and is present at a concentration of at least 40 grams per 100 ml. of solvent.

13. The method of claim 12 wherein the polyamide is poly-(p-phenylene terephthalamide) and the solvent is sulfuric acid of at least 98\% concentration.

References Cited

UNITED STATES PATENTS

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JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

260—78 S, 30.8 R; 264—203
JNTED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,767,756 Dated October 23, 1973
Inventor(s) Herbert Blades

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 51, Formula II, "-N-R'-N" should read -- -N-R'-N- --.

Column 3, line 25, insert a closing parenthesis after the benzene ring.

Column 3, line 62, - -C=C- should read

Column 5, line 25, "a" should read -- at --.

Column 5, line 28, "surface" should read -- sulfuric --.

Column 6, line 32, "(H₂SO₄), 1.83, HSO₃Cl, 1.79, HSO₃F, 1.74 g./ml.)" should read -- (H₂SO₄ 1.83, HSO₃Cl 1.79, HSO₃F 1.74 g./ml.) --.

Column 6, lines 56 and 57, "Thus, the I.V. of the dope" should read -- Thus, the I.V. of the polymer in the dope --.
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 55, "thickeneses" should read -- thickness --.

Column 10, line 23, "vibrating at" should read -- vibrating a --.

Column 12, line 29, the last number in column (c) should read -- 0.34 -- instead of "0.34".

Column 12, line 75, "at SSF" should read -- at a SSF --.

Column 13, line 5, "Conditioning testing" should read -- Conditioning and testing --.

Column 13, line 48, "canot" should read -- cannot --.

Column 14, line 41, a period should appear after (p).

Column 15, Table II, Item (e), "PPD-4,4'-bibenzoyl chloride/TC1" should read -- PPD-4,4'-bibenzoyl chloride/TC1 --.
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, Table II, Item (g), "PPD-4,4'-azobenzenedicarbonyl chloride/TC1" should read -- PPD-4,4'-azobenzenedicarbonyl chloride/TC1 --.

Column 15, Table II, Item (l), "4,4'-diamino diphenyl ether/PPD-TC1" should read -- 4,4'-diamino diphenyl ether/PPD-TC1 --.

Column 16, Table II, under Polymer Code, Item (a), "ClPPD/PPD" should read -- ClPPD/PPD-T --.

Column 16, Table II, under Polymer, Item (b), "Copoly(4,4'-bibenzylene/p-phenylene terephthalamide)" should read -- Copoly(4,4'-bibenzylene/p-phenylene terephthalamide) --.

Column 15, Table III, Solvent Monomers, Item (h), "9.5" should read -- 8.5 --.

Column 15, Table III, under Item, "(r)e" should read -- (r) --.

Column 15, line 52, "terephthaloyl chloride" should read -- terephthaloyl chloride --.
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 17, line 34, "37 g.p.d." should read -- 3.7 g.p.d. --.

Column 17, Table V, Item (e), under Inherent Viscosity Starting Polymer/Yarn, "3.7/--" should read -- 4.7/-- --.

Column 19, Claim 1, line 4, formula I,
\[
\begin{align*}
\text{"-} & \text{C-R} & \text{C"} \\
& & \\
& & \\
\text{\textsuperscript{0}} & & \text{\textsuperscript{0}}
\end{align*}
\]
should read -- \text{\textsuperscript{0}} \text{C-R} \text{\textsuperscript{0}} \text{C} --.

Column 19, line 36, Claim 9, "trans-1,4-cyclohexylene" should read -- trans-1,4-cyclohexylene --.

Column 20, line 13, Claim 10, "trans-1,4-cyclohexylene" should read -- trans-1,4-cyclohexylene --.

Column 20, line 15, Claim 10, "trans(trans-4,4'-bicyclohexylene" should read -- trans,trans-4,4'-bicyclohexylene --.

Column 20, line 16, Claim 10, "trans-vinyl-" should read -- trans-vinyl--.
UNIVERS STATES PATENT OFFICE
CERTIFICATE OF CORRECTION
Patent No. 3,767,756 Dated October 23, 1973
Inventor(s) Herbert Blades

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 20, line 18, Claim 10, "trans-vinylene" should read -- trans-vinylene --; line 18, "trans," should read -- trans, --.

Column 20, line 19, Claim 10, "trans-1,4-butadienylene" should read -- trans-1,4-butadienylene --; line 19, "2,4'-trans-vinylenephenylene" should read -- 2,4'-trans-vinylenephenylene --.

Signed and sealed this 23rd day of July 1974.

(SEAL)
Attest:

McCoy M. Gibson, Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents