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[54] **PROCESS FOR PREPARING POROUS AROMATIC POLYAMIDE FIBERS**

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[57] **ABSTRACT**

Porous fibers of an aromatic polyamide in which the void volume for pores having pore diameters of 0.12 micron or less is greater than 0.03 cc./gm., and the void volume for pores having pore diameters of more than 0.12 micron is less than 0.02 cc./gm. Such fibers are prepared by a process wherein freshly spun fibers are drawn and extracted in one or more solvent-containing aqueous baths of specified composition and temperature, subjected to steam when the drawing step is carried out at certain conditions, and are then dried. Such fibers are dyeable without the use of superatmospheric pressures or dyeing assistants.

4 Claims, No Drawings

PROCESS FOR PREPARING POROUS AROMATIC POLYAMIDE FIBERS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of copending application Ser. No. 71,286, filed Aug. 26, 1970 now issued as U.S. Pat. No. 3,695,992, which is a continuation-in-part of application Ser. No. 856,183, filed Sept. 8, 1969, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to dyeable fibers of aromatic polyamides and to a process for preparing such fibers. The term "fibers" as used herein includes continuous filaments and staple fibers made therefrom.

Fibers of aromatic polyamides, such as poly(-metaphenylene isophthalamide), possess very desirable physical and chemical properties, such as high temperature resistance, chemical stability and flame resistance. These fibers have found wide acceptance for uses requiring such properties, particularly in industrial applications such as filters and in fabrics where aesthetics are unimportant. However, aromatic polyamide fibers heretofore have been very difficult to dye, requiring the use of a combination of dyeing assistants, superatmospheric pressures and elevated temperatures. Consequently, these fibers have had limited acceptance for textile fabrics where fashionable colors are considered important.

The porous aromatic polyamide fibers prepared by the process of this invention overcome the poor dyeing characteristics of the aromatic polyamide fibers known heretofore.

SUMMARY OF THE INVENTION

The process of this invention provides a dyeable porous aromatic polyamide fiber in which the void volume for pores having pore diameters of 0.12 micron or less is greater than 0.03 cc/gm., the void volume for pores having pore diameters or more than 0.12 micron is less than 0.02 cc/gm., and the density is less than 1.3 gm/cc.; said pore diameters, void volume and density being determined by the Mercury Porosimeter Method described hereinafter. Preferably, the fiber has a void volume for pores having pore diameters of from about 0.012 to 0.12 micron of between 0.05 and 0.18 cc./gm. and a density of from 0.97 to 1.18 gm./cc. The fibers have a surprising degree of affinity for dyestuffs as compared to conventional nonporous fibers of the same aromatic polyamide.

The present invention provides a process for preparing a dyeable porous fiber of an aromatic polyamide comprising the sequential steps:

a. spinning a fiber from a solution of said polyamide in a solvent containing a solubilizing salt,
b. cooling the freshly spun fiber with aqueous liquid whereby the fiber becomes water-swollen,
c. drawing the fiber at a total draw ratio of at least 2.2:1 in one or more aqueous draw baths containing 20% to 35% by weight of said solvent and 6% to 11% by weight of said solubilizing salt, based on weight of the solution, said draw baths being heated to a temperature between about 70°C. and the atmospheric boiling point of said baths, with the proviso that when said total draw ratio of said filter in said draw baths is greater than 2.75:1, the draw baths are heated to a temperature of at least 90°C.,
d. passing the fiber through an aqueous bath to extract essentially all of said solvent and said solubilizing salt from the fiber, and
e. drying the fiber at a temperature of less than 170°C. while the fiber is free from substantial tension, with the proviso that where said draw baths contain 20% to 28% by weight of said solvent, based on weight of the draw bath, or are heated to a temperature of less than 90°C., than prior to the drying step, the fiber is subjected to saturated steam at a steam pressure of from 3 to about 60 psig. for a period of from 0.3 second to 10 minutes while the fiber is free from substantial tension.

DESCRIPTION OF THE INVENTION

The fibers prepared by the process of this invention are porous, and are defined in terms of void volumes, pore diameters, and density. For purposes of this invention, these three parameters are determined by a conventional Mercury Porosimeter Method. In this method an Aminco-Winslow Model 5–1709 Porosimeter (manufactured by the American Instrument Company, Silver Spring, Md., U.S.A.) with associated vacuum system and accessories, or equivalent standard mercury porosimeter having a pressure range of 0 to 15,000 p.s.i.a. (1,050 kg/cm.^{2} a.) is used. Thoroughly dried fibers to be evaluated are cut to lengths of 0.30 to 0.65 centimeter. A weighed sample of from 0.2 to 0.4 gram of the cut fibers are placed in an open penetrometer bulb, after which the bulb is capped and evacuated to 100 microns of mercury pressure. Mercury is then allowed to enter the bulb and the pressure is gradually raised to atmospheric pressure which fills in most of the open spaces between the cut fibers with mercury. The penetrometer is then moved from the vacuum chamber to the pressure chamber and the pressure is gradually increased. As the pressure is increased to about 100 p.s.i.a. (7 kg./cm.^{2} a.) the remaining open spaces between the cut fibers are filled. As the pressure is further increased, any penetration of mercury into pores of the fibers is detected by observing the level of mercury in the penetrometer stem. In this measurement, it is assumed that there is no penetration of the fiber at pressures up to 100 p.s.i.a. (7 kg./cm.^{2} a.), and that there is no further penetration between the cut fibers above 100 p.s.i.a. (7 kg./cm.^{2} a.). The amount of pressure required to force mercury into pores of a particular pore diameter is known in the literature, e.g., Ritter and Drake, "Pore Size Distribution in Porous Materials" Industrial and Engineering Chemistry, Analytical Edition, Volume 17, pages 782,791. The applicable equation is $P = -4\sigma \cos \theta / D$, where P is the applied pressure, σ is the surface tension of the mercury, θ is the contact angle between the mercury and the filaments, and D is the diameter of the pore. The value used for the surface tension of mercury is 474 dynes/cm. and the contact angle is 130°. Using these values, and appropriate conversion factors, the applicable equation becomes P (p.s.i.a.) = 176.8/ D (microns).

Thus, for fibers having no pores with diameters greater than 0.12 micron, there will be no penetration of mercury at pressures up to 1,450 p.s.i.a. (102 kg./cm.^{2} a.). For fibers having pore diameters of 0.012 to 0.12 micron, mercury will penetrate, and a corresponding decrease in mercury level in the penetrome-

ter stem will be observed, at pressure from 1,450 p.s.i.a. (102 kg./cm.^{2} a.) to 15,000 p.s.i.a. (1050 kg./cm.^{2} a.). The fibers of this invention may have some pore diameters greater than 0.12 micron. Therefore, a very small amount (equivalent to a void volume of less than 0.02 cc./gm. as defined hereinafter) of penetration may be observed at pressures between 100 p.s.i.a. (7 kg./cm.^{2} a.) and 1,450 p.s.i.a. (102 kg./cm.^{2} a.). The pores of the fibers may, if desired, contain a water-extractable solid material. In such instances, this solid material obviously must be water-extracted before evaluating by the Mercury Porosimeter Method. The fiber may be immersed in water at a temperature not exceeding 80°C. to extract the solid material, and then dried in air at a temperature not exceeding 110°C.

The void volume of the fibers in cubic centimeters per gram of fiber is determined by reading the penetrometer in the cubic centimeters of mercury in the predetermined stem as the pressure is increased from 100 p.s.i.a. (7 kg./cm.^{2} a.) to 15,000 p.s.i.a. (1050 kg./cm.^{2} a.) and dividing this volume by the number of grams of fiber sample in the porosimeter. The fibers have a void volume of greater than 0.03 cc./gm. for pores with pore diameters not greater than 0.12 micron and a void volume less than 0.02 cc./gm. for any pores with pore diameters greater than 0.12 micron. The preferred fibers have a void volume of about 0.05 to about 0.18 cc./gm. for pores with pore diameters of 0.012 to 0.12 micron.

Obviously, this method does not determine the entire void content of the fibers, since voids that are completely sealed, and voids accessible only by pores having pore diameters of less than 0.012 micron, will not be detected.

The density of the fibers is also determined by the Mercury Porosimeter Method. First, the volume of the sample of cut fibers in the porosimeter at 100 p.s.i.a. (7 kg./cm.^{2} a.) is determined by the equation: $[(wt._1) + (wt._2) - (wt._3)/(d)] - (V_1) = (V_2)$

wherein:

- $(wt._1)$ is the weight (gm.) of the fiber sample,
- $(wt._2)$ is the weight (gm.) of the penetrometer filled with only mercury at atmospheric pressure,
- $(wt._3)$ is the weight (gm.) of the penetrometer containing the fiber sample and filled with mercury at atmospheric pressure,
- (d) is the density (gm./cc.) of mercury at atmospheric pressure,
- (V_1) is the volume (cc.) of mercury that penetrates the spaces between the fibers as the pressure is the penetrometer is raised to 100 p.s.i.a. (7 kg./cm.^{2} a.) and
- (V_2) is the volume of the sample of the cut fibers in the penetrometer.

The density of the fibers is then determined by the equation:

$(wt._1)/(V_2)$ = density of the fibers.

The fibers have a surprising degree of affinity for dyestuffs as compared to conventional nonporous fibers of the same aromatic polyamide. It has been found that, within the range of pore diameters of 0.012 to 0.12 micron, there is a correlation between porosity and dyeability, with dyeability generally increasing with increasing porosity. It might be expected that providing pores would deleteriously affect fiber luster and tensile properties. However, the fibers show no appreciable delustering or loss of tensile strength. The clear fibers all show good reflectance levels.

The fibers are dyeable in boiling aqueous dyebaths without the use of superatmospheric pressures or dyeing assistants such as dye carriers. A wide range of dyes may be used such as acid, basic, disperse and premetallized dyes.

The term "aromatic polyamide" as used herein refers to a polymer wherein repeating units are linked by an amide group, i.e., the



radical wherein R is hydrogen or lower alkyl; the nitrogen and carbon atom of each repeating amide radical being directly attached to a carbon atom in the ring of an aromatic radical, that is, the nitrogen and carbon atom of each repeating amide group each replaces a hydrogen of an aromatic ring. The term "aromatic ring" means a carbocyclic ring possessing resonance.

The aromatic polyamides used in this invention may be prepared by reacting an aromatic diacid chloride with an aromatic diamine, the acid groups of the diacid chloride and the amine groups of the diamine being oriented ortho-, meta- or para-relative to each other (with meta-orientation being preferred), at a low temperature, e.g., a temperature below 100°C. Aromatic amino-acyl compounds also may be used in preparing suitable polymers. In addition, other polymer-forming ingredients, preferably up to about 10 mol percent, which need not contain an aromatic nucleus can be included without materially detracting from the desired physical and chemical properties of the polymers used to prepare the fibers of this invention. Substituents attached to any aromatic nucleus may be one or more or a mixture of lower alkyl, lower alkoxy, halogen, nitro, lower carbalkoxy, or other groups which do not form a polyamide during polymerization. Preferably, however, the diamine and diacid compounds utilized will be wholly aromatic, thus resulting in a polymer wherein the repeating units linked by an amide group are divalent aromatic radicals. Suitable polymers are disclosed in U.S. Pat. No. 3,094,511 and British Patent 1,106,190. The preferred aromatic polyamide is poly(-meta-phenylene isophthalamide).

The aromatic polyamides used in this invention are usually prepared in a solvent such as dimethylacetamide. The hydrogen chloride formed in the reaction is neutralized by adding an alkali or alkaline earth metal base. The salt formed by the neutralization assists in solubilizing the resulting polymer in the solvent.

Fibers may be spun by conventional dry-spinning methods. The spinning solution comprises an aromatic polyamide and an organic solvent containing a solubilizing salt. Preferably, the spinning solution contains from about 10% to about 30% polymer based on the weight of the solution. It is usually desirable to use the solution obtained during polymerization and neutralization, although the polymer may be prepared in one solvent system, isolated and redissolved in a different solvent system. Suitable spinning solvents include dimethylacetamide, dimethylformamide, and other lower alkylamides, dimethylsulfoxide and N-methyl-2-pyrrolidone. Suitable solubilizing salts include lithium bromide, lithium chloride and calcium chloride, with the latter two salts being preferred.

The spinning solution is forced through a spinneret to form fibers. These fibers then pass downward through a heated spinning cell. In the spinning cell, a large portion of the solvent is removed from the fibers, and a "skin" is formed around a highly viscous fiber core. As these fibers emerge from the spinning cell they are cooled by flooding them with an aqueous liquid. At this point the fibers become water-swollen. The swollen fibers are preferably drawn at a total draw ratio of at least 2.2:1, in one, or in a sequence of more than one, draw baths heated to a temperature of from 70°C. to the atmospheric boiling point of the bath, and each containing 20% to 35% of the same solvent as used in the spinning solution and 6% to 11% of the same solubilizing salt as used in the spinning solution. When the draw baths are at the lower end of this temperature range, higher concentrations of solvent are required, and, conversely, when the solvent concentration in the baths is at the lower end of this concentration range, higher temperatures are required. If the total draw ratio in these draw baths is greater than 2.75:1, they should be heated to a temperature of at least 90°C.; and after such drawing, the fibers are passed to following aqueous baths where they are given a moderate amount of additional draw and are extracted. If the temperature of the draw baths is less than 90°C., or if they contain less than 28% solvent, the fibers should be treated, after drawing and extraction, with saturated steam at a steam pressure of from 3 to about 60 psig. (0.21 to about 4.2 kg./cm.^{2} g.) or preferably 10 to about 55 psig. (0.7 to 3.9 kg./cm.^{2} g.), for a period of from 0.3 second to 10 minutes, while the fibers are free from substantial tension, i.e., while the fibers are free to relax or are under a minimum operable process tension. If desired, such steam treatment may also be used when the bath temperature is above 90°C., or when the bath solvent concentration is above 28%. Preferably, the fibers are drawn at least 2.8:1 in draw baths heated to a temperature of between 90° to 100°C., that contains 26 to 32 percent solvent and 6 to 9 percent solubilizing salt, after which small increments of additional draw may be given to the fibers as they are extracted in aqueous baths and the fibers then steam treated.

It is preferred that drawing and extracting be conducted in a multiple tank apparatus, wherein the first and second tanks contain the draw baths. The fibers are continuously passed from the first two tanks through the succeeding tanks wherein they are drawn lesser amounts in baths containing lesser amounts of solvent and solubilizing salt. In the final tank, or preferably the final two to five tanks, the baths consist substantially of water and the fibers are drawn to a sufficient degree to maintain operating tension. Preferably, the apparatus consists of ten adjacent tanks.

After drawing, extracting and steam treatment (if employed), the fibers are dried. Particular care must be taken in drying the fibers since improper heating will destroy the porosity essential to this invention. The fibers may be dried at room temperature, but this requires an excessive length of time. Therefore, the fibers are usually dried with air heated to a temperature of at least 100°C., but less than 170°C., and preferably between 110° to 150°C., while the fibers are free from substantial tension, i.e., while the fibers are free to relax or are under a minimum operable process tension. If desired, infrared heaters may be used to dry the fibers provided the temperature does not exceed 170°C., and the fibers are free from substantial tension.

In any subsequent processing before dyeing, it is important that the fibers not be subjected to temperatures higher than 170°C.

A suitable steaming apparatus for use herein is one containing a steaming chamber that is provided with adjustable slides at the entrance and exit to partially close them, thus permitting a buildup of steam pressure inside the chamber. For convenience, the adjustable slides can be placed adjacent the fiber entry and exit ports, which are shaped to allow the fiber to slide into and out of the chamber. The adjustable slides are shaped and positioned to close off as much open space in the fiber entry and exit ports as possible while still allowing the fiber to slide along the port openings in and out of the chambers as one step in the overall drawing, extracting, steaming and drying process.

The following examples further illustrate preferred embodiments of this invention. Inherent viscosities are determined at 25°C. using a solution of polymer in N,N-dimethylacetamide conaining 4% lithium chloride based on the weight of the solution, at a concentration of 0.5 gram of polymer per 100 cc. of solution. In the following examples, as well as elsewhere throughout the specification, all percents are by weight based on total weight unless otherwise specified.

For dyeing evaluations, dried fibers are cut by hand to staple fibers of a convenient length, e.g., less than about 10 centimeters and are dyed one hour at the boil under atmospheric pressure using a dye bath to fiber weight ratio of 133:1. The dye bath contains by weight, based on the weight of the fibers, 33.3 percent of an acid dye, C.I. Acid Blue 25 (D.I. 60255), 1.33 percent, of glacial acetic acid, and 1.6 percent of a nonionic surfactant. The surfactant is the product obtained by condensing 1 molecular proportion of oleyl alcohol with 20 molecular proportions of ethylene oxide. After completion of the dyeing cycle, the fibers are rinsed with water, then scoured twenty minutes at 80°C. using 1.5 percent by weight of the above surfactant and 1.5 percent by weight tetrasodium pyrophosphate (both based on the weight of the fibers) using a scouring bath to fiber weight ratio of 133:1. The dyed fibers are rinsed and then air dried at room temperature. Dye on fiber measurements are made by dissolving a weighed sample of dyed fiber in a 4 percent lithium chloride/96 percent N,N-dimethylacetamide solution and measuring absorbance at 586 millimicrons with a Beckman D.U. Spectrophotometer. Percent dye on fiber is calculated from the formula

$$\text{Percent dye on fiber (DOF)} = \frac{0.313 \times \text{absorbance at 586 millimicrons}}{\text{weight in grams of dyed fibers}}$$

where 0.313 is the factor derived from the slope constant (Beer's Law) for the dye, and relates dye concentration to absorbance = **100.**

In these examples, pore diameters, void volumes and densities are determined on dried, undyed fiber samples by the Mercury Porosimeter Method described above.

The K/S values are determined as described by Kubelka, P., and Munk, F. "Z. Tech. Physik" 12, 593–601 (1931). Reflectance measurements are made with the Color-master Differential reflectormeter using the red filter and the rotating assembly. A 2-gram sample of dyed fiber is hand-carded into an opaque, homoge-

neous pad (mass) measuring approximately 4 inches × 3 inches × three-fourths inch (10.2 cm. × 7.6 cm. × 1.9 cm.). The pad is placed in the instrument and a reflectance reading obtained as the sample is revolved. The pad is then turned over and another reading obtained as before. The average of these two reflectance readings is used to determine the K/S value.

EXAMPLE I

This example illustrates the preparation of three different samples of porous fibers.

Each of the three samples evaluated in this example is prepared from a spinning solution consisting of 18.5 percent, based on the weight of the solution of poly(-meta-phenylene isophthalamide) in N,N-dimethylacetamide (abbreviated hereinafter "DMAc") that contains 45 percent calcium chloride, based on the weight of the polymer. The polymer has an inherent viscosity of 1.55. For each sample, the spinning solution is passed through spinnerets into heated spinning cells. Cell temperatures are given in Table 1. The fibers are converged at a guide at the bottom of each cell, where they are flooded with water or an aqueous solution. The flooding liquids used are shown in Table 2. The fibers from adjacent spinning cells are then combined to give a large bundle of fibers referred to as "tow". Each tow is then drawn and extracted in aqueous baths contained in a ten-tank apparatus, as indicated. Draw ratios (abbreviated "D.R.") and the percent by weight of DMAc and calcium chloride are given in Table 3. After drying, a portion of the fibers are dyed as described above to determine dyeability.

Sample A: This sample is prepared using a tow containing 14,000 filaments and having a total denier of 130,000. The tow is drawn to a total draw ratio of 4.7:1 using a feed speed of 28 yards (25.6 meters) per minute. The baths are maintained at a temperature of 95°C. in all tanks. On leaving the wash-draw machine, the drain tow passes to a steam tube having a length of 5 feet (1.52 meters) where it is treated with saturated steam at a pressure of 30 psig. (2.11 kg./cm.² g.). The fibers are maintained under the lowest tension consistent with good operability in the steam tube. The steam-treated fibers then pass to a steam stuffer-box crimper where they are crimped and are free to relax. The crimped fibers are dried, while free to relax, by air heated at 110°C. for 60 minutes. The fibers are tested and results are shown in Table 4.

Sample B: This sample is prepared using a tow containing 40,800 filaments and having a total denier of 238,000. This tow is drawn at a total draw ratio of 4.9:1 at a feed speed of 26 yards (23.8 meters) per minute. All of the baths are maintained at 98°C. Steaming is carried out as in Sample A using saturated steam at a pressure of 35 psig. (2.46 kg./cm.² g.). The fibers are crimped and dried as in Sample A. Test results are shown in Table 4.

Sample C: This sample is prepared using a tow having 4,000 filaments and a total denier of 104,000. This tow is drawn at a total draw ratio of 3.0:1 at a feed speed of 30.0 yards (27.4 meters) per minute. All of the baths are maintained at 95°C. The fibers are then treated with saturated steam as in Sample A using a pressure of 40 psig. (2.81 kg./cm.² g.). The fibers are crimped and dried as in Sample A. Test results are shown in Table 4.

TABLE 1

Spinning Data

	Sample		
Cell Temperature, °C.	A	B	C
Top	280–300	260	320–330
Middle	280	260	310
Bottom	130–190	185	220

TABLE 2

Concentration of Aqueous Flooding Liquor, % By Weight

Sample	% DMAc	% $CaCl_2$
A	8–10	3–4
B	0	0
C	0	

TABLE 3

Tank number	Sample A			Sample B			Sample C		
	D. R. (X)	Percent DMAc	Percent $CaCl_2$	D. R. (X)	Percent DMAc	Percent $CaCl_2$	D. R. (X)	Percent DMAc	Percent $CaCl_2$
1	1.50	23.8	8.4	1.41	27	9	1.32	30	10
2	2.39	23.8	8.4	2.60	27	9	1.73	30	10
3	1.24	17	6	1.26	17	6	1.23	25	8
4	1.01	14	5	1.01	14	4	1.01	22	7
5	1.01	11	4	1.01	9	3	1.01	18	6
6	1.01	0	0	1.01	0	0	1.01	0	0
7	1.01	0	0	1.01	0	0	1.01	0	0
8	1.01	0	0	1.01	0	0	1.01	0	0
9	1.01	0	0	1.01	0	0	1.01	0	0
10	1.01	0	0	1.01	0	0	1.01	0	0

TABLE 4

	Sample		
	A	B	C
Denier per filament	3	1.6	10
Tenacity, gm./d.	4.0	3.9	2.5
Elongation, %	44	40	93
Void Volume, cc./gm. with pore diameters of:			
0.012–0.12 micron	0.050	0.051	0.162
0.12–1.7 microns	0.006	0.000	0.010
Density, gm./cc.	1.176	1.151	0.977
DOF, %	3.18	5.39	4.81
K/S	7.95	13.55	21.8

EXAMPLE II

Sample D of this example is prepared from an aromatic polyamide having an inherent viscosity of 1.16, obtained by reacting meta-phenylenediamine and essentially an equivalent amount of a mixture of 70 mole percent of isophthaloyl chloride and 30 mole percent of terephthaloyl chloride.

Sample E is prepared from an aromatic polyamide having an inherent viscosity of 1.10, obtained by reacting a mixture of diamines with an essentially equivalent

amount of a mixture of diacid chlorides. The diamine mixture consists of 85 mole percent of metaphenylenediamine and 15 mole percent of orthophenylenediamine. The diacid chloride mixture consists of 70 mole percent of isophthaloyl chloride and 30 mole percent terephthaloyl chloride.

Fibers are spun from each of these two polymers, using a spinning solution of 18.5 percent, based on the weight of the solution, in DMAc containing 45 percent calcium chloride based on the weight of polymer, in the manner described in Example I. The spinning cell is heated to 230°C. and water is used to flood the fibers as they exit from the cell. Tows are prepared from these fibers, drawn and extracted, steam treated and dried in the manner described in Example I except for details noted below. All the baths are maintained at 95°C. The draw ratio and the weight concentration of the DMAc and the calcium chloride is shown in Table 5. After the drawing and extracting step, the fibers are treated with saturated steam at a pressure of 15 psig. (1.05 kg./cm.^{2} g.) for 5 minutes in a pressure vessel. The filaments are dried by air heated to 110°C. for 30 minutes while free to relax. After drying a portion of the fibers are tested using procedures described above, results obtained are shown in Table 6.

TABLE 5

Tank No.	Samples D and E D.R.(X)	%DMAc	%$CaCl_2$
1	1.49	29.8	9.0
2	2.39	29.8	9.0
3	1.24	26.7	8.3
4	1.01	24.3	7.6
5	1.01	19.5	5.0
6	1.01	15.5	3.6
7	1.01	11.0	1.2
8	1.01	4.7	0.2
9	1.01	1.6	0
10	1.01	0	0

TABLE 6

	Sample D	E
Void volume, cc./gm., with pore diameters of:		
0.012–0.12 micron	0.172	0.080
0.12–1.7 microns	0.015	0.011
Density, gm./cc.	0.981	0.968
DOF, %	6.87	3.42
K/S	22.33	14.90

EXAMPLE III

This example illustrates the preparation of fibers in accordance with this invention whereby the fibers are not subjected to steam before drying. The samples evaluated in this example are prepared from a spinning solution consisting of 18.5 percent, based on the weight of the solution, of poly(metaphenylene isophthalamide) in DMAc containing 8.8 percent calcium chloride, based on the weight of the solution. The polymer has an inherent viscosity of 1.60. The solution is heated to 140°C. and passed through a spinneret containing 1,200 holes. The filaments pass downward through a spinning cell about 18 feet (5.5 meters) in length, that contains nitrogen at a temperature of about 360°C., whereby they lose a substantial portion of their dimethylacetamide. As the heated filaments emerge from the spinning cell, they are cooled with an aqueous solution containing 10 percent DMAc and 4 percent calcium chloride, based on the weight of the solution, and then wound to a package. The wound filaments contain 24 percent polymer, 29.8 percent DMAc, 8.6 percent calcium chloride and 37.6 percent water, based on the weight of the filaments. These filaments are then washed and drawn in a 10-tank apparatus containing bath solutions as described in Table 7.

TABLE 7

Tank No.	Bath Conc. Wt.% DMAc	$CaCl_2$	Bath Temp., °C.	D.R.(X)
1	1.4	6.7	95	1.33
2	31.7	7.2	95	2.33
3	20.3	6.1	95	1.21
4	14.7	4.5	95	1.01
5	9.8	2.9	95	1.01
6	5.9	1.6	95	1.01
7	3.4	0.7	95	1.01
8	1.6	0.3	95	1.01
9	0.7	0.1	95	1.01
10	0.2	0	95	1.01

The filaments enter this apparatus at a speed of 31.4 yards (28.7 meters) per minute and exit at a speed of 126 yards (115 meters) per minute and are drawn at a total machine draw ratio of 4.0:1 to provide filaments having a denier per filament of 3.0.

The drawn filaments are then crimped and dried. The filaments are dried by heating them while free to relax, with hot air for 60 minutes at a temperature of 110°C. These filaments are identified as Sample G.

In a separate experiment, filaments are prepared as for Sample G except that the bath concentration in tanks 1 and 2 is changed to 26 percent DMAc and 8 percent calcium chloride. These filaments are identified as Sample H.

In another separate experiment, filaments are prepared as for Sample G except that the temperature in the baths is decreased to 85°C., and the bath concentration in tanks 1 and 2 is changed to 26 percent DMAc and 7.3 percent calcium chloride. These filaments are identified as Sample I.

The three samples prepared in this example are tested using the previously described procedures and results obtained are shown in Table 8.

TABLE 8

	Sample G	H	I
Void volume, cc./g., with pore diameters of:			
0.012–0.12 micron	0.135	0.0213	0.0142
0.12–1.7 microns	0.0087	0.0053	0.0043
Density, gm./cc.	1.004	1.317	1.439
Tenacity, gm./d.	3.1	3.1	3.1
Elongation, %	72	75	69
DOF, %	7.55	2.24	0.75
K/S	21.7	4.9	3.5

It will be seen from these data that the fibers need not be treated with steam when the baths contain greater than 28 percent solvent and are heated to a temperature greater than 90°C. Decreasing the solvent concentration gives fibers of low dyeability unless the fibers are treated with steam before drying.

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

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

1. The process for preparing a dyeable porous fiber of an aromatic polyamide comprising the sequential steps:

a. dry spinning a fiber from a solution of said polyamide in a solvent containing a solubilizing salt,

b. cooling the fiber freshly-spun with aqueous liquid whereby the fiber becomes water-swollen,

c. drawing the fiber at a total draw ratio of at least 2.2:1 in one or more aqueous draw baths concontaining 20 to 35 percent by weight of said solvent and 6 to 11 percent by weight of said solubilizing salt, based on the weight of solution, said draw baths being heated to a temperature between about 70°C. and the atmospheric boiling point of said baths, with the proviso that when said total draw ratio of said fiber in said draw baths is greater than 2.75:1, the draw baths are heated to a temperature of at least 90°C.,

d. passing the fiber through an aqueous bath to extract essentially all of said solvent and said solubilizing salt from the fiber, and

e. drying the fiber at a temperature of less than 170°C. while the fiber is free from substantial tension, with the proviso that where said draw baths contain 20 to 28 percent by weight of said solvent, based on weight of the draw bath, or are heated to a temperature of less than 90°C., then prior to the drying step the fiber is subjected to saturated steam at a steam pressure of from 3 to about 60 psig. for a period of from 0.3 second to 10 minutes while the fiber is free from substantial tension.

2. The process of claim 1 wherein the fiber is drawn at a total draw ratio of at least 2.8:1 in a series of at least two aqueous draw baths that contain 26 to 32 percent by weight of said solvent and 6 to 9 percent by weight of said solubilizing salt, based on the weight of solution, and wherein the draw baths are heated to a temperature of between 90° to 100°C., followed by extraction of the fiber in water, and drying of the fiber with air heated to between 110° to 150°C.

3. The process of claim 2 wherein after being extracted and before being dried, the fiber is subjected to steam at a steam pressure of 10 to 55 psig. while being free from substantial tension.

4. The process of claim 3 wherein said aromatic polyamide is poly(meta-phenylene isophthalamide).

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