

- [54] **PROCESS FOR PRODUCING
HYGROSCOPIC ACRYLIC FIBERS**
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- [22] Filed: **Sept. 5, 1973**
- [21] Appl. No.: **394,502**

Related U.S. Application Data

- [62] Division of Ser. No. 143,571, May 14, 1971, now abandoned.

Foreign Application Priority Data

May 15, 1970 Japan..... 45-40910

- [52] U.S. Cl. **264/41; 8/130.1; 264/182;
264/343; 264/341**

- [51] Int. Cl.² **B29C 25/00**

- [58] Field of Search 8/115.5, 130.1; 264/343,
264/341, 182, 210 G

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[57]**ABSTRACT**

Hygroscopic acrylic fibers having high moisture regain and excellent sweat absorbing property together with the excellent characteristics of the acrylic fibers are disclosed. The fibers contain open capillary voids in a content (X) of 4.0 to 63.2 % and have a free surface area (S) of 1.0×10^4 to 1.7×10^6 cm²/g and a contact angle of the surface of the fiber with water of at most 45°.

6 Claims, 3 Drawing Figures

FIG. 1

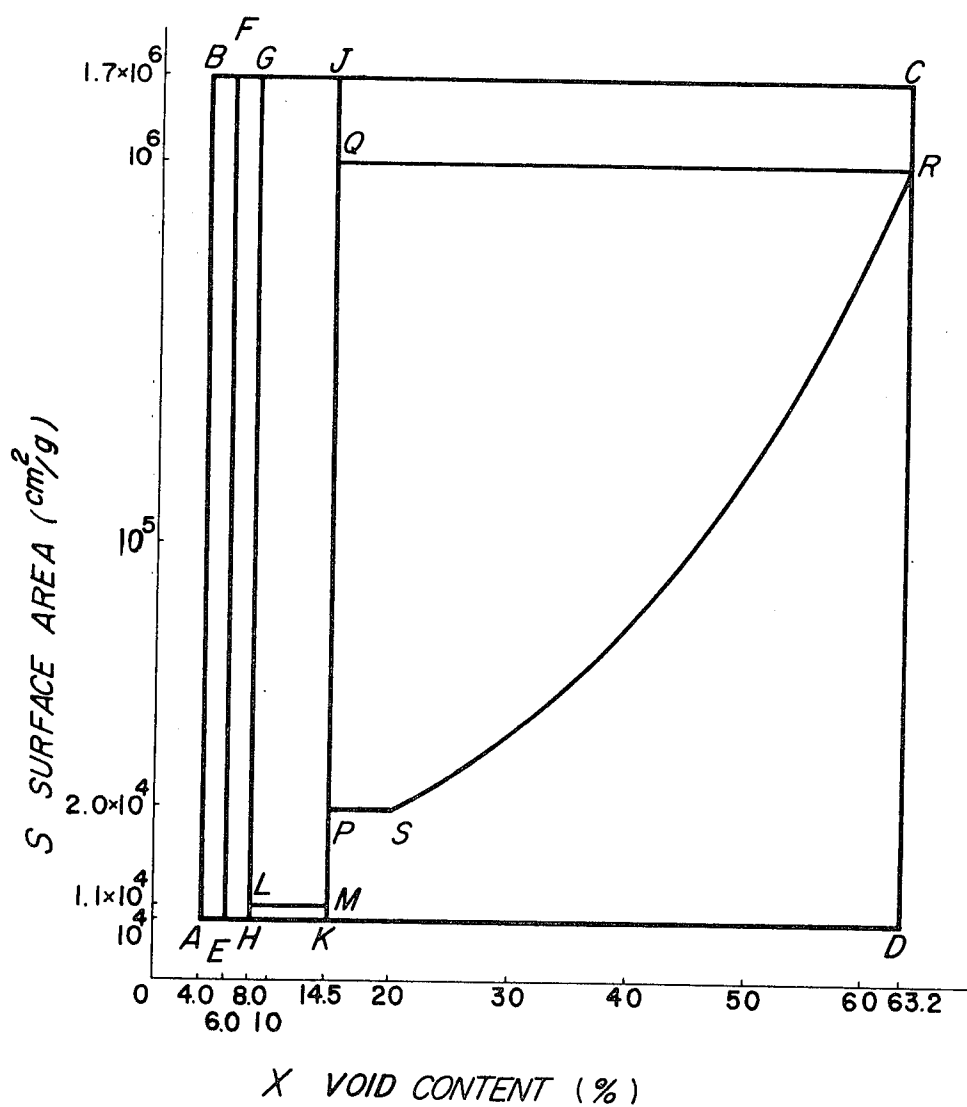


FIG. 2

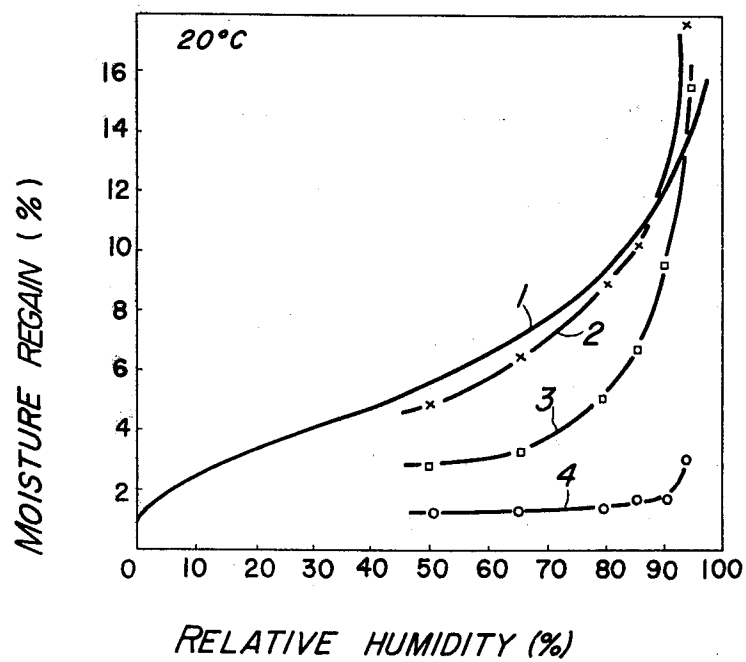
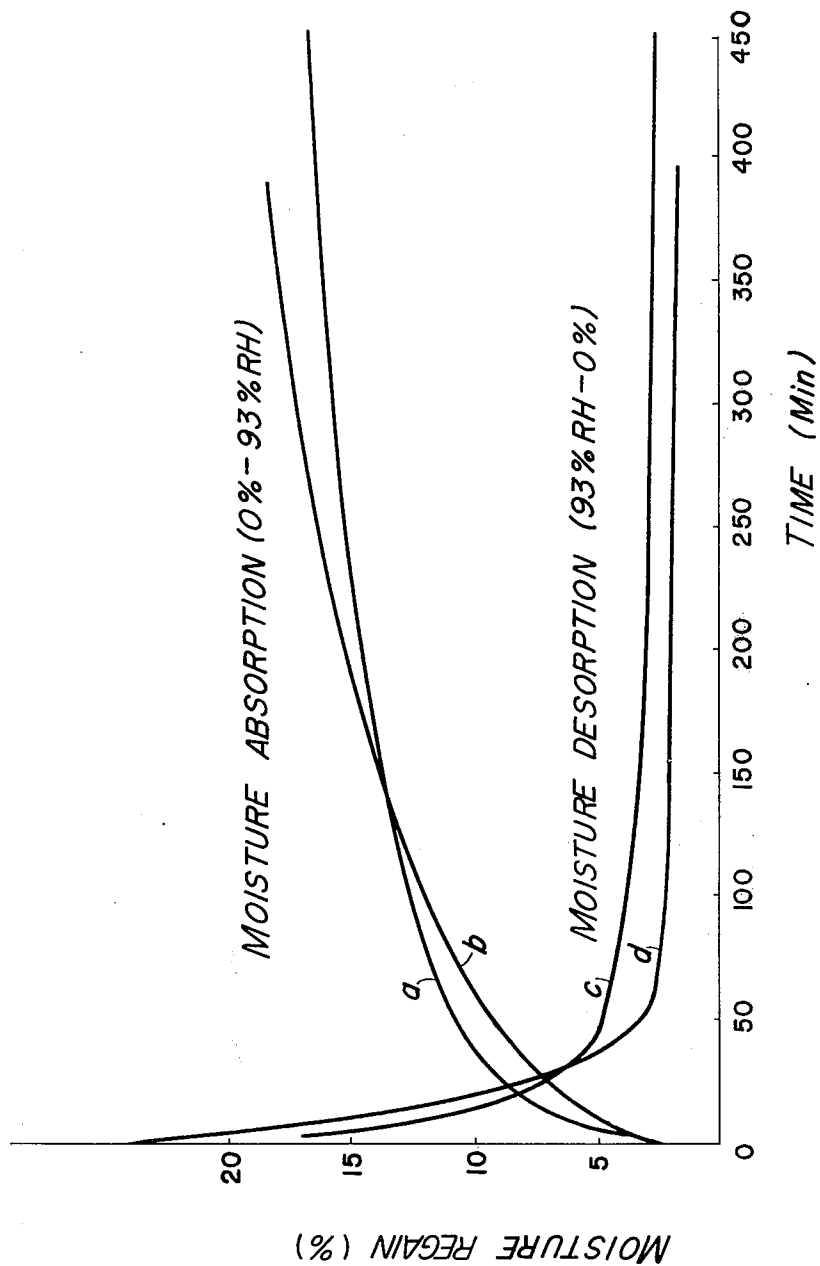


FIG. 3



PROCESS FOR PRODUCING HYGROSCOPIC ACRYLIC FIBERS

This is a division of application Ser. No. 143,571, filed May 14, 1971, and now abandoned.

The present invention relates to novel hygroscopic acrylic fibers and a process for producing the same. More particularly, it concerns hygroscopic acrylic fibers whose moisture regain is improved by subjecting acrylic fibers having voids to a treatment with a modifier. The moisture regain of acrylic fibers is extremely lower than that of natural fibers. When the acrylic fibers are converted to such clothes as underwears, hoses, bedclothes, those clothes do not provide excellent comfortableness to the human body and moreover they are not good from the hygienical standpoint and hence, the acrylic fibers have limitations in their end uses.

According to the inventors's researches, temperature and relative humidity which give comfortableness to the human body under the clothes are normally about 32°C and about 40 to 60 % RH, respectively. However, sweating causes increase of humidity under clothes and when the relative humidity exceeds about 80 %, one feels uncomfortable. When one wears clothes of non-hygroscopic fibers, sweats in hot environment or when one takes exercises wearing clothes of non-hygroscopic fibers, humidity under the cloth rapidly increases and one feels uncomfortable in short time. On the contrary, in case of wearing clothes of hygroscopic natural fibers such as cotton, increase of humidity under the clothes is slow and uncomfotableness is not rapidly caused. This is because cotton has an excellent hygroscopicity and water absorbing property. For example, moisture regain of cotton at 65 % RH at 20°C is 7.2 % and that of at 93 % RH at 20°C is 16.0 %. Thus, the difference (ΔH) in the moisture regains is 8.8 %. That is, the comfortableness in wearing clothes of cotton is attributed to the fact that the clothes of cotton have the function of controlling the increase of humidity under the clothes due to the great difference in moisture regains between at medium humidity and high humidity. Many attempts have been made to impart hygroscopicity to hydrophobic synthetic fibers such as polyesters, polyamides and acrylic fibers. For example, chemical methods such as copolymerization, graft copolymerization or blending of hydrophilic materials have been attempted as means for imparting hygroscopicity. However, according to these methods, a large amount of hydrophilic materials is required for attaining satisfactory hygroscopicity and hence, there is the defect that when a large amount of hydrophilic materials is incorporated into the polymer the properties of the fibers are degraded. Furthermore, British Pat. No. 812,460 and Japanese Patent Publication No. 538/68 mention a method for imparting hygroscopicity of hydrophobic synthetic fibers by treating them with aqueous sodium hydroxide solution and Japanese Patent Publication No. 4046/61 mentions a method for making fibers porous with foaming agent, etc. after forming of fibers. However, none of these methods can provide satisfactory hygroscopicity and furthermore, these methods have defects such as deterioration of fiber properties. Recently, researches have been made on graft polymerization of hydrophilic materials with electron rays. However, there have been problems with apparatus for attaining said purpose. Such being the

case, acrylic fibers having hygroscopicity have not yet been industrially obtained by said method.

It is an object of the present invention to provide acrylic fibers having hygroscopicity and sweat absorbing properties comparable to cellulose fibers without damaging the excellent characteristics of acrylic fibers and a process for producing such fibers on an industrial scale.

During the course of investigation, it has been found that use of mechanism of the moisture absorption with capillary condensation is very effective and the hygroscopic fibers of the present invention have been obtained by forming open capillary voids in fibers in a fiber forming step and in accelerating the capillary condensation of moisture into the voids.

That is, the hygroscopic fibers of the present invention comprise acrylonitrile copolymer, contain open capillary voids in a content (X) of 4.0 to 63.2 % and have a free surface area (S) of 1.0×10^4 to 1.7×10^6 (cm²/g), a contact angle of the surface of the fiber with water of at most 45°. The present fibers preferably have a difference (ΔH) in moisture regains between at 20°C, 93 % RH and 20°C, 65 % RH of higher than 5 % and an usual fiber diameter (about 10 μ to 50 μ).

The capillary voids are formed at the stage of removal of solvent and permeating of coagulation liquid when acrylonitrile polymer solution is extruded into coagulation liquid in wet spinning and voids thus formed are maintained in stable state in the fibers without being collapsed. The voids are fine capillaries having a distribution of diameters and different from the macroscopic and uniform hollows as in the hollow fibers. The content of voids is measured as follows:

Firstly, the density of the fibers excluding the open voids is measured by immersing a small amount of fibers in n-heptane, completely permeating n-heptane into the open voids by vacuum suction to 5 mmHg and then placing the fibers into the density-gradient tube. On the other hand, the apparent density of the fibers including the open voids is measured by placing a small amount of fibers in a picnometer, effecting between suction to a high vacuum of about 10^{-5} mmHG and then enclosing mercury thereto. Since according to this measuring method, mercury does not enter the voids having a radius of less than 7 μ , the apparent density can be measured. The content of voids is calculated in accordance with the following formula.

$$\text{Content of voids (\%)} = \frac{\text{Density obtained by using density-gradient tube} - \text{Density obtained by mercury enclosing method}}{\text{Density obtained by using density-gradient tube}} \times 100$$

The fibers which contain capillary voids have generally greater inner free surface as compared with those having no voids. The inner free surface means free surface which takes part in absorption of moisture in fiber structure. The free surface area was measured in accordance with the report of F. M. Nelson by keeping a small amount of sample at a low temperature, adsorbing nitrogen gas in the sample under a certain pressure, estimating the amount of adsorbed nitrogen by gas chromatography and calculating the free surface area in accordance with BET theory (F. M. Nelson, E. T. Eggertsen, Anal Chem, 30 1387 (1958)).

It has been found that absorption of moisture into open capillary voids increases with increase of hydrophilic degree of free surface of the voids and that it is necessary for acrylic fibers to make the surface hydrophilic in order to provide fibers of excellent hygroscopicity with the lowest possible voids content. The degree of the hydrophilic property of the surface is indicated by the contact angle of the surface of the fiber with water and is measured by keeping a single fiber perpendicular to the water surface after making it hydrophilic and reading the angle of water surface with the fiber with a microscope.

The hygroscopicity of the fibers is expressed by moisture regain and is measured by weighing the fibers in the absolutely dry state, allowing the fibers to absorb moisture in a desiccator where the humidity is adjusted to a certain relative humidity until the weight of the fibers reaches equilibrium and then weighing the fibers to calculate the moisture regain in accordance with the following formula.

$$\text{Moisture regain (\%)} = \frac{\text{Weight of the fibers after moisture absorption} - \text{Weight of fibers in absolute dry state}}{\text{Weight of fibers in absolute dry state}} \times 100$$

The difference (ΔH) in moisture regain is obtained by subtracting moisture regain at 65 % RH at 20°C from the moisture regain at 93 % RH at 20°C.

The difference (ΔH) in the moisture regain of usual acrylic fibers having no voids is about 1 to 2 %.

As the result of various researches on void content, free surface area and contact angle of the surface of the fibers with water for providing desired fiber properties and excellent hygroscopicity in acrylic fibers having usual fiber density, it has been found that a void content (x) of $4.0\% \leq x \leq 63.2\%$, a free surface area (s) of $1.0 \times 10^4 \text{ cm}^2/\text{g} \leq S \leq 1.7 \times 10^6 \text{ cm}^2/\text{g}$ and a contact angle of the surface of fibers with water of at most 45° are effective for the above mentioned purpose. That is, when the void content and the surface area exceed said ranges, the balance of fiber properties cannot be kept, mechanical properties decrease and dyeing brightness is lowered. Furthermore, relation between the void content and the free surface area, namely, average size of voids also has an effect on the fiber properties. For example, when the void content is high and the surface area is small, voids of large size are present and hence improvement of hygroscopicity due to capillary condensation is poor and the mechanical properties are also not satisfactory. Improvement of hygroscopicity can be attained when a great number of voids of small size are present and in such case, the fiber properties also tend to be satisfactory.

Referring to FIG. 1, when the void content is lower than straight line AB (void content 4.0 %) or the free surface area is less than the straight line AD (free surface area $1.0 \times 10^4 \text{ cm}^2/\text{g}$), sufficient hygroscopicity cannot be attained under usual conditions. For example, if hygroscopicity is to be increased in the above case, it is necessary to carry out the treatment for making the fibers hydrophilic under severe conditions. However, such treatment results in coloration of fibers, deterioration of mechanical properties. Furthermore, the fibers whose void content is higher than the straight line CD (void content 63.2 %) or those whose free

surface area is greater than the straight line BC (the surface area $1.7 \times 10^6 \text{ cm}^2/\text{g}$) can be produced with difficulty under the usual spinning conditions. Even if such fibers are produced employing special spinning conditions, the mechanical properties are deteriorated and the balance of the fiber properties cannot be kept.

Therefore, the hygroscopic acrylic fibers intended by the present invention can be obtained when the void content and the free surface area of the fibers are within the area surrounded by ABCD and the contact angle of the surface of the fibers with water is at most 45° . Furthermore, when the void content is higher than the straight line KJ ($X = 14.5\%$) within the area ABCD, such high hygroscopicity that ΔH is more than 8 % can be easily obtained. Especially when X and S satisfy the requirements $14.5 \leq X \leq 63.2\%$, $10^4 \leq S \leq 10^6 \text{ (cm}^2/\text{g)}$ and $\log S \geq 114/(100 - X) + 2.90$, namely, they are within the area of PQRS, the hygroscopicity, especially the value of ΔH attained is equal to or more than that of cellulosic fibers such as cotton and rayon and mechanical properties and dyeability are not lowered so much. Furthermore, the acrylic fibers above described can be easily produced on an industrial scale. When X and S have the relation $\log S < 114/(100 - X) + 2.90$, namely, they are in the range of below the curve RS, a hygroscopicity expressed by ΔH of more than 8 % can be attained, but since the average size of voids become larger, the hygroscopicity attained is not so high for the void content and mechanical properties of the fibers are somewhat deteriorated. When the void content is lower than the straight line KJ ($X = 14.5\%$), it is difficult to obtain a hygroscopicity expressed by ΔH of more than 8 % under usual conditions. However such hygroscopicity can be obtained by adopting somewhat severe treating conditions for making the surface of the fibers hydrophilic or by employing a copolymer of acrylonitrile with a hydrophilic monomer or blended polymer of such copolymer and acrylonitrile copolymer as a fiber forming polymer. That is, when the void content and the surface area satisfy the relation $8.0 \leq X \leq 14.5\%$ and $1.1 \times 10^4 \leq S \leq 1.7 \times 10^6 \text{ (cm}^2/\text{g)}$, namely, they are within LGJM, ΔH of more than 8 % can be obtained by treating the fibers comprising conventional acrylonitrile copolymer with modifier under such condition that ΔH of control fibers having the same compositions and containing no voids becomes more than 2 %. Alternatively, when the void content and surface area satisfy the relations $6.0 \leq X \leq 14.5\%$ and $1.0 \times 10^4 \leq S \leq 1.7 \times 10^6 \text{ (cm}^2/\text{g)}$, namely, they are within EFJK, ΔH of more than 8 % can be obtained by treating the fibers comprising the copolymer of blended polymer described above with modifier under such condition that ΔH of control fibers having the same compositions and containing no voids becomes more than 3 %.

FIG. 2 shows isothermal absorption curves of the fibers of the present invention, cotton fibers and conventional non-hygroscopic acrylic fibers.

In FIG. 2, curve (1) indicates scoured cotton fibers, curve (2) indicates the hydrophilic fibers of the present invention which corresponds to the fibers of Sample No. 43 in Table 3 shown hereinafter, curve (3) indicates the hydroscopic fibers of the present invention which correspond to the fibers of Sample No. 42 in Table 3 and curve (4) indicates the conventional acrylic fibers obtained by spinning a copolymer comprising 93 % of acrylonitrile and 7 % of vinyl acetate by

the usual wet spinning method. Curve (1) was obtained using values in the literature [A. R. Urquhart, A. M. Williams, J. Text. Inst. 15, T138 (1924)].

FIG. 3 illustrates the course of moisture absorption and moisture desorption of the fibers according to the present invention and the cotton fibers. The moisture absorption course is obtained by measuring the increment of weight of fibers immediately after introducing the fibers in absolute dry state into a cell in which the humidity is adjusted to 20°C, 93 % RH with a saturated aqueous solution of Glauber's salt. The moisture desorption course is obtained by measuring reduction of weight immediately after introducing the fibers in absorption equilibrium at 20°C 93 % RH into a cell which is rendered to the nearly absolute dry state with 95 % sulfuric acid. Curves (a) and (c) in FIG. 3 show the moisture absorption and desorption courses of the cotton fibers, respectively and curves (b) and (d) indicates the moisture absorption and desorption courses of the fibers of the present invention which corresponds to Sample No. 43 respectively. As is seen from FIGS. 2 and 3, the hygroscopic acrylic fibers of the present invention are comparable to natural fibers having cotton-like properties in both moisture regain and the moisture absorption and desorption rate.

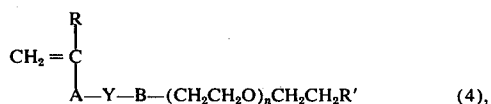
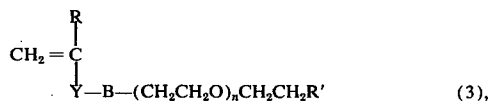
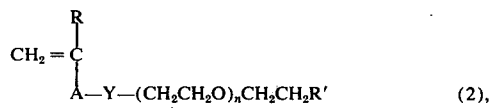
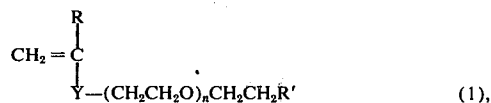
Since the hygroscopic fibers of the present invention are those in which hygroscopicity is given by open capillary voids and by making the surface of the fibers hydrophilic, there are provided characteristics that the hygroscopic effect is durably kept and moisture regain is higher than that of the fibers obtained by other methods.

Further characteristic of the present invention is that the acrylic fibers having said characteristics have water absorbability because they have a great number of open voids. This water absorption amount has a value similar to the voids content in the present invention.

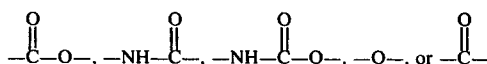
The acrylic fibers in the present invention are those made of an acrylonitrile homopolymer, an acrylonitrile copolymer containing more than 50 % by weight of acrylonitrile or a blend thereof. Copolymer components other than acrylonitrile which are copolymerizable with acrylonitrile include; however monoolefinic unsaturated compounds such as acrylic acid or esters thereof, α -chloroacrylic acid or esters thereof, methacrylic acid or esters thereof, e.g., methyl methacrylate, ethyl methacrylate, butyl methacrylate, methoxymethyl methacrylate and β -chloroethyl methacrylate, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene, methacrylonitrile, acrylamide, methacrylamide, 2-chloroacrylamide or monoalkyl substituted product of these amides, methyl vinyl ketone, vinyl carboxylic ester, e.g., vinyl acetate, vinyl chloroacetate, vinyl propionate, vinyl stearate, N-vinyl imides, e.g. N-vinyl phthalimide and N-vinyl succinimide, methylene malonic esters, itaconic acid or esters thereof, N-vinyl carbazole, vinyl furan, alkyl vinyl ethers, vinyl sulfonic acid, ethylene α,β -dicarboxylic acid or anhydrides or derivatives thereof, e.g., diethyl furmaric acid, diethyl maleic acid, diethyl citraconate and diethyl mesconate, styrene, vinyl naphthalene, vinyl substituted heterocyclic amines, e.g., vinyl pyridines, alkyl substituted vinyl pyridines, e.g., 2-vinyl pyridine, 4-vinyl pyridine, 5-methyl-2-vinyl pyridine, 1-vinyl imidazole or alkyl substituted 1-vinyl imidazoles, e.g., 2-, 4-, or 5-methyl-1-vinyl imidazole and other polymerizable materials having the $>C=C<$ structure.

Higher hygroscopicity can be obtained by using monomers having a hydrophilic property as high as possible line those to be copolymerized with acrylonitrile. The hydrophilic monomers suitable in the present invention are as follows:

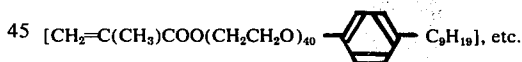
The monomers having the general formula



(wherein R is hydrogen or lower alkyl having not more than 4 carbon atoms, R' is $\text{R}_1 - \text{O} -$, $\text{R}_1\text{R}_2 - \text{N} -$, $\text{R}_1 - \text{COO} -$, $\text{R}_1 - \text{S} -$, or $\text{R}_1 - \text{CONR}_2 -$ (wherein R_1 and R_2 are alkyl, aryl or aralkyl groups which may or may not be substituted with substituents having no active hydrogen), A and B are alkylene, arylene or aralkylene groups which may or may not be substituted with substituents having no active hydrogen, Y is



and n is an integer of 5 to 100). Illustrative of these monomers are lauroxy polyethylene glycol acrylate $[\text{CH}_2=\text{CHCO}(\text{OCH}_2\text{CH}_2)_{30}\text{OC}_{12}\text{H}_{25}]$, nonyl phenoxy polyethylene glycol methacrylate



The hygroscopic acrylic fibers of the present invention can be obtained using a wet spinning apparatus used for producing conventional acrylic fibers and can be produced by wet spinning a polymer solution containing acrylonitrile copolymer to produce coagulated fibers having a large number of open capillary voids, stretching the fibers to fix the voids without collapsing them and subjecting the fibers to a treatment with a modifier. That is, acrylic fibers before being subjected to dry heat treatment generally contain a large number of voids. These voids are collapsed by drying the fibers at a high temperature under tension. On the other hand, according to the process of the present invention, a large number of voids can be maintained in the fibers without collapsing.

It has been found that said fibers having a large number of open capillary voids exhibit excellent hygroscopicity as compared with the fibers in which voids have been collapsed. However, the hygroscopicity of such fibers is still unsatisfactory and the articles made of these fibers have poor utility because they tend to

cause fibrillation and pilling. As the results of intensive researches on production of fibers having further improved hygroscopicity and causing no fibrillation and pilling, it has been found that when the surface of the acrylic fibers having open capillary voids is made hydrophilic with a modifier, capillary condensation of moisture in the voids is accelerated to highly increase hygroscopicity and to obtain useful fibers having low fibrillation and pilling tendency. Furthermore, as the result of researches on relations between properties of the fibers and the ranges of void content (X) and surface area (S) of the fibers whose surfaces are made hydrophilic, it has been found that when X and S are within the range of $4.0 \leq X \leq 63.2\%$ and $1.0 \times 10^4 \leq S \leq 1.7 \times 10^6 \text{ cm}^2/\text{g}$, namely, within the area of ABCD in FIG. 1, hygroscopic fibers having excellent properties can be obtained.

In more detail, the hygroscopic acrylic fibers of the present invention can be produced by combination of the following steps,

- a. preparing a spinning solution by dissolving an acrylonitrile copolymer in a solvent thereof,
- b. extruding said spinning solution into aqueous coagulation liquid containing said solvent to form fibers,
- c. stretching the thus formed fibers,
- d. drying the stretched fibers, and
- e. treating the fibers with a modifier.

In said steps, the capillary voids are mostly produced in the step (b) and the content and the size of the voids depend upon compositions of copolymer, compositions of spinning solution, compositions and temperature of coagulation liquid and spinning speed. In general, with rapid coagulation, the number of voids formed is increased. That is, the voids tend to be more easily formed with lower concentration of polymer in the spinning solution and of the solvent in the coagulation liquid, higher temperature of the coagulation liquid and higher spinning speed.

For example, when spinning is carried out employing a polymer concentration of 20 to 25 % in a spinning solution containing dimethyl acetamide as a solvent, a spinning speed of 0.5 to 2.5 in terms of jet stretch which is the ratio of take up speed of the first roller to extruding speed from spinneret, a concentration of dimethyl acetamide in dimethyl acetamidewater coagulation liquid of less than 80 %, and a temperature of the coagulation liquid of higher than 20°C, coagulated fibers having a void content of 10 to 70 % and a free surface area of 10^4 to $2 \times 10^6 \text{ cm}^2/\text{g}$ are obtained. The fibers having such characteristics can be produced with any commonly used solvents by suitably choosing the spinning conditions. When thus obtained coagulated fibers are stretched while washing them in a boiling water, the void content and the surface area are kept unchanged or somewhat decreased, but most of the voids are maintained without collapsing. If said stretched fibers are subjected to the usual drying treatment, most of the voids therein are collapsed and only a low hygroscopicity is obtained. Therefore, attempts have been made to keep the void content and the surface area as they are in the fibers after stretched. As the results, it has been found that this is accomplished by drying the stretched fibers at a low temperature of lower than 60°C or by subjecting them in wet state by annealing with saturated steam at a pressure of less than 2.8 kg/cm² gauge and then drying them at a temperature of lower than 110°C. The coagulated acrylic

fibers in water swollen state are sensitive to heat and therefore, drying of said fibers at a high temperature causes collapse of most of the voids. However, when the coagulated acrylic fibers are dried at a low temperature as mentioned above, open capillary voids are maintained. These drying conditions are applicable to coagulated acrylic fibers obtained by wet spinning with any solvent. Thus, the hygroscopic fibers of the present invention can be obtained by producing coagulated fibers having a void content of more than 4 % and a free surface area of more than $10^4 \text{ cm}^2/\text{g}$ by choosing suitable spinning conditions and drying the coagulated fibers under the drying conditions as mentioned above to fix the voids in a content of 4.0 to 63.2 % and a free surface area of 10^4 to $1.7 \times 10^6 \text{ cm}^2/\text{g}$.

Furthermore, it has been found that the treatment with modifier may be made before or after the drying of the fibers and the contact angle of the surface of the fibers with water or at most 45° is the most effective.

Said treatment with modifier for making the surface of the fibers hydrophilic can be accomplished by forming a hydrophilic layer on the free surface of the fibers by hydrolysis of the fibers with an aqueous solution of alkali metal hydroxide or carbonate, sulfuric acid, hydrochloric acid, or nitric acid, or amidoxime reaction with hydroxylamine aqueous solution of hydroxylamine salts such as hydroxylamine sulfate, hydroxylamine hydrochloride and hydroxylamine phosphate.

If the fibers are colored in said treatment with a modifier, the fibers can be bleached with the usual bleaching agent.

The conditions for the treatment with the above modifiers vary depending upon whether it is carried out before or after drying, and the latter generally requires severe conditions.

As mentioned above, the hygroscopic acrylic fibers of the present invention are produced by any one of the following four methods each of which comprises said steps (a) to (e).

1. Spinning conditions is extruded and the resultant fibers are coagulated and stretched. Thereafter, drying step (d) is carried out at a temperature of lower than 60°C and then the fibers are subjected to the treatment with modifiers of the step (e).
2. Spinning solution is extruded and the resultant fibers are coagulated and stretched. Thereafter, the fibers are subjected to the treatment with the modifier of the step (e) and then are subjected to drying step (d) at a temperature of lower than 60°C.
3. Spinning solution is extruded and the resultant fibers are coagulated and stretched. Thereafter, the fibers in wet state are annealed with saturated steam at a pressure of lower than 2.8 kg/cm² and then are subjected to drying step (d) at a temperature of lower than 110°C.
4. Spinning solution is extruded and the resultant fibers are coagulated and stretched. Thereafter, the fibers are subjected to the treatment with modifiers of the step (e) and then the fibers in wet state are annealed with saturated steam at a pressure of lower than 2.8 kg/cm². Thereafter, they are subjected to the drying step (d) at a temperature of lower than 110°C.

There are no differences in the void content and the surface area attained by the above four methods. However, the methods (3) and (4) have advantages over methods (1) and (2) in that according to the former, dyeability and fibrillation resistance of the resultant

fibers are improved in higher degree than according to the latter.

The present invention is illustrated more particularly by way of the following Examples, but as will be more apparent, is not limited to the details thereof.

EXAMPLE 1

A copolymer consisting of 93 % of acrylonitrile and 7 % of vinyl acetate ($[\eta] = 1.6$) was dissolved in dimethyl formamide to prepare a spinning solution having a concentration of 24 % by weight. The spinning solution was extruded through a spinneret into an aqueous solution of dimethyl formamide having various concentrations and temperatures and at various jet stretches. The

contact angle, hygroscopicity of the fibers and other fiber properties are shown in Table 1.

In Table 1, Samples No. 1 - 8, 11, 13, 16, 17 and 19 were within the area PQRS in FIG. 1 and had a ΔH of more than 8 % and good fiber properties. Samples No. 9 and 10 were within the area ABJK and had a ΔH of less than 8 %. Samples No. 12, 14 and 15 were in the area below the curve RSP and had somewhat low mechanical properties. Sample No. 18 had a surface area of larger than $10^6 \text{ cm}^2/\text{g}$ and large ΔH , but somewhat lower dyeing brightness. Samples No. 20, 21 and 23 were comparative samples and had a ΔH of less than 5 %. The fibers of Sample No. 22 had a low dyeing brightness and low fibrillation resistance.

Table 1

Sample No.	Coagulation liquid		Jet Stretch	Drying temperature (°C)	Void content (X) (%)
	Concentration (%)	Temperature (°C)			
1	55	60	0.9	40	17.7
2	"	"	1.5	"	27.4
3	"	"	2.4	"	38.4
4	"	"	1.3	"	19.7
5	"	"	1.7	"	22.2
6	"	80	0.9	"	17.9
7	65	60	"	"	16.2
8	"	80	"	"	23.1
9	55	40	"	"	4.3
10	"	60	"	53	8.6
11	"	50	"	40	15.7
12	"	"	1.3	"	20.1
13	"	"	1.7	"	28.5
14	"	"	2.0	"	37.4
15	"	"	2.0	60	34.1
16	65	40	0.9	40	17.5
17	"	"	1.3	"	26.0
18	"	"	1.7	"	29.5
19	"	"	2.0	"	40.0
20	55	40	0.9	70	5.0
21	"	60	1.7	70	24.0
22	70	30	0.9	40	33.8
23	55	60	"	80	2.3
Free surface area (S) $\times 10^4 \text{ (cm}^2/\text{g)}$	Contact angle (°)	Difference in moisture regain $\Delta H \text{ (%)}$	Denier (d)	Dry strength (g/d)	Dry elongation (%)
8.13	45	10.0	2.27	3.43	18.7
32.3	41	13.2	2.36	2.57	12.3
36.1	42	13.7	2.32	2.34	11.1
25.2	38	13.8	1.55	2.77	12.5
23.7	40	13.6	0.90	2.53	9.4
20.9	37	13.7	2.16	2.84	13.6
27.7	39	11.7	2.29	2.57	14.1
38.4	41	13.7	2.27	2.31	13.0
2.5	40	6.7	2.30	2.48	18.4
6.2	42	5.1	2.29	3.30	19.7
2.2	40	8.2	2.25	2.90	18.7
1.5	"	7.7	2.27	2.01	17.6
3.4	41	9.0	2.24	2.61	14.8
3.9	40	8.0	2.30	2.11	13.8
1.4	"	7.9	2.31	1.96	12.5
91.1	39	8.9	2.40	3.12	18.1
39.4	"	12.0	2.38	3.10	19.2
109.0	40	12.3	2.41	2.69	15.7
91.0	"	13.6	2.36	2.70	15.9
0.9	"	4.1	2.40	3.40	18.9
0.9	"	3.9	2.50	2.53	15.6
188.0	41	14.0	2.49	2.06	13.1
2.6	40	3.3	2.83	2.93	36.8

resultant fibers were stretched to 4.5 times the original length in boiling water to obtain fiber tows. Then, crimps were mechanically imparted to said tows in the wet state and the tows were cut into staples and the staples were dried at a temperature of lower than 60°C. These staples were immersed in 15 g/l of aqueous sodium hydroxide solution at 70°C for 30 minutes to make them hydrophilic and then they were washed with water and dried to produce hygroscopic fibers. Production conditions, void content, free surface area,

EXAMPLE 2

A copolymer ($[\eta] = 1.6$) consisting of 88 % of acrylonitrile, 5 % of vinyl acetate, and 7 % of methacrylic acid was dissolved in dimethyl acetamide to prepare a spinning solution having a concentration of 23.5 % by weight. This spinning solution was extruded through a spinneret into an aqueous solution of dimethyl formamide with various concentrations and temperatures and at various jet stretches. The resultant fibers were

stretched to 5 times the original length in boiling water to obtain tows. Then, the tows were treated in 10 g/l of aqueous solution of sodium hydroxide at 70°C for 5 minutes and thereafter were washed with boiling water.

The resultant fibers were mechanically crimped in the wet state and then were cut into staples and dried at a temperature of lower than 60°C. Production conditions, void content, free surface area, contact angle, hygroscopicity and other fiber properties of the thus obtained fibers are shown in Table 2.

In Table 2, samples No. 25 – 31 and 34 were within the area PQRS and had a ΔH of more than 8 %. Sample No. 24 had a surface area (S) of greater than $10^6 \text{ cm}^2/\text{g}$ and exhibited somewhat low dyeing brightness. Samples No. 32 – 35 were in the area below the curve RSP and had somewhat poor mechanical properties. Samples No. 36 to 40 were comparative samples and Samples No. 36, 37 and 40 had a void content of higher than 63.2 % and poor mechanical properties. Samples No. 38 and 39 had S of smaller than $10^4 \text{ cm}^2/\text{g}$ and ΔH of less than 5 %.

Table 2

Sample No.	Coagulation liquid		Jet Stretch	Drying temperature (°C)	Void content (X) (%)
	Concentration (%)	Temperature (°C)			
24	40	20	0.9	40	20.3
25	"	40	"	"	34.2
26	"	60	"	"	55.0
27	50	20	"	50	23.7
28	"	40	"	"	32.5
29	"	60	"	"	40.8
30	"	40	1.3	"	35.0
31	"	60	"	"	42.3
32	55	20	1.5	50	41.5
33	"	40	"	"	52.0
34	"	60	"	40	61.0
35	"	80	"	60	58.6
36	40	60	"	40	64.2
37	"	"	"	50	65.0
38	"	50	"	65	45.3
39	"	"	"	"	53.2
40	65	80	"	"	69.0
Free surface area (S) $\times 10^4 (\text{cm}^2/\text{g})$	Contact angle (°)	Difference in moisture regain ΔH (%)	Denier (%)	Dry Strength (g/d)	Dry Elongation (%)
161.0	40	14.5	2.30	2.16	22.9
90.2	41	13.6	2.10	2.80	24.1
88.3	"	15.7	2.21	2.60	22.7
5.8	40	10.1	2.09	3.20	24.8
10.2	39	11.2	2.31	3.40	25.9
12.1	"	12.3	2.20	3.42	25.8
4.5	"	10.4	2.10	3.16	24.6
9.1	42	10.9	2.15	3.38	26.1
3.2	41	8.6	2.13	2.09	15.3
11.0	"	9.3	2.16	1.98	15.4
20.2	40	9.5	2.22	1.89	12.6
3.1	"	8.0	2.21	1.93	16.1
63.0	"	10.3	2.11	1.54	19.6
10.1	"	7.9	2.28	1.69	20.1
0.9	"	4.3	2.26	1.70	19.8
0.9	41	4.5	2.24	1.91	19.8
1.3	"	5.6	2.13	1.65	10.9

EXAMPLE 3

A copolymer ($[\eta] = 1.5$) consisting of 94 % of acrylonitrile and 6 % of vinyl acetate was dissolved in dimethyl acetamide to prepare a spinning solution having a concentration of 22 % by weight. The thus obtained spinning solution was extruded into an aqueous solution of dimethyl acetamide with various concentrations and temperatures and at various jet stretches. The resultant coagulated fibers were stretched to 4.5 times the original length in boiling water and then crimps were mechanically imparted to the tows in the wet

state. These crimped tows in the wet state were annealed with saturated steam at a pressure of 0.8 to 2.8 kg/cm^2 gauge and were cut into staples and dried at a temperature of lower than 110°C. Then, these staples were subjected to treatment with aqueous solutions of sodium hydroxide, sodium carbonate, sulfuric acid and hydroxylamine sulfate, respectively. Production conditions, void content, free surface area, contact angle, hygroscopicity and other fiber properties of the thus obtained fibers are shown in Table 3. In Table 3, Samples No. 41 – 43, 56 and 56 were within the area PQRS and had a ΔH of more than 8 %. Samples No. 44 – 47 were within the area LGJM, but had a ΔH of more than 8 % because the conditions for treatment with modifier were the somewhat severe condition that the fibers were treated with 15 g/l of NaOH at 100°C for 30 minutes. It was found that when control fibers having no voids were subjected to the same treatment, ΔH of 2.2 % was obtained. The control fibers were obtained by the same method as in this Example except that the fibers were dried on a heated roller at 130°C to collapse

them. Sample No. 10 in Example 1 was within the same area as in the above, but since it was treated with 15 g/l of NaOH at 70°C for 30 minutes, ΔH thereof was 5.1 %. When fibers having no voids were subjected to the same treatment, ΔH of 1.8 was obtained. Sample No. 48 was within the area HLMK and in this case ΔH of more than 8 % cannot be attained even by a treatment with 15 g/l of NaOH at 100°C for 30 minutes. Samples No. 49 to 53, 58 and 59 and in the area below the curve RSP and had somewhat lower strength. Sample No. 60 was within the area ABFE and ΔH thereof was more than 5 %, which was less than 8 %. Samples No. 54 and

55 were comparative samples and it was found that ΔH thereof was less than 5 %.

the wet state with saturated steam at a pressure of 0.3 to 2.8 kg/cm² gauge and dried at a temperature of

Table 3

Sample No	Coagulation liquid Concentration (%)	Temperature (°C)	Jet Stretch	Steam pressure at wet annealing (kg/cm ²)	Drying temperature (°C)	Condition for treatment with modifier
41	55	60	0.9	0.8	110	NaOH 15 g/l 70°C × 30 min.
42	"	"	"	1.7	"	"
43	"	"	"	2.5	"	"
44	"	40	"	0.8	100	NaOH 10 g/l 100°C × 30 min.
45	50	"	"	"	"	NaOH 15 g/l 100°C × 30 min.
46	"	60	"	2.8	110	"
47	"	50	"	2.5	"	"
48	"	"	1.2	"	"	"
49	55	60	1.4	"	"	NaOH 10 g/l 70°C × 30 min.
50	"	"	"	1.0	100	"
51	65	"	1.5	0.8	"	"
Void content (X) (%)	Free surface area (S) × 10 ⁴ (cm ² /g)	Contact angle (°)	Difference in moisture regain ΔH (%)	Denier (d)	Dry strength (g/d)	Dry elongation (%)
39.2	41.4	40	17.9	3.26	2.06	34.0
32.4	36.1	41	12.3	3.68	1.77	41.3
20.5	25.5	40	11.0	4.42	1.43	42.5
12.0	120.0	38	9.1	3.34	1.90	40.6
8.2	30.6	"	8.5	3.29	1.85	41.0
14.4	30.0	"	8.3	4.10	1.50	38.9
10.0	1.1	"	8.1	3.86	1.53	39.0
14.0	1.0	"	7.5	3.65	1.67	40.0
43.2	2.2	40	9.6	4.30	1.26	35.0
52.1	5.5	"	10.1	3.72	1.20	34.1
54.0	19.1	"	10.3	3.89	1.31	38.3
52	65	70	1.2	2.5	110	NaOH 10 g/l 70°C × 30 min.
53	55	"	"	"	"	"
54	65	"	"	"	130	"
55	40	"	0.9	"	110	"
56	55	60	"	1.7	"	H ₂ SO ₄ 7.5 N 100°C × 30 min.
57	"	"	"	"	"	NH ₂ OH.H ₂ SO ₄ 1 % 100°C × 90 min.
58	65	70	1.2	1.2	"	Na ₂ CO ₃ 20 g/l 70°C × 30 min.
59	"	"	"	1.5	"	"
60	40	40	0.9	0.8	100	"
63.0	6.0	40	9.7	3.96	1.19	33.9
50.1	1.1	"	6.9	4.12	1.15	30.9
61.2	0.9	"	4.9	3.98	0.98	29.9
65.0	2.5	"	4.7	4.11	1.09	28.6
30.1	34.1	41	15.1	3.72	1.75	39.0
28.3	32.6	38	16.1	3.78	1.70	38.6
62.1	1.2	41	5.9	3.67	1.26	32.8
55.5	1.9	"	6.3	3.98	1.30	30.6
5.0	110	"	5.1	4.10	1.76	41.3

EXAMPLE 4

A copolymer ($[\eta] = 1.6$) consisting of 93 % of acrylonitrile and 7 % of vinyl acetate was dissolved in dimethyl acetamide to prepare a spinning solution having a concentration of 25 % by weight. This spinning solution was extruded into an aqueous solution of dimethyl acetamide with various concentrations and temperatures and at various jet stretches. The thus obtained coagulated fibers were stretched to 4.5 times the original length in boiling water to obtain fiber tows. Then, crimps were mechanically imparted to the tows in the wet state and then the tows were cut into staples. These staples were treated with 15 g/l of aqueous sodium hydroxide solution at 70°C for 30 minutes. Thereafter, the staples were washed with boiling water, annealed in

lower than 110°C.

The production conditions, void content, free surface area, contact angle, hygroscopicity and other properties of the obtained fibers are shown in Table 4.

In Table 4, Samples No. 61 to 75, 79, 80 and 82 were within the area PQRS and had a ΔH of more than 8 % and good fiber properties. Sample No. 76 was within the area LGJM and had a ΔH of more than 8 %. Samples No. 78 and 82 had a surface area of greater than 10⁶ cm²/g and large ΔH , but had somewhat lower strength. Samples No. 81 and 83 were in the area below the curve RSP and also had somewhat lower strength. Samples No. 77, 85, 86 and 87 were comparative samples and among them, No. 77, 85 and 86 had a large ΔH , but their strength were considerably low. Sample No. 87 had a ΔH of less than 5 %.

Table 4

Sample No.	Coagulation liquid Concentration (%)	Temperature (°C)	Jet Stretch	Steam pressure at wet annealing (kg/cm ²)	Drying temperature (°C)
61	50	60	0.9	0.3	40

Table 4-continued

Sample No.	Coagulation liquid Concentration (%)	Temperature (°C)	Jet Stretch	Steam pressure at wet annealing (kg/cm ²)	Drying temperature (°C)	
62	"	"	"	0.7	"	
63	"	"	"	1.2	"	
64	"	"	"	"	60	
65	"	"	"	"	80	
66	"	"	"	"	100	
67	55	20	"	"	40	
68	"	40	"	"	"	
69	"	60	"	"	"	
70	"	"	1.5	"	"	
71	"	"	2.4	"	"	
72	"	80	0.9	"	"	
73	65	60	"	"	"	
74	50	"	"	"	"	
Void content (X) (%)	Free surface area (S) × 10 ⁴ (cm ² /g)	Contact angle (°)	Difference in moisture regain ΔH (%)	Denier (d)	Dry strength (g/d)	Dry elongation (%)
52.6	34.0	40	14.5	2.88	2.52	27.3
52.6	45.8	40	16.3	2.89	2.45	33.7
52.6	55.4	44	16.2	3.23	2.44	39.2
46.6	36.6	41	15.3	3.26	2.48	43.2
43.0	34.9	40	15.2	3.28	2.45	40.3
43.0	29.5	41	14.9	3.23	2.44	42.1
28.7	20.1	43	10.4	3.00	2.50	42.2
34.4	37.8	38	18.5	3.14	2.30	36.5
39.0	45.9	40	18.2	3.16	2.48	35.4
55.0	46.3	40	19.3	3.15	1.93	33.8
57.3	47.9	39	19.3	3.13	1.72	38.9
52.6	34.6	38	18.8	3.24	1.98	41.6
52.6	37.3	39	18.2	3.20	1.85	38.0
22.4	7.1	35	13.4	2.38	2.98	14.4
75	80	20	1.5	1.2	40	
76	50	60	0.9	0.3	60	
77	55	"	2.4	"	40	
78	"	20	"	0.7	"	
79	50	40	0.9	2.5	110	
80	"	"	"	1.0	60	
81	55	20	2.0	"	40	
82	"	"	"	0.3	"	
83	"	60	"	2.5	60	
84	40	"	"	0.3	40	
85	"	"	2.4	"	"	
86	"	70	"	"	"	
87	65	40	2.0	1.2	"	
34.4	6.0	50	5.0	3.01	2.93	44.0
8.5	1.2	40	8.2	2.50	3.20	22.7
68.3	76.5	40	23.0	2.96	1.28	30.9
62.5	108.0	41	25.7	2.79	1.12	27.3
49.0	18.0	"	15.2	2.73	2.54	39.6
51.2	99.0	41	19.1	2.86	2.40	35.3
62.0	71.2	40	18.7	3.10	1.63	30.2
60.1	91.7	"	19.0	3.23	2.30	32.8
57.5	34.0	39	15.0	3.13	1.54	32.1
57.8	160.0	"	22.7	3.24	1.41	33.0
61.2	171.0	40	26.9	3.30	1.20	27.0
64.2	148.0	"	24.3	3.26	1.30	29.6
3.8	80.2	"	4.0	2.98	3.10	30.4

EXAMPLE 5

Acrylonitrile, vinyl acetate and lauroxy polyethylene glycol acrylate ($\text{CH}_2 = \text{CHCO}(\text{OCH}_2\text{CH}_2)_{30}\text{OC}_{12}\text{H}_{25}$) were polymerized at 50°C using a redox catalyst to obtain a copolymer having the following compositions.

Kind of copolymer	A	B	C	D
Acrylonitrile	93	83	68	53
Vinyl acetate	7	7	7	7
Lauroxy polyethylene glycol acrylate	—	10	25	40
Specific viscosity	0.16	0.16	0.16	0.15

Note:
Specific viscosity was measured at 0.1 g polymer/100 g DMF at 25°C.

50 The above copolymers were dissolved in dimethyl formamide (DMF) to prepare spinning solutions having a concentration of 24.0 % by weight. Furthermore, polymer B' having the same proportion of components as the polymer B was prepared by mixing polymers A and D at the ratio of 75 : 25 and 24.0 % spinning solution thereof was prepared in the same manner as mentioned above. These spinning solutions were extruded into an aqueous solution of dimethyl formamide with various concentrations and temperatures and at various
60 jet stretches. The thus obtained coagulated fibers were stretched to 4.5 times the original length in boiling water and then crimps were mechanically imparted to the tows in the wet state. The thus crimped tows in the wet state were annealed with saturated steam at a pressure of 0.8 – 2.8 kg/cm² gauge and cut into staples and
65 dried at a temperature of lower than 110°C. Thereafter, said fibers were treated with 5 g/l of aqueous sodium hydroxide solution at 70°C for 30 minutes. The production conditions, void content, free surface area, contact

angle, hygroscopicity and other fiber properties are shown in Table 5.

In Table 5, Samples No. 89 to 94 were fibers obtained by copolymerization of acrylonitrile and hydrophilic monomer. The void content and the surface area were within the area EJFK. The void content was low, but ΔH was more than 8 %.

ΔH obtained by subjecting the fibers containing no voids to the same treatment are also shown in Table 5.

- b. extruding said spinning solution into an aqueous coagulation liquid containing said solvent to form fibers, containing open capillary voids,
- c. stretching the thus formed fibers,
- d. annealing the stretched fibers in the wet state with saturated steam at a pressure of 0.3 to 2.8 kg/cm²,
- e. drying the annealed fibers at a temperature of lower than 110°C, and
- f. treating the fibers with an aqueous solution con-

Table 5

Sample No.	Polymer	Coagulation liquid		pressure Jet Stretch	Steam Drying at wet annealing (kg/cm ²)	Void content-temperature (°C)	tent (X) (%)
		Concentration (%)	Temperature (°C)				
88	A	55	60	0.9	0.8	110	37.8
89	B	"	"	"	"	"	6.1
90	B	65	"	1.2	1.7	"	14.0
91	B'	55	"	0.9	0.8	"	8.0
92	C	"	"	"	"	"	8.5
93	D	55	"	"	"	"	7.8
94	D	65	"	1.2	1.7	"	14.3
Free surface area × 10 ⁴ (cm ² /g)	Contact angle (°)	Difference in moisture regain ΔH (%)	Denier (d)	Dry strength (g/d)	Dry elongation (%)	ΔH of control fibers *	
40.0	42	11.4	3.12	2.86	31.2	1.6	
1.8	38	9.2	3.26	3.10	32.1	3.7	
5.1	"	10.5	3.20	3.21	29.8	3.7	
18.0	"	11.7	3.22	2.95	30.1	3.6	
51.2	"	12.5	3.31	3.05	27.4	4.0	
130.0	"	14.2	3.02	2.75	25.6	4.6	
90.1	"	16.0	3.10	2.78	28.1	4.6	

* The control fibers were obtained by the same method as in the present Example except that the fibers were dried on a heated roller at 130°C to collapse the voids.

REFERENCE EXAMPLE

For comparison, the void content, surface area and ΔH of the commercially available acrylic fibers are shown in Table 6. These fibers have substantially no capillary voids and their hygroscopicity was extremely low.

Table 6

Samples	Void content (%)	Surface area × 10 ⁴ (cm ² /g)	ΔH (%)
Vonnel (Mitsubishi Rayon Co., Ltd.)	0.9	less than 0.2	1.3
Toraylon (Tore Co., Ltd.)	0.8	"	1.3
Cashmilon (Asahi Kasei Kogyo K. K.)	0.7	"	1.1
Exlan (Nihon Exlan K. K.)	0.7	"	1.1
Orlon (E.I. Du Pont)	0.2	"	1.0
Dralon (Farbenfabriken Bayer A. G.)	0.2	"	1.0

What is claimed is:

1. A process for producing hygroscopic acrylic fibers which includes the steps of

- a. preparing a spinning solution by dissolving an acrylonitrile copolymer containing more than 50% by weight of acrylonitrile with at least one other polymerizable monomer having the $>C=C<$ structure and copolymerizable therewith in a solvent thereof,

taining a compound as a modifier selected from the group consisting of alkali metal hydroxide, alkali metal carbonate, sulfuric acid, hydrochloric acid and hydroxylamine salt to render the surface of the fibers hydrophilic and accelerate condensation of moisture in the voids.

2. A process according to claim 1 wherein the solvent is dimethyl acetamide.

3. A process according to claim 1, wherein the drying step (d) is carried out at a temperature of lower than 60°C.

4. A process according to claim 1, wherein the stretched fibers are subjected to the annealing step (d), the drying step (e), and then the treating step with a modifier (f).

5. A process according to claim 1, wherein the stretched fibers are subjected to the annealing step (d), the treating step with a modifier (f), and then the drying step (e).

6. A process according to claim 1, wherein after the stretching step (c), the treating step with a solution of modifier (f) is carried out and then annealing of the fibers is carried out and thereafter, the drying step (e) is carried out.

* * * * *