

[54] **ACRYLIC FIBERS HAVING EXCELLENT PILLING RESISTANCE AND A PROCESS FOR PRODUCING THE SAME**

8/114.6, 115.5; 28/76 T; 57/140 R, 140 J

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[57] **ABSTRACT**

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Acrylic fibers having excellent pilling resistance are disclosed. The acrylic fibers have a plurality of elongated wedge-shaped concave depressions extending into the fiber surface. And the acrylic fibers are produced by pre-treating acrylic fibers with a modifier to modify the outer layer of individual fiber and then after-treating the fibers with an organic solvent for acrylic fiber.

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[51] **Int. Cl.**..... D02g 3/00, D02g 3/22

[58] **Field of Search**..... 161/180, 177, 178;

3 Claims, 5 Drawing Figures

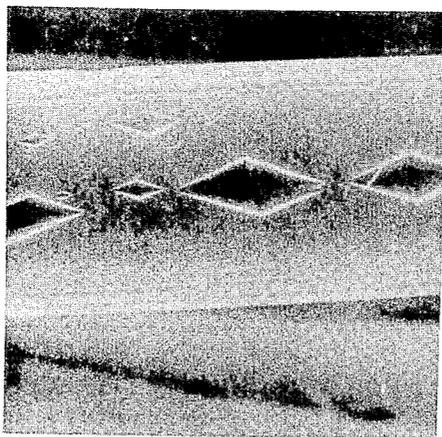


FIG. 1

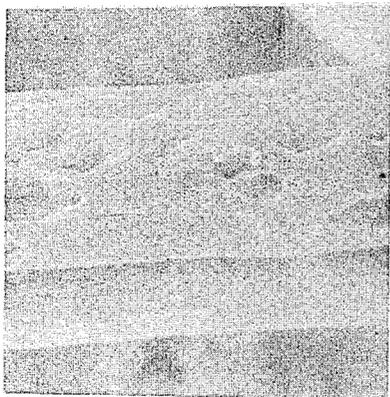


FIG. 2

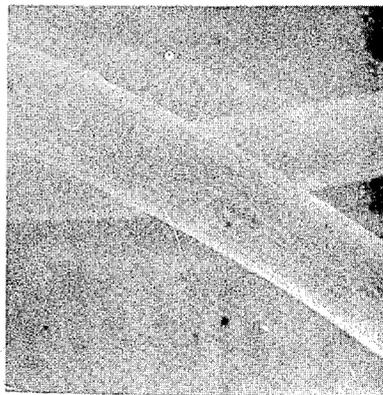


FIG. 3

FIG. 4A

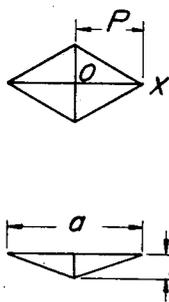
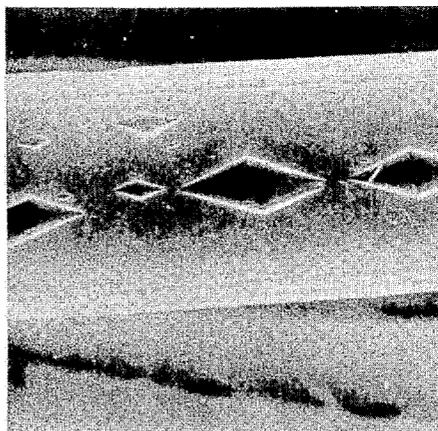
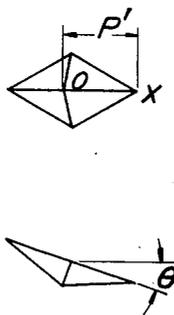


FIG. 4B



ACRYLIC FIBERS HAVING EXCELLENT PILLING RESISTANCE AND A PROCESS FOR PRODUCING THE SAME

The present invention relates to acrylic fibers having a plurality of elongated wedge shaped concave depressions extending into the fiber surface and process for producing the same.

The term "fibers" herein used includes the staple fibers, spun yarns, tow, knitted fabrics and woven fabrics.

A. fibers have various excellent physical and chemical properties so that the fibers have been used in many fields including clothes. However, acrylic fibers have a defect that when the knitted or woven fabrics made of acrylic fibers are worn for long time or put under an action of rubbing such as washing, pills are formed on the surface of the fabrics. This phenomenon is well known as pilling and the pills spoil the beautiful appearance of the fabrics. Therefore, prevention of pilling has been earnestly desired.

Many attempts have been made to prevent or eliminate the formation of pills on the surface of the fabrics.

For instance, such methods that particular conditions in fiber denier, fiber length and fiber cross section are used, or fibers are subjected to a finishing treatment with a resin have been used. However, satisfactory results have never been attained by such methods.

Further, in order to produce acrylic fibers having particular hand, the method has been used of making the fiber surface rough by embossing the fibers. However, the acrylic fibers obtained by this method has not been satisfied from the point of pilling resistance.

Accordingly, an object of the present invention is to provide acrylic fibers having excellent pilling resistance.

Another object of the present invention is to provide a process for producing acrylic fibers having excellent pilling resistance.

Further objects of the present invention will be clear from the descriptions that follows:

These objects of the present invention are achieved by pre-treating acrylic fibers with a modifier to make the outer layer of individual fiber insoluble in dimethyl formamide at 100°C. and then after-treating the acrylic fibers with an organic treating agent whereby a plurality of elongated wedge shaped concave depressions extending into the fiber surface is formed.

According to the present invention, acrylic fibers having excellent pilling resistance as well as other excellent fiber properties can be produced without losing the preferable fiber properties of acrylic fiber.

FIGS. 1, 2 and 3 are scanning electron microscopic photographs showing the concave depressions formed into the surface of fibers. FIG. 4 is to illustrate the method of measuring depth of the depression.

As is shown in the scanning electron microphotographs of FIGS. 1, 2 and 3, the important characteristic of the fibers of the present invention is that the fibers have a plurality of elongated wedge shaped concave depressions extending into the surface thereof, the number of said depressions is more than 3 per inch along the length of an individual fiber and the elongated axis of said depressions is axially aligned in the lengthwise direction of the fiber by which pilling resistance of the fiber is extremely improved.

The concave depressions shown in scanning electron microphotographs of FIGS. 1 and 2 are somewhat different from the definite rhombic concaves shown in the photograph of FIG. 3 and this is due to the difference in spinning conditions. Therefore, the elongated wedge shaped concaves into the surface of the fibers of the present invention include those having the shapes as shown in FIGS. 1 and 2 and those having the shape as shown in FIG. 3.

Acrylic fibers of the present invention have a plurality of elongated wedge shaped concave depressions described hereinbefore.

Number of the concave depressions is preferably from 5 to 50 per inch along the length of a individual fiber. And the concave depressions are preferably in rhombic shape, length (a) of the major axis (elongated axis) of the individual depression is in the range of 0.5 μ to 20 μ and the maximum depth (b) of the concave depressions is in the range of 0.2 μ to 10 μ . Major axis of the rhombic depressions is aligned in the direction of the fiber axis and the minor axis of the rhombic depressions is aligned in the direction perpendicular to the fiber axis.

The major axis and depth of the elongated wedge shaped concave depressions in the fibers of the present invention are measured with a scanning electron microscope [JSM Type II manufactured by Japan Electron Optics Laboratory Co., Ltd.]. Depth of the concave depressions is measured by taking photographs of the depression at two different angles in the same field of vision and calculating the depth in accordance with the following equation in reference to FIG. 4. FIG. 4(A) is a schematic view of the concave depression and FIG. 4(B) is an inclined schematic view of FIG. 4(A) at an angle of θ° .

$$b = p' / \sin \theta - p / \tan \theta$$

wherein

b: Maximum depth of the elongated wedge shaped concave depression.

p: Distance from the point 0 to the end point x of major axis.

p': Distance from the point 0 to the end point x of major axis after inclination by θ° .

θ : Angle of inclination of sample fiber.

For taking said two photographs, a sample inclining apparatus (Goniometer specimen stage Type JSM-GS manufactured by Japan Electron Optics Laboratory Co., Ltd.) is used with an angle of inclination of 20°.

The fibers of the present invention are produced, for example, by the following method.

In the present invention, acrylic fibers are produced from acrylonitrile homopolymer, copolymer of acrylonitrile with at least one other monomer copolymerizable with acrylonitrile or their blend by the conventional spinning methods. The acrylonitrile copolymer preferably contains more than 80 percent by weight of acrylonitrile and up to 20 percent by weight of at least one other monomer copolymerizable with acrylonitrile.

The other monomer includes vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, styrene, vinyl chloride, vinylidene chloride, vinyl bromide, vinylidene bromide, acrylamide, methacrylamide, methacrylonitrile, and monomers containing sulfoxyl group or their salts.

Acrylic fibers thus obtained are pre-treated with a modifier to modify the outer layer of individual fiber. By this treatment, the outer layer of individual fiber is made insoluble in dimethyl formamide at 100°C., and the pre-treatment is preferably carried out under such a condition that modified outer layer is 0.5 to 40 percent of the total cross sectional area of an individual fiber.

Then, thus pre-treated acrylic fibers are after-treated with at least one organic treating agent which is non-solvent for the modified outer layer, but is solvent for the un-modified inner layer of the acrylic fibers. Method of said after-treatment with the organic treating agent is as follows: (A) The pretreated acrylic fibers are immersed in the organic treating liquid and then washed with water and dried, (B) the pre-treated acrylic fibers are immersed in an aqueous organic treating liquid, then squeezed and heat treated, or (C) the pre-treated acrylic fibers are treated with a vapor of the organic treating agent.

The pre-treatment may be carried out on the acrylic fibers in a form of staple, tow, spun yarn, knitted or woven fabric.

Acrylic fibers of the present invention may be mix spun with other kind of fibers. And when the present acrylic fibers are mix spun with fibers which are degraded with the modifier to be used, it is preferable that the present acrylic fibers are pre-treated with the modifier, mix spun with other kind of fibers and then after treated with the organic treating agent.

The cross sectional area of the modified outer layer is measured as follows: that is, the sample of the pre-treated fibers is embedded in monomeric n-butyl methacrylate and heated to cause polymerization. A specimen of the cross section of the fibers is prepared by the same means as in the preparation by optical microscope. Thereafter, the specimen is immersed in dimethyl formamide at 100°C. to dissolve unmodified inner layer of the fiber and the modified outer layer remained insoluble is photographed with a scanning electron microscope. The sectional area is calculated from the photograph.

The modifiers to be used for the pre-treatment include, for example, saponifying agents such as alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and sulfuric acid and chemical reacting agents such as hydroxylamine sulfate, and hydroxylamine phosphate.

The modification treatment is carried out so that area of the modified outer layer is 0.5 to 40 percent of cross sectional area of an individual acrylic fibers. However, actual conditions vary depending upon the kind of the modifiers, size of fibers, etc. Therefore, suitable modification treatment may be carried out within the scope of the present invention.

Preferable organic treating agents for producing acrylic fibers of the present invention are as follows:

- i. Amide compounds . . . dimethyl formamide, dimethyl acetamide
- ii. Sulfon and sulfoxide compounds . . . dimethyl sulfoxide, dimethyl sulfon
- iii. Carbonate compounds . . . ethylene carbonate
- iv. Nitrile compounds . . . malononitrile, adiponitrile, acetonitrile

These organic treating agents may be used singly or jointly in the form of 100 percent solution or dilute solution. Furthermore, an inert viscosity increasing agent

such as ethylene glycol or glycerine may be added thereto.

Embodiments of the after-treating methods with these organic treating agents are as follows:

A In the method where fibers are immersed in the treating agent, the pre-treated acrylic fibers are immersed in a solution of the organic treating agent. The concentration of the solution is higher than 85 percent, treating temperature is 10° to 100°C. and treating time is 2 minutes to 1 hour. In this embodiment, a mixture such as dimethyl formamide-ethylene carbonate, dimethyl acetamide-ethylene carbonate may be used.

B. In the method where fibers are immersed in the organic agent, squeezed and then heat treated, the pre-treated fibers are immersed in an aqueous solution of the organic treating agent. Representative examples of the agents include dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide and ethylene carbonate. These organic treating agents may be preferably used in such a manner that amount of the agent adhered to the fibers immediately after squeezing is more than 15 percent, more preferably 15 percent to 100 percent of the weight of the dried fiber. The heat treating temperature is preferably 50°C. to 120°C. As to the concentration of the aqueous solution, heating temperature and heating time, there is no special limitation.

C. In the method where fibers are treated with a vapour of the organic agent, the pre-treated fibers are exposed in a vapour of organic solvents for acrylic fibers having a boiling point of lower than 250°C.

As the solvents for acrylic fibers, inorganic solvents may be used beside the organic solvents. However, the organic solvents such as dimethyl formamide, dimethyl acetamide and dimethyl sulfoxide are the most preferably used. When the pre-treated fibers are after-treated with inorganic solvents, the fibers themselves are swollen or dissolved to cause adhesion between the fibers. Furthermore, inorganic solvents are vapourized with difficulty.

It is difficult to give clear explanation of the mechanism of formation of the concave depressions extending into the fiber surface by treating the pre-treated acrylic fibers with the organic treating agent. However, it is considered that the concave depressions are formed due to extraction of the unmodified inner layer (soluble in dimethyl formamide) through the modified outer layer (insoluble in dimethyl formamide) by the treatment with the organic treating agent.

In the knitted or woven fabrics of the acrylic fibers of the present invention, the fibers have particular concave depressions, which provide weak points in strength of the fibers to cause easy falling off of pills. As the results, prevention of pilling can be accomplished.

Furthermore, the concave depressions of the fibers of the present invention have an elongated wedge shape and the major axis of the depression is aligned lengthwise direction of the fiber axis and the minor axis of the depression is aligned in the direction perpendicular to the fiber axis. Said concave depressions are extending into the surface of the fibers and are dispersed in the whole surface of the fibers. Therefore, contact area between single fibers is decreased and thus the knitted or woven fabrics have soft hand and excellent shape stability.

The present invention will be illustrated by the Examples.

EXAMPLE 1

A polymer comprising 93 percent by weight of acrylonitrile and 7 percent by weight of vinyl acetate was spun by the conventional wet spinning method to obtain a tow having monofilamentary denier of 3 and total

Ratio of area of the outer layer to that of total sectional area of the fibers is also shown in Table B.

Then, thus treated yarns were immersed in 100 percent dimethylformamide at 25°C for 20 minutes to obtain the fibers having concave depressions shown in Table B.

TABLE B

Treating agent	Concentration (%)	Temperature (°C)	Treating time (min.)	Area of outer layer (%)	Major axis (a) of depression (μ)	Maximum depth (b) of depression (μ)	Number of depression/inch
Sodium hydroxide	1.5	95	30	15	3 - 8	0.5 - 1.5	18
do.	0.5	90	30	7	5 - 12	0.5 - 2.0	40
Potassium hydroxide	3.0	95	30	13	3 - 9	0.5 - 1.5	20
Sodium hydroxide	1.5	95	30	14	3 - 10	0.5 - 1.5	20
Sulfuric acid	60.0	25	15	18	1.0 - 5	0.3 - 0.8	17

denier of 480,000. The tow was cut by the turbo stapler to obtain slivers (high bulk fibers). A part of said slivers were shrunk by a fiber setter to obtain regular fibers. Forty parts of the high bulk fibers and 60 parts of the regular fibers were worsted-spun to obtain high bulk two folded yarns (250/360 T/M) of 36 metric counts. Said high bulk yarns were pre-treated with 0.5 percent aqueous solution of sodium hydroxide at 90°C for 30 minutes, then bleached with 1 percent aqueous solution of acetic acid at 98°C for 15 minutes, washed with water and dried. The fibers were insoluble in dimethyl formamide at 100°C. Said insolubilized portion was 7 percent of total cross sectional area of the fiber.

Thus treated yarns were immersed at a liquid ratio of 1 : 50 in the treating agents as shown in Table A to form concave depressions having characteristics shown in Table A.

As one example, microphotograph of the fibers treated with treating agent (1) in Table A by a scanning electron microscope is shown in FIG. 1.

EXAMPLE 3

A copolymer of 93 percent by weight of acrylonitrile and 7 percent by weight of vinyl acetate was spun by the conventional dry spinning method to obtain staple fibers (3 deniers per filament semi dull). The staple fibers were pre-treated with 2 percent aqueous solution of sodium hydroxide at 90°C for 30 minutes, washed with water and dried.

A part of the pre-treated fibers were embedded in monomeric n-butyl methacrylate and heated to effect polymerization. Thereafter, a specimen of cross section of the fibers having a thickness of about 5 μ was prepared. This specimen was immersed in dimethylformamide kept at 100°C. to cause partial dissolution thereof. By this procedure, it was acknowledged that undissolved part was the outer layer of the fibers and the area of this outer layer was 21 percent of total cross sectional area.

The pre-treated fibers were immersed in dimethylformamide at 25°C. for 5 minutes. Then, solvent was removed by washing with water and dried. Elongated

TABLE A

Treating agent	Concentration (%)	Temperature (°C)	Immersion time (min.)	Major axis (a) of depression (μ)	Maximum depth (b) of depression (μ)	Number of depression/inch
(1) Dimethylformamide	98	25	20	5 - 12	0.5 - 2	40
(2) Dimethylformamide/Ethylene carbonate	50/50	25	20	4 - 10	0.5 - 2	25
(3) Ethylene carbonate water	90/10	28	20	3 - 8	0.4 - 2	20
(4) Dimethylacetamide	98	25	20	5 - 12	0.5 - 2	40
(5) Acetonitrile	98	50	20	2 - 8	0.5 - 2	18

EXAMPLE 2

The high bulk yarns produced by the same method as in Example 1 were pre-treated with aqueous solution of the modifiers shown in Table B to make the outer layer of the fibers insoluble in dimethyl-formamide at 100°C.

wedge-shaped concave depressions, most of which were rhombic in shape, were intermittently formed extending into the surface of the fibers. The shapes of the concaves are shown in Table C. As referential Example, non-ptreated fibers were immersed in dimethylformamide at 25°C. to cause dissolution of the fibers.

TABLE C

Fibers	Major axis (a) of depression (μ)	Depth (b) of depression (μ)	Number of depression/inch
This Example	3 - 10	0.3 - 1	12
Referential Example	0	0	0

When the fibers of this Example were made into knitted fabric, fabrics of excellent properties, especially in pilling resistance and shape stability was obtained.

A scanning electron microphotograph of the fibers obtained in this Example is shown in FIG. 3.

EXAMPLE 4

High bulk yarns in Example 1 were pre-treated with 2 percent aqueous solution of sodium hydroxide at 90°C. for 30 minutes, and then bleached with 1 percent aqueous solution of acetic acid at 98°C. for 15 minutes, washed with water and dried. The outer layer of the fibers was insoluble in dimethylformamide at 100°C. and this insolubilized part was 21 percent of total cross sectional area of the fibers.

Thus pre-treated high bulk yarns were immersed in 30 percent aqueous solution of dimethylformamide kept at 25°C. and then squeezed in such a manner that the amount of dimethylformamide solution adhered to the yarns was 70 percent of weight of dried fibers. Then, the yarns were heat treated for one hour in a drier kept at 90°C. Said yarns were dyed and subjected to softening treatment and then were made into a sweater by 14G Full Fashion knitting machine.

In the surface of the fibers, elongated wedge-shaped concave depressions were formed. The concave depressions have a length of major axis of 1.2 to 7 μ and a depth of 0.4 to 1 μ and number of depressions per 1 inch was 15.

5th grade	No formation of pills and no change of surface
4th grade	A few pills and changes
3rd grade	Medium number of pills and changes
2nd grade	Many pills and changes
1st grade	Extremely many pills and changes

Furthermore, the knitted fabric obtained in this Example had soft hand and completely maintained excellent properties of acrylic fibers.

EXAMPLE 5

A copolymer of 94 percent by weight of acrylonitrile and 6 percent by weight of methyl acrylate was spun by the conventional dry spinning method to obtain staple fibers of 3 deniers per filament. The fibers were pre-treated with 13 percent owf of hydroxylamine sulfate and 10 percent owf of sodium secondary phosphate at a liquor ratio of 1 : 10 at 98°C. for 30 minutes.

Sixty parts of thus pre-treated fibers (outer layer insoluble in dimethyl formamide at 100°C. was 23 percent) and 40 parts of Merino wool were mix spun to obtain 36 counts (metric count) two folded yarns. The yarns were immersed in aqueous solutions of the treating agents in Table E and were squeezed in such a manner that the amount of the solution adhered to the fibers was 70 percent of weight of the dried fibers. Thereafter, the yarns were heat treated for 1 hour in a drier kept at 90°C.

The states of the acrylic fibers in the yarns obtained are shown in Table E.

TABLE E

After-treating agent	Concentration (%)	Major axis (a) of depression (μ)	Maximum depth (b) of depression (μ)	Number of depression/inch
Dimethyl-acetamide	30	1.5 - 5	0.5 - 1.0	20
Dimethyl-sulfoxide	50	3.0 - 10	0.8 - 3.0	45
Ethylene carbonate	50	3.0 - 10	0.8 - 3.0	40

Said knitted fabric was tested by Random tumble type pilling tester and the results thereof are shown in Table D. It is clear from the Table D that the knitted fabric obtained in this Example had conspicuously excellent pilling resistance.

Table D comparatively shows the test results on a knitted fabric obtained from conventional acrylic fibers.

TABLE D

Fabric	Pilling resistance* (grade)
Fabric of this Example	5
Fabric of conventional acrylic fibers	2 - 3

* Grade of pilling resistance was decided by surface changes resulted after operation of random tumble type tester for 30 minutes in accordance with JIS, L-1018-1962.

EXAMPLE 6

Acrylic fibers (3 deniers per filament) were pre-treated with 2 percent aqueous solution of sodium hydroxide at 90°C. for 30 minutes and then bleached with 2 percent aqueous solution of oxalic acid at 98°C. for 15 minutes. The outer layer of the fibers thus pre-treated was insoluble in dimethylformamide at 100°C. and this outer layer was 21 percent of total cross sectional area of the fibers.

Said fibers were spun into two folded yarns (185/320 T/M) of 36 metric counts, which were exposed to saturated vapor of dimethylformamide at 100°C. for 5 minutes, washed with water and dried. Thus treated yarns were dyed and subjected to softening-treatment and then made into knitted fabric. In the fiber surface of this knitted fabric, elongated wedge-shaped concave depressions having a major axis of 1.3 μ to 5 μ and a depth of 0.4 μ to 0.8 μ were formed. Number of the de-

pressions was 20/inch.

Said knitted fabric had an excellent pilling resistance as shown in Table F.

TABLE F

Pilling resistance	
Knitted fabric of this Example	5th grade

EXAMPLE 7

Acrylic fiber two folded spun yarns (250/360 T/M) of 32 metric counts were immersed in a mixed aqueous solution of 10 percent of glycerine and 10 percent sulfuric acid, and then squeezed. Thereafter, the yarns were heated at 120°C. for 10 minutes to pre-treat the yarns, washed with water and dried. The outer layer of the fibers was insoluble in dimethylformamide at 100-°C. and said outer layer of the fiber was 25 percent of total sectional area of the fiber.

Thus pre-treated spun yarns were knitted into a fabric, which was treated in saturated vapor of the solvents shown in Table G for 5 minutes.

TABLE G

After treating agent	Vapor temperature (°C)	Length (a) of major axis of depression (μ)	Maximum depth (b) of depression (μ)	Number of depression/inch
Dimethyl-formamide	100	1.2 - 6	0.5 - 1.5	19
Dimethyl-sulfoxide	120	1.0 - 8	0.5 - 1.5	20
Acetonitrile	80	1.4 - 10	0.4 - 1.0	18

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What is claimed is:

1. Acrylic fibers each having an outer layer, and said fibers having a plurality of elongated wedge shaped concave depressions extending into the surface thereof, the number of said depressions being more than 3 per inch along the length of an individual fiber and the elongated axis of said depressions being axially aligned in the lengthwise direction of the fiber, wherein said outer layer of said fibers is insoluble in dimethyl formamide at 100°C. and said outer layer is 0.5 to 40 percent of the total cross sectional area of an individual fiber.

2. Acrylic fibers according to claim 1, wherein said concave depressions are rhombic in shape, length (a) of the elongated axis of the individual depression being in the range of 0.5 μ to 20 μ and the maximum depth (b) of said depressions being in the range of 0.2 μ to 10 μ, the major axis of said rhombic depressions being aligned in the direction of the fiber axis and the minor axis thereof being aligned in the direction perpendicular to the fiber axis.

3. Acrylic fibers according to claim 1, wherein said fibers contain at least 80 percent by weight of acrylonitrile and the number of said depressions ranges from 5 to 50 per inch along the length of an individual fiber.