Aug. 7, 1973 HIROSHI KAWAKAMI ET AL 3,751,547

PROCESS FOR PRODUCING HIGH MODULUS POLYVINYL ALCOHOL SYNTHETIC FIBERS

Filed June 28, 1971

FIG. 1

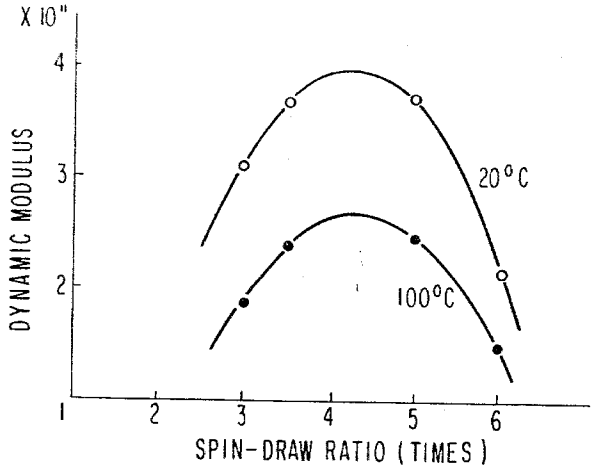
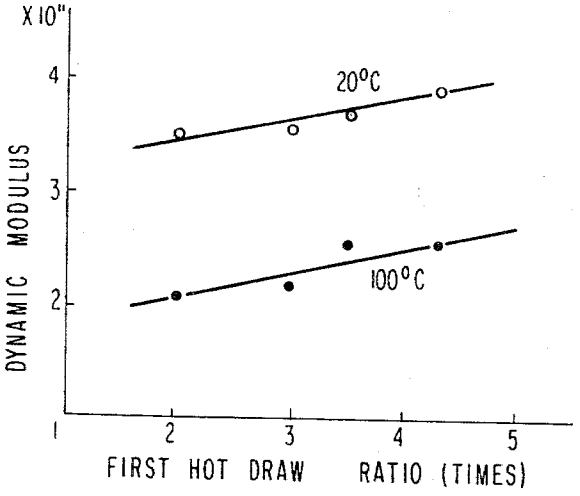


FIG. 2



INVENTORS
HIROSHI KAWAKAMI
HIDESHI SATOH
AKIRA MIYOSHI
KAZUHARU KAWABATA
KOHKICHI KIMURA

BY Sughrue, Rothwell, Mion, Zinn & Macpeak

ATTORNEYS

United States Patent Office 3,751,547 Patented Aug. 7, 1973

3,751,547

PROCESS FOR PRODUCING HIGH MODULUS POLYVINYL ALCOHOL SYNTHETIC FIBERS

Hiroshi Kawakami, Hideshi Satoh, Akira Miyoshi, Kazuharu Kawabata, and Kohkichi Kimura, Akoh, Japan, assignors to Unitika Limited, Amagasaki-shi, Hyogo-ken, Japan

Filed June 28, 1971, Ser. No. 157,246
Claims priority, application Japan, June 27, 1970, 45/56,238, 45/56,239
Int. Cl. D01f 7/00
U.S. Cl. 264—210 F 15 Claims

ABSTRACT OF THE DISCLOSURE

A process for producing high modulus polyvinyl alcohol synthetic fibers which comprises spin-drawing polyvinyl alcohol synthetic fibers having a homogeneous section and then carrying out a multistage hot drawing. Polyvinyl alcohol synthetic fibers are produced by such a process.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a process for producing polyvinyl alcohol (hereinafter called PVA) synthetic fibers having a high modulus and particularly excellent dynamic modulus, high strength and low elongation, and to PVA synthetic fibers produced by such a process, and particularly relates to providing PVA synthetic fibers which are useful as cord elements for radial tires.

Description of the prior art

It is desirable that fiber cord materials used for radial tires have a high modulus, that is, a high Young's modulus, and especially a dynamic modulus which does not decrease at high temperatures.

PVA synthetic fibers have the highest Young's modulus or dynamic modulus among various kinds of synthetic fibers. However, PVA synthetic fibers cannot be used satisfactorily as radial tire cord materials though they are promising, because the high Young's modulus and the dynamic modulus thereof decrease greatly at high temperatures. Consequently, they have not yet been practically used.

In order to improve the dynamic modulus, etc., it is necessary to highly orientate the molecular chains of the polymer by drawing. Hitherto, as the method for improving the draw ratio of PVA synthetic fibers, a process is known which comprises spinning a boric acid containing PVA solution as the spinning solution, and washing to decrease the boric acid content of the fibers to less than 0.1% before hot drawing, by which the drawability of the fibers is improved. However, by this process, the draw ratio is still only 15–16 times at the utmost.

As a result of many studies about methods for highly orientating PVA synthetic fibers by drawing in order to improve the above-mentioned faults and to produce PVA fibers having an excellent Young's modulus and dynamic modulus, the present inventors have reached the process of the present invention by which fibers having high strength, low elongation and high modulus, especially a high dynamic modulus at a high temperature, which cannot be obtained by the prior art, can be produced.

SUMMARY OF THE INVENTION

The present invention relates to a process for producing PVA fibers which have a high modulus, especially a high dynamic modulus at a high temperature, high strength and low elongation, which is characterized by carrying out the spin drawing of PVA fibers having a homogeneous section and then carrying out multistage hot drawing, and is also characterized by affording, if desired, 20–50% moisture to the fibers at the second and/or subsequent stages of the hot drawing, and PVA fibers produced by the same process.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the relationship between the spin drawing ratio and the dynamic modulus of the resulting fibers when applying the present invention.

FIG. 2 is a graph showing the relationship between the draw ratio at the first hot drawing and the dynamic modulus of the resulting fibers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As the PVA synthetic fibers having a homogeneous section produced by a wet spinning process used in the present invention, there are fibers which are prepared by spinning a PVA solution using a coagulation bath which contains caustic alkali as the main ingredient, and fibers which are prepared by spinning a PVA solution containing boric acid or borax using an alkaline coagulation bath which contains dehydrating salts. Fibers having a 2-layer structure consisting of a skin layer and a core layer which are prepared by spinning a PVA solution using a coagulation bath containing dehydrating salts, such as Glauber's salt and ammonium sulfate, do not exhibit any effect when applied to the present invention.

The spin-drawing in the present invention is carried out by taking out coagulated fibers obtained by the common spinning method from the coagulation bath, in air, by means of a first godet roll and drawing the fibers in air using guides or rolls, or drawing the fibers in an aqueous solution of salts at a high temperature, or applying both of the abovementioned treatments. The multistage hot drawing of the PVA synthetic fibers is carried out by conducting the first hot drawing at a temperature above 160° C. and below the melting point of the fibers and conducting the second and subsequent stage hot drawing at a temperature above 180° C., in which the later the stage is, the higher the temperature which is used at said hot drawing. In the multistage hot drawing, it is preferable to conduct the first hot drawing at a draw ratio as high as possible, preferably more than 3 times. In general, 3–5 times of the draw ratio is adopted. The second hot drawing is generally carried out at a 1.1–1.4 draw ratio.

In the present invention, it has been found that it is preferable to afford moisture after the first hot drawing in order to improve the drawability, because the drawability of the PVA synthetic fibers after the second and subsequent hot drawing is largely improved by affording moisture using water or an aqueous emulsion of oils. The amount of moisture is preferably 20–50% based on the fiber. In this case, it is preferable that the first hot drawing is carried out at more than 3 times the draw ratio and that the total draw ratio including the spin-drawing ratio is at least 10 times so as to prevent the rise of nap and the break of yarns upon the addition of moisture at the second hot drawing. The fibers drawn by the first hot drawing are then subjected to the second hot drawing after affording 20–50% moisture without drying.

The moisture may be added by spraying, dropping or dipping in water or an aqueous emulsion of oils such as mineral oils. If the amount of the moisture is less than 20%, it becomes difficult to carry out drawing to a high degree because of partial super-heating in a hot drawing oven at the subsequent hot drawing. If the amount of the moisture is more than 50%, a temperature in the hot drawing oven lowers by heat of vaporization of the excess moisture on the surface of fibers, and it becomes difficult to carry out the drawing.

It is preferable to carry out the second hot drawing at a slightly higher temperature, that is, more than 180° C., than the first hot drawing temperature and at more than 1.1 of the hot draw ratio. In the present invention, it is possible to repeatedly carry out the addition of moisture for the hot drawing after the second hot drawing, such as a third hot drawing and a fourth hot drawing, etc. However, where the total draw ratio is above 20 times at the second hot drawing, the third and fourth hot drawings are not required. Further, in the present invention, it is not always necessary to carry out the heat relaxing treatment of prior methods in order to remove strains and to improve hot water resistance and crystallinity. By carrying out two or more hot drawings, PVA synthetic fibers having a good dimensional stability and a good hot water resistance can be obtained without causing deformation.

It is well known that PVA fibers are subjected to spin drawing at 4 times or so of a draw ratio in the preparation of PVA fibers by a wet spinning process, washing with water, drying and hot drawing. However, in the prior methods, hot drawing is carried out only one time. If PVA fibers having a homogeneous section are subjected to spin-drawing by the prior art at the same draw ratio as in the present invention, the resulting fibers have a poor drawability and a poor dynamic modulus.

In the present invention, hot drawability is improved remarkably when affording 20–50% moisture to the PVA synthetic fibers having the homogeneous section produced by a wet spinning process. Though the reasons why the hot drawability is improved by affording the moisture to fibers after the first hot drawing are not yet clear, it is supported as follows. Namely, when the PVA synthetic fibers which are oriented and crystallized in some degree by the first hot drawing are subjected to additional hot drawing, it is necessary to weaken the firm hydrogen bond between the molecules of PVA. Water functions as the plasticizer which weakens the binding of the molecules of PVA and makes rearrangement of the molecules easy. Accordingly, by affording moisture before the second and subsequent hot drawings, it becomes possible to draw highly, above 20 times of the total draw ratio, which is impossible to obtain by the prior art methods, and the modulus of the fibers is improved remarkably.

In the following, the present invention will be explained in detail with reference to the drawings.

FIG. 1 is a graph which shows the relationship between the dynamic moduli at 20° C. and 100° C. and the spin-drawing ratio of fibers which are obtained by spinning a 15% aqueous solution of PVA having an average degree of polymerization of 1700 as the spinning solution using an aqueous solution of 400 g./l. of caustic soda as the coagulation bath, drawing with changing the spin-draw ratio, neutralizing with a bath of 300 g./l. of Glauber's salt and 50 g./l. of sulfuric acid at room temperature, treating with a bath of 300 g./l. of Glauber's salt and 30 g./l. of sulfuric acid at 90° C., washing with water and drying, conducting the first hot drawing at 225° C. so as to have 15 times the total draw ratio, affording 30% water, and conducting the second hot drawing at 238° C. in 1.27 times the drawing ratio. FIG. 2 is a graph showing the relationship between the dynamic moduli at 20° C. and 100° C. and the first hot draw ratio of fibers obtained by spinning using the same spinning solution and coagulation bath as above, conducting the spin-drawing at a 4 times draw ratio, conducting the first hot drawing of the dryed fibers by changing the drawing ratio at 225° C., affording 30% water, and conducting the second hot drawing so as to have 19.5 times the total draw ratio. The dynamic modulus is measured in the air by means of a dynamic modulus measurement device at the following conditions: length of sample: 3 cm.; initial tension: 0.2 g./d.; frequency: 10 cps.; dynamic strain: 0.6%; and rate of heating: 1.5° C./min.

It is clear from FIG. 1 that, in the case of PVA fibers having a homogeneous section prepared by the wet spinning process subjected to multistage hot drawing, fibers having an especially high dynamic modulus can be obtained when the spin draw ratio is 3.5–5 times, and the only low values are obtained when the spin-draw ratio is outside the above-mentioned range, though the total draw ratio is equal to the above-mentioned case. On the contrary, fibers which are subjected to only one-stage hot drawing after the spin-draw ratio have poor drawability and a low dynamic modulus which slightly changes depending on the spin-draw ratio.

It is also clear from FIG. 2 that it is preferable, for improving the dynamic modulus, to carry out the first hot drawing at a draw ratio as high as possible. This dynamic modulus is proportionate to Young's modulus, and accordingly fibers having a high dyanmic modulus have a high Young's modulus.

In order to make clear the characteristics of the present invention, the following experiment is shown.

EXPERIMENT

Fibers produced by spinning a 15% aqueous solution of PVA having a 1700 and 2500 average degree of polymerization as the spinning solution, using a coagulation bath containing 400 g./l. of caustic soda, were subjected to spin-drawing of 4 times. The fibers were then neutralized with a bath of 300 g./l. of Glauber's salt and 50 g./l. of sulfuric acid at room temperature and then treated with a bath having the same composition at 85° C. After washing with water, the resulting fibers having a homogeneous section were subjected to a first hot drawing at 230° C., a second hot drawing at 240° C. and a third hot drawing at 245° C. in a hot drawing oven. Just before the second and third hot drawing, the fibers were either dipped in water and squeezed to afford 30% moisture or not dipped in water. The hot draw ratio of each stage was 80% of the maximum hot draw ratio at breaking.

On the other hand, fibers having a 2-layer structure were produced by the same procedure using a 15% aqueous solution of PVA having a 1700 degree of polymerization as the spinning solution and a saturated Glauber's salt solution as the coagulation bath. The draw ratios and properties of each fiber are shown in Tables 1 and 2.

TABLE 1

Sample No.	Degree of polymerization of PVA	Coagulation bath	Spin-drawing (times)	First stage (times)
1	1,700	Alkali	3.5	4.0
2	1,700	do	3.5	4.0
3	1,700	Glauber's salt	3.5	3.0
4	2,500	Alkali	4.0	3.75
5	2,500	do	4.0	3.75

Sample No.	Moisture content (percent)	Second stage (times)	Moisture content (percent)	Third stage (times)	Whole draw ratio (times)
1	30	1.53			21.4
2		1.23			17.2
3	30	1.03			10.8
4	30	1.25	30	1.20	22.5
5		1.25		1.05	19.7

NOTE.—First stage, second stage and third stage mean the first hot drawing, the second hot drawing and the third hot drawing. Sample Nos. 1, 2, 4 and 5 are fibers having a homogeneous section, and Sample No. 3 is fibers having a double-layer structure.

TABLE 2

Sample No.	Strength (g./d.) at—		Elongation at break at—		Dynamic modulus (dyne/cm.^{2}) at—	
	20° C.	120° C.	20° C.	120° C.	20° C.	120° C.
1	15.8	13.2	4.5	6.0	3.7×10^{11}	3.0×10^{11}
2	13.2	10.6	5.5	8.0	3.0×10^{11}	2.3×10^{11}
3	9.0	5.1	8.5	9.5	1.6×10^{11}	0.9×10^{11}
4	16.4	14.0	4.0	5.5	3.9×10^{11}	3.3×10^{11}
5	14.4	11.2	5.5	7.5	3.1×10^{11}	2.4×10^{11}

NOTE.—Measurement of dynamic modulus: determined in air at the following conditions: length of sample: 3 cm.; initial tension: 0.2 g./d.; frequency: 10 c.p.s.; dynamic modulus: 0.6%; and temperature increasing rate: 1.5° C./min., by a dynamic modulus measurement device.

It is clear from the above tables that the hot drawing property is remarkably improved by carrying out the multi-stage hot drawing of fibers having a homogeneous section which are produced by spinning, using a caustic alkali solution as the coagulation bath, and that fibers having a high strength, a low elongation and a good dynamic modulus can be obtained. These fibers are suitable for use as reinforcing elements for reinforced plastics and as tire cords for radial tires. Further, drawability is further improved by repeating addition of moisture and hot drawing after the first hot drawing, and the drawn filament does not fluff. Moreover, fibers having a 2-layer structure consisting of a skin layer and a core layer which are produced by spinning in a Glauber's salt solution cannot be subjected to such drawing, even though affording moisture, and the fibers are nappy.

The denier of the filament yarn used in the process of the present invention is preferably less than 10,000 deniers so as not to cause disorder of the fibers at the addition of moisture, and so as to heat uniformly at hot drawing.

Example 1

Fibers were produced by spinning a 15% aqueous solution of PVA having an average degree of polymerization of 2500 as the spinning solution using an aqueous solution containing 350 g./l. of caustic soda as the coagulation bath. After removal from the coagulation bath, the fibers were subjected to spin-drawing at a draw ratio of 4.5 times. After neutralizing with a bath of 280 g./l. of Glauber's salt and 50 g./l. of sulfuric acid at room temperature and treating in a bath of 250 g./l. of Glauber's salt and 30 g./l. of sulfuric acid at 80° C., the fibers were washed with water and dried. The fibers were then subjected to a first hot drawing at 230° C. at a ratio of 3.6 times and a second hot drawing at 245° C. at a ratio of 1.23 times, by which the total draw ratio became 20 times. The dynamic moduli and Young's moduli of the treated filament yarn (1200 d., 500 f.) at 20° C. and 100° C. were 3.9×10^{11} dyne/cm.^{2}, 2.9×10^{11} dyne/cm.^{2}, and 4140 kg./mm.^{2}, 2110 kg./mm.^{2}, respectively. On the contrary, in the fibers which were subjected to the hot drawing without carrying out the second hot drawing, the above-mentioned values were 2.1×10^{11} dyne/cm.^{2}, 1.24×10^{11} dyne/cm.^{2} and 3060 kg./mm.^{2}, 1320 kg./mm.^{2}, respectively.

Example 2

Dried fibers obtained by the process of Example 1 were subjected to a first hot drawing at 230° C. in a ratio of 3.6 times followed by dipping in water and squeezing to afford 40% moisture. The fibers were then subjected to a second hot drawing so as to increase the total draw ratio to 21.8 times. The fibers had a 15.6 g./d. strength, a 5% elongation and a dynamic moduli at 20° C. and 100° C. of 4.1×10^{11} dyne/cm.^{2} and 3.0×10^{11} dyne/cm.^{2}, respectively.

Example 3

Fibers were produced by spinning a 15.5% aqueous solution of PVA having an average degree of polymerization of 1700 (to which 1% boric acid based on the weight of PVA was added) as the spinning solution into a coagulation bath consisting of 15 g./l. of caustic soda and 360 g./l. of Glauber's salt. After taking the fibers out, they were subjected to spin-drawing in a ratio of 4 times, neutralized in a bath of 300 g./l. of Glauber's salt and 30 g./l. of sulfuric acid at room temperature and then treated with a bath having the same composition at 85° C. After washing with water and drying, the fibers were subjected to a first hot drawing in hot air at 235° C. in a ratio of 3.75 times and then a second hot drawing at 245° C. at a ratio of 1.3 times. The resulting filament yarn (2000 d., 750 f.) had a 14.6 g./d. strength and a 5.7% elongation, and a dynamic modulus and a Young's modulus at 20° C. of 3.6×10^{11} dyne/cm.^{2}, and 4280 kg./mm.^{2}, and at 100° C. of 2.5×10^{11} dyne/cm.^{2} and 2310 kg./mm.^{2}.

In the fibers which were subjected to hot drawing without the second hot drawing, the fibers had a 12.0 g./d. strength, a 6.6% elongation and a dynamic modulus and a Young's modulus at 20° C. of 2.6×10^{11} dyne/cm.^{2} and 3160 kg./mm.^{2} and at 100° C. of 1.7×10^{11} dyne/cm.^{2} and 1560 kg./mm.^{2}. These values were inferior to those of the fibers of the present invention.

Example 4

The fibers were produced by spinning using the same procedure as in Example 3. After being subjected to spin-drawing at a spin-draw ratio of 3.5 times, the fibers were subjected to a first hot drawing at 238° C. at a ratio of 4 times and a second hot drawing at 245° C. at a ratio of 1.26 times, followed by dipping in an emulsion containing mineral oil as the main ingredient and squeezing the fibers to afford 30% moisture. Then, a third hot drawing treatment was carried out at a ratio of 1.25 times, by which the total draw ratio became 22 times. The dynamic modulus and the Young's modulus at 20° C. were 4.0×10^{11} dyne/cm.^{2} and 4630 kg./mm.^{2}, and at 100° C. were 3.1×10^{11} dyne/mm.^{2} and 2390 kg./mm.^{2}, respectively.

Example 5

Fibers were produced by spinning a 15.5% aqueous solution of PVA having an average degree of polymerization of (to which 2% boric acid based on the weight of PVA was added) as the spinning solution into a coagulation bath which consisted of a saturated Glauber's salt solution containing 15 g./l. of caustic soda. After taking the fibers out, they were subjected to spin-drawing in a ratio of 4 times followed by neutralizing with a bath containing 300 g./l. of Glauber's salt and 30 g./l. of sulfuric acid at room tempertaure and then treated with a bath having the same composition at 90° C. After washing with water and drying, the fibers were subjected to a three-stage hot drawing at the following conditions: 235° C. for 10 seconds at a ratio of 3.5 times; 238° C., for 10 seconds at a ratio of 1.15 times; and 240° C. for 10 seconds at a ratio of 1.15 times, by which the total drawing ratio became 22.5 times. The resulting filaments had a 15.8 g./d. strength and a 4.5% elongation. Dynamic moduli at 20° C. and 120° C. were 3.8×10^{11} dyne/cm.^{2} and 3.0×10^{11} dyne/cm.^{2}, respectively.

Example 6

Fibers were produced by spinning a 14% aqueous solution of PVA having an average degree of polymerization of 2500 (to which 2.0% boric acid based on the weight of PVA was added to make the pH 4) as the spinning solution using a saturated Glauber's salt solution containing 10 g./l. of caustic soda as the coagulation bath. After taking out the fibers, they were subjected to spin-drawing in a ratio of 4.5 times, neutralized with 300 g./l. Glauber's salt and 30 g./l. of sulfuric acid at room temperature and then treated with a bath having the same composition at 90° C. After washing with water and drying, the fibers were subjected to a first hot drawing at 230° C. for 10 seconds in a ratio of 4 times. The fibers were then dipped in water for 5 seconds and squeezed by rolls. The fibers were then subjected to a second hot drawing at 245° C. for 8 seconds in a ratio of 1.2 times, by which the total draw ratio became 21.6 times. The result-

ing filament yarn (1200 d., 500 f.) had a 16.2 g./d. strength and a 5% elongation. The dynamic modulus at 20° C. was 3.7×10^{11} dyne/cm.^{2} and at 120° C. was 3.1×10^{11} dyne/cm.^{2}. The fibers did not fluff as compared to the fibers obtained by the same treatment but not affording moisture at the hot drawing treatment.

Example 7

Fibers were produced by spinning an 11% aqueous solution of PVA having an average degree of polymerization of 3500 (to which 1.5% boric acid based on the weight of PVA was added) as the spinning solution with a coagulation bath having the same composition as in Example 6. The fibers were subjected to spin-drawing in a ratio of 5 times, followed by the treatment as in Example 6. After drying, the fibers were subjected to the first hot drawing at 230° C. in a ratio of 3.0 times. The fibers were then dipped into an emulsion containing mineral oil as the main component and squeezed to remove the liquid to afford 30% moisture. The fibers were then subjected to a second hot drawing at 240° C. at a ratio of 1.3 times. After affording moisture by the same emulsion of oil as the abovementioned, the fibers were subjected to a third hot drawing at 250° C. in a ratio of 1.15 times. The resulting filament yarn (1400 d., 500 f.) had a 17.2 g./d. strength and a 4% elongation. The dynamic modulus at 20° C. was 3.8×10^{11} dyne/cm.^{2} and at 120° C. was 3.2×10^{11} dyne/cm.^{2}.

Example 8

Fibers were produced by spinning a 15% aqueous solution of PVA having an average degree of polymerization of 2500 as the spinning solution using an aqueous solution of 380 g./l. of caustic soda as the coagulation bath. After taking out the fibers, they were subjected to spin-drawing at a ratio of 4.5 times. After treating with a bath of 250 g./l. of Glauber's salt and 20 g./l. of sulfuric acid at 80° C., the fibers were washed with water and dried. The dry fibers were subjected to a first hot drawing at 225° C. in a ratio of 3.0 times, followed by spraying thereon an emulsion containing a vegetable oil as the main component to afford 40% moisture. The fibers were then subjected to second drawing at 235° C. in a ratio of 1.2 times, by which the total draw ratio became 21.1 times. The filament yarn (1800 d., 750 f.) had a 16.3 g./d. strength and a 4% elongation. The dynamic modulus was 3.7×10^{11} dyne/cm.^{2}. At 120° C., the fibers had a 14.0 g./d. strength, a 5.5% elongation and a 3.1×10^{11} dyne/cm.^{2} dynamic modulus.

What is claimed is:

1. In a wet-spinning process for producing polyvinyl alcohol synthetic fibers having a homogenous cross-section comprising:
   (1) wet-spinning an aqueous polyvinyl alcohol solution into a coagulating bath to produce polyvinyl alcohol fibers having a uniform cross-section;
   (2) spin-drawing said fibers at a draw ratio of from 3.5 to 5;
   (3) washing the spin-drawing fibers with water;
   (4) drying the washed fibers;
   (5) subjecting the resulting fibers to a hot-drawing operation; and
   (6) subjecting the resulting hot-drawn fibers to a heat-relaxing step; the improvement comprising producing high modulus polyvinyl alcohol fibers of homogeneous cross-section having a high strength and low elongation without a heat relaxation step by a process which comprises:
   (7) subjecting the fibers produced in step (4) to a first-hot-drawing operation at a temperature above 160° C. but less than the melting point of the fibers and a draw ratio of at least 3;
   (8) contacting the resulting fibers with water or an aqueous oil emulsion to add moisture to the fibers in an amount of from 20 to 50 percent by weight, based on the weight of the fibers;
   (9) subjecting the resulting fibers to a second hot-drawing operation at a temperature of at least 180° C. and at a draw ratio of at least 1.1; and
   (10) repeating steps (8) and (9) until the total draw ratio is at least about 20 and wherein the temperature of the third and any subsequent hot-drawing operation is greated than the temperature of the immediately preceding hot-drawing operation.

2. The process of claim 1 further comprising, between steps (2) and (3), subjecting the fibers to a neutralization step.

3. The process of claim 2 wherein said neutralization step is conducted by contacting the fibers with a Glauber's salt solution containing sulfuric acid at room temperature and thereafter contacting the resulting fibers with a Glauber's salt solution containing sulfuric acid at a temperature of from 80 to 90° C.

4. The process of claim 1 wherein all of said hot-drawing operations are conducted in air.

5. The process of claim 1 wherein the draw ratio of said first hot-drawing operation is from 3 to 5.

6. The process of calim 5 wherein the draw ratio of said second hot-drawing operation is from 1.1 to 1.4.

7. The process of claim 1 wherein said coagulating bath comprises a caustic alkali solution.

8. The process of claim 7 wherein said coagulating bath comprises a Glauber's salt solution.

9. The process of claim 1 wherein said aqueous polyvinyl alcohol solution contains boric acid or borax and wherein said coagulating bath comprises an alkaline coagulation bath comprising dehydrating salts.

10. The process of claim 1 wherein said spin-drawing operation is conducted in air.

11. The process of claim 1 wherein said spin-drawing operation is conducted in an aqueous salt solution.

12. The process of claim 1 wherein said spin-drawing operation is conducted both in air and in an aqueous salt solution.

13. The process of claim 1 wherein the total draw ratio after step (7) but before step (8) is at least 10.

14. The process of claim 1 wherein steps (8) and (9) are repeated once and wherein the third hot-drawing operation is conducted at a draw ratio of 1.05 to 1.20 and at a temperature of from 240 to 250° C.

15. The process of claim 1 wherein the denier of the filament yarns is less than 10,000.

References Cited

UNITED STATES PATENTS

2,610,360	9/1952	Cline et al.	260—91.3 PV
3,079,640	3/1963	Kawai et al.	8—130.1
3,102,775	9/1963	Seeger	264—185
3,140,957	7/1964	Tanabe et al.	117—6
3,170,973	2/1965	Tanabe et al.	264—185
3,412,191	11/1968	Kitajima et al.	264—182
3,597,303	8/1971	Tanaka	57—157 R

JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

264—185