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POLYVINYL ALCOHOL FIBERS

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3 Claims

ABSTRACT OF THE DISCLOSURE

Polyvinyl alcohol fibers comprising an essentially water insoluble polyvinyl alcohol containing boric acid or a water soluble borate salt thereof in an amount of from 0.2 to 0.9% by weight of polyvinyl alcohol, said fibers being characterized by a half-width of (100) reflection (β) of 0.98 to 1.40 and an I_M/I_{30} of from 0.40 to 0.48 derived from the azimuthal X-ray intensity distribution at the angle of diffraction of 19.2° .

This invention is a continuation-in-part of copending application Ser. No. 90,816 filed Nov. 18, 1970 and now abandoned.

The present invention relates to improved polyvinyl alcohol fibers. More particularly, this invention relates to polyvinyl alcohol fibers which exhibit excellent properties at high temperatures such as yarn tenacity, yarn initial modulus and yarn creep.

Generally, polyvinyl alcohol (PVA) fibers surpass other synthetic fibers in breaking strength and initial modulus, and have recently found wide use in many fields, for instance, fiber reinforced plastics (FRP). It is a well-known fact that PVA fibers which are drawn to the drawable limit and minimized in heat-shrinkage exhibit outstanding breaking strength and initial modulus. However, PVA fibers, like many other synthetic fibers, undergo a deterioration in properties at high temperature in proportion to the rise in the temperature.

The primary object of the present invention is to obviate the above deficiencies in synthetic fibers by providing a PVA fiber having excellent properties at high temperature. More particularly, the synthetic fibers in accordance with the present invention are superior to conventional PVA fibers with respect to yarn tenacity, yarn initial modulus and yarn creep.

The PVA synthetic fibers of the present invention exhibit high crystallinity and molecular orientation, and are characterized by the high temperature properties indicated below and by the amount of boric acid (H_3BO_3) or a borate salt thereof contained therein, the properties at high temperature being as follows:

Yarn tenacity at $120^\circ C.$ ----- At least 7.5 g./d.
Yarn initial modulus at $120^\circ C.$ ----- At least 100 g./d.
Yarn creep at $135^\circ C.$ ----- Less than 2%.
Boric acid or borate salt content -- 0.2 to 0.9% by weight of PVA.

Generally speaking, the extensibility of synthetic fibers increases in proportion to the rise in temperature, and the strength and yarn initial modulus decrease. It can be easily speculated that this phenomenon occurs because movement is initiated in the molecular chain of the fiber in regions of low molecular orientation upon heating the fiber. This movement is soon transmitted to regions of the fiber where molecular orientation is intense. It is therefore important, in the improvement of the properties at high temperature of a synthetic fiber to suppress the

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movement of molecular chains as much as possible. This can be achieved either by (1) intensifying the orientation of the molecular chains to such an extent as to prevent them from moving, or (2) adding to the polymer a material which hinders the movement of molecular chains. These two remedies, however, when separately employed are not capable of achieving the objects of the present invention, i.e., property improvement at high temperature such as improvement in yarn tenacity, yarn initial modulus and yarn creep. For instance, improvement in yarn initial modulus may be expected in a method wherein a conventional PVA fiber is subjected to post-treatment with boric acid; however, the same process will also result in a remarkable decrease in yarn tenacity.

It has been found in accordance with the present invention that the essential factor which fulfills the primary object of the present invention is a fibrous structure wherein the orientation of the molecular chains is quite intense as a whole but which contains a substance to prohibit the movement of the molecular chains where the molecular orientation is relatively loose. That is, a portion or all of the boric acid or borate salt thereof contained in the fiber may combine with the PVA in relatively loose orientation, to prohibit the movement of the molecular chains caused by heating. When the amount of boric acid or borate salt does not measure up to 0.2% by weight of PVA, it is insufficient to restrain the chain movement. When the boric acid or borate salt content exceeds 0.9%, it will prevent the molecular chains from being highly oriented, thereby causing reduction of the yarn strength.

The novel PVA fibers of the present invention comprise PVA having an average degree of polymerization of from about 1200 to 3500 and containing from 0.2 to 0.9 weight percent boric acid or a water soluble borate salt thereof, and preferably containing from 0.2 to 0.7 weight percent boric acid or a water soluble borate salt thereof, said PVA fiber being characterized by a half width of (100) reflection (β) of 0.98 to 1.40 and (I_M/I_{30}) of 0.40 to 0.48 derived from the azimuthal X-ray intensity distribution at the angle of diffraction of 19.2° .

Among the structural parameters cited above characterizing the PVA synthetic fiber of the present invention, the half width of (100) reflection (β) is the parameter indicating the transverse magnitude of crystals in the fiber; whereas, the value of I_M/I_{30} denotes the structure of the amorphous region of said fiber.

It has now been found that a correlation exists between the advantageous characteristics of the PVA fibers of the present invention and the structural parameters of such fibers. Thus, the PVA fibers of the present invention can be characterized by the two parameters described above as will be illustrated in detail hereinbelow.

In general, 5 peaks appear in the equatorial X-ray diffraction intensity curve of a synthetic fiber of PVA within the angles of diffraction ranging from 5° to 25° , these peaks are designated, in order of increasing angle of diffraction, as (100), (001), ($10\bar{1}$), (101) and (200).

The crystallographic significance of these reflections is discussed in the literature: see, C. H. Bunn. *Nature*. 161, 929 (1948).

Crystals of PVA fiber comprise unit cells having a monoclinic crystal form characterized by: $a=7.81 \text{ \AA}$, $b=2.52 \text{ \AA}$, $c=5.51 \text{ \AA}$, $\angle ac$ (angle between a and c axes) $=91^\circ 42'$, and in the case of a heat drawn fiber, the b -axis orients along the fiber-axis direction.

The planes of (100), (001), ($10\bar{1}$), (101) and (200) are parallel to the b -axis, oriented in the parallel direction to the fiber axis and so appear on the equator on X-ray diffraction.

The sharpness of the reflections of these planes parallel to the b -axis relates to the width of the crystals, with the

broader width crystals being considered the finer crystals; whereas, the (020) reflection is in the plane perpendicular to the *b*-axis which relates to the length of the crystals.

The value of the half width of the (100) reflection (β) in the PVA fiber of the present invention ranges from 0.98 to 1.40, being considerably broader as compared to conventional PVA fibers having β values of from 0.60 to 0.98. Consequently, the PVA fibers of the present invention have considerably smaller crystal width in the crystalline structure in comparison to conventional PVA fibers.

The intensity distribution determined along the azimuthal direction at the angle of diffraction of 19.2° has heretofore been found by C. H. Mac. Gillarry to represent the orientation of the amorphous region of the PVA fiber; see, *Recueil des Travaux Chimiques des Pays-Bas* T69, 3(1950). The intensity at the meridian in the intensity distribution along the azimuthal direction of the fiber according to the present invention has been found to be weaker than those of conventional PVA fibers. Near the equator, the intensity is affected by the effect of the crystalline reflection, and so the ratio of the intensity at the meridian to the intensity at the azimuthal angle of 30° has been adopted as a parameter (I_M/I_{30}) characteristic of the fibers of the present invention. The smaller values of said parameter signify less disorder in the amorphous region of the fiber, and indicate better orientation of the molecular chain in said amorphous region.

The PVA fibers of the present invention exhibit a value of the parameter (I_M/I_{30}) ranging from 0.40 to 0.48, which is smaller than the I_M/I_{30} , typically 0.49 to 0.55 of conventional PVA fibers, thereby imparting enhanced orientation to the amorphous region of the fibers of the present invention as compared to conventional PVA fibers.

Many spinning methods have heretofore been developed for PVA fibers. For example, wet-spinning through a coagulation bath containing sodium sulfate, wet-spinning through a coagulation bath containing sodium hydroxide, dry-spinning and the like. PVA fibers manufactured by these conventional methods are characterized by a high degree of crystallization, with the width of the crystals exceeding 95 Å. In particular, PVA fibers manufactured by coagulation through a caustic soda bath exhibit a β value of below 0.83, and a crystal width of about 120 Å. Thus, the conventional PVA fibers are characterized by thorough development of the crystal width; whereas, in the PVA fibers of the present invention containing 9.2 to 0.9% of boric acid, and preferably 0.2 to 0.7% of boric acid, the crystals do not develop along the wide direction and so the width of the crystals is merely 55 to 82 Å.

In conventional PVA fibers, the length of the molecular chains of the amorphous region are irregular and scarcely oriented; hence, the structure thereof is random and loose. The structural parameter I_M/I_{30} of said conventional PVA fibers having such an irregular amorphous region ranges from 0.49 to 0.55.

In contrast, however, the PVA fibers of the present invention containing boric acid, a part of which cross links with the PVA molecule imparting difficulty in movement of the molecular chain, thereby providing considerable orientation in the amorphous region of the PVA molecule giving rise to a compact structure, exhibit a value of I_M/I_{30} below 0.48.

The excellent strength and the high temperature performance of the fibers of the present invention are considered to depend largely on the structure of the amorphous region thereof.

The novel synthetic fibers of the present invention are highly crystallized and highly oriented. These fibers are characterized by exhibiting a yarn dry break strength at room temperature of at least 10 g./d., a microcrystal length (half width of the reflection along (020) plane) of at least 125 Å. and containing 0.2 to 0.9 weight percent based on PVA of boric acid (H_3BO_3), or a borate salt thereof.

The fibers of the present invention exhibit markedly improved performance at high temperatures, thus, for example, the yarn dry break strength at 120° C. is maintained at at least 7.5 g./d., the initial modulus at 120° C. is maintained at at least 100 g./d., and the yarn creep at 135° C. is less than 2%.

In general, the elongation of break of a synthetic fiber increases with the rise in the temperature, while both the break strength and the initial modulus tend to decrease, the reason for which can be postulated as follows; on heating, molecular chains existing in the loosely oriented regions of the fiber begin to move, the motion imparted to the molecular chains by heating propagates gradually to the highly oriented regions, resulting in a loosely oriented structure of the fiber as a whole. As a consequence, it is essential to inhibit the movement of the molecular chains as much as possible. There are two possible ways to halt molecular motion: (1) by imparting extremely high orientation to the molecular chain, the whole molecular chain becomes immobile, or (2) by adding certain materials which suppress the motion of the molecular chain. However, neither method alone can improve both the break strength and the initial modulus at high temperatures which are the principal object of the present invention.

Conventional post-treatment of the fiber with boric acid provides some improvement of the initial modulus; however, the break strength is inevitably lowered to a considerable extent thereby. For example, the Latour Patent, U.S. 2,716,049, discloses a method of preparing PVA fiber consisting of spinning a solution of 82–94% saponified PVA into a coagulation bath and post-treating the fiber with boric acid. The PVA fiber produced by the process of this patent exhibits a tenacity of 2–3.4 g./d. and is soluble in water. In addition, it has been found that PVA fibers produced by this technique exhibit a yarn tenacity of 1.50 g./d., an elongation of 24.2% and a yarn initial modulus of 3.54 g./d., all measured at 120° C. In comparison, the PVA fibers of the present invention exhibit a yarn tenacity of more than 7.5 g./d. at 120° C., a yarn modulus of more than 100 g./d. at 120° C., and are essentially insoluble in water.

It has now been found that a fiber structure with markedly high orientation in the crystalline regions and containing boric acid or a borate salt to suppress the motion of the molecular chain in the amorphous regions is effective in achieving the purposes of the present invention. A part of or all the boric acid or borate salt combines with PVA in the loosely oriented regions of the fiber to suppress the motion of the molecular chain imparted thereto by heating. If the content of boric acid is less than 0.2%, it is insufficient to inhibit such molecular motion; while use of amounts of said boric acid exceeding 0.9%, precludes high orientation of the molecular chains resulting in a lowering of the tenacity or break strength. The break strength of the PVA yarn of the present invention at room temperature is at least 10 g./d. which indicates that all the molecular chains of the PVA fiber of the present invention are highly oriented to attain such a high strength.

The PVA employed in the present invention has an average degree of polymerization ranging from 1200 to 3500, and preferably ranges from 1500 to 3000. As the average degree of polymerization decreases below 1200, the viscosity of the spinning solution becomes too low to effect stable spinning of the solution and the resulting fibers exhibit insufficient strength. If the average degree of polymerization is higher than 3500, however, difficulties are encountered in the spinning operation which make the manufacture of good fibers extremely difficult. The PVA employed in the present invention exhibits an initial degree of saponification of from 97 to 99.9%; however, the PVA in the fiber is substantially completely saponified since additional saponification occurs during the fiber-forming process.

The PVA fibers of the present invention can be produced by a process comprising: preparing an aqueous solution of PVA which contains boric acid or borate salt thereof (the spinning solution); spinning in a coagulating bath comprising a major amount of water, sodium hydroxide or potassium hydroxide and sodium sulfate, said materials being present in the coagulating bath in a predetermined amount; drawing the resulting fibers between rollers; neutralizing any alkali adhered to the fibers with acid; wet-heat drawing of the fibers; water-rinsing to adjust the amount of boric acid remaining in the fiber to be within a predetermined range; dehydrating and drying; and, dry-heat drawing.

The concentration of the coagulating bath, which has heretofore been used in the conventional wet spinning method to produce PVA fibers containing no boric acid or borate, is almost saturated with sodium sulfate, when sodium sulfate is used as the dehydrating salt in the bath. This is done because the fibers will stick to one another due to insufficient coagulation, when the concentration of the dehydrating salt in said bath is lower than 100 gm./l. Accordingly, the coagulating bath used in the present invention is further combined with sodium hydroxide or potassium hydroxide in a predetermined amount, thereby facilitating the spinning of spinning solutions containing boric acid or borate. The properties of the PVA fiber thus produced depend very little on the temperature. It is often observed that when the content of sodium sulfate is high in the coagulating bath, the drawability of the product tends to decrease. The PVA synthetic fibers produced in accordance with the present invention exhibit superior drawability and less temperature dependency as compared with conventional PVA fibers which contain no boric acid.

In accordance with the present invention, it has been found that the aqueous spinning solution of PVA containing boric acid or a water soluble borate salt thereof can be coagulated to produce PVA synthetic fibers having yarn tenacity, yarn initial modulus and yarn creep which hardly depend on the temperature. The method of the present invention comprises spinning an aqueous solution of PVA containing boric acid or a borate salt thereof into a coagulating bath being kept strongly alkaline by the addition of 10 to 100 gm./l. sodium hydroxide or potassium hydroxide and 100 to 330 gm./l. sodium sulfate, which is then subjected to subsequent treatments such as roller drawing, alkali neutralization, water-rinsing to adjust the residue of boric acid in the fiber to a range of 0.2 to 0.9% by weight of PVA, and preferably to a range of 0.2 to 0.7% by weight of PVA, dehydration and drying, and dry-heat drawing.

It is preferable to add boric acid or a water soluble borate salt thereof to the spinning solution in an amount ranging between 1 and 5% by weight of PVA.

Boric acid or any water soluble borate salt thereof can be employed in accordance with the present invention. Any borate salt which is relatively soluble in the aqueous spinning solution can be suitably employed, as for example, the alkali metal borates such as sodium borate, potassium borate and the like. The solution is maintained weakly acidic, specifically between pH 3 and pH 5. The pH of the solution can be regulated, if necessary, by addition of an acid thereto. Acids which can be added to the solution can be, for example, an inorganic acid such as sulfuric, hydrochloric and nitric acid, an organic acid such as acetic acid, tartaric acid, etc.; or a combination of an organic acid and a salt of an organic acid, e.g. citric acid and sodium citrate, acetic acid and sodium acetate, tartaric acid and potassium tartaric acid and sodium citrate, etc.

When the spinning solution has a pH lower than 3, the rate of coagulation in the coagulating bath will be slower, and corrosion of the apparatus occurs due to the high acidity. On the other hand, when the pH is higher than 5, the solution becomes unstable causing an increase

in viscosity thereby greatly damaging the spinning conditions.

The concentration of PVA in the spinning solution preferably ranges between 10 and 30% by weight. The spinning solution is spun into a strongly alkaline coagulating bath containing mainly water and sodium hydroxide or potassium hydroxide in a range of 10 to 100 g./l. and sodium sulfate in a range of 100 to 330 g./l. Sodium hydroxide or potassium hydroxide concentrations of less than 10 g./l. result in unfavorable effects such as reduction in the coagulating rate and reduction of drawability at the time of spinning. It is considered undesirable to exceed a sodium hydroxide or potassium hydroxide concentration of 100 g./l. because gelling action due to alkali becomes so active, as to decrease the spinnability of the spinning solution causing such properties as the yarn tenacity, yarn initial modulus and yarn creep to be inferior. When the concentration of sodium sulfate is less than 100 g./l., gelling action due to alkali overpowers the dehydration and coagulating action of the sodium sulfate. This causes swelling of the fiber at the time of coagulation, which adversely affects the quality of the product. On the other hand, concentrations of sodium sulfate exceeding 330 g./l. cause deformation in the fiber's cross section to substantially an elliptical cross section since dehydration and coagulating action overpowers other actions. The deformed section of the fiber is a cause of reduction in drawability.

In the present invention the PVA fiber thus spun is subjected to subsequent conventional treatments such as roller drawing, neutralization of alkali by the use of acid, wet-heat drawing, and is then water-rinsed to adjust the amount of boric acid remaining in the fiber to be in a range of 0.2 to 0.9% by weight of PVA. The residue of boric acid after water-rinsing should be more than 0.2% by weight of PVA because swelling of the fiber at the time of rinsing may occur when it is less than said amount. The swelling of the fiber will cause a slack in the fiber, which can then be caught in the rollers resulting in an unstable operation, thereby decreasing such properties as the yarn tenacity, yarn initial modulus and yarn creep.

These drawbacks are not observed in the present invention because the residue of boric acid present in the fiber may either react with PVA to effect formation of inter- or intra-molecular cross linkings, hang on the PVA chains, or remain unreacted. This is one of the characteristic features of the present invention. When the amount of said boric acid exceeds 0.9% by weight, the drawability of the fiber will decrease resulting in a decrease in the absolute values of the yarn tenacity and yarn initial modulus.

Thus, by selecting the optimum conditions for coagulation, the process can be stabilized for production of fibers having high drawability. Moreover, by so determining the conditions for water-rinsing as to maintain the residue of boric acid in the range of 0.2 to 0.9 weight percent and preferably in the range of 0.2 to 0.7 weight percent, products having properties hardly dependent on temperature are obtained without reducing the dry-heat drawability.

In the present invention, it is necessary to conduct the dry-heat drawing of the PVA fiber subsequent to water-rinsing, dehydration and drying, in order to achieve a total drawing ratio of more than 1300%. If the total drawing ratio is less than 1300%, it is difficult to obtain PVA fiber exhibiting the above-mentioned properties. According to this invention, the PVA fiber can be drawn to a total drawing ratio of 1800%.

The properties of PVA fiber thus obtained are: yarn tenacity at 120° C. of at least 7.5 gms./denier (g./d.); yarn initial modulus at 120° C. of at least 100 g./d.; and yarn creep at 135° C. of less than 2% (elongation rate under the load of 1 g./d. for 60 minutes). The fibers contain 0.2 to 0.9% of boric acid or a borate salt. The

fibers of the present invention are superior to conventional PVA fibers containing no boric acid or borate with respect to high temperature properties.

The measurement of boric acid remaining in the synthetic fiber can be conducted in accordance with the following method:

A fiber weighing in terms of PVA approximately 2 g. is placed in a crucible, to which is added 0.1 mole/l. aqueous sodium hydroxide solution to cover the fiber. After placing the crucible in a dryer at 105° C. for one night, it is baked in an electric furnace at 400° C. to 500° C. for 60 minutes. The fiber in the crucible is then placed in a beaker, to which is added ion-exchanging water and maintained as it is for 60 minutes. A few drops of phenolphthalein indicator are added to the beaker. Whereupon, 0.1 mole./l. hydrochloric acid is added until the color turns from red to yellow. After boiling for 30 to 60 minutes, it is cooled and neutralized to pH 7 by sodium hydroxide or hydrochloric acid addition as may be required. Mannite is added to the beaker and the solution is again neutralized to pH 7 by titrating with 0.1 mole/l. sodium hydroxide. The volume (cc.) being titrated is measured. The amount of boric acid remaining in the fiber is calculated by the following equation wherein $W(g.)$ is the weight of PVA in the test product measured in accordance with the method given above, and f and $v(cc.)$ are the strength and the titrated volume, respectively, of the 0.1 mole aqueous solution of sodium hydroxide:

$$\frac{0.62 \times f \times v}{W}$$

The dry break strength or tenacity is determined according to JISL 1070. Thus the sample of the fiber is twisted 8 times per 10 cm., dried at 105° C., for 3 hours and then immediately tested for break strength with a sample having a length of 20 cm., at a drawing speed 10 cm./min., using a constant speed elongating tensile strength tester which has polyurethane film at the jaw face of the fastener.

The initial modulus can be obtained from the stress-strain curve given by the determination of the above dry break strength, in reference to JIS L 1073. For the determination at room temperature, it is carried out in a room kept at 20° C., while for the determination at high temperatures, the upper and lower fastener of the tester is in an atmosphere of an electric oven kept at 120° C. and the test performed until breaking of the sample occurs.

The determination of the halfwidth β in the equatorial X-ray reflection, and the azimuthal X-ray intensity distribution I_M/I_{30} will be illustrated below.

(1) Equatorial X-ray reflection.—A sample of about 125 mg. and of 2.5 cm. is made into a strip of 10 mm. in width, and then subjected to the scanning test at the equator thereof using a wide angle X-ray diffractometer, type D3F of Rigaku Denki Co. Ltd. under the conditions of 40 kv., 15 ma., Cu-cathode, the line focus and the slits of 1°/6°, 0.3 mm. and 1/3°.

(2) Length of the crystallite (half-width of the reflection along (020) plane β).—The same apparatus and sample as in (1) are used in the determination. Slit is 1 mm. pin hole collimator first slit 3 x 2, 2nd slit 1°, as the incident slit, scanning slit 1°. Recorder: range 250 c/s time constant 2 sec., scanning speed 1°/min., chart speed 1 cm./min. The half-width β of the reflection along (020) plane is measured from the data obtained above, following a correction for the deviation of interference arising from the apparatus. From Table I below, the length of the crystallite in angstrom units can be calculated from $(100/\beta)$.

(3) Determination of β .—The half-width of the reflection along (100) reflection β is determined as follows. A

base line is drawn on the scanning chart from 8° to 15° of the diffraction angle, a perpendicular line is drawn from the point of maximum intensity to the base line. The width at half of the height is determined and is considered the "apparent half width" B expressed in terms of the angle, and is corrected for the deviation of interference arising from the apparatus to obtain β . The correction to obtain β from B is found in the following Table I.

TABLE I

Correction for deviation for apparatus interference in obtaining half-width (β) from apparent half-width (B)

B	β B	β B	β B	β			
0.71	0.608	0.81	0.716	0.91	0.822	1.01	0.926
2	619	2	726	2	832	2	936
3	630	2	736	3	841	3	947
4	640	4	748	4	852	4	957
0.75	0.653	0.85	0.759	0.95	0.863	1.05	0.968
6	662	6	770	6	874	6	978
7	672	7	780	7	884	7	988
8	684	8	790	8	894	8	998
9	694	9	800	9	905	9	1.009
0.80	0.706	0.90	0.811	1.00	0.916	1.10	1.019

(4) Azimuthal X-ray intensity distribution.—The scintillation counter is fixed at $2\theta=19.2^\circ$ whereupon the azimuthal intensity distribution of reflection is measured by revolving the sample. It is measured by the number of counts per 2 minutes with the slit system of pin hole slit 3 x 3 cm., at 1°, 2°.

The PVA fiber of the present invention is characterized by having weak intensities along the azimuth angle of 60°–90°. Though a shoulder near 60° can be recognized, it is not significant, since reflections other than the amorphous scattering are included therein, as radial streaks can be seen in the X-ray photograph. The degree of orientation of the amorphous region is consequently appropriately expressed by the ratio of the intensity along the meridian to that along 30° in the azimuth angle.

The following examples further define, describe and compare the polyvinyl alcohol fibers of the present invention and their methods of preparation. Parts and percentages are by weight unless otherwise indicated.

Example 1

10 kg. of an aqueous spinning solution containing 1.7 kg. of PVA with a degree of polymerization of 1,750 and degree of saponification of 99.5 mole percent, and 34 g. of boric acid and a sufficient amount of nitric acid to adjust the pH to 4.3 is prepared. The spinning solution is passed through spinning nozzles comprising 600 spinning holes, 0.08 mm. in diameter into a coagulating bath containing 30 g./l. of sodium hydroxide and 230 g./l. of sodium sulfate. The fiber thus spun is then taken out of the bath at a rate of 10 m./min., and then subjected to subsequent treatments such as; roller drawing of 100%, neutralization in a bath comprising 70 g./l. of sulfuric acid and 300 g./l. of sodium sulfate; wet-heat drawing of 150%; water-rinsing to adjust the amount of boric acid to be 0.45%; dehydration and drying; and dry-heat drawing of 220%. The final product obtained is drawn to a total drawing ratio of 1,500%.

The product thus obtained exhibits a yarn tenacity of 9.3 g./d. at 120° C., yarn initial modulus of 135 g./d. at 120° C. and yarn creep of 1.4% at 135° C. and furthermore exhibits a β of 1.04 and I_M/I_{30} of 0.44.

In Table 2 below, comparative examples are provided which illustrate the effects on yarn properties of variations in process conditions and boric acid concentration. The conditions employed in Example I and the resulting yarn properties so obtained are also set forth to assist in these comparisons.

TABLE 2

	Example 1	Comparison						
		1	2	3	4	5	6	7
Material:								
Polymerization degree of PVA.....	1,750	1,750	1,750	1,750	1,750	1,750	1,750	1,750
Saponification degree of PVA (mol percent).....	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5
Spinning solution:								
The concentration of PVA (percent).....	17	17	17	17	17	18	18	17
The amount of boric acid added (percent).....	2.0	2.2	2.2	2.2	2.2	2.6	2.6	2.0
pH.....	4.3	4.1	4.1	4.1	4.1	4.0	4.0	4.3
Coagulation bath:								
NaOH (g./l.).....	30	8	110	80	15	40	40	30
Na ₂ SO ₄ (g./l.).....	230	260	150	90	380	220	220	230
Neutralization bath:								
H ₂ SO ₄ (g./l.).....	70	70	70	(³)	70	80	80	70
Na ₂ SO ₄ (g./l.).....	300	300	300	-----	300	320	320	300
Drawing:								
Total drawing ratio (percent).....	1,500	⁴ 1,100	⁵ 1,200	-----	⁴ 1,000	1,500	1,200	1,100
Roller drawing (percent).....	100	100	100	-----	100	100	100	100
Wet-heat drawing (percent).....	150	150	140	-----	150	150	140	150
Dry-heat drawing (percent).....	220	140	192	-----	120	220	192	140
Amount of residue of boric acid (percent).....	0.45	0.51	0.52	-----	0.49	0.15	1.00	0.46
Tenacity (120° C.) (g./d.).....	9.3	6.2	7.0	-----	5.4	7.3	7.0	6.5
Initial modulus (120° C.) (g./d.).....	135	72	82	-----	63	91	82	96
Creep (135° C.) (percent).....	1.4	2.5	2.2	-----	3.1	2.3	2.4	2.3
β	1.04	0.90	0.95	-----	0.95	0.87	0.97	0.92
I_M/I_{30}	0.44	0.52	0.42	-----	0.51	0.48	0.51	0.51

¹ Tartaric acid used to adjust pH.² Acetic acid and sodium acetate used to adjust pH.³ Incapable of being spun.⁴ Sample exhibited poor drawability.⁵ Sample exhibited poor spinability.

NOTE.—In Example 1 to comparative Example 4, nitric acid is used to adjust the pH.

EXAMPLE 2

PVA fiber containing sodium borate and drawn to a total drawing ratio of 1,500% is obtained in the same manner as in Example 1, except that sodium borate is employed in an amount of 1.5% of PVA in lieu of boric acid and tartaric acid is employed in lieu of nitric acid for adjustment of pH. The product obtained exhibits a yarn tenacity of 9.1 g./d. at 120° C., yarn initial modulus of 127 g./d. at 120° C., yarn creep of 1.5% at 135° C, a β of 0.98 and I_M/I_{30} of 0.48.

EXAMPLE 3

An aqueous PVA solution having a concentration of PVA of 15 weight percent and containing 150 g. of PVA with a degree of polymerization of 2,350 and a degree of saponification of 99.5 mole percent is admixed with 30 g. of boric acid (2% by weight of PVA) and a small amount of acetic acid to prepare a spinning solution of pH of 4.5. The spinning solution is spun into a strongly alkaline coagulating bath mainly of water containing 40 g./l. of sodium hydroxide and 250 g./l. of sodium sulfate. After taking the spun fibers out of the bath at a rate of 10 m./min., they are subjected to roller drawing of 100%, neutralization, wet-heat drawing of 150%, water-rinsing to adjust the amount of boric acid residue to 0.4% by weight of PVA, dehydration and drying, and dry-heat drawing of 200%. The product (1,200 d./600 f.) is thus drawn to a total drawing ratio of 1,400%. The product thus obtained exhibits a yarn tenacity of 9.2 g./d. at 120° C., yarn initial modulus of 131 g./d. at 120° C., yarn creep of 1.9% at 135° C., a β of 1.06 and I_M/I_{30} of 0.47; the product is superior in its properties at high temperature.

EXAMPLE 4

An aqueous solution of PVA of 17 weight percent containing 100 kg. of PVA with a degree of polymerization of 1,750 and a degree of saponification of 99.9 mole percent is admixed with 2 kg. of boric acid (2 weight percent of PVA) and 0.3 kg. of acetic acid (0.005 g. equivalent to PVA 100 g.) to prepare a spinning solution. The pH is maintained at 4.5.

The spinning solution is passed through nozzles of 1,000 holes in number and 0.15 mm. in diameter into the coagulating bath containing 50 g./l. of sodium hydroxide and 200 g./l. of sodium sulfate. Then, the fibers are taken out of the bath at a rate of 10 m./min. The spinning con-

dition is very stable in this case; during two weeks' spinning, no difficulties such as clogging of the nozzles is observed. The fiber thus spun is then subjected to the same processing as in Example 3; i.e., roller drawing, neutralization, wet-heat drawing, water-rinsing to adjust the amount of residual boric acid to 0.5% by weight of PVA, dehydration, drying, and dry-heat drawing. The product (1,800 d./1,000 f.) thus obtained is drawn to a total drawing ratio of 1,400%. The product exhibits a yarn tenacity of 9.3 g./d. at 120° C., yarn initial modulus of 134 g./d. at 120° C., yarn creep of 1.8% at 135° C., a β of 1.13 and I_M/I_{30} of 0.46.

EXAMPLE 5

1 kg. of an aqueous spinning solution containing 170 g. of PVA with a degree of polymerization of 1750 and degree of saponification of 99.5 mol percent, 5.95 g. of boric acid (3.5 weight percent on PVA) and sulfuric acid sufficient to adjust the pH to 4 is prepared. The spinning solution is passed through a nozzle into a coagulation bath containing 15 g./l. of sodium hydroxide and 230 g./l. of sodium sulfate. The resultant fiber is subjected to the same subsequent treatment as in Example 1 to obtain PVA fiber containing 0.5 weight percent of boric acid.

The product thus obtained exhibits excellent properties at 120° C. and a β of 1.11 and I_M/I_{30} of 0.45.

Example 6

A PVA aqueous spinning solution containing 17 weight percent PVA with a degree of polymerization of 1700 and degree of saponification of 99.5 mol percent, boric acid of 2 weight percent on PVA and nitric acid of 0.2 weight percent on PVA to adjust the pH to 4 is prepared.

The spinning solution is passed through a conventional nozzle comprising 600 holes into a coagulation bath at 40° C. containing 20 g./l. of sodium hydroxide and 250 g./l. of sodium sulfate. The resultant fiber is roller drawn and then subjected to subsequent treatments such as: neutralization of sodium hydroxide on the fiber with an acid, wet-heat drawing, water-rinsing of the fiber to adjust the amount of boric acid in the fiber, drying and dry-heat drawing to a total draw ratio of 1300–1500%.

In Table 3 below, the resultant PVA fibers containing various amounts of boric acid are shown with their properties.

TABLE 3

The amount of boric acid contained in the fiber (percent/PVA).....	0	0.21	0.36	0.50	0.67	0.85	0.95	1.05
Total drawing ratio (percent).....	1,200	1,500	1,500	1,500	1,500	1,400	1,200	1,140
Denier/filament.....	1,200/500	1,200/600	1,200/600	1,200/600	1,200/600	1,280/600	1,480/600	1,550/600
20° C.:								
Dry breaking tenacity (g./d.).....	9.7	11.2	11.6	11.7	11.5	10.1	9.8	9.3
Initial modulus (g./d.).....	230	240	245	250	247	236	210	204
120° C.:								
Dry breaking tenacity (g./d.).....	7.0	8.0	8.5	8.7	8.6	8.5	7.4	7.3
Initial modulus (g./d.).....	70	101	115	120	127	122	96	95
β	0.89	1.06	1.12	1.13	1.22	1.32	1.34	1.35
I_M/I_{30}	0.50	0.46	0.48	0.46	0.45	0.48	0.53	0.54

Example 7

A PVA aqueous spinning solution containing 17 weight percent of PVA with a degree of polymerization of 1750 and a degree of saponification of 99.9 mol percent, 2.8 weight percent on PVA of boric acid and 0.24 weight percent on PVA of tartaric acid to adjust the pH to 4 is prepared. The spinning solution is passed through the same nozzle as in Example 1, into a coagulation bath at 45° C. containing 30 g./l. of sodium hydroxide and 225 g./l. of sodium sulfate. The resulting fiber is then subjected to subsequent treatments such as: roller-drawing, neutralization of sodium hydroxide on the fiber with an acid, wet-heat drawing, water-rinsing of the fiber to adjust the amount of boric acid to about 0.5%, drying and dry-heat drawing to a total draw ratio of 1200-1500%.

The properties of the fibers thus obtained are shown in Table 4 below.

TABLE 4

The amount of boric acid contained in the fiber (percent/PVA).....	0.46	0.52	0.48	0.50
Total drawing ratio (percent).....	1,200	1,350	1,400	1,500
Denier/filament.....	1,200/600	1,200/600	1,200/600	1,200/600
20° C.:				
Dry breaking tenacity (g./d.).....	9.7	10.1	11.0	11.5
Initial modulus (g./d.).....	232	230	245	260
120° C.:				
Dry breaking tenacity (g./d.).....	7.0	8.0	8.2	8.6
Initial modulus (g./d.).....	75	102	109	127
β	0.92	1.01	1.03	1.15
I_M/I_{30}	0.51	0.47	0.46	0.44

The PVA synthetic fibers of the present invention which exhibit outstanding properties at high temperature find widespread application, for example, they can be employed in the tension member of V belts and for reinforcement of hoses. The high modulus and low creep of the fibers of the present invention at high temperature enables the manufacture of V belts exhibiting excellent dimensional stability under the conditions of use. High pressure hoses employed in oil pressurized machines and tools will be greatly improved by the use of the PVA fibers of the present invention because the expansion of the hose against the inner pressure is kept very small by the high modulus of the present fibers at high temperature.

Although specific materials and conditions were set forth in the above exemplary processes for preparing the outstanding polyvinyl alcohol fibers of the present invention, these are merely intended as illustrations of the present invention. Various other polyvinyl alcohols, water-soluble borates and process conditions such as those listed above may be substituted in the examples with similar results.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. Polyvinyl alcohol fibers comprising an essentially

water insoluble polyvinyl alcohol having an average degree of polymerization of from about 1200 to 3500 and containing a residue of boric acid or a water soluble borate salt thereof in an amount of from 0.2 to 0.9% by weight of polyvinyl alcohol, said fibers being characterized by a half-width of (100) reflection (β) of 0.98 to 1.40 and an I_M/I_{30} of from 0.40 to 0.48 derived from the azimuthal X-ray intensity distribution at the angle of diffraction of 19.2°.

2. Polyvinyl alcohol fibers as defined in claim 1 exhibiting a:

yarn dry break strength at room temperature of at least 10 gm./denier;

yarn tenacity at 120° C. of at least 7.5 gm./denier;

yarn initial modulus at 120° C. of at least 100 gm./denier, and

yarn creep at 135° C. of less than 2%.

3. Polyvinyl alcohol fibers as defined in claim 1 containing a residue of boric acid or a water soluble borate

salt thereof in an amount of from 0.2 to 0.7% by weight of polyvinyl alcohol.

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JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

264—185

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,850,901 Dated August 21, 1975

Inventor(s) Shoichi Tanaka et al

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

Col. 10, Table 2, 10th entry in the second column
headed "Comparison Example 1": "⁴1,100" should
be read as "1,100⁽³⁾"

Col. 10, Table 2, 10th entry in the third column
headed "Comparison Example 2": "⁵1,200" should
be read as "1,200⁽⁴⁾"

Col. 10, Table 2, 10th entry in the fifth column
headed "Comparison Example 4": "⁴1,000" should
be read as "1,100⁽³⁾"

Signed and Sealed this

twenty-eight Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,850,901

Dated November 26, 1974

Inventor(s) Shoichi Tanaka et al

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

Col. 5, line 69: "tartrate," should be inserted after "potassium".

Col. 7, line 60: "ma" should be read as "mA".

Col. 7, line 61: "1°/6°" should be read as "1/6°".

Col. 8, Table 1, third entry in the second column headed "B": "2" should be read as "3".

Signed and sealed this 8th day of April 1975.

(SEAL)

Attest:

RUTH C. HASON
Attesting Officer

C. MARSHALL DANN
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