

[54] **PROCESS FOR THE PREPARATION OF POLYVINYL ALCOHOL FIBERS**

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[58] **Field of Search**..... **264/185, 210 F; 260/29.6 BM, 91.3 VA**

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[57] **ABSTRACT**

Process for the preparation of polyvinyl alcohol fibers comprising:

- i. spinning an aqueous polyvinyl alcohol spinning solution containing boric acid or a borate salt thereof;
- ii. coagulating the spun polyvinyl alcohol solution in an aqueous solution containing sodium or potassium hydroxide and sodium sulfate to obtain fibers;
- iii. roller drawing said fibers;
- iv. neutralizing said fibers
- v. wet-heat drawing said fibers;
- vi. rinsing said fibers with water to adjust the amount of residual boric acid or borate salt to 0.2 to 0.9% by weight of polyvinyl alcohol;
- vii. dehydrating and drying said fibers; and
- viii. dry-heat drawing said fibers to a total drawing ratio of at least 1,300 percent.

**5 Claims, No Drawings**

## PROCESS FOR THE PREPARATION OF POLYVINYL ALCOHOL FIBERS

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

The present invention relates to a process for the preparation of polyvinyl alcohol fibers which exhibit excellent properties at high temperature 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 process for preparing PVA fibers having excellent properties at high temperature. More particularly, the synthetic fibers produced in accordance with the present invention are superior to conventional PVA fibers with respect to yarn tenacity, yarn initial modulus and yarn creep. Radial-ply tires which utilize the PVA fibers produced by the present invention in the cord of the breaker give excellent results in the plunger test, high speed test, cornering power test, tread wear-resistance test and durability test.

The PVA synthetic fibers produced by 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°C            | at least 7.5 g/d             |
| yarn initial modulus at 120°C.    | at least 100 g/d             |
| yarn creep at 135°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 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 may be expected in a method wherein a conventional PVA fiber is sub-

jected 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 percent by weight of PVA, it is insufficient to restrain the chain movement. When the boric acid or borate salt content exceeds 0.9 percent, it will prevent the molecular chains from being highly oriented, thereby causing reduction of the yarn strength.

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 g/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 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 g/l sodium hydroxide or potassium hydroxide and 100 to 330 g/l sodium

sulfate, which is then subjected to subsequent treatments such as roller drawing, alkali neutralization, water-rushing to adjust the residue of boric acid in the fiber to a range of 0.2 to 0.9 percent by weight of PVA, dehydration and drying, and dry-heat drawing.

It is preferable to add boric acid or a borate salt thereof to the spinning solution in an amount ranging between 1 and 5 percent 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 substantially 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 acid, nitric acid and hydrochloric 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 tartrate, 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 percent by weight; the average degree of polymerization of the PVA ranges from 1,200 to 3,500 and preferably ranges from 1,500 to 3,000. 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 percent by weight of PVA.

The residue of boric acid after water-rinsing should be more than 0.2 percent 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 percent 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 a range of 0.2 to 0.9 weight percent and preferably in a 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 1,300 percent. If the total drawing ratio is less than 1,300 percent, 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 1,800 percent.

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 percent (elongation rate under the load of 1 g/d for 60 minutes). The fibers contain 0.2 to 0.9 percent of boric acid or a borate salt and preferably contain 0.2 to 0.7 percent 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 2g 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:

$$0.62 \times f \times v/W$$

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 JISL 1073. For the determination at room temperature, it is carried out in

spinning holes, 0.08mm in diameter into a coagulating bath containing 30g/l of sodium hydroxide and 230g/l of sodium sulfate. The fiber thus spun is then taken out of the bath at a rate of 10m/min., and then subjected to subsequent treatments such as; roller drawing of 100 percent, neutralization in a bath comprising 70g/l of sulfuric acid and 300g/l of sodium sulfate; wet-heat drawing of 150 percent; water-rinsing to adjust the amount of boric acid to be 0.45 percent; dehydration and drying; and dry-heat drawing of 220 percent. The final product obtained is drawn to a total drawing ratio of 1,500 percent.

The product thus obtained exhibits a yarn tenacity of 9.3g/d at 120° C., yarn initial modulus of 135g/d at 120° C. and yarn creep of 1.4 percent at 135° C.

In Table 1 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 1 and the resulting yarn properties obtained are also set forth to assist in the comparison.

TABLE 1

|                                       | Example 1 | Comparison 1 | Comparison 2 | Comparison 3            | Comparison 4 | Comparison 5 | Comparison 6 | Comparison 7 |
|---------------------------------------|-----------|--------------|--------------|-------------------------|--------------|--------------|--------------|--------------|
| Manufacturing Conditions              |           |              |              |                         |              |              |              |              |
| 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 %)  | 99.5      | 99.5         | 99.5         | 99.5                    | 99.5         | 99.5         | 99.5         | 99.5         |
| Spinning solution:                    |           |              |              |                         |              |              |              |              |
| the concentration of PVA (%)          | 17        | 17           | 17           | 17                      | 17           | 18           | 18           | 17           |
| the amount of boric acid added (%)    | 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(1)       | 4.0(1)       | 4.3(2)       |
| Coagulation bath:                     |           |              |              |                         |              |              |              |              |
| NaOH (g/l)                            | 30        | 8            | 110          | 80                      | 15           | 40           | 40           | 30           |
| Na <sub>2</sub> SO <sub>4</sub> (g/l) | 230       | 260          | 150          | 90                      | 360          | 220          | 220          | 230          |
| Neutralization bath:                  |           |              |              |                         |              |              |              |              |
| H <sub>2</sub> SO <sub>4</sub> (g/l)  | 70        | 70           | 70           | incapable of being spun | 70           | 80           | 80           | 70           |
| Na <sub>2</sub> SO <sub>4</sub> (g/l) | 300       | 300          | 300          | —                       | 300          | 320          | 320          | 300          |
| Drawing:                              |           |              |              |                         |              |              |              |              |
| total drawing ratio (%)               | 1,500     | 1,100(3)     | 1,200(4)     | —                       | 1,000(3)     | 1,500        | 1,200        | 1,100        |
| roller drawing (%)                    | 100       | 100          | 100          | —                       | 100          | 100          | 100          | 100          |
| wet-heat drawing (%)                  | 150       | 150          | 140          | —                       | 150          | 150          | 140          | 150          |
| dry-heat drawing (%)                  | 220       | 140          | 192          | —                       | 120          | 220          | 192          | 140          |
| Yarn Properties                       |           |              |              |                         |              |              |              |              |
| Amount of residue of boric acid (%)   | 0.45      | 0.51         | 0.52         | —                       | 0.49         | 0.15         | 1.00         | 0.46         |
| Tenacity (120°C.)                     | 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.) (%)                    | 1.4       | 2.5          | 2.2          | —                       | 3.1          | 2.3          | 2.4          | 2.3          |

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 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

10kg of an aqueous spinning solution containing 1.7kg of PVA with a degree of polymerization of 1,750 and degree of saponification of 99.5 mole percent, and 34g 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

Note to Table 1:

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

1. tartaric acid used to adjust pH
2. acetic acid and sodium acetate used to adjust pH
3. sample exhibited poor drawability
4. sample exhibited poor spinnability

#### EXAMPLE 2

PVA fiber containing sodium borate and drawn to a total drawing ratio of 1,500 percent is obtained in the same manner as in Example 1, except that sodium borate is employed in an amount of 1.5 percent by 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. and yarn creep of 1.5 percent at 135° C.

## EXAMPLE 3

An aqueous PVA solution having a concentration of PVA of 15 weight percent and containing 150g of PVA with a degree of polymerization of 2,350 and a degree of saponification of 99.5 mole percent is admixed with 30g of boric acid (2 percent 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 percent, neutralization, wet-heat drawing of 150 percent, water-rinsing to adjust the amount of boric acid residue to 0.4 percent by weight of PVA, dehydration and drying, and dry-heat drawing of 200 percent. The product (1,200d/600f) is thus drawn to a total drawing ratio of 1,400 percent. 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. and yarn creep of 1.9 percent at 135° C.; the product is superior in its properties at high temperature.

## EXAMPLE 4

An aqueous solution of PVA of 17 weight percent containing 100kg of PVA with a degree of polymerization of 1,750 and a degree of saponification of 99.9 mole percent is admixed with 2kg of boric acid (2 weight percent of PVA) and 0.3kg of acetic acid (0.005g equivalent to PVA 100g) 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 0.15mm in diameter into

## EXAMPLE 5

1 Kg of an aqueous spinning solution containing 170g of PVA with a degree of polymerization of 1,750 and degree of saponification of 99.5 mol percent, 5.95g 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 15g/l of sodium hydroxide and 230g/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.

## EXAMPLE 6

A PVA aqueous spinning solution containing 17 weight percent PVA with a degree of polymerization of 1,700 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 1,300-1,500 percent.

In Table 2 below, the resultant PVA fibers containing various amounts of boric acid are shown with their properties.

Table 2

| The amount of boric acid contained in the fiber (%/PVA) | 0        | 0.21     | 0.36 | 0.50 | 0.67 | 0.85     | 0.95     | 1.05     |
|---|----------|----------|------|------|------|----------|----------|----------|
| Total drawing ratio (%)                                 | 1200     | 1500     | 1500 | 1500 | 1500 | 1400     | 1200     | 1140     |
| denier/filament   | 1200/500 | 1200/600 | do.  | do.  | do.  | 1280/600 | 1480/600 | 1550/600 |
| 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       |

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 condition is very stable in this case; during 2 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 percent by weight of PVA, dehydration drying, and dry-heat drawing. The product (1,800d/1,000f) thus obtained is drawn to a total drawing ratio of 1,400 percent. The product exhibits a yarn tenacity of 9.3 g/d at 120° C., yarn initial modulus of 134 g/d at 120° C. and yarn creep of 1.8 percent at 135° C.

## EXAMPLE 7

A PVA aqueous spinning solution containing 17 weight percent of PVA with a degree of polymerization of 1,750 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 percent, drying and dry-heat drawing to a total draw ratio of 1,200-1,500 percent.

The properties of the fibers thus obtained are shown in Table 3 below.

Table 3

| The amount of boric acid contained in the fiber (%/PVA) |          |      |      |      |
|---|----------|------|------|------|
|   | 0.46     | 0.52 | 0.48 | 0.50 |
| Total drawing ratio (%)                                 | 1200     | 1350 | 1400 | 1500 |
| denier/filament   | 1200/600 | do.  | do.  | do.  |
| 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  |

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. The excellent high temperature properties of the PVA synthetic fibers produced in accordance with the present invention are utilized to their fullest extent when the PVA fibers are employed in the cord of a radial ply or a belted bias-ply tire.

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:

- 5 1. Process for the preparation of polyvinyl alcohol fibers comprising:
  - 10 i. spinning an aqueous polyvinyl alcohol solution comprising 10 to 30 percent by weight of a polyvinyl alcohol having a degree of polymerization ranging from 1,200 to 3,500 and 1 to 5 percent boric acid or a substantially water soluble borate salt thereof based on the weight of polyvinyl alcohol;
  - 15 ii. coagulating the spun polyvinyl alcohol solution in an aqueous solution containing 10 to 100 gms/liter sodium or potassium hydroxide and 100 to 330 gms/liter sodium sulfate to obtain fibers;
  - 20 iii. roller drawing said fibers;
  - 25 iv. neutralizing alkali adhered to said fibers with acid;
  - 30 v. wet-heat drawing said fibers;
  - 35 vi. rinsing said fibers with water to adjust the amount of residual boric acid or borate salt to 0.2 to 0.9 percent by weight of polyvinyl alcohol;
  - 40 vii. dehydrating and drying said fibers; and
  - 45 viii. dry-heat drawing said fibers to a total drawing ratio of at least 1,300 percent, thereby obtaining polyvinyl alcohol fibers exhibiting the following high temperature properties:
    - Yarn tenacity at 120° c. — at least 7.5 gms/denier
    - Yarn initial modulus at 120° C. — at least 100 gms/denier
    - Yarn creep at 135° C. — less than 2 percent.
2. Process as defined in claim 1 wherein the fibers are rinsed with water to adjust the amount of residual boric acid or borate salt to 0.2 to 0.7 percent by weight of polyvinyl alcohol.
3. Process as defined in claim 1 wherein the spinning solution is maintained at a pH of from 3 to 5.
4. Process as defined in claim 3 wherein the pH of the spinning solution is adjusted by addition thereto of an inorganic acid, organic acid or mixture of an organic acid and a salt of an organic acid.
5. Process as defined in claim 1 wherein the fibers are dry-heat drawn to a total drawing ratio of from 1,300-1,800 percent.

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