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METHOD OF PRODUCING FIBERS

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5 Claims. (Cl. 264—185)

The present invention relates to polyvinyl alcohol fibers and is more particularly concerned with a method for producing polyvinyl alcohol fibers of improved characteristics.

It is known that polyvinyl alcohol fibers have strength and other desirable properties. Their hot-water resistance, however, is generally poor and much effort has been expended in seeking ways to improve this property.

It is accordingly an object of this invention to provide a process for producing polyvinyl alcohol fibers of improved hot-water resistance.

In accordance with the invention, fibers are produced from an aqueous polyvinyl alcohol spinning solution containing boric acid and, after spinning, the boric acid is completely removed from the fibers by washing. The fibers may then be drawn while being heated or subjected to after-treatments such as heat treatment, chemical treatments, e.g. acetalization or the like. In a preferred embodiment of the invention, the fibers are wet spun in a conventional coagulating bath to which boric acid has been added. By reason of the spinning of the fibers in the presence of boric acid in accordance with the invention, polyvinyl alcohol fibers of excellent hot-water resistance are produced and it has also been observed that, surprisingly, the strength of the fibers is also greatly increased.

The invention will be further understood from the following experimental data:

A 15% by weight aqueous solution of polyvinyl alcohol having an average degree of polymerization of 1700 to which was added boric acid in the amount of 0.8% based on the weight of the polyvinyl alcohol was spun into (1) a saturated aqueous ammonium sulfate solution (530 g./liter ammonium sulfate), (2) a saturated aqueous ammonium sulfate solution containing ammonium hydroxide (8 g./liter), and (3) a saturated ammonium sulfate solution containing ammonium hydroxide (8 g./liter) and boric acid (15 g./liter) all at 29° C. The fibers extended through the coagulating bath for 1 meter, the speed of removal from the bath was 10 meters/minute, the rate of drawing on a roller was 100%, and the rate of wet-heat drawing (in a saturated aqueous solution of ammonium sulfate at 90–92° C.) was 150%. The fibers were then washed free of boric acid by soaking them in running water at 50° C. for 5 minutes. After that, the fibers were heat-drawn as much as possible in polyethylene glycol at 230° C., for 5 seconds, and they were further subjected to heat treatment in polyethylene glycol at 235° C. for 5 seconds. The fibers prepared in this way were compared with fibers produced in identical manner but with no boric acid present. These fibers were then tested for dry strength, and elongation, and the hot water resistance (maximum temperature at which shrinkage of less than 10% is observed when measured by soaking the fibers with the load of 0.02 g./denier for 1 hour at temperatures from 100° C. upward at 5° C. intervals). The pertinent data are set forth below:

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Spinning Solution	Coagulation bath	Total elongation after removal from bath (percent)	Fineness (Denier)	Dry strength (g./Denier)	Dry elongation (percent)	Hot water resistance (° C.)
Without boric acid	(1)	990	1.65	10.2	7.7	100
Boric acid present	(1)	1,250	1.25	12.5	7.8	110
Do	(2)	1,500	1.06	13.1	6.7	120
Do	(3)	1,550	1.02	15.3	6.5	120

As is evident from the test results tabulated above, the dry strength and the hot-water resistance of polyvinyl alcohol fibers are markedly improved when the fibers are spun from a polyvinyl alcohol spinning solution containing boric acid.

Polyvinyl alcohol fibers with a maximum strength of 10–11 g./denier have been obtained in the past, and these were the strongest of all fibers, including natural, artificial, and synthetic fibers. The present invention has made it possible to increase the strength of polyvinyl alcohol fibers by as much as 50% while at the same time to provide fibers capable of withstanding hot water of 120° C. without the necessity of subjecting the fibers to chemical treatment such as acetalization.

The effect of this invention is obtained by adding boric acid to the polyvinyl alcohol spinning solution, spinning the fibers into a conventional wet-spinning coagulation bath, but preferably into such a bath to which boric acid has been added, washing the fibers free of boric acid after removal from the coagulation bath. Suitably the fibers are then drawn under heat in a conventional hot-drawing operation.

The amount of boric acid employed can vary but suitably the spinning solution contains about 0.4 to 1.5% based on the weight of the polyvinyl alcohol. When the boric acid is also used in the coagulation solution, it is employed in similar concentrations based on the total solution. The content of polyvinyl alcohol in the spinning solution is that conventional for wet-spinning operations. The effect seems greater when the coagulation bath is slightly alkaline, as by the presence of ammonium hydroxide, sodium hydroxide, or other like alkaline agent.

The invention will be further understood from the following specific examples of practical application. However, it will be understood that these examples are not to be construed as limiting the scope of the present invention in any manner. In the examples, all parts are by weight unless otherwise indicated.

The conditions and the relative relationships set forth in the examples are those preferred in carrying out the process of this invention, but it will be understood that other conditions and relationships may be used within the scope of the invention. In general, unless otherwise indicated, conventional operations and techniques are suitably employed.

Example 1

An aqueous solution containing polyvinyl alcohol having a degree of polymerization of 1600, and 0.8%, based on the polyvinyl alcohol, of boric acid was spun

into an aqueous solution kept at 20° C. and containing 500 g./liter of ammonium sulfate, 10 g./liter of ammonium hydroxide, and 15 g./liter of boric acid. The product fibers were drawn by 100% on a roller, and then by 150% while wet and while heated. The fibers were then washed in running water for 10 minutes, and were heat-dried in hot air at 180° C.

The fibers obtained as described above were heat drawn as much as possible for 5 seconds in polyethylene glycol at 230° C. to provide a total elongation after removal from spinning bath amounting to 1600%, followed by a heat treatment for 5 seconds in polyethylene glycol at 235 ° C.

These fibers had a dry strength of 16.0 g./denier, a dry elongation of 7.0%, and exhibited hot-water resistance at 120° C. The corresponding values obtained with fibers produced as a control by following the same procedure but omitting the presence of boric acid, were 10.0 g./denier, 7.5%, and 100° C., respectively.

Example 2

An aqueous solution containing 20% of polyvinyl alcohol, having a degree of polymerization of 1300, and 0.5%, based on the polyvinyl alcohol, of boric acid was spun into an aqueous solution at 20° C. and containing 480 g./liter of ammonium sulfate and 6 g./liter of ammonium hydroxide, followed by drawing by 100% on a roller and then by drawing by 150% while wet and heated. The product fibers were then washed in running water for 1 minute, and heat dried in hot air at 180° C.

These fibers were heat-drawn as much as possible for 5 seconds in a fused solder bath at 230° C. to provide a total elongation after removal from the spinning bath being 1550%, and subsequently, the fibers were subjected to heat treatment while being allowed to shrink or contract by 15% for 5 seconds in fused solder at 235° C.

The fibers thus obtained exhibited a much greater strength and hot water resistance than fibers subjected to the same treatment but without the presence of boric acid and the fibers had a dry strength of 12.8 g./denier, a dry elongation of 12.8%, and hot-water resistance at 125° C. The corresponding values of the control fibers which were produced without the use of boric acid were 7.8 g./denier, 12.2%, and 105° C., respectively.

Example 3

An aqueous solution containing 25% of polyvinyl alcohol, having an average degree of polymerization of 1000, was spun into an aqueous solution at 20° C. and containing 530 g./liter of ammonium sulfate, 8 g./liter of ammonium hydroxide, and 15 g./liter of boric acid. A 400% heat drawing while wet was then applied to the fibers, and they were then washed in running water at room temperature for 15 minutes. After that, the fibers were soaked in methanol for 1 minute, followed by air drying.

These fibers were heat drawn as much as possible for 5 seconds in fused Wood's metal to provide a total elongation after removal from the spinning bath of 1600%, and they were then subjected to heat treatment while permitting 10% shrinkage for 5 seconds in fused Wood's metal at 235° C.

The fibers produced in this manner exhibited very good strength and hot-water resistance compared with control fibers produced by the same procedure but without the presence of boric acid. The product fibers had a dry strength of 13.3 g./denier, a dry elongation of 9.1%, and a hot-water resistance of 120° C.

Example 4

An aqueous solution containing 11% of polyvinyl alcohol having an average degree of polymerization of 2500 and 1.5%, based on the polyvinyl alcohol, of boric acid was spun into an aqueous solution at 45° C. and containing 500 g./liter of ammonium sulfate, 8 g./liter of ammonium hydroxide, and 15 g./liter of boric acid. The fibers were then subjected to 100% drawing on a roller, and 150% heat drawing while wet was then applied. The product fibers were then washed for 5 minutes in running water at 50° C., and the fibers were finally heat-dried in air heated to 180° C.

The fibers thus obtained were heat-drawn for 5 seconds in silicon oil at 240° C., and they were then heat treated for 5 seconds in silicon oil at 245° C. The fibers had a dry strength of 12.5 g./denier, a 6.8% dry elongation, and a hot-water resistance of 115° C.

Example 5

An aqueous solution containing 15% of polyvinyl alcohol having a degree of polymerization of 1500, and 1.2%, based on the polyvinyl alcohol, of boric acid, was spun into an aqueous solution at 30° C. and containing 380 g./liter of Glauber's salt and 3 g./liter of caustic soda. After 100% drawing on a roller and 150% wet-heat drawing, the product fibers were washed for a minute in running water at 65° C., and were then heat-dried in air heated to 180° C.

These fibers were heat drawn as much as possible in fused Wood's metal at 230° C., and subsequently were heat treated in fused Wood's metal at 235° C.

The fibers obtained in this manner showed very good performance compared to control fibers produced in like manner but without the presence of boric acid. Thus, the product fibers had a dry strength of 14.7 g./denier, a dry elongation of 7.2%, and a hot-water resistance of 120° C.

Example 6

A 30% aqueous solution of polyvinyl alcohol having an average degree of polymerization of 1700, and 0.4%, based on the polyvinyl alcohol of boric acid, was dry spun into air. The fibers produced were washed for 20 minutes in running water at room temperature, and were then dried by air.

These fibers were heat-drawn for 5 seconds in silicon oil at 230° C., and were subsequently heat-treated for 5 seconds in silicon oil at 235° C.

The thus obtained product fibers had a dry strength of 11.8 g./denier, a dry elongation of 7.2%, and a hot water resistance of 115° C. On the other hand, the corresponding values of 7.5 g./denier, 11.3%, and 95° C., respectively, were exhibited by control fibers which were treated in identical manner except that boric acid was omitted.

As previously indicated, the spinning of the fibers from the spinning solution containing boric acid in accordance with the invention is effected by conventional wet-spinning techniques. Suitable spinning conditions for producing fibers from the spinning solutions of this invention are described, for example, in U.S. Patent 2,642,333 as well as in Cline et al. U.S. Patent 2,636,803 and Osugi et al. U.S. Patent 2,906,594.

The fibers may suitably be stretched and heat treated in accordance with conventional techniques as illustrated, for example, in U.S. Patents 2,636,803, 2,636,804 and 2,906,594. Thus, the fibers are suitably stretched to a draw ratio of about 2:1 to 12:1 during or after spinning. For wet spun filaments, the stretching can be carried out directly after spinning while the fibers are wet at room temperature up to 100° C. to a draw ratio of about 5:1. For stretching to higher draw ratios, it is preferred to conduct the stretching in a heated medium such as air at 100–250° C.

Heat treatment is usually carried out by heating the fibers in a medium such as air at 210–250° C. for 2 seconds to 5 minutes.

While chemical treatments such as acetalization are not necessary, such treatments may be given to the fibers

if desired such as described in the above-mentioned patents.

It will also be understood that various changes and modifications in addition to those indicated above may be made in the embodiments herein described without departing from the scope of the invention as defined in the appended claims. It is intended, therefore, that all matter contained in the foregoing description shall be interpreted as illustrative only and not as limitative of the invention.

We claim:

1. A process of forming polyvinyl alcohol fibers of increased strength and hot-water resistance which comprises introducing into a coagulation bath, an aqueous solution of polyvinyl alcohol containing at least about 0.4% by weight of boric acid to form polyvinyl alcohol fibers therefrom, removing the thus-formed fibers from the coagulation bath and washing the fibers by soaking them in running water for at least about one minute to remove boric acid therefrom and to render them free of free boric acid.

2. A process as defined in claim 1, wherein said coagulation bath contains boric acid.

3. A process as defined in claim 1, wherein said boric acid is present in said solution in the amount of about 0.4 to 1.5% by weight of the polyvinyl alcohol.

4. A process of forming polyvinyl alcohol fibers of increased strength and hot-water resistance which comprises introducing into a coagulation bath an aqueous solution of polyvinyl alcohol containing at least about 0.4% by weight of boric acid to form polyvinyl alcohol fibers therefrom, removing the thus-formed fibers from the coagulation bath, washing the fibers by soaking them in running water for at least about one minute to remove free boric acid therefrom and to render them free of free boric acid, and heat drawing said fibers.

5. A process as defined in claim 4, wherein said boric acid is present in said solution in the amount of about 0.4 to 1.5% by weight of the polyvinyl alcohol.

References Cited in the file of this patent

Jones: "Polyvinyl Alcohol," British Plastics, February 1944, pp. 77–83.

Billmeyer: Textbook of Polymer Chemistry, published in 1957 by Interscience Publishers, pp. 391–393 are relied on.