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POLYVINYL ALCOHOL SPINNING SOLUTION AND FIBERS PREPARED THEREFROM

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The present invention relates to the production of fibers of polyvinyl alcohol and is more particularly concerned with a novel spinning solution from which polyvinyl alcohol fibers of improved characteristics can be produced.

Ordinary polyvinyl alcohol fibers do not exhibit good dyeability and many proposals have been made for improving the dyeing properties of polyvinyl alcohol fibers. Many of these prior proposals for improving the dyeability of fibers of polyvinyl alcohol involve difficulties, however, in their industrialization and they are, therefore, of limited utility from a practical standpoint.

It is an object of this invention to provide a novel process for producing polyvinyl alcohol fibers of improved dyeability.

It is another object of the invention to provide means for producing fibers of the character indicated which avoids the disadvantages and drawbacks of prior proposals.

It is a further object of the invention to provide means readily adapted to commercial polyvinyl alcohol fiber producing practices which permits polyvinyl alcohol fibers of improved dyeability to be produced economically and without complex operating procedures or reactions.

In accordance with the invention, polyvinyl alcohol fibers are produced from a polyvinyl alcohol spinning solution containing glucose or a water-soluble derivative of glucose.

It is a feature of this invention that the use of a polyvinyl alcohol spinning solution containing glucose or one of its water-soluble derivatives permits polyvinyl alcohol fibers of excellent dyeability to be produced economically and efficiently and at low cost.

It is a further feature of the invention that fibers spun from a spinning solution of the character indicated are transparent after wet spinning and even after they have subsequently been subjected to an after-treatment, e.g. a heat treatment.

Other objects and features of the invention will be apparent from the following detailed description, with particular reference to illustrative embodiments of the invention.

In order to illustrate the characteristic features of this invention, there were prepared a series of aqueous polyvinyl alcohol spinning solutions. Each aqueous solution was prepared from polyvinyl alcohol having an average degree of polymerization of 1700 and in each solution was incorporated commercial glucose. The concentration of the polyvinyl alcohol had a constant value of 15% in each solution but the amounts of glucose were varied as follows: solution (1), 0% (control), solution (2), 10%, solution (3), 20%, solution (3'), 20%, and solution (4), 30%, the percentages being based on the amount of polyvinyl alcohol. The spinning solutions thus prepared were spun in a coagulation bath consisting of a saturated solution of Glauber's salt at 45° C. in accordance with conventional techniques, employing an immersion length of 1.5 meters, a take-up speed of 10 meters/min., and roller drawing of 300%. The fibers thus spun were subsequently dried in an air bath held at 180° C. The fibers from solution (3') were also drawn 50% in air held at 230° C. The fibers were then subjected to heat treatments

for 30 seconds in an air bath held at 235° C., and they were formalized at 70° C. for an hour in a formalizing solution consisting of 5% formaldehyde, 15% sulfuric acid, and 15% sodium sulfate. The strength, the elongation, the shrinkage in boiling water, the dye absorption (Congo red 2%, Na_2SO_4 10%, bath ratio 50:1, 80° C., 1 hour) and the depth of the dye shade of the dyed fibers were measured. The depth of shade was measured with varying concentrations of Congo red, Na_2SO_4 10%, bath ratio 50:1 at 80° C., 2 hours. The value of the depth of shade is expressed in terms of K/S at a dye absorption of 10 mg./g. of the material to be dyed, using the formula

$$K/S=\frac{(1-R\infty)^2}{2R\infty}$$

where $R\infty$ is the coefficient of reflection for the wavelength 520 mu. The results are tabulated in the following table:

	(1)	(2)	(3)	(3')	(4)
Strength (g./denier)	3.49	3.52	3.02	3.68	2.63
Elongation (percent)	31.8	28.9	30.0	20.1	28.0
Shrinkage in boiling water (percent)	1.5	2.0	1.8	2.5	1.5
Dye absorption (mg./g.)	4.5	10.6	16.5	8.9	18.0
Depth of shade of dyed fiber (K/S)	4.1	7.6	10.5	9.2	11.2

From the foregoing results, it will be seen that conspicuous improvements in the dyeing absorption and in the depth of shade of the dyed fibers are apparent. While the tests show that with increasing amounts of glucose the strength tends to decrease somewhat, when the same manufacturing steps are used, it will also be seen from the tests on the fibers from solution (3') that any decrease of strength can be fully compensated for by drawing. On the other hand, variations in the amount of glucose added do not significantly affect the improved elongation and the shrink-resistance in water which are achieved. The fibers from solution (1) were opaque, just as in the case of ordinary Vinylon fibers. The fibers produced from solution (2), however, were generally transparent, and conspicuously transparent fibers were produced from solutions (3) and (4), the transparency of the fibers from solution (3') lying between those from solutions (2) and (3). This activity of glucose in giving the fibers a transparent appearance is thought to be related to the marked improvement in the depth of shade of the dyed fibers which is observed.

While glucose has been referred to above, the new results provided by this invention can also be obtained by the use of water-soluble derivatives of glucose, e.g. alkyl and acetyl derivatives of glucose, such as monomethyl glucose, dimethyl glucose, trimethyl glucose, monoacetyl glucose, diacetyl glucose, triacetyl glucose, β-glucosan, and the like.

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 these examples, all parts are by weight, unless otherwise indicated.

Example 1

An aqueous solution containing 20% of polyvinyl alcohol having an average degree of polymerization of 1000, and 20% glucose (based on the amount of polyvinyl alcohol) was wet spun in conventional manner at 50° C. into an aqueous solution containing 410 g./liter of sodium sulfate, and the fibers then dried. The fibers were then subjected to heat treatment for 1 minute in air at 220° C., and the heat-treated fibers were formalized at 60° C. for 2 hours in an aqueous solution containing 4% formaldehyde and 15% sulfuric acid. The

fibers thus obtained possessed high resistance to boiling water, and excellent transparency. Fibers produced by the same procedure, but from a spinning solution to which no glucose was added, were opaque. The former fibers exhibited far better depth of shade than the latter fibers when they were dyed with Nippon Fast Violet BB Conc.

Example 2

An aqueous solution containing 15% polyvinyl alcohol having an average degree of polymerization of 1700 and 10% glucose (based on the amount of polyvinyl alcohol) was wet spun by conventional techniques into a saturated aqueous solution of Glauber's salt maintained at 45° C., and the fibers produced was roller drawn by 400%, then heat-dried in hot air at 180° C. These fibers was subjected to heat-treatment for 2 minutes at 210° C. in super-heated steam at 1 atmosphere gage pressure, and they were benzalized at 60° C. for 1 hour by immersion in an aqueous solution containing 1% benzaldehyde, 0.3% sodium dibutyl naphthalene sulfonate, and 2% sulfuric acid. The thus obtained fibers were transparent, whereas fibers produced under identical conditions, but from a spinning solution to which no glucose was added, were opaque, and the former were dyed far deeper than the latter when dyed with Celliton Fast Blue FFR.

Example 3

An aqueous solution containing 14% polyvinyl alcohol having an average degree of polymerization of 1600 and 30% glucose (based on the amount of polyvinyl alcohol) was wet spun in a saturated aqueous solution of Glauber's salt maintained at 50° C., and the fibers produced were dried without further handling. These fibers were heat-drawn by 700% in air at 230° C., then shrunk 15% in air at 235° C. The fibers were subsequently acetalized at 60° C. for 2 hours in an aqueous solution containing 0.5% formaldehyde, 2% β-cyclohexyl aminobutylaldehyde, 15% sulfuric acid, and 10% sodium sulfate. These fibers exhibited far better depth of shade than control fibers produced under the same conditions, but from a spinning solution to which no glucose was added, when they were dyed for 1 hour at 80° C. with 2% acid dye, Acid Scarlet 3R, 1% sulfuric acid (bath ratio, 50:1).

Example 4

An aqueous solution was prepared from amino-acetalized polyvinyl alcohol which was 30% acetalized with β-cyclohexyl aminobutylaldehyde and from polyvinyl alcohol having an average degree of polymerization of 1700, the quantities of the two compounds being chosen to provide an average degree of amino-acetalation of 1%, and a concentration of total polyvinyl compounds of 15%. To this solution was added glucose in the amount of 20% based on the total quantity of polyvinyl compounds. This aqueous solution was then conventionally wet spun into a saturated aqueous solution of Glauber's salt maintained at 45° C., and the fibers were roller-drawn by 200%, and heat-dried. These fibers were then heat-drawn by 200% in air at 225° C., subjected to heat-treatment at 230° C. at constant length, and subsequently benzalized for 1 hour at 60° C. in an aqueous solution containing 2% benzaldehyde, 40% methanol, and 10% sulfuric acid. These fibers surpassed in depth of shade control fibers produced without the use of glucose when the two fibers were dyed at 80° C. for 1 hour in a dyeing bath having a bath ration of 50:1 and containing 2% Acid Scarlet 3R, and 1% acetic acid. It was noted that both fibers had absorbed the dye in the dyeing bath.

Example 5

An aqueous solution containing 15% polyvinyl alcohol having an average degree of polymerization of 1700 and 25% glucose (based on the amount of polyvinyl alcohol) was wet spun into a saturated aqueous solution of Glauber's salt at 50° C. The fibers obtained was subjected to heat-treatment for 2 hours in saturated Glauber's salt maintained at 120° C., and they were then formalized as described in Example 1. These fibers were highly transparent, and exhibited better dyeability than the control fibers produced without the presence of glucose in the spinning solution.

Example 6

An aqueous solution containing 13% polyvinyl alcohol having an average degree of polymerization of 2000 and 20% trimethyl glucose (based on the amount of polyvinyl alcohol) was wet spun by extruding it into a coagulation bath containing 350 g./liter of sodium sulfate held at 55° C. The fibers obtained were subjected to heat-treatment in an air bath maintained at 230° C. at constant length, and they were subsequently formalized at 65° C. for 1 hour in an aqueous solution containing 5% formaldehyde, 20% sulfuric acid, and 5% sodium sulfate.

These fibers, in comparison with the control fibers produced without the use of glucose, had a cross-section which was almost circular, owing to the marked improvement in their solidity, and they exhibited a transparent appearance and excellent dyeability.

Example 7

An aqueous solution containing 13% polyvinyl alcohol having an average degree of polymerization of 1700, 35% diacetyl glucose (based on the amount of polyvinyl alcohol), and 1% blue pigment (based on the amount of polyvinyl alcohol), was wet spun into a saturated aqueous solution of Glauber's salt held at 45° C., and the fibers were subjected to heat-treatment in air at 220° C., and they were then formalized at 70° C. for 1 hour in an aqueous solution containing 5% formaldehyde, 15% sulfuric acid, and 15% sodium sulfate. These fibers had an extremely deep color and exhibited good coloration when dyed in comparison with the control fibers produced without the use of glucose.

The conditions and relative relationships set forth in the examples are those preferred but it will be understood that other conditions and relationships may be used within the scope of the invention. For example, the amount of glucose or glucose derivative specified in the examples of 10 to 35 percent based on the weight of the total polymer is preferred, these percentages being based on the dry weight of the additive. In general, unless otherwise indicated, conventional operations and techniques are suitably employed.

Thus, any polyvinyl alcohol suitable for spinning into fibers may be used. Typical polyvinyl alcohols which can be suitably used are described, for example, in Cline et al. U.S. Patent 2,636,803. Similarly, mixed spinning solutions may be prepared containing polyvinyl alcohol in combination with other polymers, e.g. a nitrogen-containing polyvinyl alcohol, as the polymer components, as described, for example in the co-pending application of Matsubayashi et al., Serial No. 42,998, filed July 15, 1960, now United States Patent No. 3,137,673. The spinning of the fibers from the spinning solution containing glucose or glucose derivatives in accordance with the invention is effected by conventional wet-spinning techniques.

Thus, the solutions are spun to form fibers, for example, in conventional manner by extruding the solution through small holes in a spinning jet into a medium effective to remove water therefrom. In wet spinning processes the medium can, for example, be a concentrated aqueous solution of a coagulating salt such as sodium sulfate or ammonium sulfate, while in dry spinning techniques air or an inert gas such as nitrogen is employed.

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.

Acetalization is conveniently carried out in conventional manner in an aqueous solution containing 0.2–10% aldehyde, 5–20% sulfuric acid and 0–25% sodium sulfate or ammonium sulfate at temperatures of 40–80° C. for times ranging from a few minutes, e.g. 10 minutes, to several hours, e.g. 5 hours.

The polymers contained in the solutions of this invention are similarly formed into other shapes such as films by conventional techniques. Thus, films are suitably produced by the procedure described, for example, in Izard et al. U.S. 2,236,061 and in Herrmann et al. U.S. Patent 2,837,770.

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 spinning solution effective to form polyvinyl alcohol fibers of improved dyeing characteristics which consists essentially of an aqueous solution of polyvinyl alcohol in combination with a member selected from the group consisting of glucose, monomethyl glucose, dimethyl glucose, trimethyl glucose, monoacetyl glucose, diacetyl glucose, triacetyl glucose, and beta-glucosan, said member being present in said solution in an amount of from 10% to 35% based on the weight of said polyvinyl alcohol in said solution.

2. A process of forming polyvinyl alcohol fibers having improved dyeing characteristics which comprises introducing into a coagulation bath a spinning solution which consists essentially of an aqueous solution of polyvinyl alcohol in combination with a member selected from the group consisting of glucose, monomethyl glucose, dimethyl glucose, trimethyl glucose, monoacetyl glucose, diacetyl glucose, triacetyl glucose and beta-glucosan, said member being present in said solution in an amount of from 10% to 35% based on the weight of said polyvinyl alcohol in said solution.

3. A process according to claim 2, wherein said member is glucose.

4. A process according to claim 2, wherein said member is trimethyl glucose.

5. A process according to claim 2, wherein said member is diacetyl glucose.

6. Polyvinyl alcohol fibers of improved dyeing characteristics consisting essentially of polyvinyl alcohol and a member selected from the group consisting of glucose, monomethyl glucose, dimethyl glucose, trimethyl glucose, monoacetyl glucose, diacetyl glucose, triacetyl glucose, and beta-glucosan, said member being present in said fiber in an amount of 10% to 35% based on the weight of said polyvinyl alcohol in said fiber.

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